

# Chaotic Simplicity: A Systematic Investigation of the Structure-Property Relationships in Simple $ABO_4$ Metal Oxides

A thesis submitted to The University of Sydney in fulfilment of the requirements for the degree of Doctor of Philosophy by

**Bryce G. Mullens**

Under the supervision of

**Professor Brendan J. Kennedy**

and

**Dr Zhaoming Zhang**



**School of Chemistry, Faculty of Science**

**The University of Sydney**

**November 2023**



## Declaration of Authorship

I, Bryce Geoffrey Mullens, declare that this thesis entitled “Chaotic Simplicity: A Systematic Investigation of the Structure-Property Relationships in Simple  $ABO_4$  Metal Oxides”, and the work presented herein, is my own except where otherwise acknowledged.

---

Bryce G. Mullens - November 2023





*"The important thing in science is not so much to obtain new facts, as it is to discover  
new ways of thinking about them."*

– Sir William Lawrence Bragg

Australian Physicist

Discoverer of Bragg's law of X-ray diffraction



## **Statement of Authorship Attribution**

This dissertation has been submitted to the School of Chemistry, Faculty of Science at the University of Sydney in order to fulfil the requirements for obtaining the PhD degree. The research presented here has been conducted under the supervision of Professor Brendan J. Kennedy at the School of Chemistry, the University of Sydney, and Dr Zhaoming Zhang in the Nuclear Fuel Cycle division at the Australian Nuclear Science and Technology Organisation. The research work was conducted from March 2020 to November 2023.

During this time, four months were spent at CentraleSupélec, Université Paris-Saclay, Paris, France under the supervision of Professor Gianguido Baldinozzi as part of the Scholarship AINSE ANSTO French Embassies (SAAFE) Research Internship program, funded by the Australian Institute of Nuclear Science and Engineering (AINSE). Additionally, four months were spent at the State University of New York, Stony Brook NY, USA under the supervision of Professor Karena W. Chapman as part of the Australian-American Postgraduate Fulbright Scholarship funded by the Kinghorn Foundation. Finally, two months were spent at the University of Tennessee, Knoxville TN, USA under the supervision of Professor Maik K. Lang as part of the United Uranium Scholarship administered by ANSTO.

The overall topic of the research presented here is an investigation into the various structure-functionality relationships of  $ABO_4$  metal oxides. This work was done with the following contributions. For each referenced manuscript, the PhD candidate is underlined with the corresponding author(s) bolded:

**Chapter 3** of this dissertation is published as three separate manuscripts, with a further manuscript currently under review:

- Mullens, B.G.; Avdeev, M.; Brand, H.E.A.; Mondal, S.; **Vaitheeswaran, G.**; **Kennedy, B.J.**; Insights into the Structural Variations in  $\text{Sm}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  and  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  Combined Experimental and Computational Studies. *Dalton Transactions*, **2021**, 50, 9103-9117.
- Mullens, B.G.; Saura-Múzquiz, M.; Marlton, F.P.; Avdeev, M.; Brand, H.E.A.; Mondal, S.; **Vaitheeswaran, G.**; Kennedy, B.J.; Beyond the Ionic Radii: A Multifaceted Approach to Understand Differences Between the Structures of  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  Fergusonites. *Journal of Alloys and Compounds*, **2023**, 930, 167399.
- Saura-Múzquiz, M.; Mullens, B.G.; Maynard-Casely, H.E.; **Kennedy, B.J.**; Neutron Diffraction Study of the Monoclinic–Tetragonal Phase Transition in  $\text{NdNbO}_4$  and  $\text{NdTaO}_4$ . *Dalton Transactions*, **2021**, 50, 11485-11497.
- Mullens, B.G.; Saura-Múzquiz, M.; Cordaro, G.; Marlton, F.P.; Maynard-Casely, H.E.; Zhang, Z.; Baldinozzi, G.; **Kennedy, B.J.**; Understanding the Ionic Conductivity of  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$  Through Variable Temperature *In Situ* Neutron Powder Diffraction Studies.  
*Under Revision for Chemistry of Materials.*

The study was designed with the help of Professor Brendan Kennedy and Dr Matilde Saura-Múzquiz. I synthesised each of the samples studied, with the exception of some  $LnNbO_4$  samples that were provided. Synchrotron X-ray powder diffraction data were collected by myself, Professor Brendan Kennedy, and Dr Matilde Saura-Múzquiz under the guidance of Dr Helen Brand on the Powder Diffraction beamline at the Australian Synchrotron. Neutron powder diffraction data were collected under the guidance of Dr Helen Maynard-Casely and Professor Maxim Avdeev on the Wombat and Echidna neutron diffractometers at the Australian Centre for Neutron Scattering. Computational work was conducted by Professor Ganapathy Vaitheeswaran and Dr Subrata Mondal at the University of Hyderabad, India. Ionic conductivity studies were conducted at the Université Paris-Saclay, Paris under the supervision of Dr Guilio Cordano and Professor Gianguido Baldinozzi.

**Chapter 4** of this dissertation is published as the following manuscript:

- Mullens, B.G.; Nicholas, M.K.; Marlton, F.P.; Brand, H.E.A.; Gu, Q.; Maynard-Casely, H.E.; **Kennedy, B.J.**; Long-Range A-Site Cation Disorder in  $NaA(MO_4)_2$  ( $M = Mo, W$ ) Double Scheelite Oxides. *Journal of Solid State Chemistry*, **2023**, *321*, 123871.

The study was designed with the help of Professor Brendan Kennedy. Myself and Ms Maria Nicholas synthesised each of the samples studied. Synchrotron X-ray powder diffraction data were collected by Dr Qingfen Gu during mail-in discretionary beamtime, with variable temperature data collected under the guidance of Dr Helen Brand on the Powder Diffraction beamline at the Australian Synchrotron. Neutron powder diffraction data were collected under the guidance of Dr Helen Maynard-Casely on the Echidna neutron diffractometer at the Australian Centre for Neutron Scattering. Neutron total scattering data were collected under the guidance of Drs Matt Tucker and Cheng Li on the NOMAD beamline at the Spallation Neutron Source at Oak Ridge National Laboratory, USA.

**Chapter 5** of this dissertation is published as two manuscripts, with an additional manuscript under review and a final manuscript in the early drafting stage:

- Mullens, B.G.; **Marlton, F.P.**; Nicholas, M.K.; Permana, A.J.; Avdeev, M.; **Vaitheeswaran, G.**; Li, C.; Liu, J.; Chater, P.A.; Kennedy, B.J.; Seeing the Unseen: The Structural Influence of the Lone Pair Electrons in the Photocatalyst PbWO<sub>4</sub>.  
*Under Revision for Inorganic Chemistry.*
- Mullens, B.G.; Marlton, F.P.; Nicholas, M.K.; Permana, A.J.; Brand, H.E.A.; Maynard-Casely, H.E.; Zhang, Z.; Baldinozzi, G.; **Kennedy, B.J.**; A Multifaceted Approach to Understand the Monoclinic-Tetragonal Phase Transition in BiVO<sub>4</sub>.  
*Manuscript in Preparation.*
- Hu, D.; Beauvais, M.L.; Kamm, G.E.; Mullens, B.G.; Sanchez Monserrate, B.A.; Vornholt, S.M.; Chupas, P.J.; **Chapman, K.W.**; Resolving Fast Relative Kinetics in Inorganic Solid-State Synthesis. *Journal of the American Chemical Society*, **2023**, *145* (49), 26545-26549.
- Hu, D.; Beauvais, M.L.; Mullens, B.G.; Sanchez Monserrate, B.A.; Vornholt, S.M.; Kamm, G.E.; Ferrari, J.J.; Chupas, P.J.; **Chapman, K.W.**; The RAPTR Furnace: A Rapid Heating and Cooling Sample Furnace for *In Situ* X-Ray Scattering Studies of Temperature-Induced Reactions. *Journal of Applied Crystallography*, **2024**, *57*, 88-93.

The study was designed with the help of Professor Brendan Kennedy and Dr Frederick Marlton. I synthesised each of the samples studied, with the help of Ms Maria Nicholas and Mr Ahmadi Jaya Permana. Variable temperature synchrotron X-ray powder diffraction data were collected by Professor Brendan Kennedy and Dr Helen Brand on the Powder

Diffraction beamline at the Australian Synchrotron. Variable temperature neutron powder diffraction data were collected by Professors Brendan Kennedy and Maxim Avdeev and Dr Helen Maynard-Casely, with the assistance of Ms Maria Nicholas and Mr Ahmadi Jaya Permana. X-ray total scattering data were collected during beamtime at the Argonne National Laboratory, USA, with assistance provided by Professor Karena Chapman, Dr Simon Vornholt, and Mr John Ferrari. Neutron total scattering data were collected under the guidance of Drs Matt Tucker and Cheng Li on the NOMAD beamline at the Spallation Neutron Source at Oak Ridge National Laboratory, USA. Computational work was conducted by Professor Ganapathy Vaitheeswaran and Mr Supratik Mukherjee at the University of Hyderabad, India.

**Chapter 6** of this dissertation contains references to two manuscripts already published:

- Marlton, F.P.; Mullens, B.G.; Chater, P.A.; **Kennedy, B.J.**; Tetrahedral Displacive Disorder in the Scheelite-Type Oxide  $\text{RbReO}_4$ . *Inorganic Chemistry*, **2022**, *61* (38), 15130-15137.
- Saura-Múzquiz, M; Marlton, F.P.; Mullens, B.G.; Manjón-Sanz, A.M.; Neufeind, J.C.; Everett, M.; Brand, H.E.A.; Mondal, S.; **Vaitheeswaran, G.**; **Kennedy, B.J.**; Understanding the Re-Entrant Phase Transition in a Non-Magnetic Scheelite. *Journal of the American Chemical Society*, **2022**, *144* (34), 15612-15621.

Two additional manuscripts describing this work are at the final stages of submission. The study was designed with the help of Professor Brendan Kennedy and Drs Matilde Saura-Múzquiz and Frederick Marlton.  $\text{CsReO}_4$  was synthesised with the assistance of Dr Matilde Saura-Múzquiz, and  $\text{TlTeO}_4$  was synthesised by Associate Professor Frederic Poineau at the University of Nevada, Las Vegas NV, USA. X-ray total scattering data were collected by Dr Phil Chater on the I15-1 beamline at Diamond Light Source, UK. Neutron

total scattering data were collected under the guidance of Drs Matt Tucker, Michelle Everett, Emily Van Auken, Cheng Li, and Alicia Manjón-Sanz on the NOMAD and POWGEN beamlines at the Spallation Neutron Source at Oak Ridge National Laboratory, USA. Any data that was used in this dissertation from the two previously published manuscripts was additionally reanalysed by myself.

**Chapter 7** of this dissertation is currently in the early drafting stage of a manuscript. The study was designed with the help of Professor Brendan Kennedy and Drs Matilde Saura-Múzquiz and Alex Yuen. The sample was synthesised with the assistance of Dr Alex Yuen. Laboratory X-ray powder diffraction data were collected by myself. Neutron powder diffraction data were collected with the assistance of Professor Maxim Avdeev on the Echidna beamline at the Australian Centre for Neutron Scattering. Magnetic susceptibility data were collected with the assistance of Dr Matilde Saura-Múzquiz, and analysed with the assistance of Professor Maxim Avdeev.



*In addition to the statements above, in cases where I am not the first or corresponding author of a published item, permission to include the published material has been granted by the appropriate party.*

---

Bryce G. Mullens - November 2023

*As supervisor for the candidature upon which this thesis is based, I can confirm that the authorship attribution statements above are correct.*

---

Professor Brendan J. Kennedy - November 2023



# Acknowledgements

The research work presented in this dissertation is the accumulation of the thoughts, inputs, insights, and guidance of many people from around the world. This work would not have been possible without the encouragement of the supportive environments I found myself in throughout my four years as a PhD student.

I would like to express my heartfelt gratitude to my academic supervisor, Professor Brendan Kennedy, for his unwavering support, guidance, and mentorship throughout both my Honours and PhD journeys. You not only provided me with the academic expertise necessary for this work, but offered insightful discussions, dedicated feedback, and the encouragement to think critically and to explore new ideas. I also enjoyed our more nuanced discussions, including the make-up of Australia's bowling attack in the cricket, the Melbourne Demons winning a flag after 57 years (Go Dees!), our favourite Mountain Goat brews, and the 'importance' of using double spaces in a Microsoft Word document. This simple paragraph cannot capture how much I appreciate your input.

I would also like to thank my secondary academic supervisor, Dr Zhaoming Zhang, for her assistance and encouragement since I was a bright-eyed Honours student back in 2019. I enjoyed our many journeys to the Australian Synchrotron conducting spectroscopy measurements, and our lunches in the ANSTO cafeteria. I look forward to us continuing to work together in the future.

To the Solid State Research Group at the University of Sydney, thank you for your constant encouragement and for providing the most amazing atmosphere to be apart of. To Professors Chris Ling and Siegbert ‘Siggi’ Schmid, thank you for your feedback and for providing a different and fresh perspective on my research work at the various group meetings. A big thank you to the senior members of our research group who were instrumental in getting my research started: Drs Adriano Pavan, Sean Injac, Junwei (Ben) Li, and Matt Sale. I would also like to especially thank my fellow students Alex Brown, Mia Brennan, Frederick Tiger Yang, Maria Nicholas, Ahmadi (Didi) Permana, Twishi Pandit, and Caleb Bennett. I hope to leave behind as supportive and collaborative of a research group as I initially joined.

I must also give a special thank you to the two postdocs that I worked under for a majority of my PhD studies: Drs Matilde Saura-Múzquiz and Frederick Marlton. I apologise for all the silly questions I’ve asked over the years and for being a constant pest, but thank you for allowing me to never lose my curiosity. Your hard work has allowed me to become the scientist (or, scientician) that I am today. I no longer consider you postdocs, but more like family. I look forward to the many more adventures The Golden Girls will share in the future.

I would like to extend my gratitude to the larger academic community at the University of Sydney for providing a conducive atmosphere for academic collaboration and growth. Thank you to the research groups I have worked closely with over the years within the School of Chemistry, such as the Maschmeyer Group for allowing us to synthesise materials using large amounts of hydrofluoric acid, and the Kepert and D’Alessandro Group for allowing me to use your equipment with thallium-containing sample vials. A special thank you to Drs Alex Yuen, Jyah Strachan, and Christopher Barnett for assisting in our larger collaborative projects on the structure and properties of photocatalysts and electrocatalysts. I would also like to extend my thanks to Drs Samuel Duyker, Paul

Fitzgerald, William Lewis, and Michelle Wood at Sydney Analytical for their constant upkeep of the instrumentation, as well as Dr René Macquart for his upkeep of the Thermophysical Property instruments within the School of Chemistry.

Thank you Professor Gianguido Baldinozzi for taking me on as a research student at the Université Paris Saclay for four months, providing invaluable guidance with my research, and helping me explore other possible directions including ionic conductivity, Raman spectroscopy, and group theory analysis. I will always be in awe of the sheer amount of knowledge you possess; from science, to the history of Europe, to what makes a good wine, and everything in between. This dissertation could not have been as thorough without your outstanding expertise and unwavering input. I'd also like to thank Professor Guilhem Dezanneau and Dr Giulio Cordaro for their assistance with collecting ionic conductivity data and for providing valuable insight. Thank you also to the larger research group at the Université Paris Saclay. Your farewell rendition of 'Land Down Under' by Men at Work will live in my head forever.

An enormous thank you to Professor Karena Chapman for taking me on as a visiting scholar at Stony Brook University of four months, and looking after me so well that I did not want to leave. Being a University of Sydney alumna, you have been a role model of mine since I was a senior undergraduate student. To spend time working with you and your research group (and to hopefully come back) has been a dream come true. Thank you to Professors Pete Chupas and John Parise for your constant feedback and suggestions with respect to my research. In particular, an enormous thank you to the larger Chapman Research Group: Drs Simon Vornholt and Zhihengyu (Woodrow) Chen, Ms Gabrielle Kamm, Mr John Ferrari, Ms Michelle Beauvais, Mr Bryan Sanchez Monserrate, Mr Patrick Kruszon-Oeffner, Mr Luke Tufaro, Mr Jan Hofmann, and Ms Danrui Hu. I learned far more about total scattering, the Fast & Furious Universe, and how to survive  $-19\text{ }^{\circ}\text{C}$  ( $-2\text{ }^{\circ}\text{F}$ ) winters that I thought possible. I cannot wait to see what

you all accomplish in the future.

Thank you Professor Maik Lang and Dr Eric O’Quinn for allowing me to work at the University of Tennessee, Knoxville for two months. Doing uranium synthesis is never an easy sell, but with your help we were able to collect some magnificent data. I look forward to establishing a robust collaboration with both of you in the future. Thank you also to the larger research group, especially Dr Alexandre Solomon, Mr John Hirtz, and Mr Cale Overstreet who put aside countless hours to help set up a uranium lab, synthesise uranium oxides, and collect data on them. I am truly fortunate to have had the opportunity to work in your research group.

To everybody at the Australian Centre for Neutron Scattering, but in particular Professor Maxim Avdeev and Dr Helen Maynard-Casely, thank you for your tireless efforts and constant (all hours) support in collecting the best neutron diffraction data we possibly could. Thank you for always being available, either to answer questions, discuss problems, or to perform sample changes. Thank you also to the beamline scientists I worked with at Oak Ridge National Laboratory, especially Drs Matt Tucker, Michelle Everett, Emily Van Auken, Cheng Li, and Alicia Manjón-Sanz. This work could not have been completed without your expertise and support.

A big thank you to all of the beamline scientists I have worked with over the years at the Australian Synchrotron: Drs Helen Brand, Anita D’Angelo, Qingfen Gu, Valerie Mitchell, and Bruce Cowrie. Throughout the COVID-19 lockdown, you kept my PhD research moving by remotely running experiences, and for that I am enormously thankful. I always enjoy my trips down to the Australian Synchrotron, and it means a lot to know that you always have time to help me with my research. Thank you also to Dr Phil Chater from the Diamond Light Source, who did the same thing throughout the COVID-19 lockdowns all the way over in the United Kingdom.

I would also like to acknowledge and thank all of the various scholarships and funding I have been fortunate enough to utilise in my time as a PhD student. The Research Training Program scholarship, Postgraduate Research Award (AINSE), the Postgraduate Research Support Scheme (USyd), the SAAFE Scholarship (AINSE), the United Uranium Trust Fund (ANSTO), as well as the Australian-American Fulbright Postgraduate Fellowship funded by the Kinghorn Foundation. Thank you also to AINSE for the international travel bursary to attend the North American Solid State Chemistry Conference in Calgary, Canada, and to the Society of Crystallographers in Australia and New Zealand (SCANZ) for the travel bursary to attend the International Union of Crystallography (IUCr) 26<sup>th</sup> Congress in Melbourne, Australia.

Finally, I would like to extend my most sincere thanks to my friends and family. Especially, my mother Carol and brother Daniel who has served as constant support throughout an extremely busy four years. I would also like to thank my partner, Tara, for listening to me come home each and every day talking about some silly experiment I did with potentially deadly chemicals (hydrofluoric acid, uranium oxide, thallium carbonate, sodium arsenate, accidentally synthesising polonium, *etc.*), or listening to some interesting trend I observed in my data.

*The research work presented in this dissertation was conducted on the lands of the Gadigal, Dharawal, Kulin, and Darkinjung people. I acknowledge the transition of custodianship and law of the Country on which work was performed on, and pay my respects to those who have cared and continue to care for this Country.*





# List of Publications

A number of publications have resulted or are in the process of being prepared from the research performed for this dissertation. These are included below, with publications labelled with an asterisk (\*) included in this dissertation.

- Mullens, B.G.; Saura-Múzquiz, M.; Cordaro, G.; Marlton, F.P.; Maynard-Casely, H.E.; Zhang, Z.; Baldinozzi, G.; Kennedy, B.J.; Understanding the Ionic Conductivity of HoNbO<sub>4</sub> and HoTaO<sub>4</sub> Through Variable Temperature *In Situ* Neutron Powder Diffraction Studies. *Under Revision for Chemistry of Materials*.\*
- Mullens, B.G.; Marlton, F.P.; Nicholas, M.K.; Permana, A.J.; Avdeev, M.; Vaitheeswaran, G.; Li, C.; Liu, J.; Chater, P.A.; Kennedy, B.J.; Seeing the Unseen: The Structural Influence of the Lone Pair Electrons in the Photocatalyst PbWO<sub>4</sub>. *Under Revision for Inorganic Chemistry*.\*
- Hu, D.; Beauvais, M.L.; Kamm, G.E.; Mullens, B.G.; Sanchez Monserrate, B.A.; Vornholt, S.M.; Chupas, P.J.; Chapman, K.W.; Resolving Fast Relative Kinetics in Inorganic Solid-State Synthesis. *Journal of the American Chemical Society*, **2023**, *145* (49), 26545-26549.\*

- Injac, S.D.; Mullens, B.G.; Romero, F.D.; Avdeev, M.; Barnett, C.; Yuen, A.K.L.; Patino, M.A.; Mukherjee, S.; Vaitheeswaran, G.; Singh, D.J.; Kennedy, B.J.; Shimakawa, Y.; Characterisation of  $\text{Pb}_2\text{Rh}_2\text{O}_7$  and  $\text{Y}_2\text{Rh}_2\text{O}_7$ : An Unusual Case of Pyrochlore Stabilisation Under High Pressure, High Temperature Synthesis Conditions. *Submitted to the Journal of Materials Chemistry C in November 2023.*
- Li, J.W.B.; Mullens, B.G.; Kamiyama, T.; Miao, P.; Kennedy, B.J.; Phase Transitions in  $\text{AgTaO}_4$  Using High Resolution Neutron Powder Diffraction. *Submitted to the Journal of Solid State Chemistry in November 2023.*
- Hu, D.; Beauvais, M.L.; Kamm, G.E.; Mullens, B.G.; Sanchez Monserrate, B.A.; Ferrari, J.J.; Vornholt, S.M.; Chupas, P.J.; Chapman, K.W.; The RAPTR Furnace: A Rapid Heating and Cooling Sample Furnace for *In Situ* X-Ray Scattering Studies of Temperature-Induced Reactions. *Journal of Applied Crystallography*, **2024**, 57, 88-93.\*
- Mullens, B.G.; Nicholas, M.K.; Marlton, F.P.; Brand, H.E.A.; Gu, Q.; Maynard-Casely, H.E.; Kennedy, B.J.; Long-Range A-Site Cation Disorder in  $\text{NaA}(\text{MO}_4)_2$  ( $M = \text{Mo}, \text{W}$ ) Double Scheelite Oxides. *Journal of Solid State Chemistry*, **2023**, 321, 123871.\*
- Mullens, B.G.; Saura-Múzquiz, M.; Marlton, F.P.; Avdeev, M.; Brand, H.E.A.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B.J.; Beyond the Ionic Radii: A Multifaceted Approach to Understand Differences Between the Structures of  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  Fergusonites. *Journal of Alloys and Compounds*, **2023**, 930, 167399.\*

- Saura-Múzquiz, M.; Marlton, F.P.; Mullens, B.G.; Liu, J.; Vogt, T.; Maynard-Casely, H.E.; Avdeev, M.; Blom, D.A.; Kennedy, B.J.; Cation and Lone Pair Order-Disorder in the Polymorphic Mixed Metal Bismuth Scheelite  $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$ . *Chemistry of Materials*, **2023**, *35* (1), 123-135.
- Saura-Múzquiz, M.; Mullens, B.G.; Avdeev, M.; Jharapla, P.K.; Vaitheeswaran, G.; Gupta, M.K.; Mittal, R.; Kennedy, B.J.; Experimental and Computational Insights into the Anomalous Thermal Expansion of  $(\text{NH}_4)\text{ReO}_4$ . *Journal of Solid State Chemistry*, **2022**, *315*, 123531.
- Marlton, F.P.; Mullens, B.G.; Chater, P.A.; Kennedy, B.J.; Tetrahedral Displacive Disorder in the Scheelite-Type Oxide  $\text{RbReO}_4$ . *Inorganic Chemistry*, **2022**, *61* (38), 15130-15137.\*
- Saura-Múzquiz, M.; Marlton, F.P.; Mullens, B.G.; Manjón-Sanz, A.M.; Neufeind, J.C.; Everett, M.; Brand, H.E.A.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B.J.; Understanding the Re-Entrant Phase Transition in a Non-Magnetic Scheelite. *Journal of the American Chemical Society*, **2022**, *144* (34), 15612-15621.\*
- Saura-Múzquiz, M.; Mullens, B.G.; Brand, H.E.A.; Kennedy, B.J.; Structure and Electronic Properties of a  $\mu$ -Oxo Ruthenium Bromide. *Journal of Solid State Chemistry*, **2022**, *311*, 123151.
- Mullens, B.G.; Avdeev, M.; Brand, H.E.A.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B.J.; Insights into the Structural Variations in  $\text{SmNb}_{1-x}\text{Ta}_x\text{O}_4$  and  $\text{HoNb}_{1-x}\text{Ta}_x\text{O}_4$  Combined Experimental and Computational Studies. *Dalton Transactions*, **2021**, *50*, 9103-9117.\*

- Mullens, B.G.; Zhang, Z.; Avdeev, M.; Brand, H.E.A.; Cowie, B.C.C.; D'Angelo, A.; Saura-Múzquiz, M.; Kennedy, B.J.; Average and Local Ordering of  $\text{Yb}_2(\text{Ti}_{2-x}\text{Yb}_x)\text{O}_{7-x/2}$  'Stuffed' Pyrochlores: The Development of a Robust Structural Model. *Journal of Solid State Chemistry*, **2021**, 122412.
- Mullens, B.G.; Zhang, Z.; Avdeev, M.; Brand, H.E.A.; Cowie, B.C.C.; Saura-Múzquiz, M.; Kennedy, B.J.; Effect of Long- and Short-Range Disorder on the Oxygen Ionic Conductivity of  $\text{Tm}_2(\text{Ti}_{2-x}\text{Tm}_x)\text{O}_{7-x/2}$  'Stuffed' Pyrochlores. *Inorganic Chemistry*, **2021**, 60 (7), 4517-4530.
- Saura-Múzquiz, M.; Mullens, B.G.; Maynard-Casely, H.E.; Kennedy, B.J.; Neutron Diffraction Study of the Monoclinic-Tetragonal Phase Transition in  $\text{NdNbO}_4$  and  $\text{NdTaO}_4$ . *Dalton Transactions*, **2021**, 50, 11485-11497.\*

# Table of Contents

|                                                                    |          |
|--------------------------------------------------------------------|----------|
| Declaration                                                        | i        |
| Preface                                                            | xi       |
| Acknowledgements                                                   | xvii     |
| List of Publications                                               | xxii     |
| Table of Contents                                                  | xxvii    |
| List of Figures                                                    | xxix     |
| List of Tables                                                     | li       |
| List of Abbreviations                                              | lv       |
| Abstract                                                           | lix      |
| <b>Part I: Introduction and Theoretical Background</b>             | <b>1</b> |
| <b>Chapter 1 Introduction</b>                                      | <b>3</b> |
| 1.1 The Need for a Carbon-Neutral Economy . . . . .                | 5        |
| 1.1.1 Materials Science . . . . .                                  | 6        |
| 1.1.2 The Hierarchy of Material Design . . . . .                   | 8        |
| 1.1.3 Metal Oxides as Functional Energy Materials . . . . .        | 10       |
| 1.2 Scheelite-Type Oxides . . . . .                                | 11       |
| 1.2.1 The Scheelite-Type Structure . . . . .                       | 12       |
| 1.2.2 Variations on the Scheelite-Type Structure . . . . .         | 15       |
| 1.2.2.1 Changes Due to Ionic Radii . . . . .                       | 16       |
| 1.2.2.2 Changes Due to Temperature . . . . .                       | 19       |
| 1.2.2.3 Changes Due to Pressure . . . . .                          | 24       |
| 1.2.3 Additional Changes in Symmetry Due to Substitution . . . . . | 27       |
| 1.3 Applications of $ABO_4$ -Type Materials . . . . .              | 30       |

|                  |                                                                                     |           |
|------------------|-------------------------------------------------------------------------------------|-----------|
| 1.3.1            | Solid Oxide Fuel Cells and $\text{LaNbO}_4$ . . . . .                               | 30        |
| 1.3.2            | Solid State Lasers and $\text{NaBi}(\text{WO}_4)_2$ . . . . .                       | 33        |
| 1.3.3            | Photocatalysts, $\text{BiVO}_4$ , and $\text{PbWO}_4$ . . . . .                     | 34        |
| 1.3.4            | Storage of Radioactive Waste and $\text{TlTcO}_4$ . . . . .                         | 35        |
| 1.3.5            | Spintronic Materials and $\text{CsMnF}_4$ . . . . .                                 | 37        |
| 1.4              | Dissertation Outline and Aims . . . . .                                             | 37        |
| <b>Chapter 2</b> | <b>Theory and Experimental Techniques</b>                                           | <b>41</b> |
| 2.1              | Understanding Functional Materials . . . . .                                        | 43        |
| 2.2              | Synthetic Methods . . . . .                                                         | 45        |
| 2.2.1            | Solid State Synthesis Techniques . . . . .                                          | 46        |
| 2.2.2            | Coprecipitation Synthesis Techniques . . . . .                                      | 47        |
| 2.3              | Long-Range Average Structure Determination . . . . .                                | 48        |
| 2.3.1            | Laboratory X-Ray Diffraction . . . . .                                              | 55        |
| 2.3.2            | Synchrotron X-Ray Diffraction . . . . .                                             | 58        |
| 2.3.3            | Neutron Powder Diffraction . . . . .                                                | 59        |
| 2.3.4            | Diffraction Modelling and Refinement Methods for Structure<br>Solutions . . . . .   | 60        |
| 2.4              | Short-Range Local Structure Determination . . . . .                                 | 63        |
| 2.4.1            | Pair Distribution Function Analysis . . . . .                                       | 64        |
| 2.4.2            | Total Scattering Infrastructure . . . . .                                           | 68        |
| 2.4.2.1          | X-Ray Total Scattering . . . . .                                                    | 68        |
| 2.4.2.2          | Neutron Total Scattering . . . . .                                                  | 70        |
| 2.5              | Physical Property Characterisation Techniques . . . . .                             | 72        |
| 2.5.1            | Electrochemical Impedance Spectroscopy for Ionic Conductivity                       | 72        |
| 2.5.2            | Solid State UV-Vis Spectroscopy for Band Gap Estimation . .                         | 75        |
| 2.5.3            | Physical Properties Measurement System for Magnetism . . .                          | 77        |
| <b>Part II:</b>  | <b>Deducing Structure-Property Relationships in Functional<br/>Energy Materials</b> | <b>80</b> |
| <b>Chapter 3</b> | <b>Ceramic Electrolytes for Solid Oxide Fuel Cells</b>                              | <b>81</b> |
| 3.1              | Introduction: $\text{LaNbO}_4$ as a Solid Electrolyte . . . . .                     | 83        |
| 3.1.1            | Expansion into $\text{LnNbO}_4$ and $\text{LnTaO}_4$ . . . . .                      | 83        |
| 3.2              | Synthesis Procedure and Experimental Methods . . . . .                              | 85        |
| 3.2.1            | Sample Synthesis . . . . .                                                          | 85        |
| 3.2.2            | Synchrotron X-ray and Neutron Powder Diffraction . . . . .                          | 86        |
| 3.2.3            | Physical Property Measurements . . . . .                                            | 87        |
| 3.3              | Structural Studies . . . . .                                                        | 88        |
| 3.3.1            | Structural Studies of $\text{LnNbO}_4$ . . . . .                                    | 89        |

|                  |                                                                                       |            |
|------------------|---------------------------------------------------------------------------------------|------------|
| 3.3.2            | Structural Studies of $LnTaO_4$ . . . . .                                             | 94         |
| 3.3.3            | Structural Studies of $Ln(Nb_{1-x}Ta_x)O_4$ . . . . .                                 | 99         |
| 3.3.4            | Computational Studies of $HoNbO_4$ and $HoTaO_4$ . . . . .                            | 104        |
| 3.4              | Heating and <i>In Situ</i> Studies . . . . .                                          | 106        |
| 3.4.1            | Response of $LnNbO_4$ to Heat . . . . .                                               | 107        |
| 3.4.2            | Response of $LnTaO_4$ to Heat . . . . .                                               | 115        |
| 3.4.3            | Determining Optimal Synthesis Conditions using <i>In Situ</i><br>Techniques . . . . . | 120        |
| 3.5              | Ionic Conductivity Studies of $HoNbO_4$ and $HoTaO_4$ . . . . .                       | 125        |
| 3.5.1            | Ionic Conductivity as a Function of Gas Environment . . . . .                         | 125        |
| 3.5.2            | Structural Studies of Ion Conduction Pathways . . . . .                               | 128        |
| 3.6              | Conclusions and Towards the Future Design of Solid Electrolytes . . .                 | 129        |
| <b>Chapter 4</b> | <b>Rare-Earth Ion Matrices for Solid State Lasers</b>                                 | <b>135</b> |
| 4.1              | Introduction: Solid State Lasers . . . . .                                            | 137        |
| 4.1.1            | Scheelite-Type Oxides as Solid State Lasing Materials . . . . .                       | 138        |
| 4.2              | Synthesis Procedure and Experimental Methods . . . . .                                | 141        |
| 4.2.1            | Sample Synthesis . . . . .                                                            | 141        |
| 4.2.2            | Synchrotron X-Ray and Neutron Powder Diffraction . . . . .                            | 142        |
| 4.3              | Structural Studies of $NaA(BO_4)_2$ . . . . .                                         | 143        |
| 4.3.1            | Synthesis and Space Group Determination . . . . .                                     | 143        |
| 4.3.2            | Rietveld Refinements of Double Scheelites . . . . .                                   | 146        |
| 4.3.3            | Neutron Total Scattering Studies . . . . .                                            | 150        |
| 4.3.4            | Variable Temperature Study of $NaBi(WO_4)_2$ . . . . .                                | 157        |
| 4.4              | Conclusions and Towards the Future Design of Lasing Materials . . .                   | 158        |
| <b>Chapter 5</b> | <b>Local Structure Studies of Photocatalysts</b>                                      | <b>161</b> |
| 5.1              | Introduction: Photocatalytic Water Splitting . . . . .                                | 163        |
| 5.1.1            | $BiVO_4$ and $PbWO_4$ as Photocatalysts . . . . .                                     | 164        |
| 5.2              | Synthesis Procedure and Experimental Methods . . . . .                                | 168        |
| 5.2.1            | Sample Synthesis . . . . .                                                            | 168        |
| 5.2.2            | Synchrotron X-Ray and Neutron Powder Diffraction . . . . .                            | 169        |
| 5.2.3            | X-Ray and Neutron Total Scattering . . . . .                                          | 171        |
| 5.3              | Structural Studies of $BiVO_4$ . . . . .                                              | 172        |
| 5.3.1            | Room Temperature Synchrotron X-Ray and Neutron Powder<br>Diffraction . . . . .        | 172        |
| 5.3.2            | Variable Temperature Synchrotron X-Ray Diffraction . . . . .                          | 174        |
| 5.3.3            | Variable Temperature Neutron Powder Diffraction . . . . .                             | 178        |
| 5.3.4            | X-Ray Total Scattering . . . . .                                                      | 184        |
| 5.3.5            | Neutron Total Scattering . . . . .                                                    | 189        |

|                                                                    |                                                                                          |            |
|--------------------------------------------------------------------|------------------------------------------------------------------------------------------|------------|
| 5.4                                                                | Structural Studies of $\text{PbWO}_4$ . . . . .                                          | 199        |
| 5.4.1                                                              | <i>In Situ</i> Synthesis Studies . . . . .                                               | 199        |
| 5.4.2                                                              | Room Temperature Synchrotron X-Ray and Neutron Powder<br>Diffraction . . . . .           | 202        |
| 5.4.3                                                              | Variable Temperature Neutron Powder Diffraction . . . . .                                | 203        |
| 5.4.4                                                              | X-Ray and Neutron Total Scattering . . . . .                                             | 205        |
| 5.4.5                                                              | Comparison to the Original $\text{CaWO}_4$ Scheelite . . . . .                           | 211        |
| 5.4.6                                                              | Computational Studies . . . . .                                                          | 215        |
| 5.5                                                                | Conclusions and Towards the Future Design of Photocatalysts . . . .                      | 217        |
| <b>Part III: Additional Studies of Functional Energy Materials</b> |                                                                                          | <b>222</b> |
| <b>Chapter 6</b>                                                   | <b>Safe Storage of Radioactive Waste</b>                                                 | <b>223</b> |
| 6.1                                                                | Introduction: Matrices for Radioactive Waste . . . . .                                   | 225        |
| 6.1.1                                                              | Similarities and Differences Between $\text{ATcO}_4$ and $\text{AReO}_4$ . . .           | 226        |
| 6.2                                                                | Synthesis Procedure and Experimental Methods . . . . .                                   | 228        |
| 6.2.1                                                              | Sample Synthesis . . . . .                                                               | 228        |
| 6.2.2                                                              | X-Ray and Neutron Total Scattering . . . . .                                             | 229        |
| 6.3                                                                | Structural Studies of $\text{CsReO}_4$ . . . . .                                         | 230        |
| 6.3.1                                                              | Long-Range Average Structure X-Ray Diffraction Studies . . .                             | 230        |
| 6.3.2                                                              | Short-Range Local Structure X-Ray PDF Studies . . . . .                                  | 236        |
| 6.4                                                                | Structural Studies of $\text{TlTcO}_4$ . . . . .                                         | 246        |
| 6.4.1                                                              | Long-Range Average Structure Neutron Powder Diffraction<br>Studies . . . . .             | 246        |
| 6.4.2                                                              | Short-Range Local Structure Neutron PDF Studies . . . . .                                | 251        |
| 6.5                                                                | Conclusions and Future Work . . . . .                                                    | 260        |
| <b>Chapter 7</b>                                                   | <b>Adventures Outside of Metal Oxides – Magnetism in<br/><math>\text{CsMnF}_4</math></b> | <b>263</b> |
| 7.1                                                                | Introduction: $\text{CsMnF}_4$ as a Spintronic Material . . . . .                        | 265        |
| 7.2                                                                | Synthesis Procedure and Experimental Methods . . . . .                                   | 268        |
| 7.2.1                                                              | Sample Synthesis . . . . .                                                               | 268        |
| 7.2.2                                                              | X-Ray and Neutron Powder Diffraction . . . . .                                           | 269        |
| 7.2.3                                                              | Physical Property Measurements . . . . .                                                 | 270        |
| 7.3                                                                | Room Temperature Nuclear Structure of $\text{CsMnF}_4$ . . . . .                         | 270        |
| 7.4                                                                | Magnetic Susceptibility Studies of $\text{CsMnF}_4$ . . . . .                            | 272        |
| 7.5                                                                | Magnetic Structure of $\text{CsMnF}_4$ . . . . .                                         | 274        |
| 7.6                                                                | Conclusions and Future Work . . . . .                                                    | 278        |
| <b>Part IV: Conclusions and Future Work</b>                        |                                                                                          | <b>281</b> |



---

|                   |                                                                      |            |
|-------------------|----------------------------------------------------------------------|------------|
| <b>Chapter 8</b>  | <b>Conclusion, Perspectives, and Future Work</b>                     | <b>283</b> |
| <b>Appendix A</b> | <b>Supporting Information</b>                                        | <b>289</b> |
| A.1               | Chapter 2: Theory and Experimental Techniques . . . . .              | 289        |
| A.2               | Chapter 3: Ceramic Electrolytes for Solid Oxide Fuel Cells . . . . . | 294        |
| A.3               | Chapter 4: Rare-Earth Ion Matrices for Solid State Lasers . . . . .  | 303        |
| A.4               | Chapter 5: Local Structure Studies of Photocatalysts . . . . .       | 307        |
| A.5               | Chapter 6: Safe Storage of Radioactive Waste . . . . .               | 311        |
| A.6               | Chapter 7: Adventures Outside of Metal Oxides . . . . .              | 312        |



# List of Figures

|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |    |
|-----|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 1.1 | An illustration of the materials science tetrahedron. This shows how the synthesis and processing, structure, functionality, and performance of materials are all interdependent of each other. . . . .                                                                                                                                                                                                                                                                                                                              | 7  |
| 1.2 | The $ABO_4$ tetragonal $I4_1/a$ scheelite-type structure with the (a) $AO_8$ edge-sharing polyhedra highlighted in blue, and the (b) $BO_4$ isolated tetrahedra highlighted in grey. The different bonding environments are highlighted in (c), with the two unique $A-O$ distances drawn in green and gold, and the unique $B-O$ distance drawn in purple. . . . .                                                                                                                                                                  | 12 |
| 1.3 | Phase diagram for $ABX_4$ materials by Errandonea <i>et al.</i> highlighting the possible phases accessible by altering the ionic radii of the $A$ - and $B$ -site cations, and the $X$ anions. <sup>44</sup> The phases that are the focus of this dissertation are highlighted by the shaded areas: (blue) tetragonal $I4_1/a$ scheelite, (green) monoclinic $I2/a$ and $P2/c$ fergusonite, (gold) tetragonal $I4_1/amd$ zircon, and (pink) orthorhombic $Pnma$ pseudo scheelite. . . . .                                          | 16 |
| 1.4 | The $ABX_4$ structures both stable at room temperature (a) tetragonal $I4_1/a$ scheelite-type, and (b) orthorhombic $Pnma$ pseudo scheelite-type. The difference between the two structures is the size of the $A$ -site cation (as visualised by the blue and pink spheres). The difference can also be visualised <i>via</i> the rotations of the $BO_4$ tetrahedra, with (a) rotated about the $c$ -axis, and (b) rotated about the $b$ -axis. . . . .                                                                            | 17 |
| 1.5 | The $ABX_4$ structures (a) tetragonal $I4_1/a$ scheelite-type, and two fergusonite-type structures (b) monoclinic $I2/a$ $M$ -type, and (c) monoclinic $P2/c$ $M'$ -type. By changing the ionic radii of the $B$ -site cation, the structural motif is changed from isolated $BX_4$ tetrahedra to edge-sharing $BX_6$ distorted octahedra. The difference between the $I2/a$ and $P2/c$ structures is visualised through the chains of $BX_6$ octahedra, with the chains ‘out-of-phase’ in $I2/a$ and ‘in-phase’ in $P2/c$ . . . . . | 19 |
| 1.6 | Relationships between the (top) tetragonal $I4_1/amd$ , (bottom left) monoclinic $Pnma$ , and (bottom right) tetragonal $I4_1/a$ structures. . . . .                                                                                                                                                                                                                                                                                                                                                                                 | 21 |

- 1.7 Relationship between the (left) monoclinic  $I2/a$  and (right) tetragonal  $I4_1/a$  structures. The phase transition proceeds through a breaking of the  $B-O_l$  bond governed by the  $\Gamma_2^+$  mode. . . . . 22
- 1.8 Relationship between the (a) tetragonal  $I4_1/amd$  scheelite-type aristotype, and (b) tetragonal  $I4_1/amd$  zircon-type structures. Although these phases are similar, they possess different connectivity. The different coloured spheres and tetrahedra are used to show that no phase transition occurs between these two structures. . . . . 25
- 1.9 Relationship between the (a) tetragonal  $I4_1/a$  and (b) tetragonal  $I\bar{4}$  structures. Of note is the splitting of the  $4b$  Wyckoff position in the  $I4_1/a$  structure to two distinct  $2b$  and  $2c$  Wyckoff positions in the  $I\bar{4}$  structure. This distinction allows for the possibility of cation ordering. . . . . 28
- 1.10 The crystal structure of (a)  $CsMnF_4$  and (b)  $CsFeO_4$ , both in the tetragonal  $P4/nmm$  space group. The aqua spheres represent  $Cs^+$ , the purple octahedra represent  $MnF_6$ , the brown octahedra represent  $FeF_6$ , and the white atoms represent  $F^-$ . . . . . 29
- 1.11 (a) The monoclinic  $I2/b$  crystal structure of  $BiVO_4$  consisting of  $BiO_8$  polyhedra (purple) and  $VO_4$  tetrahedra (orange), (b) the  $BiO_8$  polyhedra with four different Bi–O bond distances between 2.3–2.8 Å (indicated with different colours), (c) the tetragonal  $I4_1/a$  crystal structure of  $PbWO_4$  consisting of  $PbO_8$  polyhedra (black) and  $WO_4$  tetrahedra (grey), (d) the  $PbO_8$  polyhedra with two different Pb–O bond distances between 2.6–2.8 Å (indicated with different colours). . . . . 35
- 2.1 We often use materials science to rationalise how materials on the macroscale behave by understanding the arrangement of their atoms on the atomic scale. . . . . 44
- 2.2 Schematic diagram of Bragg diffraction using a two dimensional lattice. The atoms on the lattice are represented as blue circles, with the incoming photons as grey arrows. Photons  $A$  and  $B$  are scattered elastically from particles  $a$  and  $b$  respectively. For constructive interference between photons  $A$  and  $B$ , the extra distance travelled must be an integer multiple of the wavelength. . . . . 50

- 
- 2.3 X-ray diffraction on a sample of 8 k grit diamond powder collected on (a) a PANalytical X'Pert Pro copper source diffractometer, and (b) a STOE Stadi P monochromatic molybdenum source diffractometer. The relevant lattice planes, as notated by their ( $hkl$ ) Miller indices, are drawn on the diamond structure in (c–e). Note the ‘bump’ observed between  $10\text{--}15^\circ 2\theta$  in the molybdenum source pattern is an amorphous contribution from the borosilicate glass capillary used to house the sample. . . . . 51
- 2.4 Comparison of the different scattering of X-rays (black circles) and neutrons (blue squares) relative to atomic number,  $Z$ . For the neutron scattering lengths, the weighted average of the isotope distribution is used. The blue dashed line emphasises  $b_{\text{coh.}} = 0$ , with elements below this being negative scatterers. . . . . 54
- 2.5 X-ray diffraction on a sample of 8 k grit diamond powder collected on (blue) a PANalytical X'Pert Pro copper source diffractometer, and (green) a STOE Stadi P monochromatic molybdenum source diffractometer. The patterns have been plotted in (a)  $Q$  with (b) demonstrating the difference in peak-shape resolution, and (c)  $d$ -spacing with (d) demonstrating the difference in  $d_{\text{min.}}$ . The ‘bump’ in the STOE pattern is an amorphous contribution from the borosilicate glass capillary used to house the sample. 57
- 2.6 (a,c) X-ray Bragg diffraction and (b,d) X-ray pair distribution function data collected on lithium fluoro-sulfonylimide (Li-FSI) both (a,b) above and (c,d) below its melting point of  $T_{\text{mp}} = 143^\circ\text{C}$ . Data collected at the Argonne National Laboratory Advanced Photon Source beamline 11-ID-B. 66
- 2.7 A one dimensional chain of atoms may be arranged (a) in a ‘perfect’ line, or (b) slightly offset from each other, with the dotted line in (b) showing the ‘perfect’ line. Despite these local distortions, the average of each unit (denoted by  $\mu$ ) is still seen as the same. As diffraction averages over many hundreds of thousands of unit cells, it is often insensitive to these local distortions. . . . . 67
- 3.1 Representative Rietveld refinements against the synchrotron X-ray diffraction patterns of (a)  $\text{LaNbO}_4$  and (b)  $\text{LuNbO}_4$ . Each structure was refined to the monoclinic  $I2/a$  fergusonite-type structure. Data was collected to  $\sim 80^\circ 2\theta$ , with the insets highlighting the quality of the fit to the data. The black circles represent the data, the red line represents the calculated profile, the green line is the difference between the data and the calculated profile, and the blue ticks are the space group-allowed reflections. 89

- 
- 3.2 The refined lattice parameters for the  $LnNbO_4$  series, with (a) the  $a$  and  $c$  lattice parameters, (b) the  $b$  lattice parameter, (c) the monoclinic  $\beta$  angle, and (d) the unit cell volume. The error bars are smaller than the symbols, and the dashed lines have been drawn to guide the eyes. Note: For clarity, not all  $Ln^{3+}$  cations are listed on the top axes. . . . . 91
- 3.3 The refined structure for the  $LnNbO_4$  series, with (a)  $NbO_4$  tetrahedra, (b)  $NbO_6$  distorted octahedra, and (c)  $NbO_6$  distorted octahedra with individual Nb–O bonds labelled. The light green spheres are the  $La^{3+}$  ions and the dark green polyhedra are the  $Nb^{5+}$  environments. The blue and gold bonds are the regular  $NbO_4$  bonds, whereas the purple bonds are the Nb– $O_l$  bonds. . . . . 92
- 3.4 Composition dependence of the room temperature (a)  $Ln$ –O bond distances, and (b) Nb–O bond distances of the  $LnNbO_4$  structures. The dashed lines have been drawn to guide the eyes, with the averages drawn with a solid line. Note: For clarity, not all  $Ln^{3+}$  cations are listed on the top axes. . . . . 93
- 3.5 The (a) monoclinic  $P2_1/c$  structure, (b) monoclinic  $I2/a$  structure, and (c) monoclinic  $P2/c$  structure. The  $Ln^{3+}$  cations are drawn as coloured spheres, and the  $TaO_6$  polyhedra are drawn in brown. . . . . 94
- 3.6 Representative Rietveld plots for (a)  $PrTaO_4$  fitted to the monoclinic  $P2_1/c$  space group, (b)  $GdTaO_4$  fitted to the monoclinic  $I2/a$  space group, and (c)  $YbTaO_4$  fitted to the monoclinic  $P2/c$  space group. The black circles represent the data, the solid red lines are the calculated profile, the solid green lines are the difference between the observed and calculated intensities, and the blue ticks are the space group-allowed reflections. The insets highlight the quality of the data and fits at high  $2\theta$ . . . . . 96
- 3.7 Composition dependence of the room temperature (a) lattice parameters and (b) monoclinic  $\beta$  angle of the  $LnTaO_4$  series. Where not apparent, the error bars are smaller than the symbols. For the samples inside the grey area ( $Ln^{3+} = Ho, Dy, \text{ and } Tb$ ) single-phase samples of both the  $P2/c$  and  $I2/a$  polymorphs were recovered and studied. The dashed lines have been drawn to guide the eyes. . . . . 97
- 3.8 Composition dependence of the room temperature (a)  $Ln$ –O bond distances, (b) Ta–O bond distances, (c)  $LnO_8$  polyhedra volume, and (d)  $TaO_6$  polyhedra volume. The error bars are smaller than the symbols. For the samples inside the grey area ( $Ln^{3+} = Ho, Dy, \text{ and } Tb$ ) single-phase samples of both the  $P2/c$  and  $I2/a$  polymorphs were recovered and studied. The dashed lines have been drawn to guide the eyes, with the averages drawn with a solid line. . . . . 98

- 
- 3.9 The synchrotron X-ray diffraction data for (a)  $\text{Pr}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  probing the  $P2_1/c \rightarrow I2/a$ , (b)  $\text{Gd}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  probing the  $I2/a \rightarrow I2/a$ , and (c)  $\text{Yb}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  probing the  $P2_1/c \rightarrow I2/a$  solid solution series. . . . 100
- 3.10 The  $\text{Ln}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  solid solution series in the  $I2/a$  space group, with (a) the compositional dependence of the normalised unit cell volume. The values are normalised to the values of the corresponding  $\text{LnNbO}_4$  structure. (b) The linear dependence of the change in gradient of the unit cell volume between  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  in the  $I2/a$  space group. The dashed lines are linear fits the the data. . . . . 101
- 3.11 Composition dependence at room temperature of the solid solution series  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  for (a) Ho–O bond distances, (b) B–O bond distances, (c)  $\text{HoO}_8$  polyhedra volume, and (d)  $\text{BO}_6$  polyhedra volume. The dashed lines have been drawn the guide the eyes, with the averages drawn with a solid line. . . . . 102
- 3.12 (a) The compositional dependence of the  $B$  site  $y$  atomic coordinate in the  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  series. Where not apparent, the error bars are smaller than the symbols. (b) The  $\text{Ho}(\text{Nb,Ta})\text{O}_4$  monoclinic  $I2/a$  fergusonite-type structure, drawn with  $(\text{Nb,Ta})\text{O}_4$  tetrahedra for clarity. The  $\text{Ho}^{3+}$  cations are drawn as blue spheres, the  $\text{Nb}^{5+}$  cations as green spheres, the  $\text{Ta}^{5+}$  cations as brown spheres, and  $\text{O}^{2-}$  anions as red spheres. The unshaded tetrahedra shows the difference in position between the  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  coordinates in the tetrahedra environment. . . . . 103
- 3.13 (a) Electron charge density distribution plot of the  $I2/a$  phase of  $\text{HoTaO}_4$  in the (010) plane. The gold circle highlights the significant electron density between the  $\text{Ho}^{3+}$  and  $\text{Ta}^{5+}$  cations. (b) A skeletal crystal structure of the  $I2/a$  phase of  $\text{HoTaO}_4$  in the (010) plane, with the same area highlighted in the gold circle. This demonstrates there is significant covalent character associated with the longer Ta–O<sub>l</sub> bond. . . . . 105
- 3.14 Representative Rietveld refinements for the neutron powder diffraction data for  $\text{HoNbO}_4$ , measured at 1.54 Å. At low temperature, the structures were refined using a monoclinic  $I2/a$  model. At high temperature, the structures were refined using a tetragonal  $I4_1/a$  model. In both cases, the black circles represent the observed data, the solid red line represents the fit to the measured profile, the lower green line represents the differences between the observed and calculated profiles, and the blue tick marks show the positions of the space group-allowed reflections. . . . . 107

- 
- 3.15 Portions of the temperature dependent neutron powder diffraction patterns of  $\text{HoNbO}_4$  measured on heating to 1000 °C. The  $I2/a \rightarrow I4_1/a$  phase transition at  $\sim 775$  °C is indicated by the solid line. The data were collected at 1.54 Å. . . . . 108
- 3.16 Rietveld refinements for the variable temperature neutron diffraction of  $\text{HoNbO}_4$ , with (a) the  $a$  and  $c$  lattice parameters, (b) the unit cell volume, (c) the monoclinic  $\beta$  angle, and (d) the  $y$  atomic coordinate of  $\text{Nb}^{5+}$  plotted against the monoclinic  $\beta$  angle. The black dashed line represents the temperature of the  $I2/a \rightarrow I4_1/a$  phase transition, and the red dashed lines are fits described in the text. . . . . 110
- 3.17 Strain analysis based on the lattice parameters from the variable temperature Rietveld refinements of  $\text{HoNbO}_4$ . (a) The  $(\epsilon_1 - \epsilon_2)$  strain component, as calculated using the expressions from Equation 3.5, fitted over the whole measured temperature range, and (b) the fit performed in a range 50 °C below  $T_c$ , with  $\beta = 0.5$ . The same are shown for (c) and (d) with the  $\epsilon_6$  strain component. Although the data was fit down to 100 °C, the plots show from 400–800 °C for clarity. . . . . 113
- 3.18 The monoclinic  $\beta$  angle from the variable temperature Rietveld refinements of  $\text{HoNbO}_4$ . (a) The monoclinic  $\beta$  angle fitted over the whole measured temperature range, and (b) the fit performed in a range 50 °C below  $T_c$ , with  $\beta = 0.5$ . . . . . 114
- 3.19 Representative Rietveld refinements for the neutron powder diffraction data, measured at 1.54 Å. (c) At low temperature, the structure was refined using the monoclinic  $P2/c$  model. (b) At high temperature, the structure was refined using a tetragonal  $I4_1/a$  model. (a) Upon cooling, the structure was refined to the monoclinic  $I2/a$  model. In each case, the black circles represent the observed data, the solid red line represents the fit to the measured profile, the solid green line represents the differences between the observed and calculated profiles, and the blue tick marks show the positions of the space group-allowed reflections. . . . . 116
- 3.20 Portions of the temperature dependent neutron diffraction patterns of  $\text{HoTaO}_4$  measured on heating to 1500 °C. The  $P2/c$  and  $I4_1/a$  two-phase region is indicated by the dashed lines, whereas the  $I4_1/a \rightarrow I2/a$  phase transition upon cooling at  $\sim 1300$  °C is indicated by the solid line. The data were collected at 1.54 Å. . . . . 117



- 
- 3.21 Temperature dependence of the lattice parameters for  $\text{HoTaO}_4$  obtained by Rietveld refinements against neutron powder diffraction data. The data were collected as the sample was heated from room temperature to 1500 °C, and then as the sample was cooled to room temperature. For ease of comparison, the lattice parameters of the  $I$ -centred cells have been appropriately rescaled. The error bars are smaller than the symbols. . . . 117
- 3.22 Phase fraction the two phase first order phase transition in  $\text{HoTaO}_4$  upon heating. The two-phase region is highlighted in grey. . . . . 118
- 3.23 Temperature dependence of the (a) Nb–O bond distances calculated for  $\text{HoNbO}_4$  upon heating, and (b) Ta–O bond distances calculated for  $\text{HoTaO}_4$  upon cooling. The dotted line indicates the  $I2/a \rightarrow I4_1/a$  phase transition in both samples. Note the difference in the  $x$ -axis between the two plots. . . . . 119
- 3.24 Refined phase fraction values extracted from *in situ* neutron powder diffraction study of the  $\text{Ho}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  green powder, as a function of temperature. For clarity, data below 800 °C is not shown. Samples were rapidly heated (180 °C  $\text{hr}^{-1}$ ) to 1200 °C before being slowly heated (30 °C  $\text{hr}^{-1}$ ) to 1500 °C. The data were collected at 1.54 Å. . . . . 124
- 3.25 Conductivity results of  $\text{HoNbO}_4$  -  $I2/a$  (filled blue symbols),  $\text{HoTaO}_4$  -  $I2/a$  (filled green symbols), and  $\text{HoTaO}_4$  -  $P2/c$  (filled red symbols) in Arrhenius plots with logarithmic scale as a function of the inverse of the temperature measured at 850–600 °C in (a) air, (b) Ar, (c) wet Ar, and (d) wet 5%  $\text{H}_2$  in Ar. . . . . 126
- 3.26 Conductivity results on a logarithmic scale (left axis) and activation energy (right scale) as a function of the atmosphere measured from 850–600 °C for (a)  $\text{HoNbO}_4$ , (b)  $\text{HoTaO}_4$  -  $I2/a$ , and (c)  $\text{HoTaO}_4$  -  $P2/c$ . As  $\text{HoNbO}_4$  exhibits a  $I2/a \rightarrow I4_1/a$  phase transition, the activation energy of both the monoclinic  $I2/a$  and tetragonal  $I4_1/a$  phases are plotted. . . . . 127
- 3.27 Refined structure of  $\text{HoTaO}_4$  ( $I2/a$ ) at room temperature. The solid green and orange lines represent the O(1)–O(1) distances, whilst the dashed purple line represents the O(1)–O(2) distance. . . . . 128
- 4.1 The crystal structures of some well known solid state lasing materials. (a)  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , (b)  $\text{LaMgAl}_{11}\text{O}_{19}$ , and (c)  $\text{YVO}_4$ . The teal environments are  $\text{Y}^{3+}$ , blue environments are  $\text{Al}^{3+}$ , and orange environments are  $\text{V}^{5+}$ . The disordered environments in (b) are shown as  $\text{La}^{3+}$  green and  $\text{Mg}^{2+}$  pink partially-filled spheres, with vacancies shown in white. . . . . 137

- 
- 4.2 The  $AA'B_2O_8$  scheelite-type structure consisting of  $(A, A')O_8$  polyhedra (not drawn) and  $BO_4$  tetrahedra. (a) The  $I4_1/a$  space group, showing a random arrangement of two different cations across the  $4b$  Wyckoff position. (b) The  $I\bar{4}$  space group, showing a fully ordered arrangement of  $A$ -site cations with  $A$  on the  $2b$  and  $A'$  at the  $2c$  Wyckoff position. . . . . 139
- 4.3 (a) Synchrotron X-ray and (b) neutron powder diffraction patterns of  $NaA(WO_4)_2$  ( $A^{3+} = \text{La, Pr, Nd, Sm, Lu, and Bi}$ ). The  $NaSm(WO_4)_2$  sample was not analysed using neutron powder diffraction due to the large neutron absorption cross section of Sm. Each diffraction pattern has been offset vertically for visibility. . . . . 144
- 4.4 Influence of ordering of the  $Na^+$  and  $Bi^{3+}$  cations in  $NaBi(WO_4)_2$  across the  $2b$  and  $2c$  sites of  $I\bar{4}$  space group model. The black circles represent the observed synchrotron X-ray powder diffraction data, and the solid lines represent different extents of ordering, from 100:0  $Na^+$  to  $Bi^{3+}$  on the  $2c$  site (fully ordered) to 50:50  $Na^+$  to  $Bi^{3+}$  on the  $2c$  site (fully disordered). The fully disordered model is comparable to that of the fully disordered  $I4_1/a$  model. . . . . 145
- 4.5 Rietveld refinement plots of (a,b)  $NaLa(WO_4)_2$  and (c,d)  $NaBi(WO_4)_2$  fitted in the tetragonal space group  $I4_1/a$ . The black circles are the observed data, the solid red line is the calculated profile, and the solid green line is the difference between the observed and calculated intensities. The blue vertical tick marks show the positions of the space group-allowed reflections. The synchrotron X-ray diffraction insets highlight the quality of the data. . . . . 147
- 4.6 Composition dependence of the (a) lattice parameters and (b) unit cell volume for the  $NaA(WO_4)_2$  ( $A^{3+} = \text{La, Pr, Nd, Sm, Lu, and Bi}$ ) oxides. The values were obtained by Rietveld refinement against a combined synchrotron X-ray and neutron powder diffraction dataset to the  $I4_1/a$  structural model, except for  $A^{3+} = \text{Sm}$ , where only the X-ray dataset was used (indicated by hollow symbols) due to the large neutron absorption cross section of Sm. The error bars are smaller than the symbols, and the dashed lines have been drawn to guide the eyes. . . . . 147
- 4.7 Composition dependence of the (a)  $A$ –O bond distances, (b) W–O bond distance, (c) difference between the two  $A$ –O distances, and (d) volume of the  $AO_8$  polyhedra of the  $NaA(WO_4)_2$  oxides derived from Rietveld refinements. Where not apparent, the error bars are smaller than the symbols. The dashed lines have been drawn to guide the eyes. . . . . 149
- 4.8 Neutron pair distribution function data of (green)  $NaLa(WO_4)_2$ , (red)  $NaLu(WO_4)_2$ , and (purple)  $NaBi(WO_4)_2$ . . . . . 150

- 
- 4.9 Fits to the neutron pair distribution function data at 100 K of  $\text{NaLa}(\text{WO}_4)_2$  over a range of 1.2–30 Å to the (a) disordered  $I4_1/a$  and (b) ordered  $I\bar{4}$  models. The blue circles represent the data, the red line represents the fit to the data, and the green line represents the difference between the two. . . . . 152
- 4.10 The refined  $\text{AO}_8$  polyhedra volumes of the  $\text{NaLa}(\text{WO}_4)_2$  in (a) disordered  $I4_1/a$  and (b) ordered  $I\bar{4}$  over a range of 1.2–30 Å. The yellow spheres represent  $\text{Na}^+$ , whereas the green spheres represent  $\text{La}^{3+}$ . . . . . 154
- 4.11 Neutron pair distribution function fits to  $\text{NaLa}(\text{WO}_4)_2$  conducted over the range of 12–40 Å to the  $I\bar{4}$  model. A fixed distribution of  $\text{Na}^+$  and  $\text{La}^{3+}$  across the  $2c$  Wyckoff position was modelled, and the  $R_{wp}$  value was used to assess the quality of the fits. . . . . 154
- 4.12 Fits to the neutron pair distribution function data at 100 K of  $\text{NaBi}(\text{WO}_4)_2$  over a range of 1.2–30 Å to the (a) disordered tetragonal  $I4_1/a$ , (b) ordered tetragonal  $I\bar{4}$  and (c) disordered monoclinic  $I2/b$  models. The blue circles represent the data, the red line represents the fit to the data, and the green line represents the difference between the two. . . . . 155
- 4.13 Normalised lattice parameters and unit cell volume for  $\text{NaBi}(\text{WO}_4)_2$  upon heating, obtained from Rietveld refinements of synchrotron X-ray diffraction data. . . . . 157
- 5.1 The three phases of  $\text{BiVO}_4$ . (a) The monoclinic-fergusonite form of space group  $I2/b$ , (b) the tetragonal-scheelite form of space group  $I4_1/a$ , and (c) the tetragonal-zircon form of space group  $I4_1/amd$ . Note that the  $I2/b \rightarrow I4_1/a$  phase transition is reversible with both temperature and pressure, whereas the  $I4_1/amd \rightarrow I4_1/a$  is irreversible. . . . . 164
- 5.2 The structure of (a)  $\alpha\text{-PbO}$  ( $Pbcm$ ). The four short Pb–O bonds reflect the projection of the lone pair electron density in the opposite direction (along the  $a$ -axis). (b) The structure of  $\text{PbS}$  ( $Fm\bar{3}m$ ). The centrosymmetry of  $\text{Pb}^{2+}$  in the  $\text{PbS}_6$  octahedra, and the six Pb–S bonds of identical length indicate limited lone pair stereoactivity. . . . . 166
- 5.3 Rietveld refinements against the (a) synchrotron X-ray diffraction and (b) neutron powder diffraction data of  $\text{BiVO}_4$  at room temperature. The black circles represent the data, the red line represents the calculate profile of the monoclinic fergusonite  $I2/b$  (and diamond in the synchrotron X-ray diffraction data), the green line represents the difference between the data and the calculated profile, and the blue ( $I2/b$ ) and orange ( $Fd\bar{3}m$ ) tick marks represent the space group-allowed reflections. . . . . 173

- 
- 5.4 Rietveld refinements for the synchrotron X-ray diffraction variable temperature dataset of  $\text{BiVO}_4$ , with (a) the  $a$  and  $c$  lattice parameters, (b) the unit cell volume, (c) the monoclinic  $\gamma$  angle, and (d) the  $z$  atomic coordinates of  $\text{Bi}^{3+}$  and  $\text{V}^{5+}$  plotted against each other. The black dashed line represents the temperature of the  $I2/b \rightarrow I4_1/a$  phase transition, and the red dashed line is a fit described in the text. . . . . 175
- 5.5 (a) Synchrotron X-ray diffraction data for  $\text{BiVO}_4$  heating from 300–700 K, highlighting the (200) and (020) reflections in the low temperature data, and (004) in the high temperature data. (b) The plotted full width at half maximum of the reflections across the temperature range, fitted using two Gaussians of equal width. The dotted line indicates the  $I2/b \rightarrow I4_1/a$  phase transition. . . . . 176
- 5.6 Rietveld refinements for  $\text{BiVO}_4$  using neutron powder diffraction at (a) 723 K refined to the  $I4_1/a$  space group, (b) 300 K refined to the  $I2/b$  space group, and (c) 3 K refined to the  $I2/b$  space group. The black circles represent the data, the red lines represent the calculated profile, and the green line represents the difference between the data and the calculated profile, and the blue tick marks represent the space group-allowed reflections. 180
- 5.7 Rietveld refinements for the neutron powder diffraction variable temperature dataset of  $\text{BiVO}_4$ , with (a) the  $a$  and  $c$  lattice parameters, (b) the unit cell volume, (c) the monoclinic  $\gamma$  angle, and (d) the atomic displacement parameters of  $\text{Bi} + \text{V}$ , as well as  $\text{O}$ . The black dashed line represents the temperature of the  $I2/b \rightarrow I4_1/a$  phase transition. . . . . 181
- 5.8 Temperature dependence of the (a)  $\text{Bi-O}$  bond distances and (b)  $\text{V-O}$  bond distances upon heating. The dotted lines indicate the  $I2/b \rightarrow I4_1/a$  phase transition. . . . . 182
- 5.9 Temperature dependence of the normalised (a)  $\text{HoO}_8$  and  $\text{NbO}_4$ , and (b)  $\text{BiO}_8$  and  $\text{VO}_4$  polyhedra volumes. The dotted lines indicate the phase transition. The solid lines have been drawn to guide the eyes. . . . . 183
- 5.10 Rietveld refinements for  $\text{BiVO}_4$  using synchrotron X-ray diffraction at (a) 600 K refined to the  $I4_1/a$  space group, (b) 500 K refined to the  $I2/b$  space group, and (c) 400 K refined to the  $I2/b$  space group. The black circles represent the data, the red lines represent the calculated profile, and the green line represents the difference between the data and the calculated profile, and the blue tick marks represent the space group-allowed reflections. 185

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |     |
|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.11 | Rietveld refinements to the variable temperature datasets of $\text{BiVO}_4$ collected using (a–d) the Australian Synchrotron, (e–g) the Advanced Photon Source, and (h–k) Wombat. The black circles represent the data, the red lines represent the calculated profile, and the green line represents the difference between the data and the calculated profile. The anomalous peak shapes identified in the Australian Synchrotron data are identified as the result of domain wall broadening within $\text{BiVO}_4$ . . . . .                                                                                      | 186 |
| 5.12 | X-ray pair distribution function data for $\text{BiVO}_4$ . The data were taken at 400 K (blue), 500 K (orange), and 600 K (red). . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 187 |
| 5.13 | X-ray pair distribution function fits for the variable temperature dataset of $\text{BiVO}_4$ over a range of 1.0–30 Å. Data taken at (a) 600 K and fit to the $t$ - $s$ $I4_1/a$ model, and at (b) 400 K and fit to the $m$ - $f$ $I2/b$ model. . . . .                                                                                                                                                                                                                                                                                                                                                                | 188 |
| 5.14 | XPDF data for $\text{BiVO}_4$ at 400 K fitted over a range of (a) 1.0–30 Å and (b) 3.3–30 Å. (c) The calculated partial fits, with focus placed on the cation–cation distances. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles. . . . .                                                                                                                                                                                                                                      | 189 |
| 5.15 | Crystallographic models for (a) $t$ - $s$ $I4_1/a$ , based on the high-temperature structure of $\text{BiVO}_4$ , (b) $m$ - $f$ $I2/b$ , based on the room-temperature structure of $\text{BiVO}_4$ , and (c) the monoclinic $P2_1/c$ , based on the room temperature structure of $\text{TlReO}_4$ . . . . .                                                                                                                                                                                                                                                                                                           | 190 |
| 5.16 | Neutron pair distribution function data fits to $\text{BiVO}_4$ at 100 K for (a) $t$ - $s$ $I4_1/a$ , (b) $m$ - $f$ $I2/b$ , and (c) monoclinic $P2_1/c$ with rigid $\text{VO}_4$ tetrahedra, and (d) monoclinic $P2_1/c$ with flexible $\text{VO}_4$ tetrahedra. The data is fitted over a range of 1.2–30 Å, with the first half highlighting the fit from 1.2–6.0 Å, and the second half highlighting from 6.0–30 Å. The blue dots represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles. . . . . | 191 |
| 5.17 | Distribution of Bi–O bond distances in the $\text{BiO}_8$ polyhedra of $\text{BiVO}_4$ extracted from the small box fits of the neutron pair distribution function data using the (a) $t$ - $s$ $I4_1/a$ , (b) $m$ - $f$ $I2/b$ , (c) $P2_1/c$ with rigid $\text{VO}_4$ tetrahedra, and (d) $P2_1/c$ with flexible $\text{VO}_4$ tetrahedra models. . . . .                                                                                                                                                                                                                                                             | 193 |
| 5.18 | Distribution of V–O bond distances in the $\text{VO}_4$ tetrahedra of $\text{BiVO}_4$ extracted from the small box fits of the neutron pair distribution function data using the (a) $t$ - $s$ $I4_1/a$ , (b) $m$ - $f$ $I2/b$ , (c) $P2_1/c$ with rigid $\text{VO}_4$ tetrahedra, and (d) $P2_1/c$ with flexible $\text{VO}_4$ tetrahedra models. . . . .                                                                                                                                                                                                                                                              | 193 |

- 
- 5.19 Distribution of O–V–O bond angles in the  $\text{VO}_4$  tetrahedra of  $\text{BiVO}_4$  extracted from the small box fits of the neutron pair distribution function data using the (a)  $t$ - $s$   $I4_1/a$ , (b)  $m$ - $f$   $I2/b$ , (c)  $P2_1/c$  with rigid  $\text{VO}_4$  tetrahedra, and (d)  $P2_1/c$  with flexible  $\text{VO}_4$  tetrahedra models. . . . . 194
- 5.20 Neutron pair distribution function fits to  $\text{BiVO}_4$  at 100 K for (a) the  $m$ - $f$   $I2/b$ , and (b) the monoclinic  $P2_1/c$  model with flexible  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra. (c,d) The calculated partial contributions of each atom–atom pair. The data is fitted over a range of 1.2–30 Å, with a focus on 1.0–6.0 Å. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles. . . . . 194
- 5.21 Neutron pair distribution function fits to  $\text{BiVO}_4$  at 550 K for (a)  $t$ - $s$   $I4_1/a$ , (b)  $m$ - $f$   $I2/b$ , (c) monoclinic  $P2_1/c$  with rigid  $\text{VO}_4$  tetrahedra, and (d) monoclinic  $P2_1/c$  with flexible  $\text{VO}_4$  tetrahedra. The data is fitted over a range of 1.2–30 Å, with the first half highlighting the fit from 1.2–6.0 Å, and the second half highlighting from 6.0–30 Å. The blue dots represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles. . . . . 195
- 5.22 The (left, purple) Bi–O and (right, orange) V–O bond distances from the variable temperature neutron pair distribution function data fit to the flexible monoclinic  $P2_1/c$  model. . . . . 197
- 5.23 The phase evolution during the reaction of  $\text{PbO}$  and  $\text{WO}_3$  at 750 °C within the rapidly-actuating pneumatic thermal reactor furnace, as quantified from Rietveld refinements of the time-resolved X-ray powder diffraction data. The solid vertical line indicates a change in the  $x$ -axis scale from seconds to minutes. . . . . 200
- 5.24 The polyhedra environments for  $\text{W}^{6+}$  in each of the three Rietveld refined phases. (a)  $\text{WO}_6$  octahedra in  $\text{WO}_3$  ( $Pcnb$ ), (b) strained  $\text{WO}_6$  octahedra in  $\text{Pb}_3\text{WO}_6$  ( $P2_1/n$ ) with the four short W–O bonds drawn in blue and the two long W–O bonds drawn in green, and (c)  $\text{WO}_4$  tetrahedra in  $\text{PbWO}_4$  ( $I4_1/a$ ). . . . . 201
- 5.25 Combined Rietveld refinements against the (a) synchrotron X-ray and (b) neutron powder diffraction data of  $\text{PbWO}_4$  at room temperature. The structure was refined to the  $t$ - $s$   $I4_1/a$  space group, with the inset highlighting the quality of the fit to the synchrotron X-ray diffraction data. The black circles represent the data, the red line represents the calculated profile, the green line is the difference between the data and the calculated profile, and the blue ticks are the space group-allowed reflections. . . . . 203

- 
- 5.26 Rietveld refinements of  $\text{PbWO}_4$  to the  $t$ - $s$   $I4_1/a$  space group measured at 3 K using neutrons of wavelength (a) 1.30 and (b) 2.44 Å. The black circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles, and the blue markers are the space group-allowed reflections. . . . . 204
- 5.27 (a) X-ray pair distribution function fits of  $\text{PbMoO}_4$  at 300 K to the long-range average  $t$ - $s$   $I4_1/a$  structure. (b) Neutron pair distribution function fits of  $\text{PbWO}_4$  at 300 K to the long-range average  $t$ - $s$   $I4_1/a$  structure. The data were fitted over a range of 1.2–30 Å, with the first half highlighting the fit from 1.2–8.0 Å, and the second half highlighting from 8.0–30 Å. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles. . . . . 205
- 5.28 Neutron pair distribution function fits to  $\text{PbWO}_4$  at 115 K for (a)  $t$ - $s$   $I4_1/a$ , (b)  $m$ - $f$   $I2/b$ , (c) monoclinic  $P2_1/c$  with rigid  $\text{WO}_4$  tetrahedra, and (d) monoclinic  $P2_1/c$  with flexible  $\text{WO}_4$  tetrahedra. The data was fitted over a range of 1.2–30 Å, with the first half highlighting the fit from 1.2–5.0 Å, and the second half highlighting from 5.0–30 Å. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles. . . . . 207
- 5.29 Distribution of Pb–O bond distances in the  $\text{PbO}_8$  polyhedra of  $\text{PbWO}_4$  for the four neutron pair distribution function fits with (a) the  $t$ - $s$   $I4_1/a$ , (b) the  $m$ - $f$   $I2/b$ , (c) the monoclinic  $P2_1/c$  with rigid  $\text{WO}_4$  tetrahedra, and (d) the monoclinic  $P2_1/c$  with flexible  $\text{WO}_4$  tetrahedra angles. . . . . 208
- 5.30 Distribution of W–O bond distances in the  $\text{WO}_4$  tetrahedra of  $\text{PbWO}_4$  for the four neutron pair distribution function fits with (a) the  $t$ - $s$   $I4_1/a$ , (b) the  $m$ - $f$   $I2/b$ , (c) the monoclinic  $P2_1/c$  with rigid  $\text{WO}_4$  tetrahedra, and (d) the monoclinic  $P2_1/c$  with flexible  $\text{WO}_4$  tetrahedra angles. . . . . 208
- 5.31 Distribution of O–W–O angles in the  $\text{WO}_4$  tetrahedra of  $\text{PbWO}_4$  for the four neutron pair distribution function fits with (a) the  $t$ - $s$   $I4_1/a$ , (b) the  $m$ - $f$   $I2/b$ , (c) the monoclinic  $P2_1/c$  with rigid  $\text{WO}_4$  tetrahedra, and (d) the monoclinic  $P2_1/c$  with flexible  $\text{WO}_4$  tetrahedra angles. . . . . 209

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |     |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.32 | Partial neutron pair distribution functions plotted for $\text{PbWO}_4$ at 115 K using the (a,c) tetragonal $I4_1/a$ model, and (b,d) monoclinic $P2_1/c$ model with flexible $\text{PbO}_8$ polyhedra and $\text{WO}_4$ tetrahedra. Data was fitted across the 1.2–30 Å range. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles. . . . .                                                | 209 |
| 5.33 | Neutron pair distribution function fits to the $t$ - $s$ $I4_1/a$ structural model with anisotropic atomic displacement parameters. (a) $\text{CaWO}_4$ at 100 K, and (b) $\text{PbWO}_4$ at 115 K. The data was fitted over a range of 1.2–10 Å. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles. . . . .                                                                              | 214 |
| 6.1  | Rietveld refinements to the X-ray Bragg data of $\text{CsReO}_4$ at (a) 700 K to the tetragonal $I4_1/a$ space group, (b) 400 K to the orthorhombic $Pnma$ space group, and (c) 100 K to the orthorhombic $Pnma$ space group. The insets show the high quality fit to the data at high $Q$ . The black circles represent the data, the red line represents the fit to the data, the green line represents the difference between the data and the fit, and the blue dashes represent the space group-allowed reflections. . . . . | 231 |
| 6.2  | Rietveld refinements for the variable temperature data of $\text{CsReO}_4$ , with (a) the $a$ and $b$ lattice parameters, (b) the unit cell volume, (c) the atomic displacement parameters measured as $B_{eq.}$ , and (d) the relationship between the square of the strain in the orthorhombic $Pnma$ phase and the temperature. the black dashed line represents the temperature of the $Pnma \rightarrow I4_1/a$ phase transition, and the red dashed line represents a linear fit. . . . .                                   | 232 |
| 6.3  | (a) The $R_{wp}$ values from the Rietveld refinements of (black squares) orthorhombic $Pnma$ , (red circles) tetragonal $I4_1/a$ , and (green triangles) tetragonal $I4_1/amd$ . (b) The refined oxygen $x$ atomic coordinate from the Rietveld refinements to the tetragonal $I4_1/a$ model. . . . .                                                                                                                                                                                                                             | 235 |
| 6.4  | Variable temperature X-ray pair distribution function data of $\text{CsReO}_4$ at 100 (blue), 300 (green), 500 (orange), and 700 K (red). The vertical markers correspond to some of the nearest atom–atom pairs in both the orthorhombic $Pnma$ at 100 K (above) and the tetragonal $I4_1/a$ structure at 700 K (below). Black arrows indicate extra features in the pair distribution function that are not described by the model. . . . .                                                                                     | 237 |



- 
- 6.5 A comparison of the (a,c) synchrotron X-ray Bragg diffraction and (b,d) X-ray pair distribution function data at two pairs of temperatures: (a,b) 400 and 550 K, and (c,d) 100 and 300 K. In each panel, the red line represents the higher temperature data and the blue line represents the lower temperature data. In the synchrotron X-ray diffraction plots, the space group-allowed reflections are indicated, whereas in the X-ray pair distribution function data, the cation–cation distances are indicated. . . . 238
- 6.6 Variable temperature X-ray pair distribution function data of CsReO<sub>4</sub> at (a) 600 K fitted to the tetragonal  $I4_1/a$  model, (b) 400 K fitted to the orthorhombic  $Pnma$  model, and (c) 100 K fitted to the orthorhombic  $Pnma$  model. The blue circles represent the data, the red line represents the small box fit to the data, and the green line represents the difference between the two. . . . . 240
- 6.7 Results from the fits of the (a,c,e,g) X-ray Bragg diffraction and (b,d,f,h) X-ray pair distribution function of the CsReO<sub>4</sub> data from 100–800 K using the orthorhombic  $Pnma$  (black), tetragonal  $I4_1/a$  (red), and  $I4_1/amd$  (green) models. (a,b) The  $R_{wp}$  from the Bragg fits, and the  $R$  parameter from the X-ray pair distribution function fits, with the parameter described in text. (c,d) The unit cell volume (UCV) across the entire temperature range. (e,f) The atomic displacement parameters extracted for Cs<sup>+</sup> and Re<sup>7+</sup> from the X-ray Bragg ( $B_{eq.}$ ) and the X-ray pair distribution function ( $B_{high}$ ) fits. (g,h) The Re–O bond distances, with an additional peak-fitting technique performed for the X-ray pair distribution function data described in text. For clarity, the error bars have been omitted. The dashed line at 450 K represents the  $Pnma \rightarrow I4_1/a$  phase transition observed in the X-Ray Bragg fits, whereas the dotted line at 700 K represents the onset of local disorder in the X-ray pair distribution function. . . . . 241
- 6.8 Results from the variable  $r$  range X-ray pair distribution function fits with the  $I4_1/a$  model. The value of  $\Delta l$  is described in text, with two different  $r_{max}$  of 10 and 30 Å used. The values of  $\Delta a$ ,  $\Delta c$ , and  $\Delta UCV$  correspond to the differences between the lattice parameters between the two fits. . . . 244
- 6.9 Rietveld refinements to the neutron Bragg data of TlTcO<sub>4</sub> at (a) 600 K to the tetragonal  $I4_1/amd$  space group, (b) 450 K to the orthorhombic  $Pnma$  space group, (c) 300 K to the orthorhombic  $Pnma$  space group, and (d) 50 K to the orthorhombic  $Pnma$  space group. The black circles represent the data, the red line represents the fit to the data, the green line represents the difference between the data and the fit, and the blue dashes represent the space group-allowed reflections. . . . . 247

- 
- 6.10 Rietveld refinements to the neutron Bragg data of  $\text{TlTcO}_4$  at 600 K to the (a) tetragonal  $I4_1/a$  space group, and the (b) tetragonal  $I4_1/amd$  structure. The black circles represent the data, the red line represents the fit to the data, the green line and shaded area represent the difference between the data and the fit, and the blue dashes represent the space group allowed reflections. . . . . 249
- 6.11 Rietveld refinements for the variable temperature data of  $\text{TlTcO}_4$  with (a) the  $a$  and  $b$  lattice parameters, (b) the unit cell volume, (c) the atomic displacement parameters measured as  $B_{eq.}$ , and (d) the Tc–O bond distances, where only the uncertainties of the average value has been displayed for clarity. . . . . 250
- 6.12 Unit cell volumes of the various  $\text{ABO}_4$  phase transitions, (a)  $Pnma \rightarrow I4_1/amd$  in  $\text{TlTcO}_4$  taken from synchrotron X-ray diffraction by Kennedy *et al.*,<sup>38</sup> (b)  $I2/a \rightarrow I4_1/a$  in  $\text{NdNbO}_4$  taken from neutron powder diffraction by Saura-Múzquiz *et al.*,<sup>25</sup> (c)  $I2/b \rightarrow I4_1/a$  in  $\text{BiVO}_4$  taken from neutron powder diffraction data, and (d)  $I2/a \rightarrow I4_1/a$  in  $\text{HoNbO}_4$  taken from neutron powder diffraction data. The purple circles represent the low-temperature data, the orange circles represent the high-temperature data, the dashed line indicates the phase transition temperature, and the dotted line is extrapolated from the low-temperature data and is used to guide the eyes. . . . . 251
- 6.13 Variable temperature neutron pair distribution function data of  $\text{TlTcO}_4$  at 50 (blue), 300 (green), 450 (orange), and 600 K (red). . . . . 252
- 6.14 Neutron pair distribution function data of  $\text{TlTcO}_4$  measured at 50 K fitted to the (a) tetragonal  $I4_1/amd$ , (b) orthorhombic  $Pnma$ , and (c) monoclinic  $P2_1/c$  structure. The blue circles represent the data, the red line represents the small box fit to the data, and the green line represents the difference between the two. The  $\text{TcO}_4$  tetrahedra in the  $P2_1/c$  model were constrained to be rigid. . . . . 253
- 6.15 Variable temperature neutron pair distribution function data of  $\text{TlTcO}_4$  at 50 K fitted to the (a) tetragonal  $I4_1/amd$ , (b) orthorhombic  $Pnma$ , and (c) monoclinic  $P2_1/c$  structure with rigid  $\text{TcO}_4$  tetrahedra. The blue circles represent the data, the red line represents the small box fit to the data, and the green line represents the difference between the two. . . . . 253

- 
- 6.16 Neutron pair distribution function data of  $\text{TlTcO}_4$  at 600 K fitted to the (a) tetragonal  $I4_1/amd$ , (b) tetragonal  $I4_1/a$ , (c) orthorhombic  $Pnma$ , and (d) monoclinic  $P2_1/c$  structure. The blue circles represent the data, the red line represents the small box fit to the data, and the green line represents the difference between the two. The  $\text{TcO}_4$  tetrahedra in the monoclinic  $P2_1/c$  model were constrained to be rigid. . . . . 254
- 6.17 The  $A\text{--}O$ ,  $B\text{--}O$  bond lengths, and  $O\text{--}B\text{--}O$  bond angles from (a–c)  $\text{TlTcO}_4$ , (d–f)  $\text{PbWO}_4$ , and (g–i)  $\text{BiVO}_4$ , taken from the neutron pair distribution function fits at 300 K to the monoclinic  $P2_1/c$  model. . . . . 256
- 6.18 (a) The scheelite-type aristotype in the tetragonal  $I4_1/amd$  structure. (b) The monoclinic  $P2_1/c$  structure of  $\text{TlTcO}_4$  derived from the neutron pair distribution function refinements. Looking along the top row, one  $\text{TcO}_4$  tetrahedra is rotated about the  $b$ -axis, whereas two are rotated about the  $a$ -axis. (c) The monoclinic  $P2_1/c$  structure of  $\text{TlReO}_4$  derived from the Saura Múzquiz *et al.* neutron pair distribution function refinements.<sup>2</sup> Looking along the top row, one  $\text{ReO}_4$  tetrahedra is rotated about the  $a$ -axis, whereas two are rotated about the  $b$ -axis. . . . . 257
- 6.19 (a) The unit cell volumes of  $\text{TlTcO}_4$  and  $\text{TlReO}_4$  taken from the studies by Kennedy *et al.* and Chay *et al.*, respectively.<sup>34,38</sup> Data were taken from the Rietveld refinements of synchrotron X-ray diffraction data, with the unit cell volume tripled to allow for a comparison between the orthorhombic  $Pnma$ , tetragonal  $I4_1/a$ , and monoclinic  $P2_1/c$  structures. (b) The atomic displacement parameters of  $\text{Tc}^{7+}$  and  $\text{O}^{2-}$  in  $\text{TlTcO}_4$  compared with that of  $\text{Re}^{7+}$  and  $\text{O}^{2-}$  in  $\text{TlReO}_4$ . Data were derived from the neutron pair distribution function fits to the monoclinic  $P2_1/c$  structure, and from Saura-Múzquiz *et al.*<sup>2</sup> . . . . . 258
- 7.1 Crystal structures of (a)  $\text{RbMnF}_4$  in the space group  $P2_1/a$ , and (b)  $\text{CsMnF}_4$  in the space group  $P4/nmm$ . The pink spheres represent  $\text{Rb}^+$ , the cyan spheres represent  $\text{Cs}^+$ , and the purple octahedra represent the  $\text{MnF}_6$  octahedra. Note the difference in  $\text{Mn--F--Mn}$  bond angle between the two structures. . . . . 266
- 7.2 (a) The  $\text{MnF}_6$  octahedra in the  $\text{CsMnF}_4$  material. The red axial  $\text{Mn--F}$  bonds ( $\sim 1.8$  Å) are shorter than the blue equatorial  $\text{Mn--F}$  bonds ( $\sim 2.0$  Å). (b) The  $3d$  orbital energy diagram of  $\text{Mn}^{3+}$ . The energy levels are shown in black, with the high-spin electrons shown as blue half arrows. The energy splittings are shown in green, and are taken from Behatha *et al.*<sup>15</sup> . . . . . 267

- 
- 7.3 The Rietveld refinement of  $\text{CsMnF}_4$  immediately after synthesis using monochromatic Mo source laboratory X-ray diffraction to the tetragonal  $P4/nmm$  space group. The black circles represent the data, the red line represents the calculated profile, and the green line represents the difference between the two. The blue ticks indicate the space group-allowed reflections. 271
- 7.4 The Rietveld refinement of  $\text{CsMnF}_4$  immediately after synthesis against neutron powder diffraction to the tetragonal  $P4/nmm$  space group at room temperature. The black circles represent the data, the red line represents the calculated profile, and the green line represents the difference between the two. The blue ticks indicate the space group-allowed reflections. . . . . 271
- 7.5 Magnetic susceptibility of  $\text{CsMnF}_4$  collected under field cooled and zero field cooled conditions using a physical property measurement system. (a) The susceptibility collected between 1.8–300 K, with a focus from 1.8–40 K shown in (b). The inset shows the inverse magnetic susceptibility fit from 80–300 K, with the Curie-Weiss fit shown as a red dashed line. . . . . 273
- 7.6 Magnetisation of  $\text{CsMnF}_4$  collected with a variable magnetic field using a physical property measurement system. The data collected at 1.8 K is shown as the blue line, and the data collected at 20 K is shown as the red line. The inset highlights the opening of the hysteresis loop at 1.8 K (and lack of opening at 20 K) at low magnetic field strength. . . . . 274
- 7.7 The dependence of the structural parameters of  $\text{CsMnF}_4$  with respect to temperature based on Rietveld refinements of neutron powder diffraction data. (a) The  $a$  and  $c$  lattice parameters, (b) unit cell volume, (c) Mn–F and Mn–Mn distances, and (d) the Mn–F–Mn bond angle. Dashed lines have been drawn to guide the eyes. . . . . 275
- 7.8 Neutron powder diffraction data collected on  $\text{CsMnF}_4$  using 2.44 Å. The red line corresponds to the pattern at 30 K, the blue line at 3 K, and the green line is the difference between them. The black lines are the space group allowed reflections from the nuclear  $P4/nmm$  structure. The five prominent magnetic reflections are seen below  $55^\circ 2\theta$ . The inset highlights the presence of diffuse magnetic features above  $T_C = 18.9$  K, with the 30 K data displayed as black circles, the red line is the calculated profile, and the green shaded area as the difference between the two. . . . . 276
- 7.9 The structure of  $\text{CsMnF}_4$  derived from neutron powder diffraction data at 3 K. (a) The nuclear structure of  $\text{CsMnF}_4$  in the space group  $P4/nmm$  with (b) the magnetic structure as a result of the  $\text{Mn}^{3+}$  cations. . . . . 277

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |     |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 7.10 | Neutron diffraction data collected on CsMnF <sub>4</sub> using 2.44 Å at 3 K. The red line is the fit to the nuclear structure, the purple line is the fit to the magnetic structure, and the green line is the difference between the calculated fit and the data. The blue ticks indicate the space group-allowed reflections. . . . .                                                                                                                                          | 277 |
| A.1  | The Fourier transform, $x(\omega)$ , of the function, $x(t)$ . In this case, $x(t) = \sin(t)$ and $x(\omega) = \delta(\omega+1)$ . . . . .                                                                                                                                                                                                                                                                                                                                        | 290 |
| A.2  | The Fourier transform, $x(\omega)$ , of the function, $x(t)$ . In this case, $x(t) = \sin(t) + \sin(3t) + \sin(7t)$ and $x(\omega) = \delta(\omega+1) + \delta(\omega+3) + \delta(\omega+7)$ . . . . .                                                                                                                                                                                                                                                                            | 290 |
| A.3  | The Fourier transform, $x(\omega)$ , of the function, $x(t)$ . In this case, $x(t)$ is a Gaussian curve, and $x(\omega)$ is another Gaussian curve. . . . .                                                                                                                                                                                                                                                                                                                       | 291 |
| A.4  | The Fourier transform, $x(\omega)$ , of the function, $x(t)$ . In this case, $x(t) = \delta(t+1)$ and $x(\omega) = 1$ . . . . .                                                                                                                                                                                                                                                                                                                                                   | 291 |
| A.5  | Room temperature X-ray diffraction studies of ErTaO <sub>4</sub> heated to 1550 °C. (a) Laboratory X-ray diffraction using copper source, and (b) synchrotron X-ray diffraction. The inset highlights the split reflections between 1.9–2.2 Å <sup>-1</sup> . . . . .                                                                                                                                                                                                             | 294 |
| A.6  | Unit cell volumes of $Ln_2(Zr_{2-x}Sn_x)O_7$ ( $Ln^{3+} = La, Nd, Sm$ ) pyrochlores plotted as a difference from the original $Ln_2Zr_2O_7$ structure. The linear lines have been added as lines of best fit, with the gradients included in the legend. The inset demonstrates the lack of significant variation between the lines of best fit. . . . .                                                                                                                          | 299 |
| A.7  | The Tauc plots for (a) HoNbO <sub>4</sub> and (b) HoTaO <sub>4</sub> obtained from UV-Vis diffuse reflection spectroscopy. Data is presented as the Kubelka-Munk transform of a direct-allowed transition. The insets show the electronic band structure along the high-symmetry path $\Gamma$ -F-Q-Z- $\Gamma$ . . . . .                                                                                                                                                         | 299 |
| A.8  | Strain analysis based on the lattice parameters from the variable temperature Rietveld refinements of HoTaO <sub>4</sub> upon cooling. (a) The ( $\epsilon_1 - \epsilon_2$ ) strain component, as calculated using the expression from Equation 3.5, fitted over the whole measured temperature range, and (b) the fit performed in a range 50 °C below $T_c$ with $\beta = 0.5$ . Although the data was fit down to 100 °C, the plots show from 700–1300 °C for clarity. . . . . | 300 |
| A.9  | Strain analysis based on the lattice parameters from the variable temperature Rietveld refinements of HoTaO <sub>4</sub> upon cooling. (a) The $\epsilon_6$ strain component, as calculated using the expression from Equation 3.5, fitted over the 800–1300 °C temperature range, and (b) the fit performed in a range 50 °C below $T_c$ with $\beta = 0.5$ . Data was fit over a reduced region due to the saturation of the strain component. . . . .                          | 301 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |     |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| A.10 | The monoclinic $\beta$ angle from the variable temperature Rietveld refinements of $\text{HoTaO}_4$ upon cooling. (a) The monoclinic $\beta$ angle fitted over the whole measured temperature range, and (b) the fit performed in a range 50 °C below $T_c$ with $\beta = 0.5$ . Although the data was fit down to 100 °C, the plots show from 700–1300 °C for clarity. . . . .                                                                                                                                                                                              | 301 |
| A.11 | Relationship between the activation energy calculated from the electrochemical impedance spectroscopy measured in air, and the average O–O distances taken from the Rietveld refinements of the neutron powder diffraction datasets. . . . .                                                                                                                                                                                                                                                                                                                                 | 302 |
| A.12 | Arrhenius plots of (black squares) $\text{LaNbO}_4$ and (red circles) $\text{La}(\text{Nb}_{0.65}\text{V}_{0.30}\text{Mo}_{0.05})\text{O}_{4+\delta}$ from the electrochemical impedance spectroscopy measured in air. The activation energies are listed as an inset. . . . .                                                                                                                                                                                                                                                                                               | 302 |
| A.13 | (Left) Synchrotron X-ray and (right) neutron powder diffraction patterns of $\text{NaA}(\text{MoO}_4)_2$ ( $A^{3+} = \text{La, Eu, Lu, Bi}$ ). The $\text{NaEu}(\text{MoO}_4)_2$ sample was not analysed using neutron powder diffraction due to the large neutron absorption cross section of Eu. Each diffraction pattern has been offset vertically for visibility. . . . .                                                                                                                                                                                               | 304 |
| A.14 | Unit cell parameters of the $\text{NaA}(\text{MoO}_4)_2$ ( $A^{3+} = \text{La, Eu, Lu, Bi}$ ) series derived from combined X-ray and neutron powder diffraction Rietveld refinements. for $\text{NaEu}(\text{MoO}_4)_2$ , only the synchrotron X-ray diffraction dataset was refined (indicated with hollow symbols). Where not apparent, the errors are smaller than the symbols. The dashed lines have been drawn the guide the eyes. . . . .                                                                                                                              | 305 |
| A.15 | (Top left) The A–O, (top right) B–O, (bottom left) difference between the unique A–O distances, and (bottom right) $\text{AO}_8$ polyhedra volume of the $\text{NaA}(\text{MoO}_4)_2$ ( $A^{3+} = \text{La, Eu, Lu, Bi}$ ) series derived from combined X-ray and neutron powder diffraction Rietveld refinements. For $\text{NaEu}(\text{MoO}_4)_2$ , only the synchrotron X-ray diffraction dataset was refined (indicated with hollow symbols). Where not apparent, the errors are smaller than the symbols. The dashed lines have been drawn the guide the eyes. . . . . | 305 |
| A.16 | The monoclinic $\gamma$ angle from the variable temperature Rietveld refinements of $\text{BiVO}_4$ upon heating. (a) The monoclinic $\gamma$ angle fitted over the temperature 400–510 K (shown with the whole temperature to highlight the anomalous behaviour at low temperature. (b) The fit performed in a range 50 K below $T_c$ with $\beta = 0.5$ . . . . .                                                                                                                                                                                                          | 308 |

- 
- A.17 Rietveld refinements for the synchrotron X-ray powder diffraction variable temperature dataset of  $\text{BiVO}_4$ , with (a) the  $a$  and  $c$  lattice parameters, (b) the unit cell volume, (c) the monoclinic  $\gamma$  angle, and (d) the  $z$  atomic coordinates of  $\text{Bi}^{3+}$  and  $\text{V}^{5+}$  plotted against each other. The black dashed lines represent the temperature of the  $I2/b \rightarrow I4_1/a$  phase transition, and the red dashed line is a linear fit. . . . . 308
- A.18 (a) A photo of the rapidly-actuating pneumatic thermal reactor furnace indicating the heating assembly, the movable sample fixture, and the pneumatic linear actuator. (b) An expanded view of the sample in the hot zone. For clarify, the heat shields are not shown. . . . . 309
- A.19 Synchrotron X-ray diffraction patterns of a sample of  $\text{PbO} + \text{WO}_3$  in the hot zone of the rapidly-actuating pneumatic thermal reactor. Three patterns are displayed: after 0 seconds (blue), after 5.5 seconds (orange), and after 8.7 seconds (red). The blue asterisk indicates the prominent reflection associated with the  $\text{PbO}$  phase, which disappears after 5.5 seconds. This is accompanied by an increase in diffuse scattering. . . . . 309
- A.20 Synchrotron X-ray diffraction patterns of  $\text{CsReO}_4$  from 100–800 K in 100 K steps. The patterns have been offset vertically to enhance visibility. . . . 311
- A.21 X-ray pair distribution function data for  $\text{CsReO}_4$  from 100–800 K in 100 K steps. . . . . 311
- A.22 Neutron powder diffraction pattern of an impure sample of  $\text{CsMnF}_4$  collected at room temperature. . . . . 312





# List of Tables

|     |                                                                                                                                                                                                                                                                       |     |
|-----|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 3.1 | Selected Rietveld refinement structural parameters, bond distances, and bond valence sums for $LnNbO_4$ ( $Ln^{3+} = La, Lu$ ) against synchrotron X-ray diffraction data. . . . .                                                                                    | 90  |
| 3.2 | Final heating temperatures of the $LnTaO_4$ samples with the space group of the recovered product. The sample marked with * was found to be a mixture of $P2/c + I2/a$ using SXRD data. . . . .                                                                       | 97  |
| 3.3 | Rietveld refinement structural parameters, bond distances, and bond valence sums for $HoNbO_4$ at 50 and 1000 °C against neutron powder diffraction data. . . . .                                                                                                     | 109 |
| 4.1 | Selected Rietveld refinement structural parameters, bond distances, and bond valence sums for $NaA(WO_4)_2$ ( $A^{3+} = La, Bi$ ) against combined synchrotron X-ray and neutron powder diffraction data. . . . .                                                     | 148 |
| 4.2 | Selected Rietveld refinement structural parameters, bond distances, and bond valence sums for $NaA(WO_4)_2$ ( $A^{3+} = La, Bi$ ) against combined synchrotron X-ray and neutron powder diffraction data. . . . .                                                     | 153 |
| 5.1 | Atomic displacements allowed by the $\Gamma_1^+$ and $\Gamma_2^+$ modes in the space group $I2/b$ . In this case, the letters $a-h$ have been used to denote the magnitude of the atomic displacements, with the subscripts used to denote which are coupled. . . . . | 177 |
| 5.2 | Rietveld refinement structural parameters, bond distances, and bond valence sums for $BiVO_4$ against neutron powder diffraction data. The atomic coordinates of vanadium have been fixed as described in the text. . . . .                                           | 179 |
| 5.3 | Selected Rietveld refinement bond distances and bond angles for $PbWO_4$ and $CaWO_4$ from variable temperature neutron powder diffraction data. . . . .                                                                                                              | 212 |
| 6.1 | Selected Rietveld refinement structural parameters and bond distances for $CsReO_4$ using synchrotron X-ray diffraction data. . . . .                                                                                                                                 | 233 |
| 6.2 | Selected Rietveld refinement structural parameters and bond distances for $TlTcO_4$ using neutron powder diffraction data. . . . .                                                                                                                                    | 248 |

---

|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |     |
|-----|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 7.1 | Selected Rietveld refinement structural parameters and bond distances for $\text{CsMnF}_4$ using neutron powder diffraction data collected at room temperature. . . . .                                                                                                                                                                                                                                                                                                                                                                               | 272 |
| A.1 | Rietveld refinement parameters of $\text{LnNbO}_4$ taken from synchrotron X-ray diffraction data. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection. . . . .                                                                                                                                                                                                                            | 295 |
| A.2 | Rietveld refinement parameters of $\text{LnTaO}_4$ taken from synchrotron X-ray diffraction data. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection. . . . .                                                                                                                                                                                                                            | 296 |
| A.3 | Unit cell volumes and associated gradients across the $\text{Ln}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$ solid solution series determined from synchrotron X-ray diffraction. . . .                                                                                                                                                                                                                                                                                                                                                                    | 297 |
| A.4 | Rietveld refinement parameters of the $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$ taken from combined synchrotron X-ray and neutron powder diffraction data. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection. . . . .                                                                                                                                                           | 298 |
| A.5 | Refined parameters for $\text{HoTaO}_4$ at low and high temperatures using neutron powder diffraction. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                        | 300 |
| A.6 | Refinement parameters of $\text{NaA}(\text{WO}_4)_2$ ( $A^{3+} = \text{La, Pr, Nd, Lu, Bi}$ ) derived from combined synchrotron X-ray and neutron powder diffraction data to the tetragonal $I4_1/a$ space group. Refinement parameters for $\text{NaSm}(\text{WO}_4)_2$ are derived only from synchrotron X-ray diffraction data. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection. . | 303 |
| A.7 | Refinement parameters of $\text{NaA}(\text{MoO}_4)_2$ ( $A^{3+} = \text{La, Eu, Lu, Bi}$ ) derived from combined synchrotron X-ray and neutron powder diffraction data to the tetragonal $I4_1/a$ space group. Refinement parameters for $\text{NaEu}(\text{MoO}_4)_2$ are derived only from synchrotron X-ray diffraction data. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection. .   | 304 |

- 
- A.8 Refinement parameters of  $\text{NaBi}(\text{WO}_4)_2$  from the neutron pair distribution function fits to the tetragonal  $I4_1/a$ , tetragonal  $I\bar{4}$ , and monoclinic  $I2/b$  space groups. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection. 306
- A.9 Tabulated potential space group selections of  $\text{BiVO}_4$ . Atomic coordinates are written outside of the 0.0–1.0 range to highlight the relationship between the space groups. The high temperature tetragonal  $I4_1/a$  phase is also displayed to show its relationship. . . . . 307
- A.10 Comparison of the unit cell parameters and distortion of the  $\text{PbO}_8$  polyhedra in  $\text{PbWO}_4$ , assuming a monoclinic  $I2/b$  structure obtained by small box fitting against neutron pair distribution data measured at 115 K, with the geometry-optimised structure obtained using density functional theory calculations. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection. 310



# List of Abbreviations

| Abbreviation | Definition                                                 |
|--------------|------------------------------------------------------------|
| 1D           | One Dimension                                              |
| 2D           | Two Dimensions                                             |
| 3D           | Three Dimensions                                           |
| AC           | Alternating Current                                        |
| ADP          | Atomic Displacement Parameter                              |
| ANSTO        | The Australian Nuclear Science and Technology Organisation |
| APS          | Advanced Photon Source                                     |
| BEC          | Born Effective Charge                                      |
| BVS          | Bond Valence Sum                                           |
| CERN         | <i>Conseil Européen pour la Recherche Nucléaire</i>        |
| CHESS        | Cornell High Energy Synchrotron Source                     |
| CIF          | Crystallographic Information File                          |
| CPE          | Constant Phase Element                                     |
| DC           | Direct Current                                             |
| DFT          | Density Functional Theory                                  |
| DoS          | Density of States                                          |
| DRS          | Diffuse Reflection Spectroscopy                            |
| DSC          | Differential Scanning Calorimetry                          |
| EIS          | Electrochemical Impedance Spectroscopy                     |
| emu          | Electromagnetic Units                                      |
| EXAFS        | Extended X-Ray Absorption Fine Structure                   |
| FC           | Field-Cooled                                               |
| FWHM         | Full Width at Half Maximum                                 |
| GKA          | Goodenough-Kanamori-Anderson                               |
| HER          | Hydrogen Evolution Reaction                                |
| HF           | Hartree-Fock                                               |
| HRMC         | Hybrid Reverse Monte Carlo                                 |
| ICSD         | Inorganic Crystal Structural Database                      |
| IR           | Ionic Radii                                                |
| <i>irrep</i> | Irreducible Representation                                 |
| Laser        | Light amplification by stimulated emission of radiation    |
| LED          | Light-Emitting Diode                                       |

| Abbreviation | Definition                                           |
|--------------|------------------------------------------------------|
| MD           | Molecular Dynamics                                   |
| MOF          | Metal-Organic Framework                              |
| mPDF         | Magnetic Pair Distribution Function                  |
| NIST         | National Institute of Standards and Technology       |
| NMR          | Nuclear Magnetic Resonance                           |
| NPD          | Neutron Powder Diffraction                           |
| NPDF         | Neutron Pair Distribution Function                   |
| OPAL         | Open-Pool Australian Lightwater Reactor              |
| ORNL         | Oak Ridge National Laboratory                        |
| PBE          | Perdew-Burke-Ernzerhof                               |
| PDF          | Pair Distribution Function                           |
| pDoS         | Partial Density of States                            |
| PPMS         | Physical Property Measurement System                 |
| PWS          | Photocatalytic Water Splitting                       |
| RAPTR        | Rapidly-Actuating Pneumatic Thermal Reactor          |
| Redox        | Reduction-Oxidation                                  |
| SNAP         | Spallation Neutrons and Pressure                     |
| SOFC         | Solid-Oxide Fuel Cell                                |
| SXRD         | Synchrotron X-Ray Diffraction                        |
| ToF          | Time-of-Flight                                       |
| TCH          | Thompson-Cox-Hastings                                |
| UCV          | Unit Cell Volume                                     |
| UV-Vis       | Ultraviolet-Visible Light                            |
| VASP         | Vienna <i>ab initio</i> Simulation Package           |
| VESTA        | Visualization for Electronic and STructural Analysis |
| VSEPR        | Valence Shell Electron Pair Repulsion                |
| VSM          | Vibrating Sample Magnetometry                        |
| XANES        | X-Ray Absorption Near-Edge Spectroscopy              |
| XPDF         | X-Ray Pair Distribution Function                     |
| XRD          | X-Ray Diffraction                                    |
| ZFC          | Zero Field-Cooled                                    |

# Abstract

The replacement of carbon-emitting energy sources with cleaner alternatives on an industrial scale is regarded as a critical priority for limiting the effects of anthropogenic climate change. The global economy needs ways to limit the carbon emissions produced from energy generation and manufacturing processes. Current research is focusing on the use of solid-oxide fuel cells for carbon-neutron energy generation, the production of hydrogen gas for energy storage, and the safe sequestering of radioactive waste from carbon-neutral nuclear energy. Each of these technologies, as well as applications in solid state lasing and spintronics, can be addressed using a single structure type – the  $ABO_4$  scheelite-type structure.

The  $ABO_4$  structure type has found application in a variety of processes due to the diverse array of chemical substitutions that can be made into its structure. For example,  $LaNbO_4$  has found application as a ceramic electrolyte for solid-oxide fuel cells,  $BiVO_4$  and  $PbWO_4$  as catalysts for photocatalytic water splitting, and  $ATcO_4$  salts as a solid for immobilising highly active  $^{99}Tc$  nuclear fission products. Despite the wide applicability of these materials, a full description of their structure-functionality relationships remains elusive; how their structure on the atomic scale affects their application in functional devices.

This dissertation focuses on a small class of  $ABO_4$  materials, with a focus on understanding and developing their structure-functionality relationships. The structures

of these materials were first characterised using a combination of synchrotron X-ray and neutron powder diffraction in order to understand their long-range average structure. This was followed by a study of their short-range local structure using X-ray and neutron total scattering techniques, where the pair distribution function of each is modelled to identify and quantify local distortions and disordering processes that occur on the atom-by-atom scale. Finally, the accurate establishment of these structures are related to their application as functional energy materials, with their ionic conductivity, band gap, and magnetic susceptibility quantified. This allows for a detailed understanding of the structure, which is used to identify engineering choices that should be made to design and manufacture the next generation of these functional materials.

LaNbO<sub>4</sub> ceramic electrolytes, and their extension into the generalised  $LnBO_4$  ( $Ln^{3+} = \text{La-Lu}$ ;  $B^{5+} = \text{Nb, Ta}$ ) structures, were studied for their ability to act as mixed oxygen ion/proton conductors. A delicate interplay between the  $AO_8$  polyhedra and  $BO_6$  distorted octahedra was uncovered that appears to be unique to this structure class. These interactions could then be either strengthened or weakened depending on the size of the  $Ln^{3+}$  cation and the strength of orbital interaction between the  $B$ -site and the oxygen anionic sublattice.

NaBi(WO<sub>4</sub>)<sub>2</sub> materials have been studied for their ability to host rare-earth ions in a stable lattice for solid state lasing applications. Changes in their properties, such as a broadening of their emission spectra, have been previously identified despite no changes to its long-range average structure. Although no long-range average ordering between the  $A$ -site cations was identified using a combination of synchrotron X-ray and neutron powder diffraction, two unique  $A$ -site polyhedra were identified using total scattering techniques. This study explains the broadening of the emission spectra detected in previous studies, but also identifies a way in which these interactions may be tuned through cation doping, allowing for greater control over the delicate balance between



---

thermal stability and structural disorder required for solid state lasing materials.

$\text{BiVO}_4$  and  $\text{PbWO}_4$  have both been identified in the literature as materials capable of performing photocatalytic water splitting. However, an incomplete structural model currently exists for these materials. Although  $\text{PbWO}_4$  and  $\text{CaWO}_4$  exhibit the same long-range average structure, only  $\text{PbWO}_4$  has been identified as a photocatalyst in the literature. A study of the long-range average structure confirms that  $\text{PbWO}_4$  and  $\text{CaWO}_4$  are isostructural down to 3 K. However, neutron total scattering identified structural distortions in the  $\text{PbO}_8$  polyhedra and  $\text{WO}_4$  tetrahedra that were not observed in the isostructural  $\text{CaWO}_4$  as a result of the  $\text{Pb}^{2+}$   $6s^2$  stereochemically active lone pair electrons. Similar short-range structural distortions were also observed in  $\text{BiVO}_4$  as a result of its  $\text{Bi}^{3+}$   $6s^2$  lone pair. By understanding the local structure of  $\text{PbWO}_4$ , and identifying distortions that are common with the the industrial photocatalyst  $\text{BiVO}_4$ , a model was proposed to explain its photocatalytic properties.

The final section of this dissertation examined other local scale phenomena that have not previously been reported in similar  $\text{ABO}_4$  materials. A study of  $\text{CsReO}_4$  identified local scale incoherent  $\text{ReO}_4$  tetrahedra translations that appear to be unique to the  $\text{AReO}_4$  family of materials. A study of  $\text{TlTcO}_4$  was used to develop a robust understanding of different distortions that have been identified in  $\text{ABO}_4$  structure with lone pair-bearing cations on the  $A$  site, such as  $\text{Tl}^+$ ,  $\text{Pb}^{2+}$ , and  $\text{Bi}^{3+}$ . Depending on the oxidation state of the  $A$ -site cation and the polarisability of the  $B\text{--O}$  bonds, different distortions in either the  $\text{AO}_8$  polyhedra or  $\text{BO}_4$  tetrahedra are observed. Finally, a brief excursion was taken outside of the world of metal oxides, where the two dimensional ferromagnetism of  $\text{CsMnF}_4$  was explored. The magnetic structure is determined using neutron powder diffraction, which due to its difficult synthesis process and hydroscopic nature, had not been reported previously.



---

**Part I:**  
**Introduction and Theoretical**  
**Background**

---



# Chapter 1

## Introduction



## 1.1 The Need for a Carbon-Neutral Economy

The world's economy operates through a network of transactions between countries such as international trade, currency exchange, global investing, and immigration. Underpinning many of these economical demands, on both an global and individual scale, is the need for a secure source of energy. Energy is required for transport in international trade, for driving industrial and scientific developments, and for fulfilling the needs of individuals such as food, heating, and shelter. Current sources of global energy are dominated by unsustainable, carbon-based fuels, which account for almost 80% of the world's energy usage.<sup>1</sup> These include coal, oil, and gas, which account for over 75% of global greenhouse gas emissions and 90% of global carbon dioxide emissions.<sup>2</sup> This has seen the development of large-scale anthropogenic climate change in the form of rising sea levels effecting low-lying Pacific Island countries,<sup>3</sup> a lack of nutrients in the North Atlantic Ocean due to increased glacier melting,<sup>4</sup> and longer and more intense bushfire seasons in both the northern and southern hemispheres.<sup>5</sup>

Australia is particularly susceptible to the effects of climate change, with its dry climate and coastal-based population. This was seen recently with the 2019–2020 'Black Summer' bushfires, where 5.8 million hectares of Australia's land was burned (larger than the land mass of Croatia),<sup>6</sup> almost three billion animals were lost,<sup>7</sup> and the air pollution was so intense it depleted the Earth's ozone layer by an additional 3–5%.<sup>8</sup> Additional climate change events have been recorded in Australia more recently, with five extensive 'once in a 100 year' flooding events recorded in the year 2022 alone, as well as increased rates of coral bleaching in the Great Barrier Reef.<sup>9</sup> This also has an effect on international trade, with the Australian Department of the Treasury estimating severe flooding in 2022 cost the economy \$11.7 billion Australian dollars in lost produce, disaster relief, and damage to fertile land.<sup>10</sup> Given Australia's large dependence on fossil fuels, with 71% of Australia's electricity generation being derived from carbon-based sources,<sup>11</sup> Australia is in need of developing forms of carbon-neutral energy in order to mitigate the effects of anthropogenic climate change and its subsequent effect on the global economy.

Australia's energy share in renewables has increased significantly in recent years. The amount of energy derived from renewables – such as wind, solar, and biomass – has doubled over the last decade.<sup>12</sup> This has been in conjunction with a large increase in household solar, with nearly one in three homes in Australia now equipped with rooftop solar panels.<sup>13</sup> Key to driving the technological innovation of solar and wind power – as well as other global carbon-neutral energy developments in batteries, photocatalysts, and nuclear power – is the further development of the materials used to perform these tasks efficiently, effectively, and safely.

### 1.1.1 Materials Science

The study of materials science is seen as an interdisciplinary field between physics, chemistry, and engineering devoted to researching and discovering materials capable of performing a particular task or technological operation. The human race has long been advanced by the materials they are capable of developing, with distinct eras of advancement being named after materials humans were able to work with at the time: namely the Copper Age (3200–2300 BCE), the Bronze Age (2300–700 BCE), and the Iron Age (700–1 BCE).<sup>14,15</sup> Today, materials science is driven by the development of revolutionary technologies for everyday objects, such as polymers for fabric and clothing, semiconductors for computing, and biomaterials for medical purposes. This has led to major advancements such as the Apollo 11 moon landing in 1969 which would not have been possible without the invention of the transistor, or the observation of Albert Einstein's long-hypothesised gravitational waves in 2015 that relied on the invention of the light-emitting diode (LED) laser.<sup>16</sup>

The basis of materials science involves studying the delicate interplay between the structure of a material, the synthesis and processing methods required to make the material, and its resulting functional properties and performance (Figure 1.1). The structure of a material is of utmost importance due to its ability to be manipulated and controlled, and hence, will be the major focus of this dissertation. The structure of materials can vary based on length scale, with the ordering of materials on an atomic



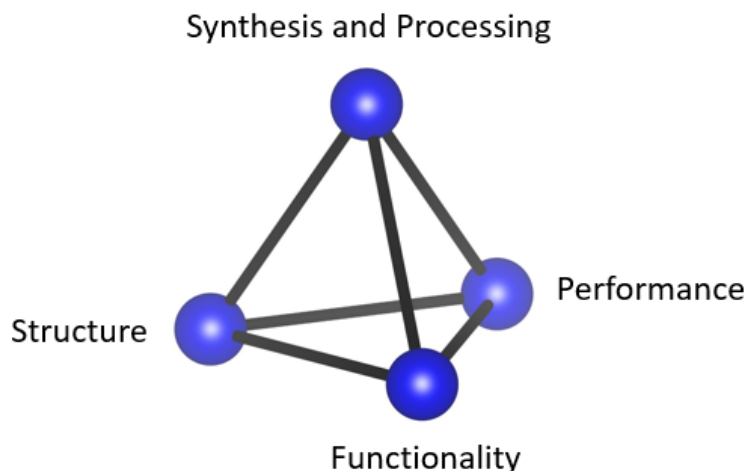


Figure 1.1: An illustration of the materials science tetrahedron. This shows how the synthesis and processing, structure, functionality, and performance of materials are all interdependent of each other.

scale (that is, atom by atom on the scale of a few Ångströms, or  $10^{-10}$  m) leading to large scale symmetry relations described by crystallography (observable on the milliscale or  $10^{-3}$  m). By understanding inherent chemical phenomena, such as atomic size, chemical bonding, and polarisability, we are able to understand their role in particular materials to further develop their applications. The language and techniques used for the structural characterisation of materials will be explored in more detail in Chapter 2 of this dissertation. Synthesis and processing involves designing optimal pathways to create the desired material. Ideally, this should use as little energy as possible by balancing the thermodynamic and kinetic requirements of forming the desired chemical product, as well as being able to produce it on a large scale for industrial applications. Finally, it is essential to explore the properties and functionality of these materials to determine their potential uses. These include (but are by no means limited to) mechanical properties for high-tensile strength materials, electrical properties for lower resistance electricity conduction, optical properties for photonics, and magnetic materials for computer storage.

In recent times, the designing and manufacturing of materials has become so complicated and complex that many materials are often studied for their properties without a full understanding of the influence of their structure. This has led to the importance of identifying *structure-functionality relationships* to better understand these materials, and to ‘tailor make’ them better suited for their applications. For example,

the pyrochlore oxide material  $\text{Y}_2\text{Ru}_2\text{O}_7$  has shown great promise as an electrocatalyst; a material capable of splitting water into hydrogen and oxygen gas using a small amount of electricity. Recent studies have identified that substituting a small amount ( $<10\%$ ) of another metal (such as zinc, or  $\text{Zn}^{2+}$ ) into the structure can double its activity.<sup>17–20</sup> Despite this, a full understanding of where the dopant sits within the structure, as well as why  $\text{Zn}^{2+}$  causes the twofold increase in activity whereas  $\text{Cu}^{2+}$  causes its activity to decrease, remains elusive. In simple terms, the most recent goal of materials science has become finding and understanding materials that *break* our current knowledge of materials science.

### 1.1.2 The Hierarchy of Material Design

The process of functional material identification and design is best summarised in the following sequential order:

**Step 1: Synthesis.** A material is traditionally synthesised in a conventional way, from a solid state synthesis technique (combining reagents and heating to high temperatures for long periods of time), to a coprecipitation synthesis (combining water-soluble salts and allowing a product to precipitate), to hydrothermally (reacting precursors under elevated temperatures and pressures).

**Step 2: Characterisation.** If a material is successfully synthesised, it is then taken for further analysis. At the University of Sydney, materials are routinely characterised using X-ray diffraction to determine whether or not they are phase pure. If they are deemed not to be phase pure, they are either ground and reannealed again, or resynthesised completely. If a material is determined to be phase pure, information may be extracted from its diffraction pattern, such as its space group and arrangement of atoms. Other characterisation techniques are also available at large scale research facilities, such as synchrotron X-ray and neutron powder diffraction, and total scattering techniques to provide more information on the material.

**Step 3: Structure Solution.** On top of the characterisation, additional techniques may be performed in order to obtain a complete structural solution of the material. This is usually in the form of a complete description of where the atoms in the material are, as well as their associated symmetries. Using diffraction, a Rietveld refinement can be performed to obtain this information. This information is stored in a crystallographic information file (CIF).

**Step 4: Computational Analysis.** Once a CIF has been established for a material, further analysis may be performed using a combination of density functional theory (DFT) and/or molecular dynamics (MD) simulations. This provides an understanding of the nuclear structure of the material (such as the positions of the atoms), as well as its electronic structure (how the atoms interact with each other). Modelling the electronic structure allows for an understanding of structural requirements (such as bonding between atoms), as well as physical phenomena (such as magnetism and band gaps). This helps to better understand why certain materials are structured the way they are.

**Step 5: Property Studies.** If a material is deemed to have interesting structural properties, whether it be atomic or electronic, they can be investigated further using physical property measurements. This can range from assessing their ionic conductivity using electronic impedance spectroscopy (EIS), to testing their photocatalytic and electrocatalytic properties using gas chromatography, to measuring their response to external magnetic fields using magnetic calorimetry.

It is clear from this brief outline that the road to functional material design can be long and difficult. A combination of all five steps can lead to an understanding of what makes a material applicable for a particular purpose (developing a structure-functionality relationship). In turn, this can lead to the development of carbon-neutral energy innovations, such as more efficient battery materials, more stable catalysts, and purposefully-engineered magnetic interactions.

### 1.1.3 Metal Oxides as Functional Energy Materials

Many avenues have been explored for the design of functional energy materials. These include, but are not limited to, organic polymers, metal-organic frameworks (MOFs), nitrides and carbides, and metallurgy. The focus of this dissertation will be on metal oxides, which are crystalline solids consisting of metal cations and oxygen anions. Metal oxides are often studied because of their stability and response to external stimuli. In fact, most of the Earth's crust consists of different oxides that have remained stable and unreacted for millions of years. These include sand (also known as silicon dioxide, or  $\text{SiO}_2$ ) as well as various mineral deposits like iron ore (in the form of hematite  $\text{Fe}_2\text{O}_3$  or magnetite  $\text{Fe}_3\text{O}_4$ ). With the exception of the lighter inert gases – helium, neon, argon, and krypton – oxygen forms at least one binary oxide with each of the elements of the Periodic Table (up to Einsteinium(III) oxide,<sup>21</sup> or  $\text{Es}_2\text{O}_3$ ).

Even the most simple binary oxides have been studied in great detail due to their functional properties. In 1972, titanium dioxide ( $\text{TiO}_2$ ) was first reported to be capable of performing photocatalytic water splitting; splitting water into hydrogen and oxygen gas in the presence of light.<sup>22,23</sup> Additionally, the highest solid state ionic conductivity recorded to date is in the cubic phase of bismuth oxide, known as  $\delta\text{-Bi}_2\text{O}_3$ .<sup>24–26</sup> However, significant drawbacks are associated with each of these materials, with  $\text{TiO}_2$  suffering from a low quantum yield and low light absorption,<sup>27–30</sup> and  $\delta\text{-Bi}_2\text{O}_3$  being a poor electrical conductor and a metastable structure that is only accessible at elevated temperatures.<sup>25,31</sup> Given the inherent compositional simplicity of these materials, metal oxides have provided a rich tapestry for additional structural modifications in an attempt to improve their performance as functional materials. In  $\text{TiO}_2$  photocatalysts, a great deal of research has focused on engineering different morphologies of  $\text{TiO}_2$  particles, such as synthesising particular nanostructures or thin-film substrates to improve efficiency.<sup>32–37</sup> Similarly in  $\delta\text{-Bi}_2\text{O}_3$ , attempts to stabilise the high-temperature  $\delta\text{-Bi}_2\text{O}_3$  material at lower temperatures through morphology design and chemical doping have been reported.<sup>38–40</sup>

Other ways in which metal oxides can be explored is by combining two binary metal oxides to yield a ternary oxide. These are given the form  $A_aB_bO_c$ , where  $A$  and  $B$  are different metal cations, and  $a, b$  and  $c$  are stoichiometric coefficients. Ternary oxides have also led to great scientific advancement, such as 8% yttria-stabilised zirconia ( $Y_{0.16}Zr_{0.92}O_{2.08}$ ) as an ionic conductor,<sup>41</sup>  $CsOs_2O_6$  as a superconductor,<sup>42</sup> and  $LiCoO_2$  as a commercially-available battery electrode.<sup>43</sup> However, the addition of more chemical elements can lead to complicated relationships within the structure, with other phenomena such as reduction-oxidation potentials, stacking faults, and antisite defects all becoming possible and difficult to quantify. Developing structure-functionality relationships in ternary oxides (and quaternary oxides and beyond) remains one of the great challenges of material science.

This dissertation will focus on exploring the phase space of  $ABO_4$  metal oxides, where  $A$  and  $B$  are different metal cations. By varying the different  $A$ - and  $B$ -site metal cations, different materials with different crystal structures are formed, leading to applications as functional energy materials including ceramic ionic conductors, lasing materials, photocatalysts, and matrices of safely storing radioactive waste. The next section of this introduction will focus on an archetype  $ABO_4$  metal oxide; the scheelite-type oxide. The phase space of different  $ABO_4$  materials will then be explored using the Periodic Table, changing the oxidation states and ionic radii of the  $A$ - and  $B$ -site cations to form new materials with different symmetries and applications. A brief aside will be given to  $ABX_4$  materials, where the oxygen anions have been replaced with other anions, such as sulfur, tellurium, and fluorine to explore an even greater phase space.

## 1.2 Scheelite-Type Oxides

Scheelite-type oxides of the form  $ABO_4$  have generated a lot of interest due to the large amount of chemical and charge combinations available within their structure type. In fact, almost every cation in the Periodic Table has been reported within the  $ABO_4$  structure type in some way.<sup>44,45</sup> Different combinations of charge cations have been incorporated within the structure, leading to a diverse range of materials properties.

As a brief example, the alkali metal ( $A^+$ ) and transition metal ( $B^{7+}$ ) combination  $\text{KOsO}_4$  has been identified as a  $5d^1$  quantum magnet oxide,<sup>46</sup> whereas the  $A^{4+}$  and  $B^{4+}$  combination  $\text{ThGeO}_4$  has been identified as a potential host matrix for high-activity radioactive waste.<sup>47</sup> Understanding their nuclear and electronic structure is critical to further developing structure-functionality relationships within this diverse class of metal oxides.

### 1.2.1 The Scheelite-Type Structure

The archetype scheelite  $\text{ABO}_4$  metal oxide structure is tetragonal ( $a = b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$ ) in the space group  $I4_1/a$  (space group #88). The structure consists of two unique cation sites; the  $A$  and  $B$  sites (Figure 1.2). The  $A$  site consists of  $\text{AO}_8$  polyhedra, expressed as two unique  $A\text{--O}$  bond distances. The  $A$ -site cation is confined to the special symmetry-constrained Wyckoff position  $4b$  ( $0, 1/4, 5/8$ ), meaning it has little freedom of movement within the structure. The  $B$ -site cation is found in a similarly constrained special Wyckoff position  $4a$  ( $0, 1/4, 1/8$ ) with a single unique  $B\text{--O}$  bond distance. There is one oxygen position at the  $16f$  Wyckoff position with general coordinates  $(x, y, z)$ . The  $\text{ABO}_4$  structure is arranged in such a way that the  $\text{AO}_8$  polyhedra and  $\text{BO}_4$  tetrahedra alternate within the structure, leading to edge-sharing  $\text{AO}_8$  polyhedra and isolated  $\text{BO}_4$  tetrahedra.

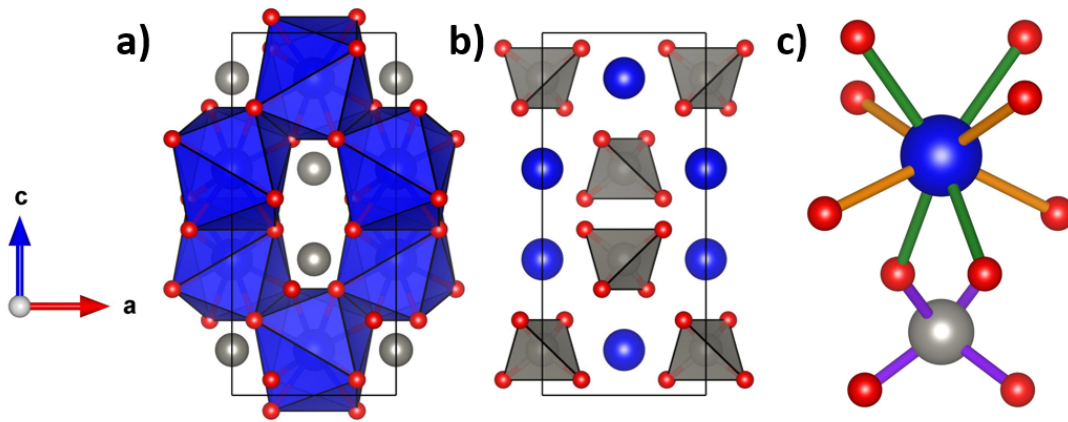


Figure 1.2: The  $\text{ABO}_4$  tetragonal  $I4_1/a$  scheelite-type structure with the (a)  $\text{AO}_8$  edge-sharing polyhedra highlighted in blue, and the (b)  $\text{BO}_4$  isolated tetrahedra highlighted in grey. The different bonding environments are highlighted in (c), with the two unique  $A\text{--O}$  distances drawn in green and gold, and the unique  $B\text{--O}$  distance drawn in purple.

The first and ‘original’ scheelite structure identified was  $\text{CaWO}_4$ ; the original ore of tungsten. Scheelite was first described in 1751 from Mount Bispergs Klack in Sweden and named after Carl Wilhelm Scheele, the Swedish-German chemist credited with the discovery of oxygen in 1773, a year before Joseph Priestley independently published the same discovery.<sup>48</sup> Owing to its unusual heaviness, the ore was named ‘*tung sten*’ meaning ‘heavy stone’ in Swedish. This eventually became the name of purified tungsten metal, with ‘scheelite’ remaining the name of the mineral ore itself. Since then, materials deviating from the  $\text{CaWO}_4$  chemical composition, but retaining the same  $\text{AO}_8$  and  $\text{BO}_4$  structural motifs and tetragonal  $I4_1/a$  structure, have been referred to as scheelite-type materials.

Since its discovery, a wide variety of scheelite-type oxides have been studied in the literature. The original  $\text{CaWO}_4$  material, consisting of a II-VI combination of  $\text{Ca}^{2+}$  and  $\text{W}^{6+}$ , was investigated for its high luminescent properties. Early studies by Kröger presented a thorough investigation of its properties,<sup>49</sup> as well as the effect of chemical substitution of similar cations. This led to the identification of  $\text{PbWO}_4$  as a scintillator, used in ordinary lab equipment through to the detectors used in the Large Hadron Collider at the *Conseil Européen pour la Recherche Nucléaire* (CERN), or the European Organization for Nuclear Research.<sup>50</sup>  $\text{PbWO}_4$  has demonstrated great chemical stability and resistance to radiation, making it a perfect detector material in high-energy applications.<sup>51</sup>

Apart from  $\text{CaWO}_4$ , other II-VI charge combination scheelites have been investigated due to their functional material properties. Moving one period down the Periodic Table from  $\text{Ca}^{2+}$  to  $\text{Sr}^{2+}$ ,  $\text{SrWO}_4$  has been investigated as a ceramic host matrix for radioactive  $^{90}\text{Sr}$  immobilisation.<sup>52</sup> Furthermore, both  $\text{SrMoO}_4$  and  $\text{SrWO}_4$  have been investigated as self-activating phosphors,<sup>53–55</sup> with possible applications in solid state lasers,<sup>56–58</sup> LEDs,<sup>59,60</sup> and optoelectronic devices.<sup>61</sup> This is due to the excellent photoluminescence, high chemical stability, and low thermal expansion of the material.<sup>62</sup> Moving yet another period down the Periodic Table to  $\text{Ba}^{2+}$ ,  $\text{BaWO}_4$  has been extensively investigated as a photocatalyst due to its chemical and thermal stability, as well as its favourable direct band gap.<sup>63–66</sup> The synthesis, long-range average, and short-range local ordering of the

II-VI charge combination scheelites is the focus of Chapter 5 of this dissertation, with a particular focus on  $\text{PbWO}_4$ , its application as a photocatalyst, and local scale distortions that are not found in the isostructural ‘original’ scheelite  $\text{CaWO}_4$ .

Moving away from II-VI charge combinations, significant applications have also been found for I-VII scheelite-type oxides. As mentioned previously, the  $\text{KOsO}_4$  metal oxide was recently identified as a  $5d^1$  quantum magnet oxide due to the isolated  $\text{Os}^{7+} 5d^1$  ( $S = 1/2$ ) cations.<sup>46</sup> Previously, oxides containing  $5d$  transition metals, such as Os and Ir, have demonstrated unusual magnetic properties, from the ferromagnetic insulator  $\text{Ba}_2\text{NiOsO}_6$ , to the superconducting  $\text{CsOs}_2\text{O}_6$  mentioned above.<sup>42,67</sup> This has been attributed to the diffuse nature of the  $5d$  orbitals, which has been proposed to give rise to itinerant, rather than localised, electronic effects.<sup>46</sup> Furthermore, the spin-orbit coupling often results in a significant decrease in the observed magnetic moment, as illustrated in various Re-, Os-, and Ir-containing compounds.<sup>68–71</sup> Although a majority of these magnetic phenomena have been reported in structures containing corner-sharing octahedral motifs such as pyrochlores and perovskites, the ionic nature of the larger  $A$ -site cation and the isolated  $\text{BO}_4$  tetrahedra in the  $\text{ABO}_4$  structure allow for the study of these materials whilst removing the oxygen-mediated superexchange interactions.<sup>46</sup> In addition to the magnetism studies, scheelite-type systems with  $B^{7+} = \text{Re}$  have been investigated as potential host matrices for radioactive waste due to the similarities between  $\text{Re}^{7+}$  and the highly mobile fission product  $\text{Tc}^{7+}$ .<sup>72–74</sup> Work concerning the  $\text{ATcO}_4$  and  $\text{AReO}_4$  scheelite-type oxides is the subject of Chapter 6 of this dissertation.

The III-V combinations have received a large amount of attention due to the prevalence of potential  $A^{3+}$  cations available, from transition metals ( $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ , *etc.*) to a majority of lanthanoids ( $\text{Ln}^{3+} = \text{lanthanoid}$ , La–Lu) and actinoids ( $\text{An}^{3+} = \text{Am–Cf}$ ). One of the most well-studied III-V combination scheelites is  $\text{LaNbO}_4$ , although it should be noted that it only adopts the scheelite-type structure at elevated temperatures ( $>500\text{ }^\circ\text{C}$ ).<sup>75</sup> This has been investigated as a potential proton-conducting solid-oxide fuel cell (SOFC) material due to its lack of electronic conductivity,<sup>76–78</sup> as well as its high chemical stability in harsh, acidic environments containing  $\text{H}_2\text{S}$  or  $\text{CO}_2$  gases.<sup>79</sup> The abundance of chemical substitutions possible on either the  $A$ - and  $B$ -sites leads to a



great deal of flexibility in terms of the size of the ionic radii (IR), such as substituting  $\text{La}^{3+}$  for  $\text{Lu}^{3+}$  (1.16 *vs.* 0.977 Å in eight-coordinate geometry) whilst maintaining charge balance.<sup>80</sup> This is observed to have an impact on the ionic conductivity of these materials, as well as influencing any potential phase transitions they may undergo. The identification of structure-functionality relationships in the III-V combinations is the main focus of Chapter 3 of this dissertation.

Finally, combinations of different oxidation states can be substituted onto either the *A* or *B* sites of these scheelite-type oxides to produce an even greater array of applications. The most notable of these concerns mixing  $\text{Na}^+$  and  $\text{Y}^{3+}$  onto the *A* site to form  $\text{NaYMo}_2\text{O}_8$  (sometimes written as  $(\text{Na}_{0.5}\text{Y}_{0.5})\text{MoO}_4$  to emphasise its relationship with other  $\text{ABO}_4$  materials and highlight the mixed cations on the *A* site).<sup>81</sup> These materials have been identified as potential host crystals for luminescent rare-earth ions for solid state lasing due to their excellent thermal and hydrolytic stability.<sup>82</sup> Furthermore, combining different cation oxidation states has also led to the study of  $\text{CaANb}_2\text{O}_8$  ( $A^{4+} = \text{U}, \text{Th}$ ) as a potential host matrix for radioactive waste.<sup>83</sup> Understanding the structures of these mixed-site scheelite-type oxides is the subject of Chapter 4 of this dissertation, with a particular focus on their local environment and their potential influence on their application as solid state lasers.

Although the present discussion has focused on the scheelite-type structure, there are a variety of other structures closely related to the scheelite-type structure that possess different symmetries and structural motifs. By using different cation combinations, vacancy creation, or external stimuli, different  $\text{ABO}_4$  structures may be synthesised with vastly different properties.

### 1.2.2 Variations on the Scheelite-Type Structure

The richness of the  $\text{ABX}_4$  phase space has been extensively explored.<sup>44,45</sup> In particular, changing the ionic ratios  $r_A/r_X$  and  $r_B/r_X$ , where  $r_A$  is the IR of the *A*-site cation,  $r_B$  is the IR of the *B*-site cation, and  $r_X$  is the IR of the anion (where *X* is not necessarily oxygen), can lead to either increases or decreases in crystal symmetry. Here, the phase

diagram proposed by Errandonea *et al.* is presented in Figure 1.3,<sup>44</sup> giving a ‘map’ of different crystal symmetries in the  $ABX_4$  materials. This diagram is adapted from the less-comprehensive version first published by Bastide in 1987.<sup>45</sup> The next section will introduce ways of moving around this phase diagram, by changing the ionic ratios through the application of temperature, pressure, or through chemical substitution. In turn, this gives access to an increasingly rich phase space which can be used to further tailor  $ABX_4$  materials for use as functional materials.

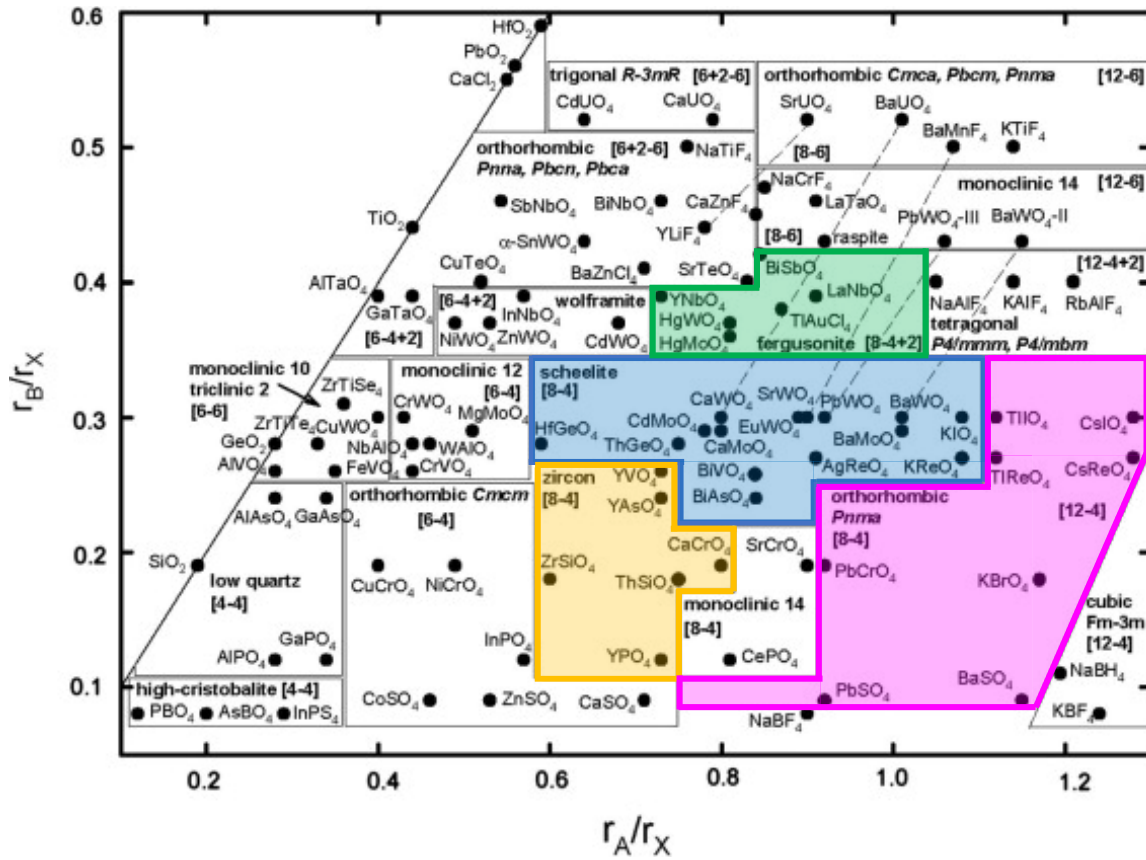


Figure 1.3: Phase diagram for  $ABX_4$  materials by Errandonea *et al.* highlighting the possible phases accessible by altering the ionic radii of the A- and B-site cations, and the X anions.<sup>44</sup> The phases that are the focus of this dissertation are highlighted by the shaded areas: (blue) tetragonal  $I4_1/a$  scheelite, (green) monoclinic  $I2/a$  and  $P2/c$  fergusonite, (gold) tetragonal  $I4_1/amd$  zircon, and (pink) orthorhombic  $Pnma$  pseudo scheelite.

### 1.2.2.1 Changes Due to Ionic Radii

As outlined above, the  $ABO_4$  metal oxides can accommodate a wide variety of different cations and charge combinations. However, not each of these combinations will produce the tetragonal  $I4_1/a$  scheelite-type structure, with many other phases also observed.

Crucially, the tetragonal  $I4_1/a$  scheelite-type structure only occurs within a ‘sweet spot’ of the  $r_A/r_O$  and  $r_B/r_O$  ratios (where  $r_A/r_O \sim 0.65\text{--}1.15$ , and  $r_B/r_O \sim 0.25\text{--}0.35$ ) (Figure 1.3, blue area). Therefore, by altering the IR of either the  $A$ - or  $B$ -site cations, we can alter the long-range symmetry of the structure.

#### Orthorhombic $Pnma$ Pseudo Scheelite-Type

By increasing the IR of the  $A$ -site cation, such as substituting  $\text{Rb}^+$  (IR = 1.61 Å,  $r_{\text{Rb}}/r_O \sim 1.13$ ) for  $\text{Cs}^+$  (IR = 1.74 Å,  $r_{\text{Cs}}/r_O \sim 1.23$ ), a change in long-range symmetry is expected. In  $A\text{ReO}_4$ , this results in a decrease in symmetry from tetragonal  $I4_1/a$  to orthorhombic ( $a \neq b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$ )  $Pnma$  (space group #62) structure (Figure 1.3, pink area). This has been seen previously, with  $\text{RbReO}_4$  and  $\text{CsReO}_4$  observed in the tetragonal  $I4_1/a$  and orthorhombic  $Pnma$  structures respectively.<sup>73</sup>

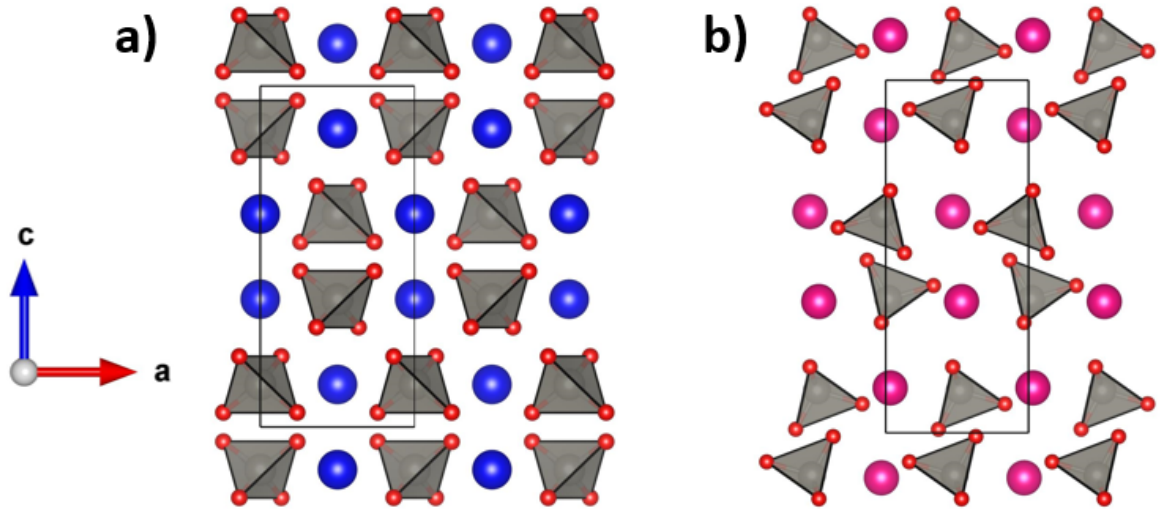


Figure 1.4: The  $ABX_4$  structures both stable at room temperature (a) tetragonal  $I4_1/a$  scheelite-type, and (b) orthorhombic  $Pnma$  pseudo scheelite-type. The difference between the two structures is the size of the  $A$ -site cation (as visualised by the blue and pink spheres). The difference can also be visualised *via* the rotations of the  $BO_4$  tetrahedra, with (a) rotated about the  $c$ -axis, and (b) rotated about the  $b$ -axis.

The  $Pnma$  structure has mostly been observed at room temperature for  $ABO_4$  materials with  $A^+ = \text{Cs}$ , such as  $\text{CsMnO}_4$ ,<sup>84</sup>  $\text{CsTeO}_4$ ,<sup>72</sup>  $\text{CsRuO}_4$ ,<sup>85</sup>  $\text{CsReO}_4$ ,<sup>73</sup>  $\text{CsOsO}_4$ ,<sup>85</sup>  $\text{CsClO}_4$ ,<sup>86</sup> and  $\text{CsIO}_4$ .<sup>87</sup> This has been previously referred to as the ‘baryte-type’ structure, due to its similarity to  $\text{BaSO}_4$ ,<sup>85</sup> but is more often called the ‘pseudo scheelite-type’ structure. The orthorhombic ‘ $Pnma$ ’ structure is similar to the tetragonal  $I4_1/a$  scheelite-type structure, but incorporates different rotations of the  $BO_4$  tetrahedra (Figure 1.4). Where the  $BO_4$  tetrahedra are rotated around the  $c$ -axis in  $I4_1/a$ , the  $BO_4$  tetrahedra are

rotated around the  $b$ -axis in  $Pnma$ .<sup>73</sup> This also leads to other losses of symmetry in the structure, such as the  $A$ - and  $B$ -site cations moving from their symmetry-constrained sites to the more free  $(x, 3/4, z)$  and  $(x', 1/4, z')$  positions respectively. This is also accompanied by the splitting of one anion position to three different anion positions.

### Monoclinic $I2/a$ Fergusonite-Type

By increasing the IR of the  $B$ -site cation, such as substituting  $W^{6+}$  (IR = 0.42 Å,  $r_W/r_O \sim 0.30$ ) for  $Nb^{5+}$  (IR = 0.48 Å,  $r_{Nb}/r_O \sim 0.34$ ), a lowering in symmetry from tetragonal  $I4_1/a$  to monoclinic ( $a \neq b \neq c$ ,  $\alpha = \beta \neq \gamma = 90^\circ$ )  $I2/a$  (space group #15) is observed (Figure 1.3, green area). This is most commonly described in  $LnNbO_4$  (where  $Ln^{3+} = La-Lu$ ). This structure is often referred in the literature as the  $M$ -type fergusonite-type structure, analogous to similar labels used in perovskites such as  $NaNbO_3$  and  $AgNbO_3$  to denote lower-symmetry distortions of an aristotype.<sup>88,89</sup> The fergusonite-type structure is named after the British politician and mineral collector Robert Ferguson of Raith, and is usually found in the form  $ANbO_4$  in nature (with  $A^{3+} = \text{rare-earth elements, such as Y and } Ln^{3+}$ ). It also naturally occurs in a metamictic state (amorphous, or with a loss of crystalline structure), due to its sequestering of naturally-occurring radioactive elements such as uranium and thorium.<sup>90</sup>

The increased size of the  $B$ -site cation provides additional flexibility within the structure. Namely, each cation site goes from a symmetry-constrained  $4b$  site  $(0, 1/4, 5/8)$  to a more general  $4e$  site  $(0, 1/4, 5/8 + \delta)$ , with freedom along a particular axis. The unique anion position is also split into two, allowing for distortions in the  $BO_4$  tetrahedra, giving two pairs of different bond lengths. These further deformations in the tetrahedra also lead to the inclusion of an additional two  $B$ -O distances (denoted as  $B-O_l$ , for ‘long’), causing the  $BO_4$  tetrahedra to become  $BO_6$  distorted octahedra (Figure 1.5b).<sup>91</sup> This causes a departure from the  $AO_8$  polyhedra and  $BO_4$  tetrahedra networks seen in the tetragonal  $I4_1/a$  scheelite-type structure to a network of  $AO_8$  polyhedra and  $BO_6$  octahedra. Nevertheless, it is usual to describe the fergusonite-type structure as a distorted scheelite.

### Monoclinic $P2/c$ Fergusonite-Type

Similar to the monoclinic  $I2/a$  structure, increasing the IR of the  $B$ -site cation can also lower the symmetry to the monoclinic  $P2/c$  structure (space group #13). The monoclinic  $P2/c$  is given the  $M'$ -type label, due to its similarity to the monoclinic  $I2/a$  structure (Figure 1.5c). However, the topology of these two phases is distinct, with differences observed in the chains of  $BO_6$  octahedra within the structure. In the  $I2/a$  space group, these octahedra run ‘out-of-phase’, whereas in the  $P2/c$  space group they run ‘in-phase’ or ‘interdigitated’ (Figure 1.5). The  $P2/c$  structure is often observed in  $ATaO_4$  materials, where the  $A$ -site cations are the smaller rare-earth lanthanoids (such as Tb–Lu). Like the  $I2/a$  structure, the  $A$ - and  $B$ -site cations exhibit crystallographic freedom along a particular direction, with two general anion positions. There is no obvious structural relationship between this  $M'$ -type structure and the  $I4_1/a$  tetragonal scheelite-type structure.

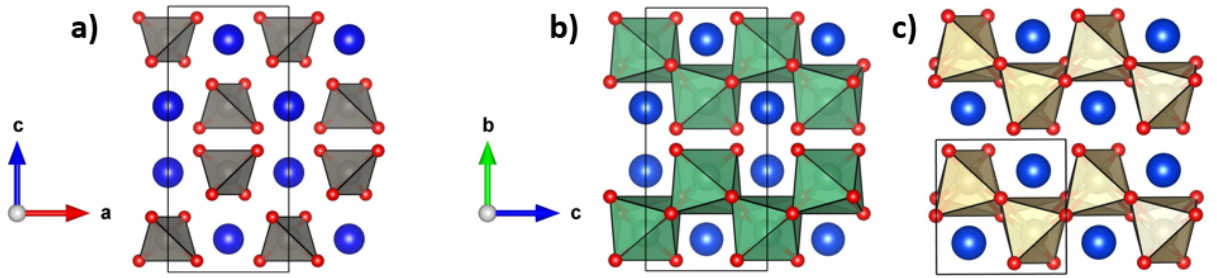


Figure 1.5: The  $ABX_4$  structures (a) tetragonal  $I4_1/a$  scheelite-type, and two fergusonite-type structures (b) monoclinic  $I2/a$   $M$ -type, and (c) monoclinic  $P2/c$   $M'$ -type. By changing the ionic radii of the  $B$ -site cation, the structural motif is changed from isolated  $BX_4$  tetrahedra to edge-sharing  $BX_6$  distorted octahedra. The difference between the  $I2/a$  and  $P2/c$  structures is visualised through the chains of  $BX_6$  octahedra, with the chains ‘out-of-phase’ in  $I2/a$  and ‘in-phase’ in  $P2/c$ .

#### 1.2.2.2 Changes Due to Temperature

In many crystallographic structures, heating a material results in an increase in the thermal motion of atoms, as well as an increase in the size of its unit cell. This can lead to an increase in symmetry, as the atoms have enough energy to overcome energy-lowering phenomena such as Jahn-Teller distortions and rigid unit mode packing such as polyhedra tilting. It is important to understand how the symmetry of these  $ABO_4$  structures change upon heating, as applications such as ceramic electrolytes for SOFCs require the application of heat to operate.

### Tetragonal $I4_1/a \rightarrow$ Tetragonal $I4_1/amd$

In some cases, the scheelite-type structure increases in symmetry from  $I4_1/a \rightarrow I4_1/amd$  upon heating. This has been identified as the true scheelite aristotype, with additional symmetry elements present. However, this structure is seldom observed in the scheelite-type oxides. Similar to the tetragonal  $I4_1/a$  structure, the  $I4_1/amd$  (space group #141) polymorph consists of networks of  $AO_{12}$  polyhedra and isolated  $BO_4$  tetrahedra. Notably, this phase transition has only been reported for  $A^+ = \text{Rb}$  scheelite-type oxides, such as  $\text{RbTcO}_4$ ,<sup>72</sup>  $\text{RbReO}_4$ ,<sup>73,92</sup>  $\text{RbOsO}_4$ .<sup>85</sup> The  $I4_1/a \rightarrow I4_1/amd$  phase transition is continuous by group theory, with the two structures differing by the rotation of their  $BO_4$  tetrahedra around the  $c$ -axis (governed by the  $\Gamma_3^+$  mode).<sup>73</sup> The general  $(x, y, z)$   $16f$  anion position in the  $I4_1/a$  structure moves to the semi-constrained  $(0, y, z)$   $16h$  position.

### Orthorhombic $Pnma \rightarrow$ Tetragonal $I4_1/a$ or Tetragonal $I4_1/amd$

Similar to the  $I4_1/a \rightarrow I4_1/amd$  phase transition reported in  $A^+ = \text{Rb}$  materials, attempts have been made to observe the  $Pnma \rightarrow I4_1/amd$  phase transition. This phase transition is also predicted to be continuous by group theory as the structures differ in the rotation of the  $BO_4$  tetrahedra about the  $c$ -axis governed by the  $M_4^+$  mode.

Early work identified both  $\text{CsTcO}_4$  and  $\text{CsReO}_4$  to be isostructural in the orthorhombic  $Pnma$  space group. Upon heating, both of these materials are reported to undergo a phase transition from orthorhombic to tetragonal ( $\text{CsTcO}_4$   $T_c \sim 450$  K,  $\text{CsReO}_4$   $T_c \sim 500$  K). However, the exact structure of this high-temperature phase remains unclear, with both  $I4_1/a$  and  $I4_1/amd$  proposed. Work on  $\text{CsTcO}_4$  by Kennedy *et al.* identified features characteristic of a first order phase transition associated with the transformation, such as a discontinuous jump in both the  $c$  lattice parameter and the unit cell volume, as well as the coexistence of both the orthorhombic and tetragonal phases between 400–450 K.<sup>72</sup> Similar features were noted for  $\text{CsRuO}_4$  and  $\text{CsOsO}_4$ , with the coexistence of both the orthorhombic and tetragonal phases over particular temperature ranges.<sup>85</sup>

The exact mechanism of the phase transition and the structure of the high-temperature phases of  $\text{CsTcO}_4$  and  $\text{CsReO}_4$  remains unresolved. The aristotype  $I4_1/amd$  structure can be obtained from  $Pnma$  by rotation of the  $BO_4$  tetrahedra around the  $b$ -axis. Conversely, the aristotype structure can be derived from the  $I4_1/a$  structure by rotation of the  $BO_4$

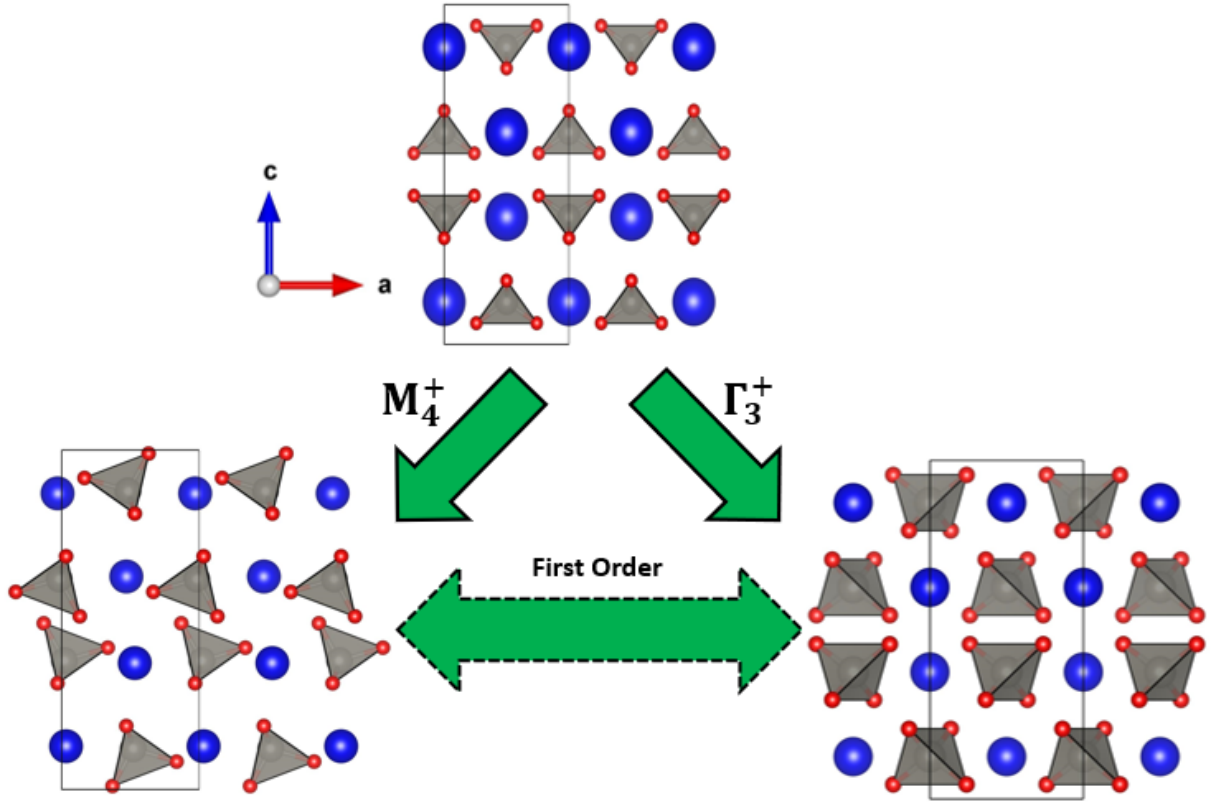


Figure 1.6: Relationships between the (top) tetragonal  $I4_1/amd$ , (bottom left) monoclinic  $Pnma$ , and (bottom right) tetragonal  $I4_1/a$  structures.

tetrahedra around the  $c$ -axis (Figure 1.5). However, it is not possible for a material to continuously transform from  $Pnma \rightarrow I4_1/a$ , as the rotations are about orthogonal axes. Therefore, any transition between these two structures must be first order. Differentiating whether an additional  $I4_1/a \rightarrow I4_1/amd$  phase transition occurs at higher temperature is difficult. Work by both Kennedy *et al.* and Chay *et al.* attempted to identify the exact space group of the high-temperature structures, but the process was problematic due to the relative weak scattering of  $O^{2-}$  ( $Z_{O^{2-}} = 10$ ) compared to either  $Cs^+$  ( $Z_{Cs^+} = 54$ ),  $Tc^{7+}$  ( $Z_{Tc^{7+}} = 36$ ), and  $Re^{7+}$  ( $Z_{Re^{7+}} = 68$ ). They tentatively identified the high-temperature structure of  $CsTcO_4$  to be  $I4_1/a$  due to the nonzero refinement of the  $O(1)$   $x$  atomic coordinate. Attempts were made to identify reflections unique to  $I4_1/a$ , but absent in the  $I4_1/amd$  structure. However, overlap between the diagnostic (114) and common (202) reflections made this difficult. A similar observation was made for  $TlTcO_4$ , whereby the high-temperature structure was postulated to be the  $I4_1/amd$  structure based on the absence of the (114) reflection.<sup>72</sup> However, this is also yet to be confirmed.



### Monoclinic $I2/a \rightarrow$ Tetragonal $I4_1/a$

As stated above, the  $\text{LaNbO}_4$  material exhibits the monoclinic  $I2/a$  fergusonite-type structure at room temperature. This material undergoes a phase transition from  $I2/a \rightarrow I4_1/a$  upon heating at  $\sim 500^\circ\text{C}$  (Figure 1.7).<sup>75</sup> This phase transition is accompanied by anisotropic expansion of the  $a$  and  $c$  lattice parameters, as well as a decrease in the monoclinic  $\beta$  angle. Upon transformation,  $a = c$  and  $\beta = 90^\circ$ , as seen in the tetragonal  $I4_1/a$  structure.

The nature of this phase transition has been investigated in-depth, as it plays a role in its potential material applications. Early work by Stubičan identified the  $I2/a \rightarrow I4_1/a$  phase transition in several  $M$ -type orthoniobates ( $\text{ANbO}_4$ ) as continuous and reversible ferroelastic phase transitions.<sup>93</sup> This was further supported by other studies that observed second order phase transition behaviour.<sup>94–97</sup> Recent literature work has identified the coexistence of both the  $I2/a$  and  $I4_1/a$  phases around the phase transition, as well as a small thermal hysteresis upon heating and cooling.<sup>75,95,98</sup> Such behaviour is inconsistent with a continuous phase transition, suggesting that the  $I2/a \rightarrow I4_1/a$  transformation is first order in nature. Furthermore, neutron powder diffraction studies have identified the long  $B\text{--}O_l$  bond to be crucial to the phase transition, with this bond being essential in optimising the coordination environment of the  $B$ -site cations at room temperature. The breaking of this bond transforms the  $\text{BO}_6$  octahedra to  $\text{BO}_4$  tetrahedra in the higher symmetry scheelite-type structure.<sup>91,94</sup> This is due to the  $\Gamma_2^+$  mode, and governs the movement of the cations and rotation of the  $\text{BO}_6$  tetrahedra.<sup>91,99</sup>

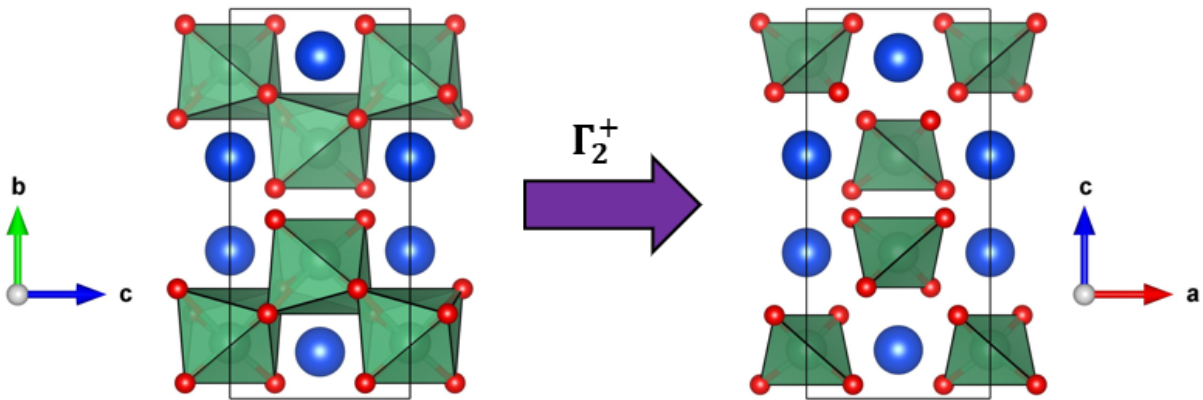


Figure 1.7: Relationship between the (left) monoclinic  $I2/a$  and (right) tetragonal  $I4_1/a$  structures. The phase transition proceeds through a breaking of the  $B\text{--}O_l$  bond governed by the  $\Gamma_2^+$  mode.



Hypothesised Monoclinic  $P2/c \rightarrow$  Monoclinic  $I2/a$ 

Although the monoclinic  $I2/a$  and  $P2/c$  structures are closely related, there has been substantially less reported on the analogous potential phase transitions for the  $P2/c$  structures. Previous work has identified the tendency of  $LnNbO_4$  materials to crystallise in the  $I2/a$  space group, whereas the  $LnTaO_4$  materials crystallise in different groups depending on the IR of the  $Ln^{3+}$  cation.<sup>75,100,101</sup> The larger  $Ln^{3+}$  cations (La–Pr) crystallise in the monoclinic  $P2_1/c$  space group (space group #14), the intermediate cations (Nd–Er) crystallise in the  $I2/a$  space group (isostructural to the  $LnNbO_4$  analogues), and the smaller cations (Ho–Lu) crystallise in the  $P2/c$  space group. This is particularly remarkable, as  $Nb^{5+}$  and  $Ta^{5+}$  cations are expected to exhibit near-identical chemistry due to their identical oxidation state and IR ( $Nb^{5+} = Ta^{5+} = 0.64 \text{ \AA}$  in octahedral geometry), and hence occupy the same space in the Errandonea *et al.* phase diagram (Figure 1.3, blue area).<sup>44,80</sup>

Various changes in the structure of  $LnTaO_4$  materials have been reported using *ex situ* diffraction. The pioneering study by Brixner *et al.* reported that  $LnTaO_4$  ( $Ln^{3+} = \text{Sm–Lu}$ ) could crystallise in either the  $I2/a$  or  $P2/c$  space group depending on whether a flux (such as  $LiSO_4$  or  $LiCl$ ) was used.<sup>102</sup> Other reports have also detailed the effect of longer heating times and higher temperatures on the structure of  $LnTaO_4$  materials, with materials transforming from the  $P2/c$  space group to the  $I2/a$  structure after being heated in a muffle furnace to temperatures exceeding  $1400 \text{ }^\circ\text{C}$ .<sup>103</sup> Although *in situ* diffraction studies have been reported describing the  $I2/a \rightarrow I4_1/a$  phase transition,<sup>75,91,93</sup> there are no equivalent *in situ* diffraction studies of the irreversible  $P2/c \rightarrow I2/a$  phase transformation.

The difference between the phase transitions in  $LnNbO_4$  and  $LnTaO_4$  structures were first explored by Stubičan, who identified that the  $I2/a \rightarrow I4_1/a$  phase transition occurs at a much higher temperature in  $LnTaO_4$  orthotantalates than the corresponding  $LnNbO_4$  orthoniobates.<sup>93</sup> This was further investigated by Saura-Múzquiz *et al.*, using neutron diffraction, where the  $I2/a \rightarrow I4_1/a$  phase transition was observed for both  $NdNbO_4$  and  $NdTaO_4$ . Each structure underwent the same  $I2/a \rightarrow I4_1/a$  phase transition *via* the same mechanism, although the orthotantalate proceeded at almost double the

temperature ( $\text{NdNbO}_4$   $T_c \sim 660$  °C,  $\text{NdTaO}_4$   $T_c \sim 1220$  °C). Interestingly, there appears to be a correlation between the preferred ( $I2/a$  or  $P2/c$ ) structure, and the temperature of the reversible  $I2/a \rightarrow I4_1/a$  phase transition. Therefore, based on this data, it is hypothesised that the  $P2/c \rightarrow I2/a$  phase transition occurs through the high-temperature  $I4_1/a$  scheelite-type phase. However, this remains to be investigated.

### 1.2.2.3 Changes Due to Pressure

Whereas increasing the temperature of a material can lead to an increase in its unit cell volume, an increase in pressure has the opposite effect. A decrease in unit cell volume can lead to changes in the coordination number of cations, as well as strengthening the orbital overlap between atoms resulting in stronger interactions. Therefore, increasing pressure is often described as the inverse of increasing temperature in terms of controlling the thermodynamics of a system. Increasing the coordination environment of cations leads to an increase in its effective IR, as seen in the  $I2/a \rightarrow I4_1/a$  phase transition of  $\text{LaNbO}_4$ , where  $\text{Nb}^{5+}$  undergoes a change in its coordination environment from  $\text{NbO}_6$  octahedra to  $\text{NbO}_4$  tetrahedra. Increasing the coordination number of the  $\text{Nb}^{5+}$  cation (from four-coordinate tetrahedra to six-coordinate octahedra) has a secondary effect of increasing the effective size of  $\text{Nb}^{5+}$  (from 0.48 to 0.64 Å).<sup>80</sup> This presents as yet another mechanism to traverse the Errandonea *et al.* phase diagram of  $ABX_4$  compounds, where an increase in pressure can result in an increase in both the  $r_A/r_X$  and  $r_B/r_X$  ratios.<sup>44</sup> Although this dissertation does not focus on the use of high pressure to explore the phase space of additional  $ABO_4$  materials, various parallels are drawn between the use of high temperature and high pressure. Therefore, it is included here in the form of a review to provide perspective on symmetry-lowering external stimuli and their relationship to temperature-induced phase transitions.

A majority of  $ABO_4$  high-pressure work has looked at  $B = \text{V}^{5+}$  and  $\text{W}^{6+}$  materials.<sup>104–106</sup> The  $AVO_4$  orthovanadates have found applications as photocatalyst materials for degrading propane and phenol,<sup>107,108</sup> as well as thermophosphors,<sup>109</sup> ionic conductors,<sup>110</sup> and optical materials.<sup>111</sup> Likewise, the  $AWO_4$  materials are currently used to fabricate scintillation detectors, as mentioned above with  $\text{PbWO}_4$ .<sup>50,51,112</sup> More recently,

high-pressure studies have been performed on  $\text{ANbO}_4$  orthoniobates to better understand the differences between these systems.

#### Tetragonal $I4_1/amd \rightarrow$ Tetragonal $I4_1/a$

One of the earliest high-pressure studies was performed on the tetragonal-zircon  $\text{YVO}_4$  in 1987.<sup>113</sup> This material has important applications in solid state lasing, where it serves as a host material for rare-earth ions. The pressure behaviour of this material was of interest due to the interpretation and modelling of the  $4f$  crystal field of  $\text{Nd}^{3+}$  as a function of interatomic distances to alter its lasing properties. The tetragonal-zircon phase is observed in the Errandonea *et al.* phase diagram (Figure 1.3, golden area), however this differs slightly from the  $I4_1/amd$  scheelite aristotype structure observed upon heating. The tetragonal-zircon structure has significantly different connectivity ( $\text{AO}_8$  *vs.*  $\text{AO}_{12}$  polyhedra), and has a smaller unit cell by approximately  $1/\sqrt{2}$  along the  $c$ -axis (Figure 1.8).

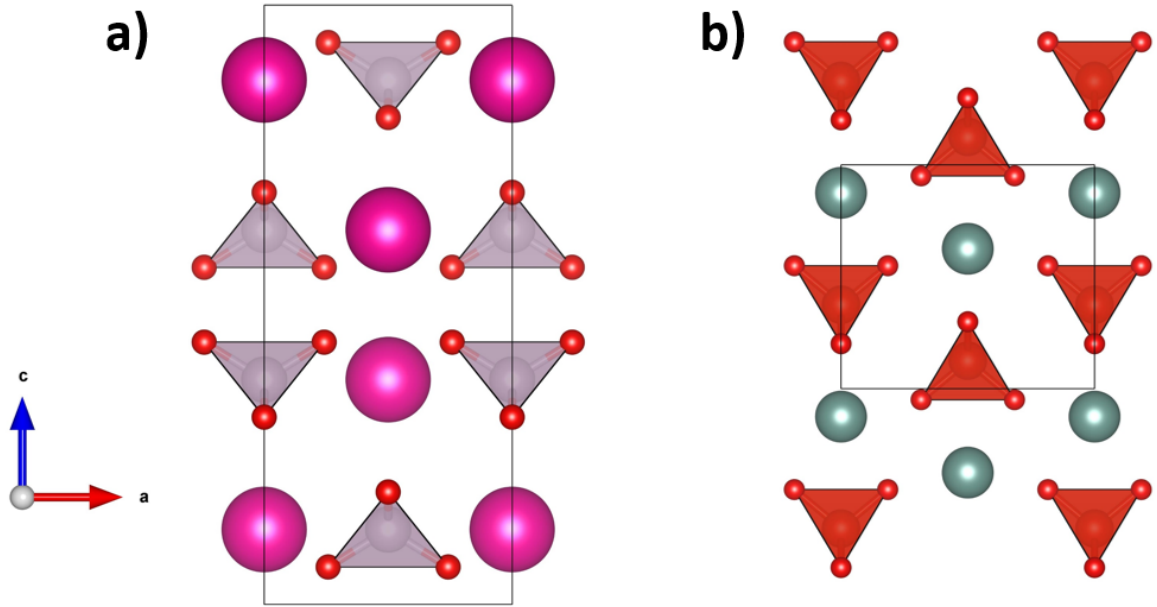


Figure 1.8: Relationship between the (a) tetragonal  $I4_1/amd$  scheelite-type aristotype, and (b) tetragonal  $I4_1/amd$  zircon-type structures. Although these phases are similar, they possess different connectivity. The different coloured spheres and tetrahedra are used to show that no phase transition occurs between these two structures.

An *in situ* high pressure structural study by Wang *et al.* reported a  $I4_1/amd \rightarrow I4_1/a$  phase transition in  $\text{YVO}_4$  at 8.5 GPa.<sup>114</sup> Contrary to the high temperature scheelite-type aristotype seen in  $\text{RbBO}_4$ ,<sup>73,85,92</sup> this phase transition is irreversible, with the

scheelite-type  $I4_1/a$  phase recovered upon releasing the pressure to ambient conditions.<sup>114</sup> The phase transition is also described as ‘sluggish’, with both phases coexisting over a pressure range of  $\sim 10$  GPa. A similar phase transition has been reported for other rare-earth orthovanadates such as  $\text{ScVO}_4$  (8.7 GPa),  $\text{EuVO}_4$  (7.8 GPa),  $\text{HoVO}_4$  (4.5 GPa),  $\text{YbVO}_4$  (5.9 GPa), and  $\text{LuVO}_4$  (8.9 GPa).<sup>115–117</sup> Various theoretical modelling techniques have been used to develop insight into this phase transition, with DFT calculations of the high pressure infrared modes used to understand the influence of pressure on the electronic structure of  $\text{AVO}_4$ .<sup>117</sup> It was identified that the pressure-driven instability of the tetragonal-zircon phase is due to the softening of the  $B_{1u}$  mode.<sup>118–120</sup> The high-pressure  $I4_1/amd \rightarrow I4_1/a$  phase transition has also been reported in other  $\text{ABO}_4$  materials, such as silicates,<sup>121</sup> phosphates,<sup>122</sup> chromates,<sup>123</sup> and arsenates.<sup>124</sup>

#### Tetragonal $I4_1/a \rightarrow$ Monoclinic $I2/a$

The high-pressure study of  $\text{EuVO}_4$  demonstrated the phase transition between  $I4_1/amd \rightarrow I4_1/a$ , with a coexistence of the two phases present between 7.8–15.1 GPa.<sup>115</sup> However, upon further pressurising above 20.9 GPa, a second pressure-induced phase transition was observed. This was determined to be a tetragonal-to-monoclinic phase transition of the form  $I4_1/a \rightarrow I2/a$ . Unlike the  $I4_1/amd \rightarrow I4_1/a$  transformation, this phase transition was identified to be reversible, with the  $I2/a$  structure not observed upon depressurising. This same phase transition was also noted in  $\text{LuVO}_4$  ( $\sim 21.9$  GPa).<sup>125</sup> Similar phase transitions have also been reported in other room temperature scheelite-type structures, including  $\text{CaWO}_4$  (10 GPa),<sup>126</sup>  $\text{SrWO}_4$  (11.5 GPa),<sup>127</sup>  $\text{SrMoO}_4$  (12.2 GPa),<sup>128</sup>  $\text{CdMoO}_4$  (12 GPa),<sup>129</sup> and  $\text{EuMoO}_4$  (8.8 GPa).<sup>129</sup>

Interestingly, the  $I4_1/a \rightarrow I2/a$  high pressure phase transition has been studied through the lens of the similar (but reversed)  $I2/a \rightarrow I4_1/a$  phase transition that occurs in  $\text{LaNbO}_4$  upon heating. Like the high-temperature studies, the nature of this phase transition is also believed to be weakly first order, with a soft mode being identified and remaining nonzero within the pressure range.<sup>127,130</sup> Studies also describe the distortion of the  $I4_1/a \rightarrow I2/a$  structure as being governed by the changing coordination environment of the  $B$ -site cation with the coordination increasing from  $\text{BO}_4$  tetrahedra to  $\text{BO}_6$  octahedra upon pressurising, similar to the high-temperature studies.<sup>104,131</sup>

### Other High Pressure Phase Transitions in $ANbO_4$

In comparison to  $AVO_4$  and  $AWO_4$ , the  $ANbO_4$  class of materials has been studied much less due to the higher pressures required for phase transformations. Early reports of high pressure phase transitions in  $LaNbO_4$ ,  $GdNbO_4$ , and  $EuNbO_4$  showed high pressure phases to exist, however no full structural models were reported.<sup>132–134</sup> It was not until Garg *et al.* performed a study combining high pressure X-ray powder diffraction and *ab initio* DFT calculations that a model for the phase transition in  $HoNbO_4$  was established.<sup>135</sup> Their study demonstrated that  $HoNbO_4$  undergoes a reversible phase transition to a second monoclinic polymorph, indexed to the  $P2_1/c$  space group, at around 19 GPa. It should be noted, however, that differences have been observed in the high-pressure behaviour of most  $ANbO_4$  materials, with isostructural compounds seemingly not undergoing the same phase transitions. For example,  $GdNbO_4$  apparently does not undergo a structural transformation up to 25 GPa,<sup>136</sup> whereas a  $I2/a \rightarrow P\bar{1}$  (space group #2) transition is reported in  $YbNbO_4$  near 11.6 GPa.<sup>137</sup> This indicates that the  $4f$  electrons play a role in the compressibility of these materials, leading to a potential way of fine-tuning their response.<sup>105,138</sup>

### 1.2.3 Additional Changes in Symmetry Due to Substitution

So far, only ternary oxides of the form  $ABO_4$  have been discussed. Making substitutions at either the  $A$  or  $B$  sites of the material gives a mechanism to traverse the Errandonea *et al.* phase diagram, as well as predicting their response to a range of external stimuli.<sup>44</sup> However, there are additional ways in which we can induce changes within the  $ABO_4$  structure, which are outlined below:

#### Multiple Cation Substitutions: Tetragonal $I\bar{4}$

As stated above, due to the chemical and thermal stability of  $ABO_4$  materials, they are remarkably robust to mixed cation occupancies. As an example, the family of  $ABO_4$  scheelite-type oxides may be extended to include ‘double scheelites’ of the form  $(A_{0.5}A'_{0.5})BO_4$  [sometimes written as  $AA'(BO_4)_2$ , where  $A$  and  $A'$  are two different  $A$ -site cations]. Oxides of this type, such as  $NaY(MoO_4)_2$ , have found applications as host crystals for luminescent ions in solid state lasing.<sup>82,139</sup>

It is important to note that  $A$  and  $A'$  are two cations of different sizes and oxidation states (in the case above,  $A = \text{Na}^+$  and  $A' = \text{Y}^{3+}$ ). The presence of two different cations on the  $A$  site may result in either incomplete or partial ordering across the site. This lowers the symmetry by splitting the  $A$  site of the  $I4_1/a$  structure into two distinct positions. This symmetry lowering is identified as tetragonal  $I\bar{4}$  (space group #82). Crystallographically, the  $4b$  Wyckoff position in the  $I4_1/a$  structure is split into two distinct  $2b$  and  $2c$  positions, where different occupancies of the  $A$  and  $A'$  cations are permitted (Figure 1.9). In most metal oxides, differences in the oxidation state or size of cations can lead to ordering, as illustrated in other materials such as the double perovskite  $\text{Ba}_2\text{InTaO}_6$ ,<sup>140,141</sup> as well as  $\text{Ln}_2\text{Ti}_2\text{O}_7$  pyrochlores and defect fluorites.<sup>142,143</sup> It should also be noted that scheelite-type oxides are not just limited to mixed occupancies on the  $A$  site, with interesting phenomena also identified in  $\text{La}_2\text{SiMoO}_8$ ,<sup>144</sup> as well as  $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$ .<sup>145,146</sup>

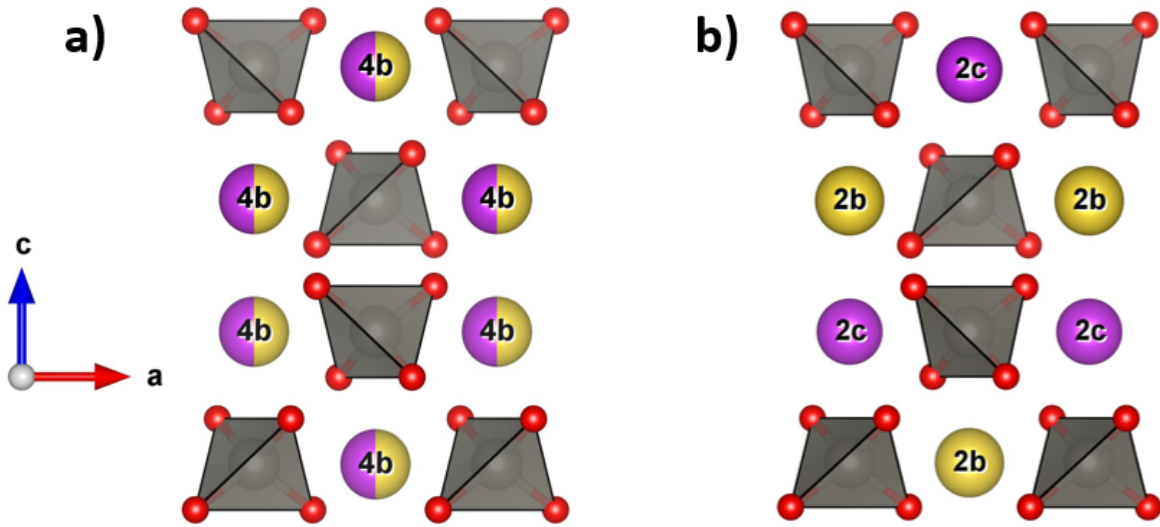


Figure 1.9: Relationship between the (a) tetragonal  $I4_1/a$  and (b) tetragonal  $I\bar{4}$  structures. Of note is the splitting of the  $4b$  Wyckoff position in the  $I4_1/a$  structure to two distinct  $2b$  and  $2c$  Wyckoff positions in the  $I\bar{4}$  structure. This distinction allows for the possibility of cation ordering.

Although partial ordering between  $A^+$  and  $A^{3+}$  cations has been reported, it remains a controversial topic within the literature. Early studies by Perera *et al.* indexed the  $\text{NaLn}(\text{BO}_4)_2$  materials to the archetype scheelite-type  $I4_1/a$  space group using X-ray powder diffraction, with the  $\text{Na}^+$  and  $\text{Ln}^{3+}$  cations disordering across a single  $4b$  Wyckoff position.<sup>147</sup> However, previous studies by Hanuza *et al.* reported vibrational states using polarised infrared and Raman spectroscopy that were postulated to be a result of short-range ordering between the  $\text{Na}^+$  and  $\text{Bi}^{3+}$  cations (and, subsequently,

lowering the symmetry from  $I4_1/a$  to  $I\bar{4}$ ).<sup>148,149</sup> This has also been reported in other spectroscopy studies, with Rico *et al.* relating the large spectroscopic bandwidths observed in some  $\text{Na}^+$ - and  $\text{Ln}^{3+}/\text{Bi}^{3+}$ -containing double scheelites to partial cation ordering,<sup>150</sup> and Volkov *et al.* relating the optical absorption and photoluminescence properties to the local ordering between Yb–Yb pairs in  $\text{LiYb}(\text{MoO}_4)_2$ .<sup>151</sup> Therefore, it is possible that partial ordering exists between the  $A$  and  $A'$  cations, leading to interesting interactions that can alter their lasing properties.

#### Anionic Substitution: Tetragonal $P4/nmm$

Another way of navigating the  $ABX_4$  phase diagram is by changing the  $X$  anion used in the structure. For example, replacing  $\text{O}^{2-}$  ( $\text{IR} = 1.40 \text{ \AA}$ ) with the slightly larger  $\text{S}^{2-}$  ( $\text{IR} = 1.84 \text{ \AA}$ ) can decrease the  $r_A/r_X$  and  $r_B/r_X$  ratios, going from orthorhombic  $Cmcm$  in  $\text{InPO}_4$  to tetragonal  $I\bar{4}$  in  $\text{InPS}_4$ .<sup>152,153</sup> By incorporating anions of different valencies (such as  $\text{F}^-$ ,  $\text{Cl}^-$ , or  $\text{N}^{3-}$ ), different charge combinations may also be accessed outside of the regular I–VII (such as  $\text{KOsO}_4$ ), II–VI ( $\text{CaWO}_4$ ), and III–V ( $\text{LaNbO}_4$ ) pairs.

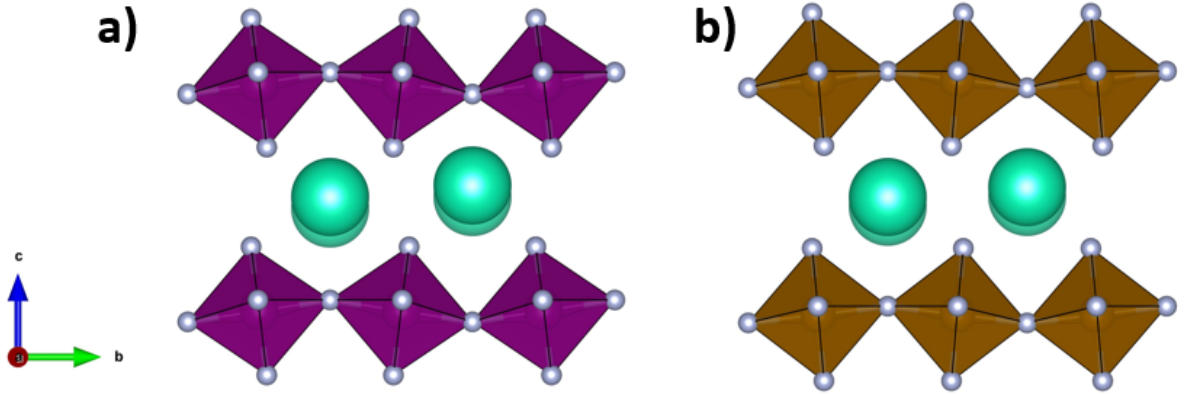


Figure 1.10: The crystal structure of (a)  $\text{CsMnF}_4$  and (b)  $\text{CsFeO}_4$ , both in the tetragonal  $P4/nmm$  space group. The aqua spheres represent  $\text{Cs}^+$ , the purple octahedra represent  $\text{MnF}_6$ , the brown octahedra represent  $\text{FeF}_6$ , and the white atoms represent  $\text{F}^-$ .

One example of this is  $\text{CsMnF}_4$ , where  $\text{F}^-$  has replaced  $\text{O}^{2-}$  in the structure allowing for a I–III cation charge combination. This material consists of corner-sharing  $\text{MnF}_6$  octahedra in 2D layers, separated by 12-coordinate  $\text{Cs}^+$  polyhedra. This 2D arrangement of the  $\text{MnF}_6$  octahedra is key, along with the coupling of the strong Jahn–Teller distortions as a result of the  $\text{Mn}^{3+}$  high spin cation complex and the weak field  $\text{F}^-$  ligands. As the Jahn–Teller distortions cause the  $\text{MnF}_6$  octahedra to distort into a two short

axial, four long equatorial bonding arrangement, a slight ‘puckering’ is observed in their arrangement (Figure 1.10a).<sup>154</sup> These slight distortions has led to various investigations into these materials, in particular with  $\text{CsMnF}_4$  displaying ferromagnetic ordering below 20 K,<sup>155</sup> whereas the isotypic material  $\text{CsFeF}_4$  displays antiferromagnetic ordering (Figure 1.10b). One particular explanation regarding this behaviour involves the superexchange angle between  $B\text{--F--}B$  (where  $B^{3+} = \text{Fe, Mn}$ ). However, this has not been confirmed experimentally. This is of particular interest in the field of magnetism, as controlling and optimising magnetic interactions is important for the development of various spintronic devices.<sup>156,157</sup>

## 1.3 Applications of $ABO_4$ -Type Materials

Based on the rich chemistry associated with the possible phases and atomic substitutions of  $ABO_4$ -type materials, these materials have received considerable attention in recent years. As mentioned, these materials have been investigated as potential ceramic electrolytes for SOFCs, solid state lasers, photocatalysts, spintronic devices, and matrices for safely storing radioactive waste. An outline of these applications, as well as the project aims of this dissertation, are presented below.

### 1.3.1 Solid Oxide Fuel Cells and $\text{LaNbO}_4$

The replacement of carbon-emitting energy sources with cleaner alternatives on an industrial scale is regarded as a critical priority for limiting the effects of anthropogenic climate change. The development of ceramic electrolytes for SOFCs offers a technological alternative to fossil fuel combustion by facilitating safe electrochemical oxidation of hydrogen-rich fuels in an all-solid-state environment. Central to the operation of SOFCs is the presence of a material with high ionic conductivity, as well as thermal and chemical stability in a variety of different chemical environments.



SOFCS operate by producing electrical energy directly from chemical energy *via* an oxidation-reduction reaction. They are seen as a viable alternative to current coal-fired power stations as they are not bound by the Carnot limit; energy is transferred from chemical directly into electrical energy allowing for greater efficiency in energy conversion, and is not lost in stepwise energy transformations along the way.<sup>158</sup> SOFCs operate by oxidising a fuel at the anode and reducing an oxidant at the cathode. In an ideal set-up, hydrogen gas is used as a fuel and oxygen from air is used as the oxidant, producing water as a carbon-neutral byproduct. The cathode acts as a catalyst by reducing oxygen to create oxygen ions, which then diffuse through the solid electrolyte to be oxidised at the anode to form water. The electrons liberated in the process travel through an external electrical circuit, being used to do electrical work. Essential to the operation of SOFCs is a ceramic electrolyte that possesses high ionic conductivity, low electrical conductivity, excellent thermal stability, and good chemical stability to a variety of gaseous environments. A significant drawback of SOFCs is that the metal oxide-based solid electrolytes used are restricted to high operating temperatures (between 500–800 °C), limiting their efficiency, large-scale usability, and commercialisation.

Various  $ABO_4$  materials have been intensively studied for their ionic conductivity properties. Purely stoichiometric materials – such as  $\text{LaNbO}_4$  and  $\text{SrWO}_4$  – have displayed promising ionic conductivity.<sup>159,160</sup> However, small amounts of dopants have been shown to increase their ionic conductivity by up to three orders of magnitude.<sup>99,161,162</sup> As ionic mobility proceeds through  $ABO_4$  materials *via* ions jumping between interstitial sites, the stability of  $\text{LaNbO}_4$  to its chemical substitutions makes it an ideal candidate to explore both oxygen ion and proton conductivity.<sup>163</sup> The enhanced oxygen ionic conductivity has been observed in Mo- or W-doped  $\text{LaNbO}_4$ , forming  $\text{La}(\text{Nb}_{1-x}\text{B}_x)\text{O}_{4+\delta}$  (where  $\text{B}^{6+} = \text{Mo}, \text{W}$ ).<sup>99,161,164–166</sup> The difference in oxidation state between  $\text{Nb}^{5+}$  and  $\text{B}^{6+}$  introduces additional oxygen ions into the structure (as indicated by the  $+\delta$  in the chemical formula) which are free to contribute to the ionic conduction. On the other hand, enhanced proton conductivity has also been observed in Ca-doped  $\text{LaNbO}_4$ , forming  $(\text{Ca}_x\text{La}_{1-x})\text{NbO}_{4-\delta}$ , with differences between the  $\text{La}^{3+}$  and  $\text{Ca}^{2+}$  oxidation state inducing oxygen vacancies that lead to enhanced proton conductivity.<sup>159,167,168</sup>

Despite their promise, various issues exist with the pursuit of  $\text{LaNbO}_4$  (and the isostructural  $\text{LnNbO}_4$  counterparts) as a potential SOFC ceramic electrolyte. Firstly, the addition of dopants alters the behaviour of these materials at moderate operating temperatures, leading to complex relationships between dopant and conductivity. This has been reinforced by MD simulations, which have confirmed that total conductivity is affected by the local structure distortions that are common in non-stoichiometric systems.<sup>163,169,170</sup> Secondly, it is desirable for solid electrolytes to avoid first order phase transitions, such as the  $I2/a \rightarrow I4_1/a$  phase transition that occurs in  $\text{LaNbO}_4$  at  $\sim 500^\circ\text{C}$ .<sup>75</sup> Properties associated with first order phase transitions, such as thermal hysteresis and discontinuities in volume expansion, can lead to induced strain within the material and a high chance of performance degradation with thermal cycling.

One way to avoid each of these issues is to look at the analogous  $\text{LnTaO}_4$  materials. Whilst  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  are described as ‘inseparable twins’ due to their identical oxidation state and IR, several differences have been observed in their crystal chemistry. Whilst the orthoniobates ( $\text{LnNbO}_4$ ) have been reported to crystallise in the  $I2/a$  structure, the orthotantalates ( $\text{LnTaO}_4$ ) can crystallise in the monoclinic space groups  $P2_1/c$ ,  $I2/a$ , or  $P2/c$  depending on the size of the  $\text{Ln}^{3+}$  cation.<sup>75,100,101</sup> Furthermore, the  $I2/a \rightarrow I4_1/a$  phase transition observed in  $\text{ABO}_4$  materials is tunable depending on the  $A$ - and  $B$ -site cations used. Larger  $\text{Ln}^{3+}$  cations traditionally lead to lower phase transition temperatures ( $\text{LaNbO}_4$   $T_c \sim 500^\circ\text{C}$  and  $\text{HoNbO}_4$   $T_c \sim 800^\circ\text{C}$ ), whereas the orthotantalates exhibit higher transition temperatures ( $\text{NdNbO}_4$   $T_c \sim 660^\circ\text{C}$  and  $\text{NdTaO}_4$   $T_c \sim 1220^\circ\text{C}$ ).<sup>91,93</sup> Therefore, the chemical tunability of both the  $A$  and  $B$  sites present an opportunity to specifically tailor these materials for ionic conductivity applications by altering the temperature of its first order phase transition.

### 1.3.2 Solid State Lasers and $\text{NaBi}(\text{WO}_4)_2$

Solid state lasers have gained a lot of attention due to their application in printing, semiconductor chip manufacturing, and medical procedures. The most commonly used solid state lasers require a medium for  $\text{Nd}^{3+}$  ions, where the crystal field splitting in the  $5d$  and  $4f$  energy levels provide the lasing activity of the crystal. The crystal field splitting of the  $\text{Nd}^{3+}$  ion is influenced by its local coordination environment, with a delicate balance between crystallinity and local disorder required to ensure good lasing efficiency and performance.

Scheelite-type structures have found application as solid state lasing materials due to their common structural motif of  $\text{AO}_8$  polyhedra environments with industrially-used lasing materials such as  $\text{Nd}^{3+}$ -doped yttrium aluminium garnets (Nd:YAGs). However, substitution of rare-earth ions onto the  $A$  site of the  $ABO_4$  structures may lead to partial ordering, which lowers the symmetry of the structure from tetragonal  $I4_1/a$  to  $I\bar{4}$ . This has led to controversy within the literature, with different studies concluding different structural models depending on the types of analysis performed.<sup>147,148</sup> Long-range average techniques, such as X-ray and neutron powder diffraction, seemingly conclude that the  $A^+$  and  $A^{3+}$  cations are disordered across a single site, leading to the identification of the tetragonal  $I4_1/a$  structure.<sup>147</sup> However, local structure probes such as infrared and Raman spectroscopy have observed additional vibrational states that require the lowering of symmetry from tetragonal  $I4_1/a$  to tetragonal  $I\bar{4}$  to be indexed. This local ordering between the  $A^+$  and  $A^{3+}$  cations has also been used to explain the optical and lasing properties of some  $A^+A^{3+}(\text{BO}_4)_2$  double scheelite materials.<sup>151</sup> As it currently stands, there is an incomplete understanding as to whether the  $A^+$  and  $A^{3+}$  cations disorder across a single cation position in the tetragonal  $I4_1/a$  structure, or partially order leading to two unique cation positions in the tetragonal  $I\bar{4}$  structure. This ordering can persist on different length scales, with an ordered arrangement possible on the local scale (as observed using spectroscopy) that is lost on the long-range scale (as observed using diffraction). An in-depth understanding of whether this local ordering occurs, and how it may be tuned to engineer more favourable local environments for the lasing rare-earth ions, is required.

### 1.3.3 Photocatalysts, $\text{BiVO}_4$ , and $\text{PbWO}_4$

In order for the full commercialisation of SOFCs, a carbon-neutral method of generating hydrogen gas is also required. Currently, hydrogen gas is produced through steam-methane reforming, which produces either carbon monoxide or carbon dioxide as a byproduct. One carbon-neutral process for hydrogen gas production is through photocatalytic water splitting (PWS), where water is ‘split’ into its constituent hydrogen and oxygen gases. In a hydrogen evolution reaction (HER), a catalyst captures the energy of a photon which is then used to break the oxygen–hydrogen bond of a water molecule. The most commonly studied materials for PWS are semiconductors, due to their ability to separate the charge carriers necessary for PWS reactions.<sup>171,172</sup> Despite its apparent simplicity, PWS has not been fully commercialised due to its low efficiency using visible light.<sup>173</sup> Current research is focused on exploring metal oxides that have a band gap suitable for multistep PWS using more of the visible light spectrum, as well as being able to maintain their crystallinity over time, and to be manufactured from low-cost and abundant materials.<sup>174</sup>

In recent years,  $\text{BiVO}_4$  and  $\text{PbWO}_4$  have been identified as promising candidates for photocatalysis due to their favourable band gaps.<sup>175,176</sup>  $\text{BiVO}_4$  adopts the monoclinic  $I2/a$  fergusonite-type structure, whereas  $\text{PbWO}_4$  adopts the higher-symmetry tetragonal  $I4_1/a$  scheelite-type structure.<sup>177,178</sup> A feature of these particular  $\text{ABO}_4$  materials is the presence of the  $6s^2$  lone pair electrons on  $\text{Bi}^{3+}$  and  $\text{Pb}^{2+}$ . Materials with lone pair electrons are well known for their unique polar properties, as evident in many Pb-based perovskites actively utilised as ferroelectrics.<sup>179–181</sup> In the case of  $\text{BiVO}_4$  and  $\text{PbWO}_4$ , the stereochemical activity of the  $6s^2$  electrons are directly related to the band gap of the material, thus influencing their applicability as visible light-driven photocatalysts.<sup>182</sup> The stereochemical activity of the lone pairs are found to exhibit distortions within the crystal structure.<sup>183–185</sup> This is of particular note in  $\text{BiVO}_4$  and  $\text{PbWO}_4$ , where the  $\text{BiO}_8$  polyhedra show distinctly more distortion than their  $\text{PbO}_8$  counterparts (Figure 1.11). These distortions are observed using X-ray and neutron diffraction, where the  $\text{BiO}_8$  polyhedra display four pairs of different Bi–O bond lengths (all ranging between 2.3–2.8 Å), whereas the  $\text{PbO}_8$  polyhedra display two different Pb–O distances (ranging between

2.6–2.8 Å). Whether a lone pair is stereochemically active or inactive appears to be related to the energy separation between the cation  $ns$  and anion  $2p$  levels.<sup>186</sup> This has been used to explain why materials such as  $\alpha$ -PbO exhibit lone pair stereochemical activity, whereas the  $Pb^{2+}$  cations in PbS do not. For metal oxides, this trend is also observed with SnO crystallising in a distorted litharge structure, whereas  $PbO_2$  forms the centrosymmetric fluorite structure.<sup>183</sup>

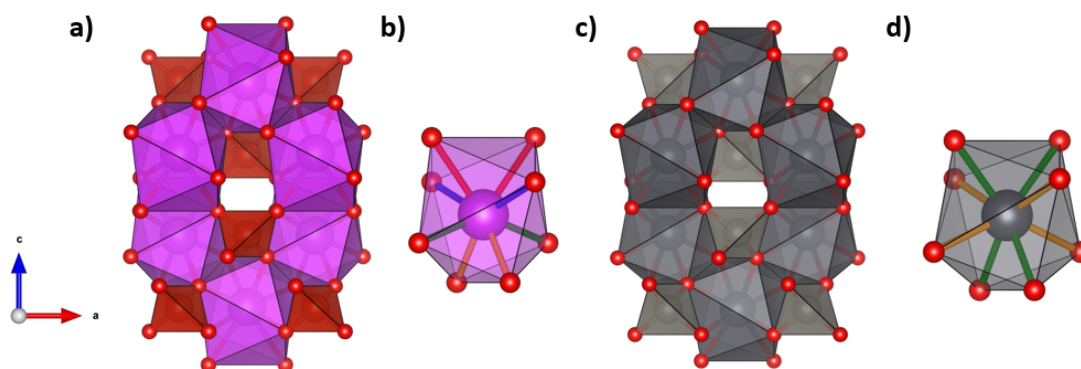


Figure 1.11: (a) The monoclinic  $I2/b$  crystal structure of  $BiVO_4$  consisting of  $BiO_8$  polyhedra (purple) and  $VO_4$  tetrahedra (orange), (b) the  $BiO_8$  polyhedra with four different Bi–O bond distances between 2.3–2.8 Å (indicated with different colours), (c) the tetragonal  $I4_1/a$  crystal structure of  $PbWO_4$  consisting of  $PbO_8$  polyhedra (black) and  $WO_4$  tetrahedra (grey), (d) the  $PbO_8$  polyhedra with two different Pb–O bond distances between 2.6–2.8 Å (indicated with different colours).

The stereochemical activity of the  $Bi^{3+}$  lone pair in  $BiVO_4$ , but the apparent lack of stereochemical activity of  $Pb^{2+}$  lone pair in  $PbWO_4$  is not explained by current experimental or computational models. Previous computational studies have demonstrated that the predicting the ground state energy structure of lone pair-bearing materials such as  $BiVO_4$  is nontrivial, where a hybrid density functional of about 60% Hartree-Fock (HF) exchange was required to model the subtle interplay between the structural and electronic properties.<sup>187</sup> Therefore, it is of critical importance to further establish the structure of these two materials in order to inform further experimental and computational studies dedicated to improving their applicability as photocatalysts.

### 1.3.4 Storage of Radioactive Waste and $TlTcO_4$

Another potential avenue of carbon-neutral energy generation is through the use of nuclear power. Nuclear power plants generate electricity by driving a steam turbine, similar

to coal-fired power stations. However, where coal-fired power plants use the heat from burning coal, nuclear power plants source their heat from the nuclear fission of uranium. In nuclear fission, uranium nuclei undergo neutron capture and radioactively decay into smaller nuclei, releasing more energy and neutrons in the process, leading to a sustained chain reaction.

A major issue with the nuclear fuel cycle is the production of high-level radioactive waste with long half lives. Some high-activity nuclear waste byproducts have extensive half lives and can remain active for long periods of time, such as  $^{239}\text{Pu}$  ( $\sim 24\,100$  years),  $^{137}\text{Cs}$  ( $\sim 30$  years), and  $^{99}\text{Tc}$  ( $\sim 221\,000$  years), as well as being environmentally hazardous due to the amount of ionising radiation they emit. Current research is focused on ways to securely store this high-activity nuclear waste, such as glasses,<sup>188,189</sup> MOFs,<sup>190,191</sup> and crystalline ceramics.<sup>188,192</sup> Two main issues are associated with the safe storage of radioactive waste. Firstly, the high mobility of smaller fission products, such as  $^{99}\text{Tc}$ , means they are problematic to sequester and can lead to long term environmental damage. Secondly, the high radioactivity of some nuclearisotopes, such as  $^{135}\text{Cs}$ , means their decay chain can lead to numerous elastic collisions within their storage matrix.<sup>193</sup> This, in turn, can lead to substantial volume expansion, microfracturing, and reduced chemical durability which can contribute to degradation of the crystalline structure of the matrix and lead to environmental leaching.

While various  $\text{ABO}_4$  structures have been shown to amorphise,<sup>194–196</sup> and hence, not be suitable for radioactive waste storage, greater promise lies in the complexing of the highly mobile pertechnetate ion ( $\text{TcO}_4^-$ ) in the form of  $\text{ATcO}_4$  salts. Technetium is one of the most challenging fission products, accounting for a mass yield of  $\sim 6\%$  in fission reactions.<sup>72</sup> Although  $^{99m}\text{Tc}$  is used as a medical radioisotope for selective imaging diagnosis, the decay product  $^{99}\text{Tc}$  presents an environmental challenge due to its high mobility, high  $\beta^-$  emission, and long half life.<sup>197</sup>

As Tc has no stable isotopes, it is common for studies to use Re as a nonradioactive surrogate.<sup>198–201</sup> This is due to the predicted similarities in the chemical behaviour of  $\text{Tc}^{7+}$  and  $\text{Re}^{7+}$  attributed to their identical oxidation state and similar IR ( $0.37$  vs.  $0.38\text{ \AA}$  in tetrahedra geometry).<sup>80</sup> However, there is a growing body of literature showing that  $\text{Tc}^{7+}$

and  $\text{Re}^{7+}$  materials do not always act similarly.<sup>202,203</sup> Although several  $\text{ATcO}_4$  and  $\text{AReO}_4$  salts have been identified as being isostructural, there have been recorded differences in their phase transitions at high temperature.<sup>72–74</sup> It is currently uncertain as to what the origin of these subtle differences are. Furthermore, the high-temperature behaviour of some  $\text{ATcO}_4$  and  $\text{AReO}_4$  salts are worth investigating due to the current unresolved phase transitions that occur at elevated temperatures. In investigating these phase transitions, it may be possible to further understand why  $\text{Tc}^{7+}$  and  $\text{Re}^{7+}$  act differently in these materials.

### 1.3.5 Spintronic Materials and $\text{CsMnF}_4$

Spintronic materials have led to the discovery of many different phenomena, such as giant magnetoresistance and the quantum Hall effect which are used in many different technological applications.<sup>204,205</sup> Important spintronic materials are topological materials, such as the 2D magnetism exhibited in the layered  $\text{CsMnF}_4$  structure. A majority of 2D magnetic materials order antiferromagnetically, such as the related  $\text{AMnF}_4$  ( $A^+ = \text{K}, \text{Rb}$ ), and the isotopic material  $\text{CsFeF}_4$ .<sup>206,207</sup> Therefore,  $\text{CsMnF}_4$  is somewhat of an anomaly. Although  $\text{CsMnF}_4$  has been studied computationally,<sup>208</sup> very few experimental studies have been performed to verify structural details such as its magnetic space group, the temperature-dependent behaviour of the Mn–F–Mn bond angles governing its superexchange interactions, and its magnetic susceptibility.

## 1.4 Dissertation Outline and Aims

The overall topic of this dissertation is to build on the various structure-functionality relationships in  $\text{ABO}_4$  metal oxides for their application as functional energy materials. This will be done by addressing previous gaps in the literature, as well as providing focus on some current unanswered questions. This dissertation has been separated into four main sections, which are outlined below:

**PART 1** provides the literature review, motivation, and theoretical background for the presented work, and consists of two chapters:

- **Chapter 1** gives a literature review into various  $ABO_4$  metal oxide structures, as well as introducing ways in which different phases may be formed, such as varying temperature, pressure, and chemical substitution. This chapter also gives a perspective on the gaps in the literature and how they will be explored in this dissertation.
- **Chapter 2** gives a brief introduction into the field of science in which this work sits at the intersection of: materials chemistry and crystallography. Introductions to various terminology is given, as well as an in-depth explanation of the analytical techniques used within this dissertation.

**PART 2** serves as the main body of work. It explores three systems in-depth and their applications as functional energy materials. This part consists of three chapters:

- **Chapter 3** introduces  $\text{LaNbO}_4$  as a potential ceramic electrolyte for solid oxide fuel cells. It looks at common structural trends in the  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  materials, as well as similarities and differences in their response to temperature. This is then used to explain trends in their ionic conductivities.
- **Chapter 4** extends the  $ABO_4$  scheelite-type structure to  $AA'(BO_4)_2$  double scheelites. An in-depth structural model is identified for these materials on both the long-range average and short-range local structure scale. The discrepancies between these structures is relevant to their application as solid state lasers.
- **Chapter 5** introduces both  $\text{BiVO}_4$  and  $\text{PbWO}_4$  as potential catalysts for PWS and the carbon-neutral production of hydrogen and oxygen gas. A full structural model is provided to understand the role of the  $6s^2$  lone pair electrons on the photocatalytic activity of the two materials.



**PART 3** is a space for additional studies performed within the author's time as a PhD student. It explores matrices capable of storing radioactive waste and spintronic materials. This part consists of two chapters:

- **Chapter 6** introduces the possible wasteform  $\text{CsReO}_4$  and compares it with  $\text{TlTeO}_4$ ; a material capable of complexing with highly mobile Tc nuclear fission products to appropriately store radioactive waste.
- **Chapter 7** takes a brief look at the synthesis, nuclear and magnetic structure, and physical properties of the layered perovskite  $\text{CsMnF}_4$ .

**PART 4** details the final chapter of the dissertation; identifying possible future avenues for additional studies.

- **Chapter 8** provides a summation of the advances made within this dissertation in understanding structure-functionality relationships in some  $ABX_4$  materials, and places these into the context of their applications as functional energy materials.



# Bibliography

- (1) US Energy Information Administration. Energy and the Environment Explained: Where Greenhouse Gases Come From, <https://www.eia.gov/energyexplained/energy-and-the-environment/where-greenhouse-gases-come-from.php> Last accessed on 2023-06-18.
- (2) United Nations. Causes and Effects of Climate Change. <https://www.un.org/en/climatechange/science/causes-effects-climate-change> Last accessed on 2023-06-18.
- (3) France24. Pacific Island Countries Fight to Ensure Future Before Rising Sea Levels Swallow Them Up, <https://www.france24.com/en/asia-pacific/20221124-pacific-islands-fight-for-existence-before-rising-sea-levels-swallow-them-up> Last accessed on 2023-06-18.
- (4) Axios. New Alarms Over Consequences of Antarctic Ice Melt, <https://www.axios.com/2023/05/30/climate-antarctic-ice-melt-slowing-global-ocean-currents> Last accessed on 2023-06-18.
- (5) USA Today. Another Above-Average Wildfire Season for 2022. How Climate Change is Making Fires Harder to Predict and Fight. <https://www.usatoday.com/story/news/2022/12/24/us-wildfire-season-2022-again-above-average-amid-climate-change/10811014002/> Last accessed on 2023-06-18.
- (6) Phys Org. Australia's 'Black Summer' Fires Affected Ozone Layer: Study. <https://phys.org/news/2022-08-australia-black-Australia's 'BlackSummer' firesaffectedozonelayer:studysummer-affected-ozone.html> Last accessed on 2023-06-18.

- (7) British Broadcasting Corporation (BBC). Australia's Fires 'killed or Harmed Three Billion Animals'. <https://www.bbc.com/news/world-australia-53549936> Last accessed on 2023-06-18.
- (8) The Guardian. Smoke from Australian Bushfires Depleted Ozone Layer by Up to 5% in 2020, Study Finds. <https://www.theguardian.com/environment/2023/mar/08/smoke-from-australian-bushfires-depleted-ozone-layer-by-up-to-5-in-2020-study-finds> Last accessed on 2023-06-18.
- (9) Bloomberg. Visit the Great Barrier Reef Before Climate Change Kills the Coral. <https://www.bloomberg.com/news/features/2022-10-19/visit-the-great-barrier-reef-before-climate-change-kills-the-coral> Last accessed on 2023-06-18.
- (10) The Sydney Morning Herald. Floods Cost Australian Economy \$5 Billion Last Year, <https://www.smh.com.au/politics/federal/floods-cost-economy-5-billion-last-year-20230112-p5cc1t.html> Last accessed on 2023-06-18.
- (11) Australian Government. Australian Electricity Generation - Fuel Mix. <https://www.energy.gov.au/data/australian-electricity-generation-fuel-mix> Last accessed on 2023-06-18.
- (12) Australian Government. Renewables, <https://www.energy.gov.au/data/renewables> Last accessed on 2023-06-18.
- (13) CleanTechnica. Nearly 1 In 3 Homes In Australia Covered In Solar Panels, <https://cleantechnica.com/2023/02/28/nearly-1-in-3-homes-in-australia-covered-in-solar-panels/> Last accessed on 2023-06-18.
- (14) Encyclopedia Britannica. History of Europe – The Metal Ages, <https://www.britannica.com/topic/history-of-Europe/The-Metal-Ages> Last accessed on 2023-06-18.
- (15) Billinge, S. J. The rise of the X-ray atomic pair distribution function method: A series of fortunate events. *Philosophical Transactions of the Royal Society A* **2019**, 377, 20180413.

## BIBLIOGRAPHY

---

- (16) Aasi, J.; Abadie, J.; Abbott, B.; Abbott, R.; Abbott, T.; Abernathy, M.; Adams, C.; Adams, T.; Addesso, P.; Adhikari, R. Enhanced sensitivity of the LIGO gravitational wave detector by using squeezed states of light. *Nature Photonics* **2013**, *7*, 613–619.
- (17) Kim, J.; Shih, P.-C.; Tsao, K.-C.; Pan, Y.-T.; Yin, X.; Sun, C.-J.; Yang, H. High-performance pyrochlore-type yttrium ruthenate electrocatalyst for oxygen evolution reaction in acidic media. *Journal of the American Chemical Society* **2017**, *139*, 12076–12083.
- (18) Feng, Q.; Zou, J.; Wang, Y.; Zhao, Z.; Williams, M. C.; Li, H.; Wang, H. Influence of surface oxygen vacancies and ruthenium valence state on the catalysis of pyrochlore oxides. *ACS Applied Materials & Interfaces* **2020**, *12*, 4520–4530.
- (19) Kuznetsov, D. A.; Naeem, M. A.; Kumar, P. V.; Abdala, P. M.; Fedorov, A.; Müller, C. R. Tailoring lattice oxygen binding in ruthenium pyrochlores to enhance oxygen evolution activity. *Journal of the American Chemical Society* **2020**, *142*, 7883–7888.
- (20) Wu, J.; Han, T.; Tang, X. First principle calculations of structural and electronic properties of pyrochlore  $\text{Y}_2\text{Ru}_2\text{O}_7$  and  $\text{Y}_{1-x}\text{M}_x\text{Ru}_2\text{O}_{7-\delta}$  ( $M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Zn}, \text{Cd}$  and  $\text{Hg}$ ). *Journal of Physics and Chemistry of Solids* **2021**, *156*, 110145.
- (21) Haire, R.; Baybarz, R. Identification and analysis of einsteinium sesquioxide by electron diffraction. *Journal of Inorganic and Nuclear Chemistry* **1973**, *35*, 489–496.
- (22) Fujishima, A.; Rao, T. N.; Tryk, D. A. Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2000**, *1*, 1–21.
- (23) Nakata, K.; Fujishima, A.  $\text{TiO}_2$  photocatalysis: Design and applications. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2012**, *13*, 169–189.
- (24) Qin, T.; Wang, D.; Zhang, X.; Wang, Y.; Drewett, N. E.; Zhang, W.; Dong, T.; Li, T.; Wang, Z.; Deng, T. Unlocking the optimal aqueous  $\delta\text{-Bi}_2\text{O}_3$  anode *via* unifying octahedrally liberated Bi-atoms and spilled nano-Bi exsolution. *Energy Storage Materials* **2021**, *36*, 376–386.

- (25) Sanna, S.; Esposito, V.; Andreasen, J. W.; Hjelm, J.; Zhang, W.; Kasama, T.; Simonsen, S. B.; Christensen, M.; Linderöth, S.; Pryds, N. Enhancement of the chemical stability in confined  $\delta$ -Bi<sub>2</sub>O<sub>3</sub>. *Nature Materials* **2015**, *14*, 500–504.
- (26) Su, D.; Dou, S.; Wang, G. Bismuth: A new anode for the Na-ion battery. *Nano Energy* **2015**, *12*, 88–95.
- (27) Dharma, H. N. C.; Jaafar, J.; Widiastuti, N.; Matsuyama, H.; Rajabsadeh, S.; Othman, M. H. D.; Rahman, M. A.; Jafri, N. N. M.; Suhaimin, N. S.; Nasir, A. M. A review of titanium dioxide (TiO<sub>2</sub>)-based photocatalyst for oilfield-produced water treatment. *Membranes* **2022**, *12*, 345.
- (28) Tang, Q.; Meng, X.; Wang, Z.; Zhou, J.; Tang, H. One-step electrospinning synthesis of TiO<sub>2</sub>/*g*-C<sub>3</sub>N<sub>4</sub> nanofibers with enhanced photocatalytic properties. *Applied Surface Science* **2018**, *430*, 253–262.
- (29) Wang, T.; Xu, J.; Zhang, Z.; Bian, H.; Xiao, H.; Sun, T. *g*-C<sub>3</sub>N<sub>4</sub> composited TiO<sub>2</sub> nanofibers were prepared by high voltage electrostatic spinning to improve photocatalytic efficiency. *Journal of Materials Science: Materials in Electronics* **2021**, *32*, 1178–1186.
- (30) Liu, B.; Chen, B.; Zhang, B. Oily wastewater treatment by nano-TiO<sub>2</sub>-induced photocatalysis: Seeking more efficient and feasible solutions. *IEEE Nanotechnology Magazine* **2017**, *11*, 4–15.
- (31) Prasad, N.; Karthikeyan, B. Broad band and enhanced photocatalytic behaviour of Ho<sup>3+</sup>-doped Bi<sub>2</sub>O<sub>3</sub> micro-rods. *Applied Physics A* **2018**, *124*, 1–8.
- (32) Ohno, T.; Sarukawa, K.; Tokieda, K.; Matsumura, M. Morphology of a TiO<sub>2</sub> photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline phases. *Journal of Catalysis* **2001**, *203*, 82–86.
- (33) Leary, R.; Westwood, A. Carbonaceous nanomaterials for the enhancement of TiO<sub>2</sub> photocatalysis. *Carbon* **2011**, *49*, 741–772.
- (34) Xiang, L.; Zhao, X. Wet-chemical preparation of TiO<sub>2</sub>-based composites with different morphologies and photocatalytic properties. *Nanomaterials* **2017**, *7*, 310.

## BIBLIOGRAPHY

---

- (35) Negishi, N.; Iyoda, T.; Hashimoto, K.; Fujishima, A. Preparation of transparent  $\text{TiO}_2$  thin film photocatalyst and its photocatalytic activity. *Chemistry Letters* **1995**, *24*, 841–842.
- (36) Kim, S. B.; Hong, S. C. Kinetic study for photocatalytic degradation of volatile organic compounds in air using thin film  $\text{TiO}_2$  photocatalyst. *Applied Catalysis B: Environmental* **2002**, *35*, 305–315.
- (37) Lee, S.-H.; Kang, M.; Cho, S. M.; Han, G. Y.; Kim, B.-W.; Yoon, K. J.; Chung, C.-H. Synthesis of  $\text{TiO}_2$  photocatalyst thin film by solvothermal method with a small amount of water and its photocatalytic performance. *Journal of Photochemistry and Photobiology A: Chemistry* **2001**, *146*, 121–128.
- (38) Gomez, C. L.; Depablos-Rivera, O.; Medina, J. C.; Silva-Bermudez, P.; Muhl, S.; Zeinert, A.; Rodil, S. E. Stabilization of the delta-phase in  $\text{Bi}_2\text{O}_3$  thin films. *Solid State Ionics* **2014**, *255*, 147–152.
- (39) Turkoglu, O.; Soylak, M. Synthesis of the beta and delta phases of  $\text{Bi}_2\text{O}_3$  stabilized by  $\text{Gd}_2\text{O}_3$ . *Asian Journal of Chemistry* **2002**, *14*.
- (40) Ling, C. D.; Withers, R. L.; Schmid, S.; Thompson, J. G. A review of bismuth-rich binary oxides in the systems  $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ ,  $\text{Bi}_2\text{O}_3\text{--Ta}_2\text{O}_5$ ,  $\text{Bi}_2\text{O}_3\text{--MoO}_3$ , and  $\text{Bi}_2\text{O}_3\text{--WO}_3$ . *Journal of Solid State Chemistry* **1998**, *137*, 42–61.
- (41) Zakaria, Z.; Abu Hassan, S. H.; Shaari, N.; Yahaya, A. Z.; Boon Kar, Y. A review on recent status and challenges of yttria stabilized zirconia modification to lowering the temperature of solid oxide fuel cells operation. *International Journal of Energy Research* **2020**, *44*, 631–650.
- (42) Hiroi, Z.; Yamaura, J.-i.; Hattori, K. Rattling good superconductor:  $\beta$ -pyrochlore oxides  $\text{AOs}_2\text{O}_6$ . *Journal of the Physical Society of Japan* **2011**, *81*, 011012.
- (43) Lyu, Y.; Wu, X.; Wang, K.; Feng, Z.; Cheng, T.; Liu, Y.; Wang, M.; Chen, R.; Xu, L.; Zhou, J. An overview on the advances of  $\text{LiCoO}_2$  cathodes for lithium-ion batteries. *Advanced Energy Materials* **2021**, *11*, 2000982.
- (44) Errandonea, D.; Manjon, F. J. Pressure effects on the structural and electronic properties of  $\text{ABX}_4$  scintillating crystals. *Progress in Materials Science* **2008**, *53*, 711–773.

- (45) Bastide, J. Systématique simplifiée des composés  $ABX_4$  ( $X = O^{2-}, F^{-}$ ) et evolution possible de leurs structures cristallines sous pression. *Journal of Solid State Chemistry* **1987**, *71*, 115–120.
- (46) Injac, S.; Yuen, A. K.; Avdeev, M.; Orlandi, F.; Kennedy, B. J. Structural and magnetic studies of  $KOsO_4$ , a  $5d^1$  quantum magnet oxide. *Physical Chemistry Chemical Physics* **2019**, *21*, 7261–7264.
- (47) Ennaciri, A.; Kahn, A.; Michel, D. Crystal structures of  $HfGeO_4$  and  $ThGeO_4$  germanates. *Journal of the Less Common Metals* **1986**, *124*, 105–109.
- (48) West, J. B. Carl Wilhelm Scheele, the discoverer of oxygen, and a very productive chemist. *American Journal of Physiology - Lung Cellular and Molecular Physiology* **2014**, *307*, L811–L816.
- (49) Kröger, F. A.; Urbach, F. Some aspects of the luminescence of solids. *Physics Today* **1948**, *1*, 24.
- (50) Dorenbos, P.; Van Eijk, C. W., *Proceedings of the International Conference on Inorganic Scintillators and their Applications, Delft, The Netherlands, 28 August–September 1, 1995: SCINT 95*; Delft University Press: 1996.
- (51) Adzic, P.; Almeida, N.; Andelin, D.; Anicin, I.; Antunovic, Z.; Arcidiacono, R.; Arenton, M.; Auffray, E.; Argiro, S.; Askew, A. Radiation hardness qualification of  $PbWO_4$  scintillation crystals for the CMS Electromagnetic Calorimeter. *Journal of Instrumentation* **2010**, *5*, P03010.
- (52) Papynov, E.; Shichalin, O.; Buravlev, I. Y.; Belov, A.; Portnyagin, A.; Fedorets, A.; Azarova, Y. A.; Tananaev, I.; Sergienko, V. Spark plasma sintering-reactive synthesis of  $SrWO_4$  ceramic matrices for  $^{90}Sr$  immobilization. *Vacuum* **2020**, *180*, 109628.
- (53) Shruthi, D.; Reddy, A. J.; Kumar, G. A. Structural, Judd-Ofelt, photoluminescence properties of  $Eu^{3+}$  activated  $SrWO_4$  phosphors: Electronic, vibrational, elastic properties from *ab initio* study. *Optical Materials* **2021**, *118*, 111243.



## BIBLIOGRAPHY

---

- (54) Pandey, A.; Rai, V. K.; Kumar, V.; Kumar, V.; Swart, H. Upconversion based temperature sensing ability of  $\text{Er}^{3+}\text{--Yb}^{3+}$  codoped  $\text{SrWO}_4$ : An optical heating phosphor. *Sensors and Actuators B: Chemical* **2015**, *209*, 352–358.
- (55) Shivakumara, C.; Saraf, R.  $\text{Eu}^{3+}$ -activated  $\text{SrMoO}_4$  phosphors for white LEDs applications: Synthesis and structural characterization. *Optical Materials* **2015**, *42*, 178–186.
- (56) Ivleva, L.; Basiev, T.; Voronina, I.; Zverev, P.; Osiko, V.; Polozkov, N.  $\text{SrWO}_4\text{:Nd}^{3+}$  – New material for multifunctional lasers. *Optical Materials* **2003**, *23*, 439–442.
- (57) Errandonea, D.; Tu, C.; Jia, G.; Martín, I.; Rodríguez-Mendoza, U.; Lahoz, F.; Torres, M.; Lavin, V. Effect of pressure on the luminescence properties of  $\text{Nd}^{3+}$  doped  $\text{SrWO}_4$  laser crystal. *Journal of Alloys and Compounds* **2008**, *451*, 212–214.
- (58) Basiev, T. T.; Smetanin, S. N.; Fedin, A. V.; Shurygin, A. S. Intracavity SRS conversion in diode-pumped multifunctional  $\text{Nd}^{3+}\text{:SrMoO}_4$  laser crystal. *Quantum Electronics* **2010**, *40*, 704.
- (59) Ju, Z.; Wei, R.; Gao, X.; Liu, W.; Pang, C. Red phosphor  $\text{SrWO}_4$ :  $\text{Eu}^{3+}$  for potential application in white LED. *Optical Materials* **2011**, *33*, 909–913.
- (60) Li, X.; Yang, Z.; Guan, L.; Guo, Q. A new yellowish green luminescent material  $\text{SrMoO}_4\text{:Tb}^{3+}$ . *Materials Letters* **2009**, *63*, 1096–1098.
- (61) Benzineb, M.; Chiker, F.; Khachai, H.; Meradji, H.; Uğur, Ş.; Naqib, S.; Omran, S. B.; Wang, X.; Khenata, R. A comparative study of structural, thermal, and optoelectronic properties between zircon and scheelite type structures in  $\text{SrMoO}_4$  compound: An *ab-initio* study. *Optik* **2021**, *238*, 166714.
- (62) Gao, H.; Yu, C.; Wang, Y.; Wang, S.; Yang, H.; Wang, F.; Tang, S.; Yi, Z.; Li, D. A novel photoluminescence phenomenon in a  $\text{SrMoO}_4/\text{SrWO}_4$  micro/nano heterojunction phosphors obtained by the polyacrylamide gel method combined with low temperature calcination technology. *Journal of Luminescence* **2022**, *243*, 118660.

- 
- (63) Khan, M. Y. A.; Zahoor, M.; Shaheen, A.; Jamil, N.; Arshad, M. I.; Bajwa, S. Z.; Shad, N. A.; Butt, R.; Ali, I.; Iqbal, M. Z. Visible light photocatalytic degradation of crystal violet dye and electrochemical detection of ascorbic acid & glucose using BaWO<sub>4</sub> nanorods. *Materials Research Bulletin* **2018**, *104*, 38–43.
- (64) Yanalak, G.; Ozen, A.; Sarilmaz, A.; Keles, A.; Aslan, E.; Ozel, F.; Patir, I. H. Scheelite-type BaMoO<sub>4</sub> and BaWO<sub>4</sub> based dye sensitized photocatalytic hydrogen evolution by water splitting. *Journal of Physics and Chemistry of Solids* **2022**, *168*, 110821.
- (65) Sahmi, A.; Omeiri, S.; Bensadok, K.; Trari, M. Electrochemical properties of the scheelite BaWO<sub>4</sub> prepared by co-precipitation: Application to electro-photocatalysis of ibuprofen degradation. *Materials Science in Semiconductor Processing* **2019**, *91*, 108–114.
- (66) Shan, Z.; Wang, Y.; Ding, H.; Huang, F. Structure-dependent photocatalytic activities of MWO<sub>4</sub> ( $M = \text{Ca, Sr, Ba}$ ). *Journal of Molecular Catalysis A: Chemical* **2009**, *302*, 54–58.
- (67) Feng, H. L.; Calder, S.; Ghimire, M. P.; Yuan, Y.-H.; Shirako, Y.; Tsujimoto, Y.; Matsushita, Y.; Hu, Z.; Kuo, C.-Y.; Tjeng, L. H. Ba<sub>2</sub>NiOsO<sub>6</sub>: A Dirac-Mott insulator with ferromagnetism near 100 K. *Physical Review B* **2016**, *94*, 235158.
- (68) Cavichini, A.; Orlando, M.; Depianti, J.; Passamai Jr, J.; Damay, F.; Porcher, F.; Granado, E. Exotic magnetism and spin-orbit-assisted Mott insulating state in a 3d–5d double perovskite. *Physical Review B* **2018**, *97*, 054431.
- (69) Chen, Q.; Svoboda, C.; Zheng, Q.; Sales, B. C.; Mandrus, D. G.; Zhou, H.; Zhou, J.-S.; McComb, D.; Randeria, M.; Trivedi, N. Magnetism out of antisite disorder in the  $J = 0$  compound Ba<sub>2</sub>YIrO<sub>6</sub>. *Physical Review B* **2017**, *96*, 144423.
- (70) Kim, B.; Jin, H.; Moon, S.; Kim, J.-Y.; Park, B.-G.; Leem, C.; Yu, J.; Noh, T.; Kim, C.; Oh, S.-J. Novel  $J_{\text{eff}} = 1/2$  Mott state induced by relativistic spin-orbit coupling in Sr<sub>2</sub>IrO<sub>4</sub>. *Physical Review Letters* **2008**, *101*, 076402.
- (71) Shinaoka, H.; Miyake, T.; Ishibashi, S. Noncollinear magnetism and spin-orbit coupling in 5d pyrochlore oxide Cd<sub>2</sub>Os<sub>2</sub>O<sub>7</sub>. *Physical Review Letters* **2012**, *108*, 247204.

## BIBLIOGRAPHY

---

- (72) Kennedy, B. J.; Injac, S.; Thorogood, G. J.; Brand, H. E.; Poineau, F. Structures and phase transitions in pertechnetates. *Inorganic Chemistry* **2019**, *58*, 10119–10128.
- (73) Chay, C.; Avdeev, M.; Brand, H. E.; Injac, S.; Whittle, T. A.; Kennedy, B. J. Crystal structures and phase transition behaviour in the 5d transition metal oxides  $A\text{ReO}_4$  ( $A = \text{Ag, Na, K, Rb, Cs and Tl}$ ). *Dalton Transactions* **2019**, *48*, 17524–17532.
- (74) Reynolds, E. M.; Yu, M.; Thorogood, G. J.; Brand, H. E.; Poineau, F.; Kennedy, B. J. Thermal expansion of ammonium pertechnetate and ammonium perrhenate. *Journal of Solid State Chemistry* **2019**, *274*, 64–68.
- (75) Arulnesan, S. W.; Kayser, P.; Kimpton, J. A.; Kennedy, B. J. Studies of the fergusonite to scheelite phase transition in  $\text{LnNbO}_4$  orthoniobates. *Journal of Solid State Chemistry* **2019**, *277*, 229–239.
- (76) Magrasó, A.; Fontaine, M.-L.; Larring, Y.; Bredesen, R.; Syvertsen, G.; Lein, H.; Grande, T.; Huse, M.; Strandbakke, R.; Haugsrud, R. Development of proton conducting SOFCs based on  $\text{LaNbO}_4$  electrolyte – Status in Norway. *Fuel Cells* **2011**, *11*, 17–25.
- (77) Tolchard, J.; Lein, H. L.; Grande, T. Chemical compatibility of proton conducting  $\text{LaNbO}_4$  electrolyte with potential oxide cathodes. *Journal of the European Ceramic Society* **2009**, *29*, 2823–2830.
- (78) Magrasó, A.; Fontaine, M.-L.; Bredesen, R.; Haugsrud, R.; Norby, T. Cathode compatibility, operation, and stability of  $\text{LaNbO}_4$ -based proton conducting fuel cells. *Solid State Ionics* **2014**, *262*, 382–387.
- (79) Shahid, M. Recent advances in proton conducting electrolytes for solid oxide fuel cells. *Ionics* **2022**, *28*, 3583–3601.
- (80) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **1976**, *32*, 751–767.

- (81) Yang, X.; Fu, Z.; Yang, Y.; Zhang, C.; Wu, Z.; Sheng, T. Optical temperature sensing behavior of high-efficiency upconversion:  $\text{Er}^{3+}\text{-Yb}^{3+}$  co-doped  $\text{NaY}(\text{MoO}_4)_2$  phosphor. *Journal of the American Ceramic Society* **2015**, *98*, 2595–2600.
- (82) Stedman, N. J.; Cheetham, A. K.; Battle, P. D. Crystal structures of two sodium yttrium molybdates:  $\text{NaY}(\text{MoO}_4)_2$  and  $\text{Na}_5\text{Y}(\text{MoO}_4)_4$ . *Journal of Materials Chemistry* **1994**, *4*, 707–711.
- (83) Fonteneau, G.; L’Helgoualch, H.; Lucas, J. Les niobates  $\text{CaUNb}_2\text{O}_8$  et  $M\text{ThNb}_2\text{O}_8$  ( $M = \text{Ca}, \text{Sr}, \text{Cd}$ ). Etude des transformations monoclinique-quadratique. *Materials Research Bulletin* **1977**, *12*, 25–33.
- (84) Prout, E.; Nassimbeni, L. Crystal structure of caesium permanganate. *Nature* **1966**, *211*, 70–71.
- (85) Injac, S.; Yuen, A. K.; Avdeev, M.; Wang, C.-H.; Turner, P.; Brand, H. E.; Kennedy, B. J. Structural and magnetic studies of  $\text{ABO}_4$ -type ruthenium and osmium oxides. *Inorganic Chemistry* **2020**, *59*, 2791–2802.
- (86) Granzin, J. Refinement of the crystal structures of  $\text{RbClO}_4$  and  $\text{CsClO}_4$ . *Zeitschrift für Kristallographie-Crystalline Materials* **1988**, *184*, 157–160.
- (87) Waal, D. d.; Zabel, M.; Range, K.-J. The crystal structure of  $\beta\text{-CsIO}_4$ , the room-temperature modification of cesium periodate. *Zeitschrift für Naturforschung B* **1996**, *51*, 441–443.
- (88) Megaw, H. D. The seven phases of sodium niobate. *Ferroelectrics* **1974**, *7*, 87–89.
- (89) Farid, U.; Khan, H. U.; Avdeev, M.; Whittle, T. A.; Kennedy, B. J. Preparation and high resolution structural studies of  $\text{Li}_x\text{Ag}_{1-x}\text{NbO}_3$  lead free piezoelectrics. *Journal of Solid State Chemistry* **2019**, *269*, 401–408.
- (90) Gieré, R.; Williams, C. T.; Wirth, R.; Ruschel, K. Metamict fergusonite-(Y) in a spessartine-bearing granitic pegmatite from Adamello, Italy. *Chemical Geology* **2009**, *261*, 333–345.
- (91) Saura-Múzquiz, M.; Mullens, B. G.; Maynard-Casely, H. E.; Kennedy, B. J. Neutron diffraction study of the monoclinic–tetragonal phase transition in  $\text{NdNbO}_4$  and  $\text{NdTaO}_4$ . *Dalton Transactions* **2021**, *50*, 11485–11497.

## BIBLIOGRAPHY

---

- (92) Marlton, F. P.; Mullens, B. G.; Chater, P. A.; Kennedy, B. J. Tetrahedral displacive disorder in the scheelite-type oxide  $\text{RbReO}_4$ . *Inorganic Chemistry* **2022**, *61*, 15130–15137.
- (93) Stubičan, V. High-temperature transitions in rare-earth niobates and tantalates. *Journal of the American Ceramic Society* **1964**, *47*, 55–58.
- (94) David, W. The high-temperature paraelastic structure of  $\text{LaNbO}_4$ . *Materials Research Bulletin* **1983**, *18*, 749–756.
- (95) Kuroiwa, Y.; Muramoto, H.; Shobu, T.; Tokumichi, H.; Yamada, Y. Pretransitional phenomena at the first-order phase transition in  $\text{LaNbO}_4$ . *Journal of the Physical Society of Japan* **1995**, *64*, 3798–3803.
- (96) Fjeld, H.; Toyoura, K.; Haugrud, R.; Norby, T. Proton mobility through a second order phase transition: Theoretical and experimental study of  $\text{LaNbO}_4$ . *Physical Chemistry Chemical Physics* **2010**, *12*, 10313–10319.
- (97) Hara, K.; Sakai, A.; Tsunekawa, S.; Sawada, A.; Ishibashi, Y.; Yagi, T. A soft acoustic mode in the ferroelastic phase transition of  $\text{LaNbO}_4$ . *Journal of the Physical Society of Japan* **1985**, *54*, 1168–1172.
- (98) Sarin, P.; Hughes, R. W.; Lowry, D. R.; Apostolov, Z. D.; Kriven, W. M. High-temperature properties and ferroelastic phase transitions in rare-earth niobates ( $\text{LnNbO}_4$ ). *Journal of the American Ceramic Society* **2014**, *97*, 3307–3319.
- (99) Auckett, J. E.; Lopez-Odriozola, L.; Clark, S. J.; Evans, I. R. Exploring the nature of the fergusonite–scheelite phase transition and ionic conductivity enhancement by  $\text{Mo}^{6+}$  doping in  $\text{LaNbO}_4$ . *Journal of Materials Chemistry A* **2021**, *9*, 4091–4102.
- (100) Haugrud, R.; Norby, T. Proton conduction in rare-earth ortho-niobates and ortho-tantalates. *Nature Materials* **2006**, *5*, 193–196.
- (101) Machida, M.; Murakami, S.; Kijima, T.; Matsushima, S.; Arai, M. Photocatalytic property and electronic structure of lanthanide tantalates,  $\text{LnTaO}_4$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{and Sm}$ ). *The Journal of Physical Chemistry B* **2001**, *105*, 3289–3294.
- (102) Brixner, L. On the structural and luminescent properties of the  $M'$   $\text{LnTaO}_4$  rare earth tantalates. *Journal of the Electrochemical Society* **1983**, *130*, 2435.

- (103) Wang, J.; Chong, X.; Zhou, R.; Feng, J. Microstructure and thermal properties of  $RETaO_4$  ( $RE = Nd, Eu, Gd, Dy, Er, Yb, Lu$ ) as promising thermal barrier coating materials. *Scripta Materialia* **2017**, *126*, 24–28.
- (104) Errandonea, D.; Garg, A. B. Recent progress on the characterization of the high-pressure behaviour of  $AVO_4$  orthovanadates. *Progress in Materials Science* **2018**, *97*, 123–169.
- (105) Errandonea, D. High pressure crystal structures of orthovanadates and their properties. *Journal of Applied Physics* **2020**, *128*, 040903.
- (106) Lacomba-Perales, R.; Errandonea, D.; Segura, A.; Ruiz-Fuertes, J.; Rodríguez-Hernández, P.; Radescu, S.; López-Solano, J.; Mujica, A.; Muñoz, A. A combined high-pressure experimental and theoretical study of the electronic band-structure of scheelite-type  $AWO_4$  ( $A = Ca, Sr, Ba, Pb$ ) compounds. *Journal of Applied Physics* **2011**, *110*, 043703.
- (107) Fukudome, K.; Ikenaga, N.-o.; Miyake, T.; Suzuki, T. Oxidative dehydrogenation of propane using lattice oxygen of vanadium oxides on silica. *Catalysis Science & Technology* **2011**, *1*, 987–998.
- (108) Ozturk, B.; Soylu, G. S. P. Synthesis of surfactant-assisted  $FeVO_4$  nanostructure: characterization and photocatalytic degradation of phenol. *Journal of Molecular Catalysis A: Chemical* **2015**, *398*, 65–71.
- (109) Palilla, F. C.; Levine, A. K.  $YVO_4:Eu$ : A highly efficient, red-emitting phosphor for high pressure mercury lamps. *Applied Optics* **1966**, *5*, 1467–1468.
- (110) Katari, V.; Patwe, S. J.; Achary, S. N.; Tyagi, A. K. High temperature structural, dielectric, and ion conduction properties of orthorhombic  $InVO_4$ . *Journal of the American Ceramic Society* **2013**, *96*, 166–173.
- (111) Piotrowski, W.; Dalipi, L.; Elzbieciak-Piecka, K.; Bednarkiewicz, A.; Fond, B.; Marciniak, L. Self-Referenced Temperature Imaging with Dual Light Emitting Diode Excitation and Single-Band Emission of  $AVO_4: Eu^{3+}$  ( $A = Y, La, Lu, Gd$ ) Nanophosphors. *Advanced Photonics Research* **2022**, *3*, 2100139.

## BIBLIOGRAPHY

---

- (112) Hizhnyi, I.; Nedilko, S.; Nikolaenko, T. Electronic structures of luminescence centers in pure and defective scintillation crystals  $AWO_4$  ( $A = \text{Pb}, \text{Cd}, \text{Zn}$ ). *Moldavian Journal of the Physical Sciences* **2006**, *5*, 15–19.
- (113) Jayaraman, A.; Kourouklis, G.; Espinosa, G.; Cooper, A.; Van Uitert, L. A high-pressure Raman study of yttrium vanadate ( $YVO_4$ ) and the pressure-induced transition from the zircon-type to the scheelite-type structure. *Journal of Physics and Chemistry of Solids* **1987**, *48*, 755–759.
- (114) Wang, X.; Loa, I.; Syassen, K.; Hanfland, M.; Ferrand, B. Structural properties of the zircon-and scheelite-type phases of  $YVO_4$  at high pressure. *Physical Review B* **2004**, *70*, 064109.
- (115) Errandonea, D.; Lacomba-Perales, R.; Ruiz-Fuertes, J.; Segura, A.; Achary, S.; Tyagi, A. High-pressure structural investigation of several zircon-type orthovanadates. *Physical Review B* **2009**, *79*, 184104.
- (116) Garg, A. B.; Rao, R.; Sakuntala, T.; Wani, B.; Vijayakumar, V. Phase stability of  $YbVO_4$  under pressure: *In situ* X-ray and Raman spectroscopic investigations. *Journal of Applied Physics* **2009**, *106*, 063513.
- (117) Garg, A. B.; Errandonea, D.; Rodríguez-Hernández, P.; López-Moreno, S.; Muñoz, A.; Popescu, C. High-pressure structural behaviour of  $HoVO_4$ : Combined XRD experiments and *ab initio* calculations. *Journal of Physics: Condensed Matter* **2014**, *26*, 265402.
- (118) Panchal, V.; Errandonea, D.; Segura, A.; Rodriguez-Hernandez, P.; Muñoz, A.; Lopez-Moreno, S.; Bettinelli, M. The electronic structure of zircon-type orthovanadates: Effects of high-pressure and cation substitution. *Journal of Applied Physics* **2011**, *110*, 043723.
- (119) Panchal, V.; Manjón, F.; Errandonea, D.; Rodriguez-Hernandez, P.; López-Solano, J.; Muñoz, A.; Achary, S.; Tyagi, A. High-pressure study of  $ScVO_4$  by Raman scattering and *ab initio* calculations. *Physical Review B* **2011**, *83*, 064111.
- (120) Gomis, O.; Lavina, B.; Rodríguez-Hernández, P.; Muñoz, A.; Errandonea, R.; Errandonea, D.; Bettinelli, M. High-pressure structural, elastic, and

- thermodynamic properties of zircon-type  $\text{HoPO}_4$  and  $\text{TmPO}_4$ . *Journal of Physics: Condensed Matter* **2017**, *29*, 095401.
- (121) Scott, H. P.; Williams, Q.; Knittle, E. Ultralow compressibility silicate without highly coordinated silicon. *Physical Review Letters* **2001**, *88*, 015506.
- (122) Lacomba-Perales, R.; Errandonea, D.; Meng, Y.; Bettinelli, M. High-pressure stability and compressibility of  $\text{APO}_4$  ( $A = \text{La, Nd, Eu, Gd, Er, and Y}$ ) orthophosphates: An X-ray diffraction study using synchrotron radiation. *Physical Review B* **2010**, *81*, 064113.
- (123) Pascual, E. C.; Amores, J. G.; Puche, R. S.; Castro, M.; Taira, N.; De Paz, J. R.; Chapon, L. Zircon to scheelite phase transition induced by pressure and magnetism in  $\text{TbCrO}_4$ . *Physical Review B* **2010**, *81*, 174419.
- (124) Errandonea, D.; Kumar, R.; Lopez-Solano, J.; Rodriguez-Hernandez, P.; Muñoz, A.; Rabie, M.; Puche, R. S. Experimental and theoretical study of structural properties and phase transitions in  $\text{YAsO}_4$  and  $\text{YCrO}_4$ . *Physical Review B* **2011**, *83*, 134109.
- (125) Mittal, R.; Garg, A. B.; Vijayakumar, V.; Achary, S.; Tyagi, A.; Godwal, B.; Busetto, E.; Lausi, A.; Chaplot, S. Investigation of the phase stability of  $\text{LuVO}_4$  at high pressure using powder X-ray diffraction measurements and lattice dynamical calculations. *Journal of Physics: Condensed Matter* **2008**, *20*, 075223.
- (126) Grzechnik, A.; Crichton, W. A.; Hanfland, M.; van Smaalen, S. Scheelite  $\text{CaWO}_4$  at high pressures. *Journal of Physics: Condensed Matter* **2003**, *15*, 7261.
- (127) Santamaria-Perez, D.; Errandonea, D.; Rodriguez-Hernandez, P.; Muñoz, A.; Lacomba-Perales, R.; Polian, A.; Meng, Y. Polymorphism in strontium tungstate  $\text{SrWO}_4$  under quasi-hydrostatic compression. *Inorganic Chemistry* **2016**, *55*, 10406–10414.
- (128) Errandonea, D.; Kumar, R. S.; Ma, X.; Tu, C. High-pressure X-ray diffraction study of  $\text{SrMoO}_4$  and pressure-induced structural changes. *Journal of Solid State Chemistry* **2008**, *181*, 355–364.



## BIBLIOGRAPHY

---

- (129) Errandonea, D.; Santamaria-Perez, D.; Achary, S.; Tyagi, A.; Gall, P.; Gougeon, P. High-pressure X-ray diffraction study of  $\text{CdMoO}_4$  and  $\text{EuMoO}_4$ . *Journal of Applied Physics* **2011**, *109*, 043510–043510.
- (130) Botella, P.; Lacombe-Perales, R.; Errandonea, D.; Polian, A.; Rodriguez-Hernandez, P.; Munoz, A. High-pressure Raman scattering of  $\text{CaWO}_4$  up to 46.3 GPa: Evidence of a new high-pressure phase. *Inorganic Chemistry* **2014**, *53*, 9729–9738.
- (131) Errandonea, D.; Pellicer-Porres, J.; Manjón, F.; Segura, A.; Ferrer-Roca, C.; Kumar, R.; Tschäuner, O.; López-Solano, J.; Rodríguez-Hernández, P.; Radescu, S. Determination of the high-pressure crystal structure of  $\text{BaWO}_4$  and  $\text{PbWO}_4$ . *Physical Review B* **2006**, *73*, 224103.
- (132) Mariathasan, J.; Finger, L.; Hazen, R. High-pressure behavior of  $\text{LaNbO}_4$ . *Acta Crystallographica Section B: Structural Science* **1985**, *41*, 179–184.
- (133) Hou, J.; Zhou, R.; Zhang, J.; Wang, Z.; Zhang, Z.; Ding, Z. Pressure and temperature study on the structural stability of  $\text{GdNbO}_4\text{:Eu}^{3+}$ . *The Journal of Physical Chemistry C* **2017**, *121*, 14787–14794.
- (134) Jiwei, H.; Qiao, C.; Chan, G.; Rucheng, D.; Zhang, J.; Zhongping, W.; Zhang, Z.; Zejun, D. Raman and luminescence studies on phase transition of  $\text{EuNbO}_4$  under high pressure. *Journal of Rare Earths* **2014**, *32*, 787–791.
- (135) Garg, A.; Errandonea, D.; Rodríguez-Hernández, P.; Muñoz, A. High-pressure monoclinic–monoclinic transition in fergusonite-type  $\text{HoNbO}_4$ . *Journal of Physics: Condensed Matter* **2021**, *33*, 195401.
- (136) Pellicer-Porres, J.; Garg, A.; Vázquez-Socorro, D.; Martínez-García, D.; Popescu, C.; Errandonea, D. Stability of the fergusonite phase in  $\text{GdNbO}_4$  by high pressure XRD and Raman experiments. *Journal of Solid State Chemistry* **2017**, *251*, 14–18.
- (137) Garg, A.; Liang, A.; Errandonea, D.; Rodríguez-Hernández, P.; Muñoz, A. Monoclinic–triclinic phase transition induced by pressure in fergusonite-type  $\text{YbNbO}_4$ . *Journal of Physics: Condensed Matter* **2022**, *34*, 174007.
- (138) Errandonea, D.; Boehler, R.; Ross, M. Melting of the rare earth metals and  $f$ -electron delocalization. *Physical Review Letters* **2000**, *85*, 3444.

- 
- (139) Shi, F.; Meng, J.; Ren, Y. Structure and luminescent properties of three new silver lanthanide molybdates. *Journal of Solid State Chemistry* **1996**, *121*, 236–239.
- (140) Song, K.; Yang, J.; Jiang, P.; Gao, W.; Cong, R.; Yang, T. Ba<sub>2</sub>InTaO<sub>6</sub> – A partially B-site-ordered double perovskite for overall water splitting. *European Journal of Inorganic Chemistry* **2015**, *2015*, 5786–5792.
- (141) Zhou, Q.; Tan, T.-Y.; Kennedy, B. J.; Hester, J. R. Crystal structures and phase transitions in Sr-doped Ba<sub>2</sub>InTaO<sub>6</sub> perovskites. *Journal of Solid State Chemistry* **2013**, *206*, 122–128.
- (142) Mullens, B. G.; Zhang, Z.; Avdeev, M.; Brand, H. E.; Cowie, B. C.; Saura Múzquiz, M.; Kennedy, B. J. Effect of long- and short-range disorder on the oxygen ionic conductivity of Tm<sub>2</sub>(Ti<sub>2–x</sub>Tm<sub>x</sub>)O<sub>7–x/2</sub> “stuffed” pyrochlores. *Inorganic Chemistry* **2021**, *60*, 4517–4530.
- (143) Mullens, B. G.; Zhang, Z.; Avdeev, M.; Brand, H. E.; Cowie, B. C.; D’Angelo, A.; Saura-Múzquiz, M.; Kennedy, B. J. Average and local ordering of Yb<sub>2</sub>(Ti<sub>2–x</sub>Yb<sub>x</sub>)O<sub>7–x/2</sub> ‘stuffed’ pyrochlores: The development of a robust structural model. *Journal of Solid State Chemistry* **2021**, *302*, 122412.
- (144) Lacorre, P.; Pautonnier, A.; Coste, S.; Barré, M.; Béchade, E.; Suard, E. Cationic order–disorder in double scheelite type oxides: The case study of fergusonite La<sub>2</sub>SiMoO<sub>8</sub>. *Inorganic Chemistry* **2021**, *60*, 2623–2633.
- (145) Krenzke, L. D.; Keulks, G. W. The catalytic oxidation of propylene: VIII. An investigation of the kinetics over Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>, Bi<sub>2</sub>MoO<sub>6</sub>, and Bi<sub>3</sub>FeMo<sub>2</sub>O<sub>12</sub>. *Journal of Catalysis* **1980**, *64*, 295–302.
- (146) Saura-Múzquiz, M.; Marlton, F. P.; Mullens, B. G.; Liu, J.; Vogt, T.; Maynard-Casely, H. E.; Avdeev, M.; Blom, D. A.; Kennedy, B. J. Cation and lone pair order–disorder in the polymorphic mixed metal bismuth scheelite Bi<sub>3</sub>FeMo<sub>2</sub>O<sub>12</sub>. *Chemistry of Materials* **2022**, *35*, 123–135.
- (147) Perera, S. S.; Munasinghe, H. N.; Yatooma, E. N.; Rabuffetti, F. A. Microwave-assisted solid-state synthesis of NaRE(MO<sub>4</sub>)<sub>2</sub> phosphors (RE = La, Pr, Eu, Dy; M = Mo, W). *Dalton Transactions* **2020**, *49*, 7914–7919.

## BIBLIOGRAPHY

---

- (148) Hanuza, J.; Maczka, M.; Van der Maas, J. Polarized IR and Raman spectra of tetragonal  $\text{NaBi}(\text{WO}_4)_2$ ,  $\text{NaBi}(\text{MoO}_4)_2$  and  $\text{LiBi}(\text{MoO}_4)_2$  single crystals with scheelite structure. *Journal of Molecular Structure* **1995**, *348*, 349–352.
- (149) Hanuza, J.; Haznar, A.; Maczka, M.; Pietraszko, A.; Lemiec, A.; Van der Maas, J.; Lutz, E. Structure and vibrational properties of tetragonal scheelite  $\text{NaBi}(\text{MoO}_4)_2$ . *Journal of Raman Spectroscopy* **1997**, *28*, 953–963.
- (150) Rico, M.; Méndez-Blas, A.; Volkov, V.; Monge, M. Á.; Cascales, C.; Zaldo, C.; Kling, A.; Fernández-Díaz, M. T. Polarization and local disorder effects on the properties of  $\text{Er}^{3+}$ -doped  $X\text{Bi}(\text{YO}_4)_2$ ,  $X = \text{Li}$  or  $\text{Na}$  and  $Y = \text{W}$  or  $\text{Mo}$ , crystalline tunable laser hosts. *Journal of the Optical Society of America B* **2006**, *23*, 2066–2078.
- (151) Volkov, V.; Cascales, C.; Kling, A.; Zaldo, C. Growth, structure, and evaluation of laser properties of  $\text{LiYb}(\text{MoO}_4)_2$  single crystal. *Chemistry of Materials* **2005**, *17*, 291–300.
- (152) Dwivedi, A.; Kaiwart, R.; Varma, M.; Velaga, S.; Poswal, H. High-pressure structural investigations on  $\text{InPO}_4$ . *Journal of Solid State Chemistry* **2020**, *282*, 121065.
- (153) Diehl, R.; Carpentier, C.-D. The structural chemistry of indium phosphorus chalcogenides. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* **1978**, *34*, 1097–1105.
- (154) Massa, W.; Steiner, M. Crystal and magnetic structure of the planar ferromagnet  $\text{CsMnF}_4$ . *Journal of Solid State Chemistry* **1980**, *32*, 137–143.
- (155) Morón, M. C.; Palacio, F.; Rodríguez-Carvajal, J. Neutron powder diffraction experiments on  $\text{AMnF}_4$  ( $A = \text{K}, \text{Rb}$ ): Nuclear and magnetic structures. *Physica B: Condensed Matter* **1992**, *180*, 125–127.
- (156) Huang, P.; Zhang, P.; Xu, S.; Wang, H.; Zhang, X.; Zhang, H. Recent advances in two-dimensional ferromagnetism: materials synthesis, physical properties and device applications. *Nanoscale* **2020**, *12*, 2309–2327.

- (157) Arockiaraj, M.; Kavitha, S. R. J.; Mushtaq, S.; Balasubramanian, K. Relativistic topological molecular descriptors of metal trihalides. *Journal of Molecular Structure* **2020**, *1217*, 128368.
- (158) Jacob, K. A new type of SOFC for conversion of high temperature heat to electricity without carnot limitation. *ECS Transactions* **2011**, *35*, 573.
- (159) Haugrud, R.; Norby, T. High-temperature proton conductivity in acceptor-doped  $\text{LaNbO}_4$ . *Solid State Ionics* **2006**, *177*, 1129–1135.
- (160) Arab, M.; Lopes-Moriyama, A. L.; dos Santos, T. R.; de Souza, C. P.; Gavarri, J. R.; Leroux, C. Strontium and cerium tungstate materials  $\text{SrWO}_4$  and  $\text{Ce}_2(\text{WO}_4)_3$ : Methane oxidation and mixed conduction. *Catalysis Today* **2013**, *208*, 35–41.
- (161) Cao, Y.; Duan, N.; Wang, X.; Chi, B.; Jian, L. Enhanced electrical conductivity of Mo-doped  $\text{LaNbO}_4$ . *Journal of the European Ceramic Society* **2015**, *35*, 1979–1983.
- (162) Li, C.; Pramana, S. S.; Skinner, S. J. Room temperature structure and transport properties of the incommensurate modulated  $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4.06}$ . *Dalton Transactions* **2019**, *48*, 1633–1646.
- (163) Toyoura, K.; Sakakibara, Y.; Yokoi, T.; Nakamura, A.; Matsunaga, K. Oxide-ion conduction *via* interstitials in scheelite-type  $\text{LaNbO}_4$ : A first-principles study. *Journal of Materials Chemistry A* **2018**, *6*, 12004–12011.
- (164) Canu, G.; Giannici, F.; Chiara, A.; Confalonieri, G.; Longo, A.; Buscaglia, M. T.; Dapiaggi, M.; Buscaglia, V.; Martorana, A. Characterisation of scheelite  $\text{LaW}_{0.16}\text{Nb}_{0.84}\text{O}_{4.08}$  ion conductor by combined synchrotron techniques: Structure, W oxidation state and interdiffusion. *Journal of Alloys and Compounds* **2021**, *857*, 157532.
- (165) Li, C.; Bayliss, R. D.; Skinner, S. J. Crystal structure and potential interstitial oxide ion conductivity of  $\text{LnNbO}_4$  and  $\text{LnNb}_{0.92}\text{W}_{0.08}\text{O}_{4.04}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$ ). *Solid State Ionics* **2014**, *262*, 530–535.

## BIBLIOGRAPHY

---

- (166) Li, C.; Pramana, S. S.; Bayliss, R. D.; Grey, C. P.; Blanc, F.; Skinner, S. J. Evolution of structure in the incommensurate modulated  $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+x/2}$  ( $x = 0.04\text{--}0.16$ ) oxide ion conductors. *Chemistry of Materials* **2020**, *32*, 2292–2303.
- (167) Norby, T.; Magrasó, A. On the development of proton ceramic fuel cells based on Ca-doped  $\text{LaNbO}_4$  as electrolyte. *Journal of Power Sources* **2015**, *282*, 28–33.
- (168) Mather, G. C.; Fisher, C. A.; Islam, M. S. Defects, dopants, and protons in  $\text{LaNbO}_4$ . *Chemistry of Materials* **2010**, *22*, 5912–5917.
- (169) Wang, J.; Zhou, L.; Wang, Y.; Xu, J.; Yang, X.; Kuang, X. Molecular dynamic simulation of interstitial oxide ion migration in  $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$  scheelite. *Journal of Solid State Chemistry* **2018**, *268*, 16–21.
- (170) Ferrara, C.; Mancini, A.; Ritter, C.; Malavasi, L.; Tealdi, C. Interstitial oxide ion migration in scheelite-type electrolytes: A combined neutron diffraction and computational study. *Journal of Materials Chemistry A* **2015**, *3*, 22258–22265.
- (171) Mills, A.; Le Hunte, S. An overview of semiconductor photocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry* **1997**, *108*, 1–35.
- (172) Zhang, F.; Wang, X.; Liu, H.; Liu, C.; Wan, Y.; Long, Y.; Cai, Z. Recent advances and applications of semiconductor photocatalytic technology. *Applied Sciences* **2019**, *9*, 2489.
- (173) Wang, L.; Zhao, J.; Liu, H.; Huang, J. Design, modification and application of semiconductor photocatalysts. *Journal of the Taiwan Institute of Chemical Engineers* **2018**, *93*, 590–602.
- (174) Serpone, N.; Emeline, A. Semiconductor photocatalysis – Past, present, and future outlook. *The Journal of Physical Chemistry Letters* **2012**, *3*, 673–677.
- (175) Lotfi, S.; Ouardi, M. E.; Ahsaine, H. A.; Assani, A. Recent progress on the synthesis, morphology and photocatalytic dye degradation of  $\text{BiVO}_4$  photocatalysts: A review. *Catalysis Reviews* **2022**, 1–45.
- (176) Zinatloo-Ajabshir, S.; Baladi, M.; Salavati-Niasari, M. Enhanced visible-light-driven photocatalytic performance for degradation of organic contaminants using  $\text{PbWO}_4$  nanostructure fabricated by a new, simple and green sonochemical approach. *Ultrasonics Sonochemistry* **2021**, *72*, 105420.

- (177) Sleight, A.; Chen, H.-Y.; Ferretti, A.; Cox, D. Crystal growth and structure of  $\text{BiVO}_4$ . *Materials Research Bulletin* **1979**, *14*, 1571–1581.
- (178) Groenink, J.; Blasse, G. Some new observations on the luminescence of  $\text{PbMoO}_4$  and  $\text{PbWO}_4$ . *Journal of Solid State Chemistry* **1980**, *32*, 9–20.
- (179) Li, F.; Lin, D.; Chen, Z.; Cheng, Z.; Wang, J.; Li, C.; Xu, Z.; Huang, Q.; Liao, X.; Chen, L.-Q. Ultrahigh piezoelectricity in ferroelectric ceramics by design. *Nature Materials* **2018**, *17*, 349–354.
- (180) Shrout, T. R.; Zhang, S. J. Lead-free piezoelectric ceramics: Alternatives for PZT? *Journal of Electroceramics* **2007**, *19*, 113–126.
- (181) Wang, Y.; Zhang, Z.; Usui, T.; Benedict, M.; Hirose, S.; Lee, J.; Kalb, J.; Schwartz, D. A high-performance solid-state electrocaloric cooling system. *Science* **2020**, *370*, 129–133.
- (182) Walsh, A.; Yan, Y.; Huda, M. N.; Al-Jassim, M. M.; Wei, S.-H. Band edge electronic structure of  $\text{BiVO}_4$ : Elucidating the role of the Bi *s* and V *d* orbitals. *Chemistry of Materials* **2009**, *21*, 547–551.
- (183) Walsh, A.; Payne, D. J.; Egdell, R. G.; Watson, G. W. Stereochemistry of post-transition metal oxides: Revision of the classical lone pair model. *Chemical Society Reviews* **2011**, *40*, 4455–4463.
- (184) Payne, D.; Egdell, R.; Walsh, A.; Watson, G.; Guo, J.; Glans, P.-A.; Learmonth, T.; Smith, K. Electronic origins of structural distortions in post-transition metal oxides: Experimental and theoretical evidence for a revision of the lone pair model. *Physical Review Letters* **2006**, *96*, 157403.
- (185) Halasyamani, P. S. Asymmetric cation coordination in oxide materials: Influence of lone-pair cations on the intra-octahedral distortion in  $d^0$  transition metals. *Chemistry of Materials* **2004**, *16*, 3586–3592.
- (186) Payne, D.; Robinson, M.; Egdell, R.; Walsh, A.; McNulty, J.; Smith, K.; Piper, L. The nature of electron lone pairs in  $\text{BiVO}_4$ . *Applied Physics Letters* **2011**, *98*, 212110.

## BIBLIOGRAPHY

---

- (187) Liu, T.; Zhang, X.; Guan, J.; Catlow, C. R. A.; Walsh, A.; Sokol, A. A.; Buckeridge, J. Insight into the Fergusonite–Scheelite phase transition of  $ABO_4$ -type oxides by density functional theory: A case study of the subtleties of the ground state of  $BiVO_4$ . *Chemistry of Materials* **2022**, *34*, 5334–5343.
- (188) Lee, W.; Ojovan, M.; Stennett, M.; Hyatt, N. Immobilisation of radioactive waste in glasses, glass composite materials and ceramics. *Advances in Applied Ceramics* **2006**, *105*, 3–12.
- (189) Gin, S.; Abdelouas, A.; Criscenti, L. J.; Ebert, W. L.; Ferrand, K.; Geisler, T.; Harrison, M. T.; Inagaki, Y.; Mitsui, S.; Mueller, K. T. An international initiative on long-term behavior of high-level nuclear waste glass. *Materials Today* **2013**, *16*, 243–248.
- (190) Jakobsen, S.; Gianolio, D.; Wragg, D. S.; Nilsen, M. H.; Emerich, H.; Bordiga, S.; Lamberti, C.; Olsbye, U.; Tilset, M.; Lillerud, K. P. Structural determination of a highly stable metal-organic framework with possible application to interim radioactive waste scavenging: Hf–UiO-66. *Physical Review B* **2012**, *86*, 125429.
- (191) Shen, N.; Yang, Z.; Liu, S.; Dai, X.; Xiao, C.; Taylor-Pashow, K.; Li, D.; Yang, C.; Li, J.; Zhang, Y.  $^{99}TcO_4^-$  removal from legacy defense nuclear waste by an alkaline-stable 2D cationic metal organic framework. *Nature Communications* **2020**, *11*, 5571.
- (192) Terra, O.; Clavier, N.; Dacheux, N.; Podor, R. Preparation and characterization of lanthanum–gadolinium monazites as ceramics for radioactive waste storage. *New Journal of Chemistry* **2003**, *27*, 957–967.
- (193) Lang, M.; Zhang, F.; Zhang, J.; Wang, J.; Lian, J.; Weber, W. J.; Schuster, B.; Trautmann, C.; Neumann, R.; Ewing, R. C. Review of  $A_2B_2O_7$  pyrochlore response to irradiation and pressure. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **2010**, *268*, 2951–2959.
- (194) Meldrum, A.; Boatner, L.; Ewing, R. A comparison of radiation effects in crystalline  $ABO_4$ -type phosphates and silicates. *Mineralogical Magazine* **2000**, *64*, 185–194.

- (195) De Los Reyes, M.; Aughterson, R. D.; Gregg, D. J.; Middleburgh, S. C.; Zaluzec, N. J.; Huai, P.; Ren, C.; Lumpkin, G. R. Ion beam irradiation of  $ABO_4$  compounds with the fergusonite, monazite, scheelite, and zircon structures. *Journal of the American Ceramic Society* **2020**, *103*, 5502–5514.
- (196) Meldrum, A.; Zinkle, S.; Boatner, L.; Ewing, R. Heavy-ion irradiation effects in the  $ABO_4$  orthosilicates: Decomposition, amorphization, and recrystallization. *Physical Review B* **1999**, *59*, 3981.
- (197) Xie, W.; Koyama, M. Theoretical design of a technetium-like alloy and its catalytic properties. *Chemical Science* **2019**, *10*, 5461–5469.
- (198) Dickson, J. O.; Harsh, J. B.; Lukens, W. W.; Pierce, E. M. Perrhenate incorporation into binary mixed sodalites: The role of anion size and implications for technetium-99 sequestration. *Chemical Geology* **2015**, *395*, 138–143.
- (199) Favre-Réguillon, A.; Draye, M.; Cote, G.; Czerwinsky, K. R. Insights in uranium extraction from spent nuclear fuels using dicyclohexano-18-crown-6 – Fate of rhenium as technetium homolog. *Separation and Purification Technology* **2019**, *209*, 338–342.
- (200) Fei, H.; Bresler, M. R.; Oliver, S. R. A new paradigm for anion trapping in high capacity and selectivity: Crystal-to-crystal transformation of cationic materials. *Journal of the American Chemical Society* **2011**, *133*, 11110–11113.
- (201) McCloy, J. S.; Riley, B. J.; Goel, A.; Liezers, M.; Schweiger, M. J.; Rodriguez, C. P.; Hrma, P.; Kim, D.-S.; Lukens, W. W.; Kruger, A. A. Rhenium solubility in borosilicate nuclear waste glass: Implications for the processing and immobilization of technetium-99. *Environmental Science & Technology* **2012**, *46*, 12616–12622.
- (202) Lukens, W. W.; McKeown, D. A.; Buechele, A. C.; Muller, I. S.; Shuh, D. K.; Pegg, I. L. Dissimilar behavior of technetium and rhenium in borosilicate waste glass as determined by X-ray absorption spectroscopy. *Chemistry of Materials* **2007**, *19*, 559–566.
- (203) Gan, H.; McKeown, D. A.; Xie, X.; Pegg, I. L. Assessment of rhenium as a surrogate for technetium in Hanford low activity waste borosilicate glasses:



- Speciation, solubility, and redox effects. *International Journal of Applied Glass Science* **2023**, *14*, 97–112.
- (204) Yakout, S. M. Spintronics: Future technology for new data storage and communication devices. *Journal of Superconductivity and Novel Magnetism* **2020**, *33*, 2557–2580.
- (205) Binasch, G.; Grünberg, P.; Saurenbach, F.; Zinn, W. Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange. *Physical Review B* **1989**, *39*, 4828.
- (206) Morón, M. C.; Palacio, F.; Rodríguez-Carvajal, J. Crystal and magnetic structures of  $\text{RbMnF}_4$  and  $\text{KMnF}_4$  investigated by neutron powder diffraction: The relationship between structure and magnetic properties in the  $\text{Mn}^{3+}$  layered perovskites  $\text{AMnF}_4$  ( $A = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ). *Journal of Physics: Condensed Matter* **1993**, *5*, 4909.
- (207) Eibschütz, M.; Guggenheim, H.; Holmes, L.; Bernstein, J.  $\text{CsFeF}_4$ : A new planar antiferromagnet. *Solid State Communications* **1972**, *11*, 457–460.
- (208) Behatha, A.; Roy, A. J.; Anusree, C.; Ponvijayakanthan, L.; Sharma, V. K.; Kanchana, V. Correlation driven topological nodal ring ferromagnetic spin gapless semimetal:  $\text{CsMnF}_4$ . *Journal of Physics: Condensed Matter* **2021**, *33*, 165803.



## Chapter 2

# Theory and Experimental Techniques



## 2.1 Understanding Functional Materials

The ultimate goal of materials science is to design, manufacture, and understand objects that are capable of advancing technology for humankind. Work is currently being carried out to develop superconductors for zero resistance electricity transfer, photovoltaics for harnessing renewable solar energy, and large-scale batteries for energy storage. However, in order to purposely design these materials for particular functions, we must first understand how their properties are derived from their structure. That is, establish the role of the precise arrangement of atoms and their interactions on the functionality of the material.

We will first approach this by considering a material with a simple structure: diamond. Diamond is a solid form of carbon that is naturally synthesised under high temperature and pressure environments, at depths between 150–250 kilometres below the Earth's surface. Every carbon atom in the diamond structure possess four strong covalent bonds to its four nearest-neighbour carbons. This arrangement motif repeats in all three dimensions (3D), with each neighbouring carbon atom also bound to a further four carbon atoms, and so on. This can become difficult to visualise, so in crystallography the arrangement is represented by drawing a smaller volume that is representative of the entire structure. This is known as a *unit cell*. A unit cell may be translated in 3D to accurately represent the structure of a material; capturing the arrangement of the networked carbon atoms.

By translating the unit cell, it is apparent that the carbon atoms are arranged in a very regular pattern. To visualise this, we start with a *lattice*; a spatial pattern of points of equal and equally oriented surroundings. Each lattice point may then be *decorated* with a group or structural motif of atoms, leading to a regularly repeating array of atoms by way of translational symmetry. In the case of diamond, there are two carbon atoms per lattice point, leading to eight atoms per unit cell in a face-centred arrangement. With different atomic motifs, other arrangements are possible, such as primitive cubic (one atom per unit cell), and body-centred cubic (two atoms per unit cell). Through translation symmetry, this gives primitive Bravais lattices as well as other settings such as body-centred, face-centred, and hexagonal lattices. There are 14 types of translational

symmetry in 3D lattice space, giving rise to 14 Bravais lattices. By further combining the 14 Bravais lattices with the 32 unique symmetry elements (known as their geometric symmetries, or *point groups*), we have the possibility of 230 space groups.

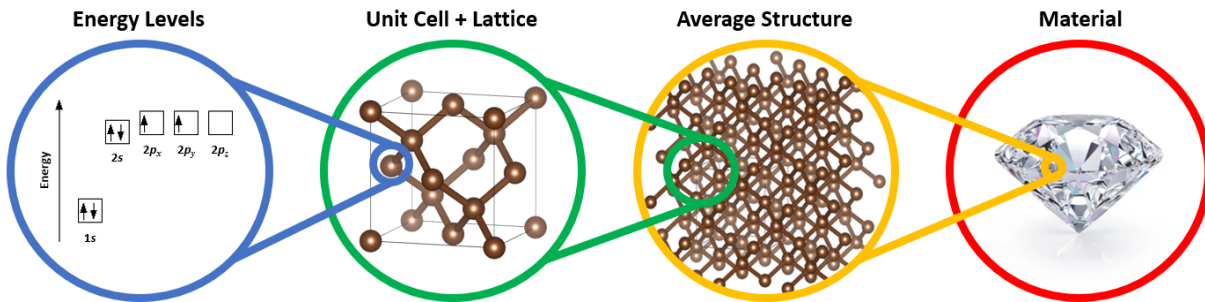


Figure 2.1: We often use materials science to rationalise how materials on the macroscale behave by understanding the arrangement of their atoms on the atomic scale.

By understanding how individual atoms are arranged in space (on a lattice), and the relevant symmetry of them (governed by the point groups), we can begin to understand how the structure of materials on the *atomic* level can influence their functionality on the *macroscopic* level. By considering each individual carbon atom on a cubic lattice, the six electrons of each carbon atom fill their respective energy levels ( $1s$ ,  $2s$ ,  $2p$ , *etc.*) following rules such as the Aufbau Principle and the Pauli Exclusion Principle. As is the case with individual molecules, two atomic orbitals can combine to form a molecular orbital with two distinct energy levels. However, in solids, there is an enormous number of atomic (and by extension, molecular) orbitals that are required to have *slightly* different energies due to the Pauli Exclusion Principle. This leads to many different energy levels stacked with an infinitesimal energy difference between them, forming an energy continuum known as a *band*.

The energy between these bands (more specifically, the valence and conduction bands) can determine how well electrons can move through the material: categorising them as metallic, semi-metallic, and insulators. In the case of diamond, its band gap (the energy difference between the top of the valence and bottom of the conduction bands) is roughly 5.6 eV, meaning it is a strong electrical insulator and electrons do not readily move throughout the structure. However, in copper, the valence and conduction bands overlap, meaning the electrons can easily move from the valence band into the conduction band, making it a strong electrical conductor.

Diamond, at the atomic scale, consists of an intricate network of carbon atoms with their electrons bound together in strong covalent bonds. This explains why diamond exhibits such high hardness and limited electrical conductivity on the macroscale. The implication of this is that by understanding the structure of materials on the atomic scale, we can understand why materials have particular properties on the macroscopic scale. Therefore, it is important that we understand the nuclear and electronic structure of materials to fully understand their structure-functionality relationships.

This chapter of the dissertation will take an in-depth look at the ways this is achieved. We first start by focusing on how we can synthesise metal oxides, then move onto how we can classify their long-range average structures (using diffraction) as well as their short-range local interactions (using total scattering). Additionally, computational methods such as DFT and MD can be used to build up more comprehensive structural models. Although computational methods are not the focus of this dissertation, they will be briefly mentioned to provide a more encompassing picture of the materials being studied. Finally, we will look at how we can quantify their physical properties in order to develop structure-functionality relationships in these systems.

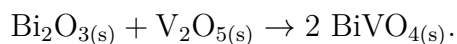
## 2.2 Synthetic Methods

The structure of materials can often be sensitive to the technique in which they have been prepared. In the case of the photocatalyst  $\text{BiVO}_4$ , heating up a stoichiometric mixture of its reagent oxides,  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ , to  $\sim 700^\circ\text{C}$  results in the formation of the monoclinic-fergusonite  $I2/b$  form of  $\text{BiVO}_4$ . However, if a solution of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NH}_4\text{VO}_3$  are mixed at room temperature, the dropwise addition of  $\text{NH}_4\text{OH}$  results in precipitation of the tetragonal-zircon  $I4_1/amd$  form of  $\text{BiVO}_4$ . It is important to understand the advantages and limitations to each synthetic technique in preparing a material of choice for its specific application.

### 2.2.1 Solid State Synthesis Techniques

Solid state methods are based on the mixing of reagents in a particular stoichiometry, then heating to a temperature that is close to, but below, their melting points. In a typical reaction, two or more predried metal oxides are weighed out and mixed together. This can be done in a variety of ways, such as in an agate mortar and pestle with a milling medium (such as acetone or ethanol), or in a ball mill to ensure adequate mixing and smaller particle sizes for better contact to aid cation diffusion. The reagents are mixed until a homogeneous sample is obtained. Before heating, the reagents may be pressed into pellets or rods using a uniaxial or hydrostatic press to further improve the contact between the reagent particles. These pellets or rods are then heated to high temperatures for prolonged periods of time. The heating temperature is traditionally determined by Tamman's Rule: a temperature of about two-thirds of the melting point of the reagent with the lowest melting point to have a reaction occur in a reasonable time.<sup>1</sup> This also facilitates avoiding possible eutectic points; where a homogeneous mixture has a lower melting point than that of its constituent metal oxides.<sup>2</sup> The elevated temperature and prolonged heating time drives the reaction to the thermodynamically stable product, as opposed to a metastable kinetic product.

Consider  $\text{BiVO}_4$  as an example of a typical solid state reaction. To synthesise 4 g (12.3 mmol) of product, 12.3 mmol of  $\text{Bi}^{3+}$  and 12.3 mmol of  $\text{V}^{5+}$  are needed. The source of these are their respective metal oxides, such that 2.8656 g of  $\text{Bi}_2\text{O}_3$  (6.15 mmol, as each mole of  $\text{Bi}_2\text{O}_3$  contributes 2 moles of  $\text{Bi}^{3+}$ ) and 1.1186 g of  $\text{V}_2\text{O}_5$  (6.15 mmol) would be weighed out. The reaction would proceed as



As an additional check, as no gas is released from this reaction (which is often the case when the reagents are oxides, and not carbonates or nitrates), the masses of  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  should sum to 4 g. The sample would then be pressed as a pellet or rod and heated to temperature in a muffle furnace.

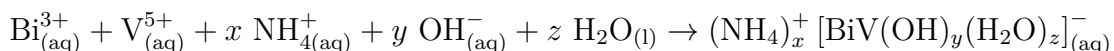


### 2.2.2 Coprecipitation Synthesis Techniques

Coprecipitation synthesis is based on the mixing of two metallic salts in order to precipitate a third salt. It has been extensively utilised in the literature due to the process being fast, cost effective, and easily adapted to a larger scale for industrial processes. Coprecipitation methods involve many more variables than solid state methods, such as the types of reagents used, the concentration of the reagents, reaction temperature, mixing conditions, spectator ions present, and pH. In turn, these variables may be explored to determine their effect on the particle size, morphology, and composition of the final material. In a typical coprecipitation synthesis, two standardised solutions of metallic salts are mixed together in an aqueous acid. After stirring for a particular time and at a particular temperature, a base (usually ammonia) is slowly added to neutralise the metallic acidic solution. Eventually, a solid precipitates out of the mixture due to the change in pH, and the solid can then be filtered, washed, dried, and collected.

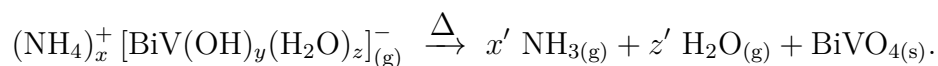
Consider again the synthesis of  $\text{BiVO}_4$ . To synthesise the tetragonal-zircon form of  $\text{BiVO}_4$ , a coprecipitation reaction is performed instead of a solid state reaction, as heating to high temperatures can cause an irreversible transformation to the monoclinic-fergusonite  $I2/b$  structure. Two sources of  $\text{Bi}^{3+}$  and  $\text{V}^{5+}$  are chosen such that they are soluble in an acidic solution, but not in a neutral solution. As such, standardised solutions of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NH}_4\text{VO}_3$  are each prepared in dilute nitric acid and mixed at room temperature for 10 minutes. A solution of  $\text{NH}_4\text{OH}$  is then added dropwise until a pale-yellow solid precipitates out. The solid is then filtered using vacuum filtration, and dried overnight at  $120^\circ\text{C}$  to evaporate any excess liquid and help crystallise the product.

The reaction would proceed as



where the exact identity of the precipitate is unknown.

The precipitate is then heated in a muffle furnace to remove the ammonium (as ammonia gas) and water to form the desired precipitate



Coprecipitation reactions lead to a more homogeneous product and more uniform particle size, which can be advantageous for specific applications such as catalysis.

## 2.3 Long-Range Average Structure Determination

As stated above, it is important to understand how atoms are arranged on the microscopic scale in order to fully understand how materials function on the macroscopic scale. By understanding the chemical species present and their arrangement, we can begin to understand the structure-property relationships in various materials. We need techniques that probe structure in a non-destructive way to locate the atoms on their respective Bravais lattice.

One such technique is diffraction, which is the primary technique used for crystal structure determination. In a quest to determine whether the X-rays discovered by Wilhelm Röntgen in 1895 acted as either waves or particles, the diffraction of X-rays by crystalline materials was identified by Max von Laue in 1912 (subsequently earning him the Nobel Prize in Physics in 1914).<sup>3</sup> This was further developed by the father-son team Sir William Henry and Sir William Lawrence Bragg, where the results of their experiments laid the mathematical foundations of explaining why crystalline solids produced patterns of reflected X-rays due to their regularly repeating structure, whereas amorphous materials such as liquids did not. This was a result of the comparative wavelengths of X-rays to the interatomic distances of atoms within a crystal structure. The Braggs were awarded the Nobel Prize in Physics in 1915 for their work in determining the crystal structures of common materials such as rock salt (NaCl), zinc blende (ZnS), and diamond.<sup>4</sup>

Diffraction exploits the regular, semi-infinite arrangement of unit cells within a material. When a photon of an initial wavelength,  $\lambda_i$ , interacts with a point-like particle (such as an atom in a crystal structure) along an initial wavevector,  $\vec{k}_i$ , at an angle  $\theta_i$ , it may be scattered elastically ( $\lambda_i = \lambda_f$ ), inelastically ( $\lambda_i > \lambda_f$ ), or completely absorbed ( $\lambda_f = 0$ ). For elastic scattering under point-like conditions, the initial wavevector and wavelength will be equal to the scattered wavevector and wavelength, such that  $|\vec{k}_i| = |\vec{k}_f|$  and  $\lambda_i = \lambda_f$ . After scattering elastically at an angle of  $\theta_i$ , the difference between the two scattering vectors is defined as  $\vec{Q} = \vec{k}_f - \vec{k}_i$ , which gives the relationship of

$$Q = \frac{4\pi \sin(\theta_i)}{\lambda_i}. \quad (2.1)$$

This is also known as the momentum transfer vector. Elastic diffraction occurs when the *Laue condition* is satisfied, such that the momentum transfer vector is compromised of an integer number of unit cell vectors:  $\vec{Q} \cdot \vec{a} = h$ ,  $\vec{Q} \cdot \vec{b} = k$ , and  $\vec{Q} \cdot \vec{c} = l$  where  $h, k, l$  are integers and known as *Miller indices*.

This example of elastic scattering can now be thought of in two dimensions to explain diffraction (Figure 2.2), where X-rays are not scattered from point-like particles, but *planes* of particles. When particles are arranged on a lattice, diffraction occurs when the distances between the particles is comparable to that of the wavelength of the incident photon. Consider two incident in-phase photons,  $A$  and  $B$ , with incident wavevectors  $\vec{k}_{Ai}$  and  $\vec{k}_{Bi}$ . Photon  $A$  elastically scatters from particle  $a$ , whereas photon  $B$  elastically scatters from particle  $b$ , with a distance  $d$  between the two layers of atoms. Each photon has been elastically scattered by an angle of  $2\theta$ , however photon  $B$  has travelled a further distance of  $d \sin \theta$ . Therefore, in order to have constructive interference between photons  $A$  and  $B$ , the two photons must be in-phase such that the extra distance is equal to an integer number of wavelengths.

This is known as *Bragg's law* (which is equivalent to the Laue condition) and is expressed as

$$n\lambda = 2d \sin \theta. \quad (2.2)$$

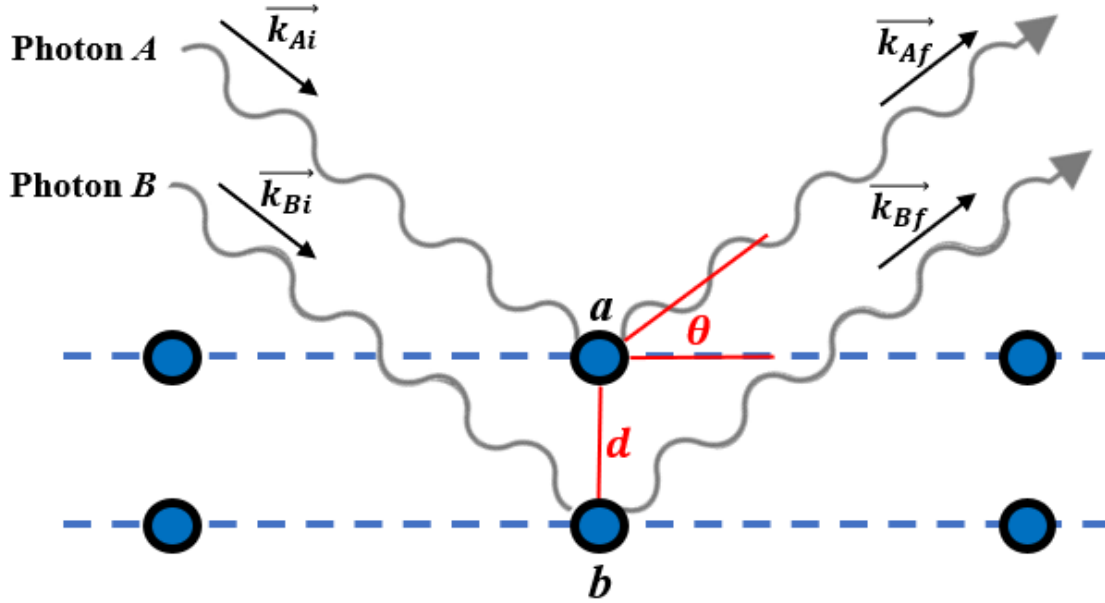


Figure 2.2: Schematic diagram of Bragg diffraction using a two dimensional lattice. The atoms on the lattice are represented as blue circles, with the incoming photons as grey arrows. Photons *A* and *B* are scattered elastically from particles *a* and *b* respectively. For constructive interference between photons *A* and *B*, the extra distance travelled must be an integer multiple of the wavelength.

If this condition is satisfied we get Bragg diffraction, which contains information about how far apart atoms are in a unit cell. In generalising from 2D to 3D, we observe many families of planes in each of the three dimensions of the crystal structure. For diffraction, the wavelength is traditionally kept constant and different interplanar distances are detected (as a peak of constructive interference) by changing the detector angle  $\theta$ . These planes are known as *Miller planes* and are related by the Miller indices  $h$ ,  $k$ , and  $l$ . To illustrate this, consider the structure of diamond from earlier. If we expose diamond to a radiation source and scan through the possible diffraction angles, Bragg peaks are observed corresponding to where Bragg's law is satisfied. If the wavelength  $\lambda$  of the radiation source is known, and the angle  $\theta$  between the incident photon and the diffracted photon is measured, the interatomic distances between planes of carbon atoms in diamond can be determined (Figure 2.3).

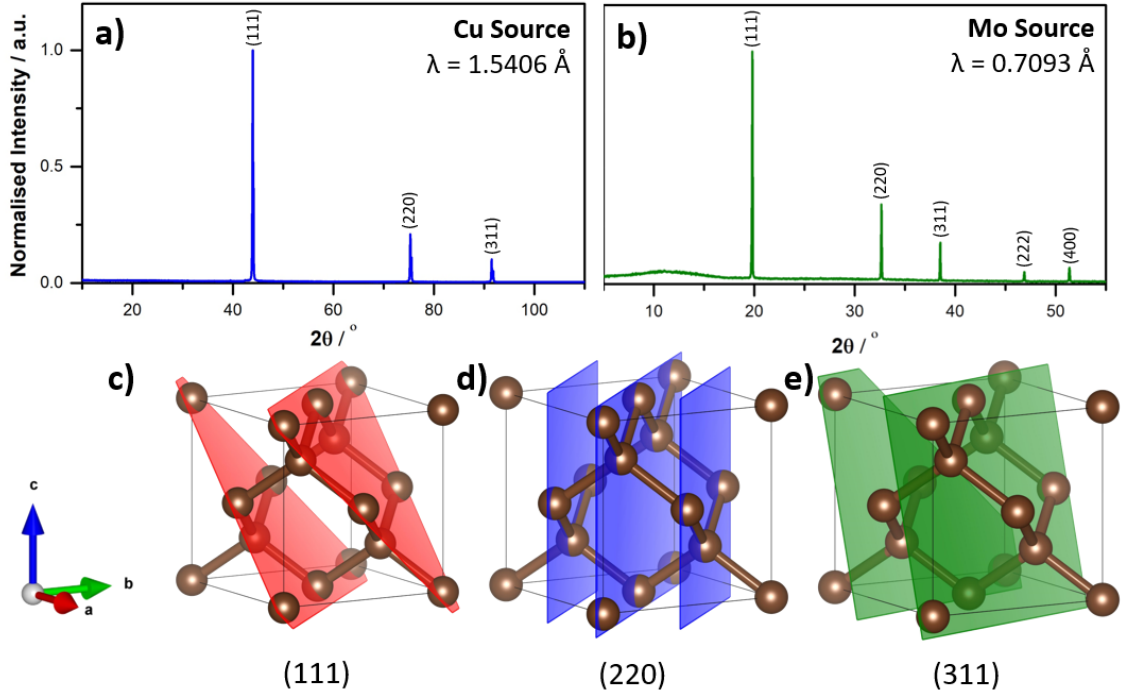


Figure 2.3: X-ray diffraction on a sample of 8 k grit diamond powder collected on (a) a PANalytical X'Pert Pro copper source diffractometer, and (b) a STOE Stadi P monochromatic molybdenum source diffractometer. The relevant lattice planes, as notated by their  $(hkl)$  Miller indices, are drawn on the diamond structure in (c–e). Note the ‘bump’ observed between  $10$ – $15^\circ 2\theta$  in the molybdenum source pattern is an amorphous contribution from the borosilicate glass capillary used to house the sample.

Each Bragg peak corresponds to a set of Miller planes within the crystal structure. The distance between the lattice planes ( $d_{hkl}$ ) can be used to calculate the length of the unit cell. In the case of cubic structures such as diamond, the relationship is

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \quad (2.3)$$

where  $a$  is the length of the unit cell, known as the lattice parameter. This can also be generalised to other lattice systems.

It is worth recapping what has just been discussed. Atoms arranged in a regular array can be reduced to a unit cell, which repeats in a semi-infinite array through translational symmetry. We can understand how the atoms are arranged within a unit cell by calculating how far apart they are using diffraction. Using a radiation source of sufficiently short wavelength (and, by extension, a high enough energy), the incoming waves may be elastically scattered by the Miller planes within the material, allowing us to calculate the size of the unit cell.

Diffraction isn't just limited to determining distances within a unit cell. The number of reflections observed in the diffraction pattern can also be used to determine its symmetry. For example, diamond is a face-centred cubic structure, meaning that the  $h, k$ , and  $l$  Miller indices must be all odd or all even for a Bragg peak to be observed. This explains why the (221) reflection in diamond is not observed (*forbidden*) as it interferes destructively with a different reflection. Another fundamental property that can be understood using diffraction is the contents of a unit cell; what elements are in the unit cell and how well they scatter the incoming radiation. We can understand this information by the observation of the intensity of the Bragg peak (or, in other words, *how much* scattering is observed). The observable intensity,  $I(\vec{Q})$ , is determined by the relationship

$$I(\vec{Q}) = S \cdot LP \cdot |F(\vec{Q})|^2 \quad (2.4)$$

where  $S$  is the source intensity and detector efficiency,  $LP$  are the Lorentz and polarisation parameters of the incident beam, and  $F(\vec{Q})$  is the structure factor. The most important of these is  $F(\vec{Q})$ , as it has the greatest effect on the relative magnitude of the various reflections and is dependent on the sample.

The structure factor describes the contributions of each atom towards the scattering from the Miller planes. For interactions consisting of X-rays, it is defined as

$$F_{\text{X-ray}}(\vec{Q}) = F_{\text{X-ray}}(Q)e^{i\phi} = \left| f_i(\vec{Q}) \sum_i e^{i\vec{Q} \cdot \vec{r}_i} \right|^2 e^{\frac{-Q^2 \langle u^2 \rangle}{2}} \quad (2.5)$$

where  $\phi$  is the phase of the diffracted X-ray over the  $i$ -th scattering surface (known as an Ewald sphere) of radius  $\vec{r}_i$ , and  $\langle u^2 \rangle$  is the average of the squared displacement of atoms from their equilibrium lattice sites with both a static and dynamic component. The final term in the expression is known as the Debye-Waller factor, and describes the decrease in scattering intensity as a result of thermal motion.

The most important term in the structure factor expression is the atomic scattering factor,  $f_i(\vec{Q})$ , which is a Fourier transform of the scatterer. This is defined as

$$f_i(\vec{Q}) \sim \int \rho(\vec{r}) e^{-i\vec{Q} \cdot \vec{r}} d\vec{r} \quad (2.6)$$

where  $\rho(\vec{r})$  is the spatial density of the particle. In the case of X-rays, this is equal to the electron charge density of the particle, meaning the magnitude of the scattering is proportional to the number of electrons in the atom (in this dissertation, notated as  $Z$  but may also stand for atomic number). X-rays are scattered most intensely from heavy atoms.

For neutron scattering, we can describe a similar structure factor to Equation 2.5 with

$$F_{\text{neut.}}(\vec{Q}) = \left| b_{\text{coh.}}(\vec{Q}) \sum_i e^{i\vec{Q} \cdot \vec{r}_i} \right|^2 e^{\frac{-Q^2 \langle u^2 \rangle}{2}} \quad (2.7)$$

where the structure factor is dependent on  $b_{\text{coh.}}(\vec{Q})$ , the coherent scattering cross section of the atom. This also has a similar expression to Equation 2.6, where

$$b_{\text{coh.}} \sim \int \rho(\vec{x}) e^{i\vec{Q} \cdot \vec{x}} d\vec{x}. \quad (2.8)$$

As neutrons possess no charge, they scatter through nuclear effects mediated by the short-range strong nuclear force. As the magnitude of this force is derived from the number of protons and neutrons within the nucleus of an atom, different isotopes inherently have different magnitudes (and signs) of scattering. For example, two common isotopes of gadolinium,  $^{155}\text{Gd}$  and  $^{157}\text{Gd}$ , have a large neutron absorbing cross-section and a large amount of incoherent scattering resulting in poor coherent scattering from neutron diffraction. However,  $^{160}\text{Gd}$  has a very low absorbance cross-section and a large scattering length, making it ideal for neutron scattering experiments. This has led to some neutron studies using isotopically-pure  $^{160}\text{Gd}$ .<sup>5-8</sup> The weighted average of the naturally-occurring isotopes is used for all  $b_{\text{coh.}}$ , resulting in a sporadic relationship between  $b_{\text{coh.}}$  and  $Z$ , as evident in Figure 2.4.

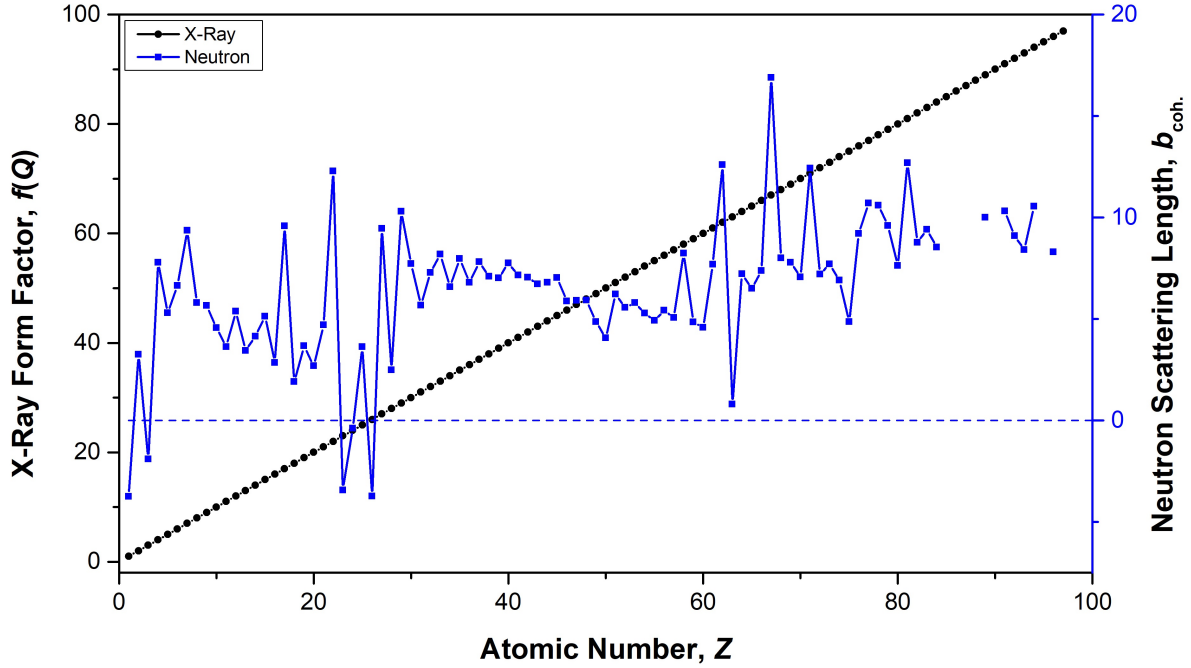


Figure 2.4: Comparison of the different scattering of X-rays (black circles) and neutrons (blue squares) relative to atomic number,  $Z$ . For the neutron scattering lengths, the weighted average of the isotope distribution is used. The blue dashed line emphasises  $b_{\text{coh.}} = 0$ , with elements below this being negative scatterers.

There are other significant differences between X-ray and neutron diffraction that are worth noting. Firstly, as the atomic scattering factor is a Fourier transform of the scattering density, different interactions lead to different angular dependent scattering intensities. As X-rays are scattered from the electron density, we may approximate the atomic electron density as a Gaussian distribution that drops off as a function of  $r$ . As the Fourier transform of a Gaussian curve is another Gaussian curve, the X-ray form factor also drops off with a Gaussian envelope, with  $f_i(\vec{Q}) \rightarrow 0$  as  $r \rightarrow \infty$ . This means that reflections at high  $2\theta$  are less intense than those at low  $2\theta$ . However, neutrons are scattered from the nuclear density, which can be approximated as an infinitesimal point or a Dirac  $\delta$ -function. As the Fourier transform of a  $\delta$ -function is 1, there is no such angular dependency for neutron scattering. An introduction to Fourier transforms is found in the Appendix.

Secondly, neutrons may experience either a repulsive or attractive potential when interacting with the nucleus of an atom. This results in either positive or negative scattering lengths (commonly referred to as a phase shift), which can give large contrast



between similar elements (Figure 2.4). This property is particularly useful for studying  $3d$  transition metals, where  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  are isoelectric (meaning their X-ray scattering factors are identical to a first approximation), but their neutron scattering lengths are significantly different ( $b_{\text{Mn}} = -3.73$  and  $b_{\text{Fe}} = 9.45$  fm). This difference in interaction also gives vanadium a near-zero neutron scattering length ( $b_{\text{V}} = -0.38$  fm), meaning samples can be housed in vanadium cans and placed in sample environments with vanadium heating elements for neutron diffraction measurements without having a large effect on the measurement.

Finally, neutrons are a spin-1/2 ( $S = 1/2$ ) particle, meaning they have an inherent nuclear spin and magnetic moment. They can interact with the unpaired electrons (spins) of ions ordered across a lattice, giving neutrons two ways to interact with materials: through conventional neutron scattering (with the nucleus), or through magnetic scattering (with the unpaired electrons). This can lead to two sets of Bragg peaks in some neutron diffraction patterns: contributions from the nuclear, as well as the magnetic structure. As magnetic scattering occurs through an interaction with the electron cloud (in this case, a spin-spin interaction between the neutron and an unpaired electron), its scattering factor decreases rapidly at larger  $\theta$ . The use of neutron diffraction to probe magnetic structures is the topic of Chapter 7 of this dissertation.

### 2.3.1 Laboratory X-Ray Diffraction

Laboratory X-ray diffraction is routinely available in many materials science laboratories around the world. This is a bulk-sensitive analytical method that is able to provide information regarding the crystal structure, crystallite strain, and domain size of a material.

Traditionally, X-rays diffraction works by directing X-rays onto a sample and detecting the diffracted rays and their intensity by scanning a detector through a  $2\theta$  range (Figure 2.2). Conventionally, X-rays are generated by heating a filament of highly heat-resistant metal (such as tungsten), which emits electrons that are accelerated towards an anode target. The accelerated electrons interact with the inner core ( $K$  shell) electrons

of the target, causing them to be ejected from the metal atom. This causes higher ( $L, M$ ) shell electrons to ‘relax’ into the lower shells to take their place, losing energy that is then emitted as X-rays. Electrons falling from the  $L \rightarrow K$  shell produce  $K_\alpha$  X-rays with two distinct wavelengths in a 2:1 ratio, due to the difference in spin and angular momentum between the  $2p_{3/2}$  and  $2p_{1/2}$  electrons. Electrons falling from the  $M \rightarrow K$  shell produce  $K_\beta$  X-rays of a single wavelength. As this process is quantised, the energy emitted is of a specific wavelength due to Moseley’s law, stating that the energy of the emitted X-ray is inversely proportional to the square of the atomic number ( $E \propto Z^2$ ).

The emitted X-rays are characteristic of the anode material, and different anode targets can be employed in X-ray diffraction to garner different information. For example, Cu  $K_\alpha$  X-rays have a lower energy than Mo  $K_\alpha$  X-rays, providing different sensitivities to unit cell content and peak splitting. The anode targets used at Sydney Analytical, a core research facility at the University of Sydney, include Cu ( $\lambda_{K\alpha_1} = 1.5406$ ,  $\lambda_{K\alpha_2} = 1.5444$  Å) and Mo ( $\lambda_{K\alpha_1} = 0.7093$  with  $\lambda_{K\alpha_2}$  filtered out). A comparison of the X-ray diffraction patterns of diamond using different radiation sources are shown in Figure 2.3. In this dissertation, two main laboratory X-ray diffraction instruments were used in the characterisation of materials. For high throughput sample analysis, a Bragg-Brentano PANalytical X’Pert Pro equipped with a Cu source was used. For precise structure determination or where very little sample was produced, a Debye-Scherrer STOE Stadi P equipped with a Mo source was used. The choice of two different X-ray wavelengths also allows for fluorescence to be avoided, such as occurring for elements close to Cu in the Periodic Table when using Cu radiation.

The PANalytical X’Pert Pro operates in a Bragg-Brentano (reflection) geometry, where a sample of polycrystalline material, usually in the form of a fine powder, is placed on a stage and flattened to reduce surface effects and absorption. The incident X-rays are then ‘reflected’ off the sample and detected, with the sample rotated on a stage to reduce the effects of crystallite orientation. The instrument performs a  $\theta : 2\theta$  scan, where the X-ray source is fixed, and the sample stage and detector move at a rate of  $\theta \text{ min}^{-1}$ . For the PANalytical, the large angular range ( $5 \leq 2\theta \leq 110^\circ$ ) allows for a large range of  $d$ -space to be probed ( $\sim 0.94\text{--}18$  Å). This allows for the accurate quantification

of different phases with larger unit cells that may be present within a polycrystalline sample, as well as spacing out the major Bragg reflections across the entire  $2\theta$  range to observe any additional reflections from impurities or pseudosymmetries. An additional advantage of the PANalytical X'Pert Pro is that it is capable of scanning up to 15 samples in series, allowing for large batches of samples to be analysed overnight. Effects associated with Bragg-Brentano geometry, such as microroughness and microabsorption, can increase the background of the measurement, and can be navigated by changing to transmission geometry.

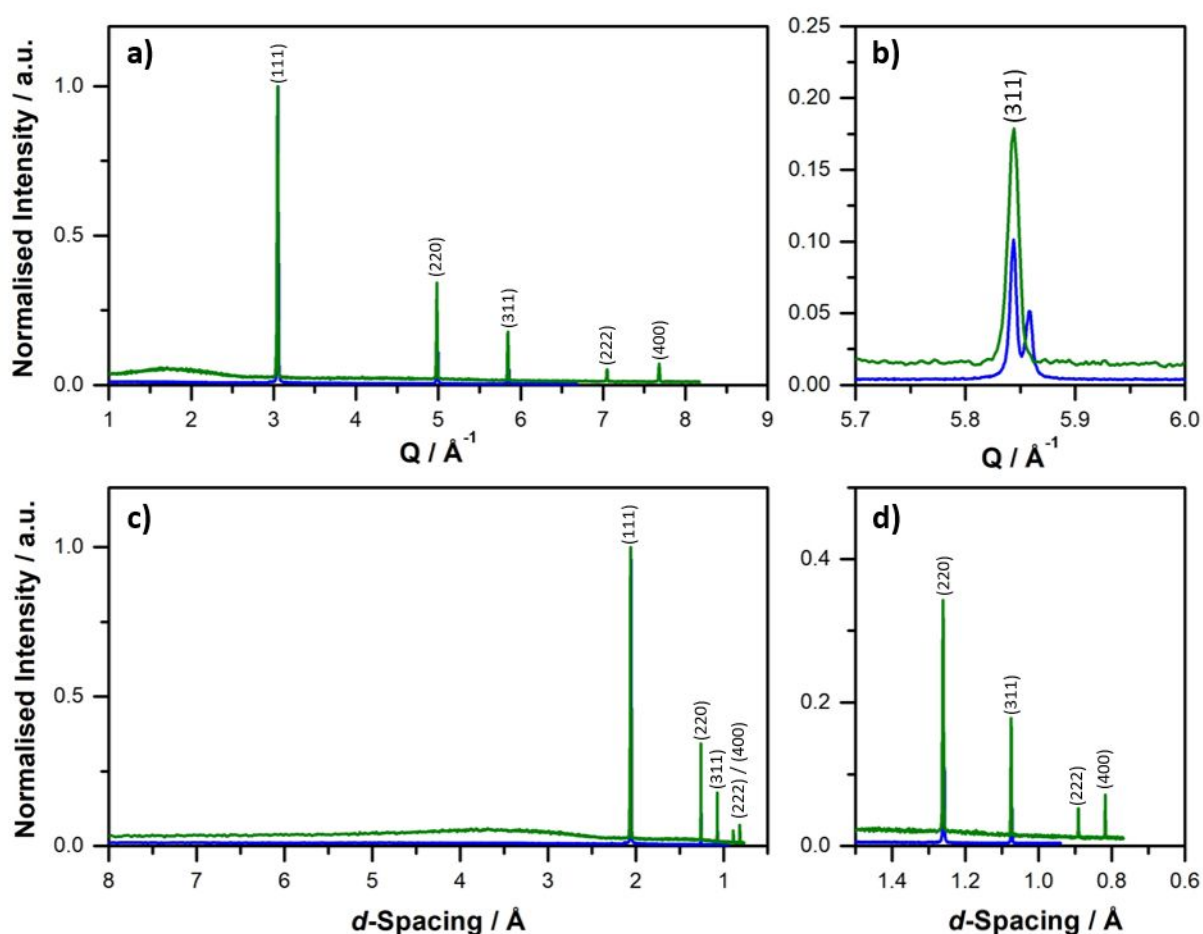


Figure 2.5: X-ray diffraction on a sample of 8 k grit diamond powder collected on (blue) a PANalytical X'Pert Pro copper source diffractometer, and (green) a STOE Stadi P monochromatic molybdenum source diffractometer. The patterns have been plotted in (a)  $Q$  with (b) demonstrating the difference in peak-shape resolution, and (c)  $d$ -spacing with (d) demonstrating the difference in  $d_{\min}$ . The 'bump' in the STOE pattern is an amorphous contribution from the borosilicate glass capillary used to house the sample.

The STOE Stadi P operates in a Debye-Scherrer (transmission) geometry, which requires less sample than its PANalytical counterpart. The higher energy of the Mo-source radiation allows for transmission geometry, leading to fewer problems associated

with sample absorption and surface effects. In this geometry, the sample is contained in a narrow capillary (made of a material semitransparent to X-rays such as borosilicate glass, quartz, or Kapton. See Figure 2.3) and is illuminated by incident X-rays. The X-rays are then ‘transmitted’ through the sample, with the diffracted X-rays detected. The STOE uses an arrangement of three MYTHEN detectors, covering a range of  $5 \leq 2\theta \leq 55^\circ$ . However, these detectors are placed closer to the sample than the detector of the PANalytical, giving less peak-shape resolution. Due to the shorter wavelength, the STOE can probe a lower  $d_{min}$ . (or larger  $Q$ ) giving it greater sensitivity to smaller atomic displacements. It is helpful to observe this by measuring the same sample of diamond powder on both a Cu- and Mo-source instrument (Figure 2.5). Therefore, the PANalytical was often used for assessing the purity of synthesised samples due to its lower energy radiation and greater peak-shape resolution, whereas the STOE was used to determine the atomic structure of materials with greater precision.

### 2.3.2 Synchrotron X-Ray Diffraction

Synchrotrons are large-scale facilities used for cutting edge scientific research around the world. They operate by accelerating electrons through a sequence of magnets until they reach close to the speed of light. The electrons travel around in a circular path, where they give off electromagnetic radiation (or *synchrotron light*) when their direction is changed by a strong magnetic field. Synchrotron light has many advantages over laboratory X-ray diffraction, such as being extremely bright and highly collimated, allowing for shorter data acquisition times and higher resolution datasets. Synchrotron light is also produced as a wide energy spectrum, with beamlines capable of utilising radiation from infrared ( $E_{h\nu} \sim 1.2$  eV) to X-ray diffraction and absorption studies ( $E_{h\nu} \sim 150$  keV).

In this dissertation, synchrotron X-ray diffraction (SXRD) data were primarily collected at BL-10, the Powder Diffraction beamline at the Australian Synchrotron.<sup>9</sup> The Powder Diffraction beamline is located on a bending magnet, operating at energies between 8–22 keV. Due to the short data acquisition times, *in situ* experiments were conducted at the Powder Diffraction beamline, such as monitoring the formation of

intermediate phases and changes in symmetry with respect to temperature. At this beamline, temperature control was achieved using either an Oxford cryostream from 90–500 K, or a hot air blower for temperatures up to 1000 °C. Data were collected using a bank of 16 1D MYTHEN strip detectors covering an angular range of approximately  $80^\circ \pm 2\theta$ . Due to the spaces between the MYTHEN strip detectors, each measurement was repeated with the detectors shifted by  $0.5^\circ$  from their initial positions to cover these spaces. These datasets were then merged using the program PDViPeR.

### 2.3.3 Neutron Powder Diffraction

Neutron powder diffraction (NPD) uses similar principles to X-ray diffraction, however an incident neutron beam is used instead of X-rays. As outlined previously, X-rays and neutrons scatter differently due to their form factors. One advantage of neutron scattering is that there is no simple relationship between scattering intensity and atomic number, meaning that it is possible to have a larger proportion of the total scattered intensity derived from lighter elements. This is particularly useful in studies of metal oxide materials, such as those studied in this dissertation. Take the photocatalyst  $\text{BiVO}_4$  as an example. Although X-rays scatter very strongly from heavier elements such as  $\text{Bi}^{3+}$  ( $Z = 80$ ) and  $\text{V}^{5+}$  ( $Z = 18$ ), there is very limited scattering from the lighter  $\text{O}^{2-}$  atoms ( $Z = 10$ ) reducing the amount of information available on their atomic positions and thermal displacements. In contrast, all three atoms possess sufficiently different coherent neutron scattering lengths ( $b_{\text{Bi}} = 8.53, b_{\text{V}} = -0.38, b_{\text{O}} = 5.80$  fm), meaning neutron measurements are sensitive to oxygen structural and atomic displacement parameters in the presence of heavier elements (although, it should be noted that neutrons are very insensitive to vanadium due to its near-zero scattering length). In this dissertation, both X-ray and neutron diffraction techniques were used complementary to each other. As X-rays generally have a superior signal-to-noise ratio and higher peak-shape resolution, they are often used to quantify structural features such as the lattice parameters and cation positions within the unit cell. By contrast, neutrons provide excellent sensitivity to lighter atoms such as oxygen, as well as thermal displacement parameters due to their point-like scattering from the nucleus.

In this dissertation, NPD measurements were performed on the Echidna high resolution, and Wombat high intensity, diffractometers at the Open Pool Australian Lightwater (OPAL) reactor, operated by the Australian Nuclear Science and Technology Organisation (ANSTO).<sup>10,11</sup> Both Echidna and Wombat utilise a neutron beam generated by the 20 MW OPAL research reactor with a constant thermal neutron flux of  $4 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ . On Echidna, the beam is monochromated using a variable-curvature Ge monochromator, allowing for a neutron wavelength selection between  $0.8 \leq \lambda \leq 3.3 \text{ \AA}$ . In this work, wavelengths of 1.30  $\text{\AA}$  (using the Ge 337 reflection), 1.62  $\text{\AA}$  (using the Ge 335 reflection), and 2.44  $\text{\AA}$  (using the Ge 331 reflection) were used. The diffracted neutrons are then detected using 128  $^3\text{He}$  detector tubes spaced  $1.25^\circ$  apart, covering up to  $165^\circ 2\theta$ . On Wombat, two monochromators are available: a pyrolytic graphite or Ge 115 monochromator. In this dissertation, the Ge monochromator was used, allowing for 1.54  $\text{\AA}$  neutrons. The detector consists of eight  $15^\circ$  curved panels, filled with a mixture of  $^3\text{He}$  and propane, without any ‘gap’ between the modules. This allows for  $120^\circ 2\theta$  continuous coverage.

For either room temperature or variable temperature data collection, samples were housed in vanadium cans due to their near-zero neutron scattering length. For low temperature measurements (down to 3 K), samples were loaded into a cryostat. For high temperature measurements (up to 1000  $^\circ\text{C}$ ), samples were loaded into an ILL-type furnace operating at  $<10^{-4} \text{ Pa}$ . For higher temperature measurements (over 1000  $^\circ\text{C}$ , but lower than 1500  $^\circ\text{C}$ ), vanadium cans could not be used due to their low melting point. Samples were loaded into open niobium cans, with the top of the can covered with a niobium wire mesh.

### 2.3.4 Diffraction Modelling and Refinement Methods for Structure Solutions

Diffraction patterns are comprised of multiple Bragg peaks that differ in position, shape, and intensity depending on the unit cell parameters, atomic coordinates, and amount of crystalline order in the system. In contrast to single crystal diffraction,

the one dimensional powder diffraction patterns often results in different  $hkl$  reflections overlapping in  $2\theta$ . This means that it can often be difficult to experimentally determine accurate intensities of individual reflections, which in turn can reduce the precision of the determined structure. As a result, a whole pattern fitting approach is often undertaken in which a structural model is used to calculate a powder pattern and compared to the experimental data. This structural model may then be *refined* to better match the experimental pattern, by changing parameters within the structure such as the lattice parameters, atomic coordinates, site occupancy, and thermal displacements of the atoms.

There are many whole pattern fitting methods used in powder diffraction analysis. The most simple method is referred to as indexing, where the  $2\theta$  and intensities are freely refined (as in, without constraints) without a full structural model. This may be used to determine information such as the unit cell parameters of a structure. Additionally, Pawley and Le Bail methods may be used where the values of  $2\theta$  are constrained to a particular space group, giving information on the symmetry of a crystal structure.<sup>12,13</sup> However, as the intensities of Pawley and Le Bail refinements are freely fit, information regarding the site occupancy and atomic coordinates due to potential Bragg reflection overlap is lost.

The most comprehensive refinement technique for powder diffraction data is Rietveld refinement, and will be the focus of this dissertation.<sup>14</sup> Rietveld refinement takes a calculated pattern from a starting structural model, and the calculated intensity ( $y_{calc.}$ ) at each step in  $2\theta$  is compared to the experimental intensity ( $y_{obs.}$ ). The difference between the two values is then minimised by changing certain parameters within the model. This is written as minimising the quantity  $M$  by using a least-squares refinement

$$M = \sum w (y_{obs.} - y_{calc.})^2 \quad (2.9)$$

where  $w$  is a weighting factor used (equal to  $1/\sigma$ , where  $\sigma$  is the measurement uncertainty).

Rietveld refinement is an iterative, multistep process in which the agreement between  $y_{calc.}$  and  $y_{obs.}$  is improved upon in each cycle. This can be measured by monitoring the weighted profile  $R$  factor,  $R_{wp}$ , which should tend to a low value.

The value is defined as

$$R_{wp} = \sqrt{\frac{\sum_{i=1}^N w_i (y_{obs.} - y_{calc.})^2}{\sum_{i=1}^N w_i y_{obs.}^2}} \quad (2.10)$$

where  $N$  is the number of points used in the Rietveld refinement. There are other goodness-of-fit parameters that are often monitored to determine how well a refined crystal structure matches the experimental dataset. These are detailed further in the Appendix.

The types of parameters that can be determined using Rietveld refinement are split into three classes: instrumental, sample, and structural parameters. Instrument parameters are the result of the source (such as resolution and divergence), whereas the properties of the material are captured by the sample (such as residual stress or crystallite size) and structural (such as scattering factors and degree of crystallinity) parameters. Within this dissertation, the Thompson-Cox-Hastings pseudo-Voigt profile model was used to account for the asymmetry of the peaks due to axial divergence.<sup>15</sup> Rietveld refinements were conducted by fitting the Bragg reflections with a pseudo-Voigt function comprising of a Gaussian component capable of modelling instrument parameters, and a Lorentzian component capable of modelling the sample parameters. The expressions for these parameters are given in the Appendix.<sup>16</sup>

In this dissertation, Rietveld refinements were performed using the software TOPAS6.<sup>17</sup> Before undertaking a traditional refinement, a Le Bail fit would first be performed on an instrument standard such as a sample of LaB<sub>6</sub> or CeO<sub>2</sub> from the National Institute of Standards and Technology (NIST). This allows for accurate quantification of profile parameters, such as resolution and axial divergence, as well as the wavelength of the radiation source. Then, a similar structure (similar atomic composition and space group) would be used as a starting point for the Rietveld refinement sourced from the Inorganic Crystal Structure Database (ICSD), often from highly accurate single crystal studies. Structure parameters such as the crystallite size and strain would be refined, along with the unit cell dimensions, atomic coordinates, and atomic displacement parameters (ADPs). In the final refinement cycles, all altered structural parameters would have their constraints relaxed and be allowed to freely refine. The crystal structures were then drawn in VESTA.<sup>18</sup>



It should be noted that single crystal diffraction is considered the ‘gold standard’ of determining unknown crystal structures. The 3D nature of single crystal diffraction patterns allows for accurate quantification of structures by separating out different  $hkl$  contributions to the diffraction pattern. However, it can often be difficult to grow diffraction quality single crystals for analysis, and single crystals limit the ability of materials to be studied either *in situ* or *operando*, such as observing phase changes in battery materials or activation sites in catalysts. Therefore, Rietveld refinement is used as a high throughput method to quantify structural changes in a material under a variety of different conditions. This has led to great scientific breakthroughs in the past for many diverse materials science fields, such as high-temperature superconductors,<sup>19</sup> batteries,<sup>20</sup> ferroelectric materials,<sup>21</sup> zeolite catalysts,<sup>22</sup> pharmaceutical polymorphism,<sup>23</sup> and many more.

## 2.4 Short-Range Local Structure Determination

Up to now in this dissertation, the description of materials has focused on their crystal structure. To put it simply, we can understand materials by modelling where the atoms are in an averaged unit cell of a few cubic Ångstroms. This technique has proven successful in describing many different materials, but is unsuitable in describing many modern-day materials, such as nanomaterials or other materials that feature disorder. This is due to the functionality of many materials deriving from other structural factors separate from the average crystal structure, such as surface morphology, heterogeneities, point defects, and chemical/distorted short-range order, amongst many other things. New techniques beyond traditional Bragg diffraction are needed to gain a more complete understanding of modern-day materials.

Consider the example of diamond from earlier. Diffraction allows for the development of a structure-functionality relationship, such as the highly symmetric network of strongly-bound carbon atoms used to explain the high density and hardness of diamond. However, different types of diamonds also exist aside from the ‘perfect’ white diamonds that are found in some jewellery. A small amount of nitrogen present in the diamond structure can

give it a yellow colour, and the presence of boron can give it a blue colour. The doping of these atoms can change the band structure of diamond, leading to different interactions with visible light and different colours being observed. However, these impurities are so rare (about  $\sim 0.1\%$ , or one in every 1000 unit cells) that diffraction is insensitive to any overall structural change. To put it simply, the presence of a nitrogen atom in one in every thousand unit cells is missed by Bragg diffraction that averages over many hundreds of thousands of unit cells. We need a technique capable of understanding the presence local defects in various materials.

### 2.4.1 Pair Distribution Function Analysis

One approach to this ‘local scale’ problem is the use of the pair distribution function (PDF) method.<sup>24</sup> This method is derived from conventional diffraction, where high energy radiation (such as X-rays or neutrons) is scattered off a material and detected. However, the extremely high energy and wide-angular range detected results in a wide range of reciprocal space being probed. This method is not only sensitive to elastic Bragg scattering, but also to short-length elastic diffuse scattering sensitive to short-range atom–atom correlations and disorder. In terms of the magnitude of the scattering vector, PDF experiments measure to a much higher  $Q$  (typically  $Q_{max} > 30 \text{ \AA}^{-1}$ ) compared to conventional diffraction (typically  $Q_{max} < 6 \text{ \AA}^{-1}$ ). As PDF experiments take into account both the Bragg and diffuse scattering, they are referred to as *total scattering* experiments.

We can understand PDF by first considering the radial distribution function,  $R(r)$ . This function acts as a scaled histogram, whereby we take each atom  $i$  in the structure and measure the distance to every other atom  $j$  in the material. This results in a 1D plot ‘counting’ how many times different atoms appear at a distance  $r_{ij}$ . This count is then scaled by the relative scattering power of each pair of atoms, which is different depending on whether X-ray or neutron radiation is used.

This can be summarised as

$$R(r) = \frac{1}{N} \sum_{i,j \neq 1} \frac{b_i^* b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \quad (2.11)$$

where  $N$  is the number of atoms,  $b$  is the weight of the scattering factor of each atom, the asterisk denotes the complex conjugate, and  $\langle b \rangle$  denotes the stoichiometric average.

The radial distribution function can be inconvenient when studying bulk materials. As  $r$  increases, the number of atoms lying on a spherical surface away from the central atom also increases, leading to a larger number of interatomic distances. This renders the radial distribution function inconvenient when dealing with atom–atom correlations beyond the first few coordination shells. A more helpful representation is to normalise the distribution function by the spherical surface area and the average number density to get a *reduced* PDF by

$$G(r) = \frac{R(r)}{r} - 4\pi r \rho_0 \gamma_0 \quad (2.12)$$

where  $\rho_0$  is the average atom number density, and  $\gamma_0$  is a characteristic function describing the autocorrection of the shape of the scattering domains. This factor is important for samples with different nanostructuring and particle shapes, but reduces to  $\gamma_0 = 1$  for the crystalline materials studied in this dissertation.

PDF data is obtained by taking the total scattering structure function,  $S(Q)$ , as the measured intensity weighted by the compositional average as  $S(Q) = I(Q)/\langle b \rangle^2$ . From this, we take the reduced structure function,  $F(Q)$ , derived as

$$F(Q) = Q [S(Q) - 1]. \quad (2.13)$$

Finally, the reduced PDF,  $G(r)$ , and the reduced structure function,  $F(Q)$ , are related by the sine Fourier transform. This gives a direct relationship between the experimentally measured pattern and the PDF by

$$G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} F(Q) \sin(Qr) dQ \quad (2.14)$$

where  $Q_{min}$  and  $Q_{max}$  are set by the instrumentation and experimental set-up.

The reduced PDF,  $G(r)$ , can be thought of as a weighted histogram of all atom-atom distances within a material. This method has the advantage over traditional Bragg diffraction in that it does not require long-range crystallographic ordering. The peaks in  $G(r)$  can detail information about the atomic distances (by the position of each peak), the coordination environment (by the area of each peak), the amount of thermal and/or chemical disorder (by the width of the peak), and the particle size (by the  $r_{max}$ ).

To truly understand the power of PDF analysis, consider lithium fluorsulfonylimide (Li-FSI). This has been proposed as a novel electrolyte in lithium-ion batteries due to its lack of organic component, offering a nonflammable, nonvolatile, and highly stable medium.<sup>25</sup> Another key component of its applicability is that Li-FSI has a low melting point ( $T_{mp} = 143$  °C), allowing for high ionic mobility at moderate operating temperatures. However, once the material melts it loses all crystalline order, meaning the key information on how the material acts *in situ* (such as what structural changes are occurring upon melting and recrystallising) cannot be probed using X-ray Bragg diffraction alone (Figure 2.6). X-ray pair distribution function (XPDF) analysis provides an avenue in which structural trends between the crystalline and melted phases can be identified by comparing its structure at low  $r$ .

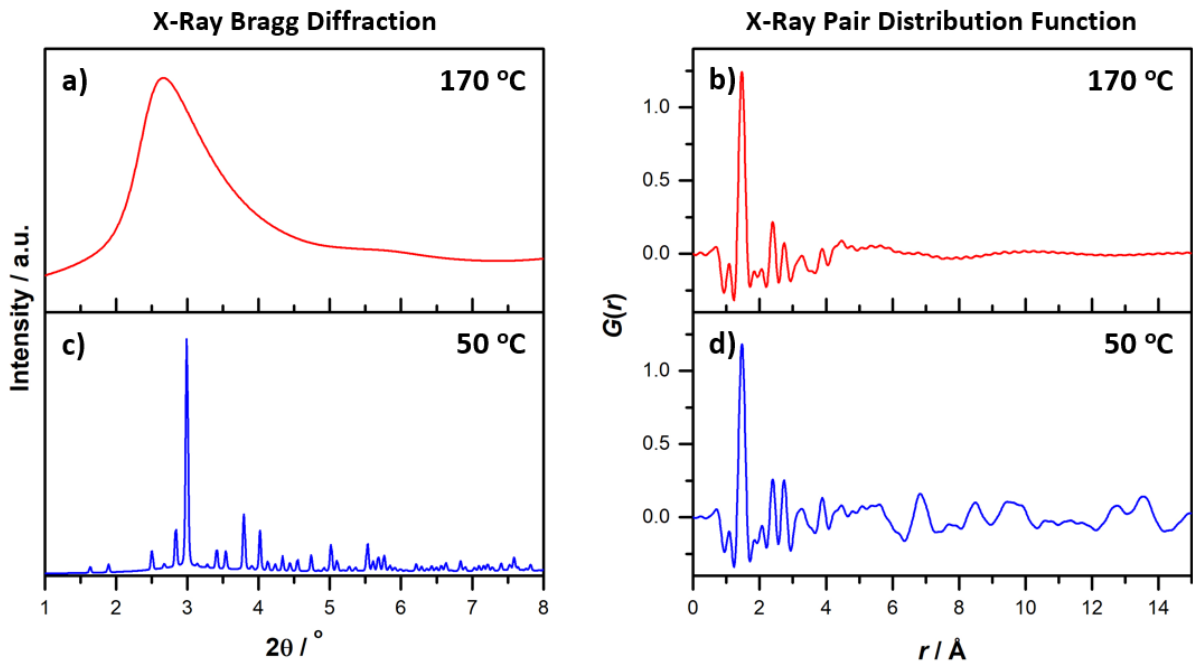


Figure 2.6: (a,c) X-ray Bragg diffraction and (b,d) X-ray pair distribution function data collected on lithium fluorsulfonylimide (Li-FSI) both (a,b) above and (c,d) below its melting point of  $T_{mp} = 143$  °C. Data collected at the Argonne National Laboratory Advanced Photon Source beamline 11-ID-B.

PDF analysis has brought about a revolution in terms of the analysis of non-crystalline materials. Examples of these include understanding the formation of nanoparticles and nanoclusters,<sup>26</sup> precipitation behaviour in water and aqueous solutions,<sup>27</sup> node distortions in MOFs,<sup>28</sup> and small molecules such as pharmaceuticals and saccharides.<sup>29</sup> This has not just been limited to non-crystalline materials, with PDF analysis also being used to understand short-range local distortions that can exist in long-range ordered crystalline materials.<sup>30</sup>

Local structure analysis provides important information on materials where the characteristics may be ‘lost’ or averaged over many unit cells. It is best understood by considering a chain of 1D atoms (Figure 2.7). At very low temperatures, they have limited dynamic motion meaning that each atom is confined to a static position. In real space, these atoms may not sit completely centred on a line, but may sit slightly offset from each other as a localised distortion. PDF analysis is sensitive to these local coherent atom-atom displacements, allowing for a greater understanding of the material. Traditional Bragg diffraction would only see the average across thousands of unit cells, approximating the position of each atom at the centre of its respective unit cell.

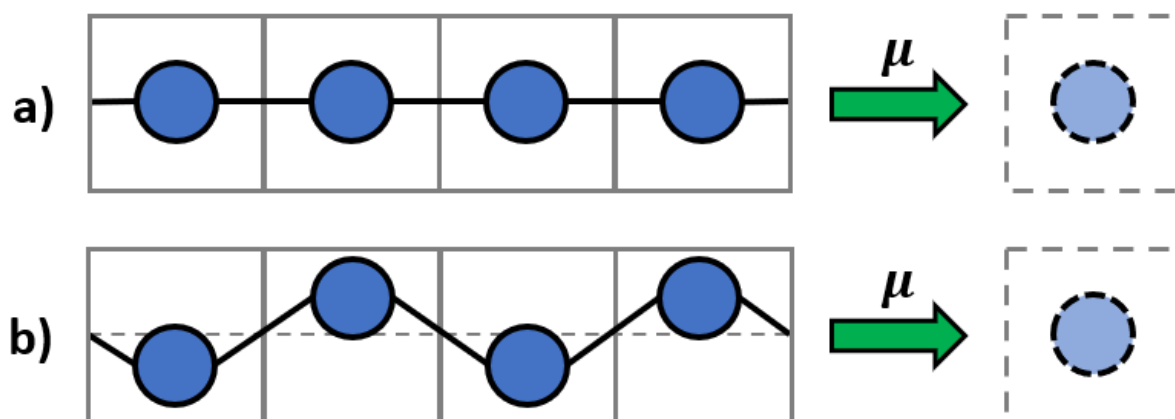


Figure 2.7: A one dimensional chain of atoms may be arranged (a) in a ‘perfect’ line, or (b) slightly offset from each other, with the dotted line in (b) showing the ‘perfect’ line. Despite these local distortions, the average of each unit (denoted by  $\mu$ ) is still seen as the same. As diffraction averages over many hundreds of thousands of unit cells, it is often insensitive to these local distortions.

There have been two prominent examples of PDF analysis in the literature that have showcased the power behind this technique. The first was an experiment performed at the Cornell High Energy Synchrotron Source (CHESS) in the late 1990s on samples of  $(\text{In}_{1-x}\text{Ga}_x)\text{As}$  semiconducting alloys.<sup>31</sup> Refinements from traditional Bragg diffraction

data identified that these materials all exhibited the zinc blende structure, with an average bond length of 2.52 Å. However, previous extended X-ray absorption fine structure (EXAFS) spectroscopy measurements revealed that each of the In–As and Ga–As pairs should take their ideal lengths of 2.437 and 2.610 Å respectively, and not an averaged bond length of 2.52 Å.<sup>32,33</sup> By collecting multiple X-ray diffraction datasets (taking upwards of 12 hours), high resolution atomic PDFs were calculated from the X-ray diffraction data that showed distinct In–As and Ga–As bond lengths differing by the same amount predicted by theoretical models.<sup>34</sup> The second such example is in the perovskite  $\text{YCrO}_3$ , which exhibits biferroic properties despite its highly symmetric structure.<sup>35</sup> For a material to be biferroic, it cannot exhibit an inversion centre found in all high-symmetry perovskites. To break this inversion centre symmetry, the atoms must sit away from their centrosymmetric positions, resulting in lower symmetry and a greater number of Bragg peaks. However, a lack of additional diffraction peaks indicated that the  $\text{Cr}^{3+}$  atoms were confined to their centrosymmetric position within the  $\text{CrO}_6$  octahedra. High resolution neutron total scattering data was used to identify that the  $\text{Cr}^{3+}$  does not sit in the centrosymmetric position, but sits slightly along the  $z$  direction, displaying asymmetric Cr–O bond lengths that differed by  $\sim 1$  pm. This highly accurate structural model allowed for an in-depth understanding of its biferroic behaviour. The implication of these two examples is that understanding the local correlated interactions of atoms is important, and can lead to breakthroughs in the understanding and designing of new functional materials.

## 2.4.2 Total Scattering Infrastructure

### 2.4.2.1 X-Ray Total Scattering

Despite the early success of total scattering measurements being able to model local phenomena in the 1990s, suitable X-ray diffraction datasets often took upwards of 12 hours to collect, meaning materials with organic coatings such as CdSe quantum dots (subject of the 2023 Nobel Prize in Chemistry)<sup>36</sup> were unable to be measured due to risk of being damaged by prolonged exposure to the high-energy X-ray beam. In 2003, the development

of large 2D area plate detectors vastly decreased the acquisition time of diffraction data. In an experiment conducted at the Argonne National Laboratory Advanced Photon Source (APS), image plate detectors were used to collect the diffraction data of a Ni standard. Data that previously took 12 hours to collect could now be collected in 1 second.<sup>37</sup> The rapid data collection time opened up XPDF studies to a wider audience.

In this dissertation, X-ray total scattering data were acquired at beamline I15-1 of Diamond Light Source, UK ( $\lambda = 0.161669 \text{ \AA}$ , 76.69 keV). Small amounts of finely ground samples were loaded into quartz capillaries with an inner diameter of 0.78 mm to a height of 3.5 cm. Data were collected under ambient conditions for the sample, an empty capillary, and the empty instrument for background subtraction. Data were collected from 100–500 K using an Oxford Cryostream, and from 400–800 K using a Cyberstar hot air blower. Diffraction data is collected using a 2D area detector at two different distances relative to the sample: 860 mm for Rietveld refinement, and 200 mm for PDF analysis.

X-ray total scattering data were also acquired at beamline 11-ID-B of Argonne National Laboratory APS, Chicago IL, USA ( $\lambda = 0.2116 \text{ \AA}$ , 58.59 keV). A small amount of finely ground sample was loaded into a quartz capillary with an inner diameter of 1.1 mm to a height of 2 cm. Data were collected under ambient conditions for the sample, an empty capillary, and the empty sample environment for background subtraction. Temperatures were probed from 300–650 K using a single point heater developed by the Chapman Research Group at Stony Brook University.<sup>38</sup> Diffraction data were collected using a 2D area detector at two different distances: 1000 mm for Rietveld refinement, and 180 mm for PDF analysis.

For all XPDF datasets, a  $\text{CeO}_2$  calibration standard was used to correct for the polarisation, detector transmission, and flat field, with badly performing pixels masked prior to integration using either DAWN (Diamond Light Source) or GSAS-II (Argonne National Laboratory).<sup>39,40</sup> The PDF  $G(r)$  were calculated using PDFgetX3,<sup>41</sup> part of the software package from the xPDFsuite.<sup>42</sup> Rietveld refinements to the Bragg diffraction data, as well as small-box fitting against the XPDF data were performed using TOPAS6.<sup>17</sup>

### 2.4.2.2 Neutron Total Scattering

Similar to X-ray total scattering measurements, different experimental set-ups from conventional diffraction are required to measure neutron total scattering data. In fact, total scattering measurements using neutron diffraction were first conceived due to the lack of intensity drop off at high  $Q$  (Equations 2.6 and 2.8). Neutron total scattering studies are traditionally performed, not at reactor-based instruments such as the OPAL reactor, but at spallation neutron sources that are capable of probing higher  $Q$ . Whereas neutrons are generated at a fission reactor through nuclear decay, spallation neutrons are produced using pulses of protons accelerated to high energies and directed onto a heavy metal target, such as liquid mercury at the Spallation Neutron Source at Oak Ridge National Laboratory, TN, USA. The collision between the high-energy protons and the heavy metal target produces lots of fragments, including neutrons, with a wide range of energies. These neutrons are then transported to different beamlines.

Whereas reactor neutron sources are better at time-averaged studies, spallation neutron sources have an advantage in that a sample is exposed to a much greater peak flux of neutrons. This is only the case if *all* of the neutrons are used, with no neutrons filtered out (or monochromated) based on their wavelength. As a result, time-of-flight (ToF) instruments are traditionally used for undertaking neutron total scattering experiments. These instruments rely on the fact that neutrons with different energies, and hence different wavelengths, travel at different velocities due to the de Broglie relationship of

$$\lambda_{\text{neut.}} = \frac{h}{p_{\text{neut.}}} = \frac{h}{m_{\text{neut.}} v_{\text{neut.}}} \quad (2.15)$$

where  $\lambda_{\text{neut.}}$ ,  $m_{\text{neut.}}$ , and  $v_{\text{neut.}}$  are the wavelength (in m), mass (in kg), and velocity (in  $\text{ms}^{-1}$ ) of the neutron respectively, and  $h$  is Planck's constant.

The implication of the de Broglie relationship is that if all neutrons from a given proton-target collision are created at the same time ( $t_0$ ), the higher energy (shorter wavelength) neutrons will travel faster, first to the sample, then following diffraction to a detector, than the lower energy (longer wavelength) neutrons. By measuring the time it takes for a neutron to travel from the source to the detector ( $t$ ), its wavelength can be



calculated. The wavelength and time-of-flight are related by the following expression

$$\lambda_{\text{neut.}} = \frac{ht}{m_{\text{neut.}}L} \quad (2.16)$$

where  $t$  is the time-of-flight, and  $L$  is the total flight path of the neutron from the source to the detector.

By substituting in Bragg's law (Equation 2.2) and the expression for wavevector transfer, we arrive at an expression relating  $d$ -spacing and ToF as

$$d \sim \frac{t}{506L \sin \theta}. \quad (2.17)$$

While monochromatic instruments have a fixed wavelength and measure various  $d$ -spacings by varying the detector angle  $\theta$ , ToF instruments have a fixed scattering angle  $\theta$  and measure various  $d$ -spacings by using incoming radiation of different energies (or  $\lambda$ ). ToF neutron powder diffractometers have large banks of fixed detectors covering a wide range of scattering angles and, for PDF measurements, typically record data for wavelengths in the range of  $0.1 < \lambda < 4.0$  Å. This results in a wide range of momentum transfer, typically between  $0.1 < Q < 50$  Å<sup>-1</sup>.

In this dissertation, neutron total scattering data were collected using either the Nanoscale Ordered MAterials Diffractometer (NOMAD) or POWGEN located at Oak Ridge National Laboratory (ORNL), TN, USA.<sup>43,44</sup> Samples were loaded into 6 mm vanadium cans. For PDF calculation, the neutron scattering data were corrected for instrument background, the incident neutron spectrum, absorption, multiple scattering, and finally normalised. The  $G(r)$  PDFs were then calculated using either PDFgetN3,<sup>45</sup> or software available at the beamline. Rietveld refinements to the Bragg diffraction data, as well as small-box fitting against the neutron PDF (NPDF) data were performed using TOPAS6.<sup>17</sup>

## 2.5 Physical Property Characterisation Techniques

After determining the long-range average and short-range local structure of various promising materials, their physical properties were also analysed in order to develop structure-functionality relationships.

### 2.5.1 Electrochemical Impedance Spectroscopy for Ionic Conductivity

In order to determine how well a material can act as an ion conductor, measurements regarding how well ions can move through their structure were undertaken using electrochemical impedance spectroscopy (EIS). The ionic conductivity of a sample is calculated by measuring the reactance of a material, or more specifically, how well charge-carrying species can pass through it.

Consider the response of a system to a direct current (DC). The voltage is known to be impacted by the magnitude of the current and resistance, as per Ohm's law

$$R = \frac{V}{I} \quad (2.18)$$

where  $R$  is the resistance (in  $\Omega$ ),  $V$  is the voltage (in V), and  $I$  is the current (in A).

However, various parasitic phenomena can arise from using a DC potential (such as charge accumulation and concentration gradients) that can effect the measured resistance. Using an alternating current (AC) provides a potential that varies in a sinusoidal matter and allows for a linear relationship between reactance and applied potential by limiting the effects of these parasitic phenomena. The AC potential means the voltage and the current vary as sine waves. The voltage and current are calculated as

$$\begin{aligned} V(t) &= V_0 \sin(\omega t) \\ I(t) &= I_0 \sin(\omega t + \phi) \end{aligned} \quad (2.19)$$

where  $V(t)$  is the potential at time  $t$ ,  $\omega$  is the radial frequency (where  $\omega = 2\pi f$  and  $f$  is in Hz), and  $\phi$  is a phase shift induced by AC phenomena such as capacitance (the ability

of a system to store electric charge) or inductance (the ability of a conductor to oppose a change in electric current flowing through it).

Combining expressions Equations 2.18 and 2.19 gives

$$Z = \frac{V}{I} = \frac{|V| \sin(\omega t)}{|I| \sin(\omega t + \phi)} = |Z| \frac{\sin(\omega t)}{\sin(\omega t + \phi)} = |Z| e^{i\phi} \quad (2.20)$$

after switching to polar coordinates, where  $Z$  is the reactance (expressed as  $Z = Z' + iZ''$ , where  $Z'$  is the real resistance analogous to DC, and  $Z''$  is the complex component on the reactance attributed to AC phenomena such as capacitance and/or inductance).

The impedance spectra are measured by applying a small voltage ( $\sim 100$  mA), and measuring the impedance over a range of frequencies. This generates a Nyquist plot, where the values of  $Z'$  and  $-Z''$  are plotted. Curves are fitted to these Nyquist plots by using *equivalence circuits*, where the physical phenomena of a material (such as bulk conductivity, intergrain boundaries, sample-electrode interfaces, *etc.*) are modelled using analogous AC phenomena (such as capacitance, reactance, *etc.*). The contribution of resistors and capacitors to impedance are modelled by

$$Z_R = R \quad \text{and} \quad Z_C = \frac{1}{i\omega C} \quad (2.21)$$

where  $Z_R$  is the impedance contribution from a resistor,  $Z_C$  is the impedance contribution from a capacitor, and  $C$  is the capacitance (in F).

When two circuit elements are placed in parallel, such as modelling the resistance and capacitance of the bulk material, we take the reciprocal of their sum. The equivalence circuit of the bulk material is given as

$$Z_B = (Z_R^{-1} + Z_C^{-1})^{-1} = \left( \frac{1}{R} + i\omega C \right)^{-1} = \frac{R}{1 + i\omega RC}. \quad (2.22)$$

Traditionally for solid electrolytes, two parallel circuits – consisting of a resistor and a capacitor – are used to model the bulk conductivity of an electrolyte, as well as other contributions such as intergrain boundaries.

This gives a total impedance of

$$Z = R_1 + \frac{R_2}{1 + i\omega R_2 C_2} + \frac{R_3}{1 + i\omega R_3 C_3} \quad (2.23)$$

where  $R_1$  is the inherent resistance of the instrument,  $R_2$  and  $C_2$  are the resistance and capacitance associated with the bulk material, and  $R_3$  and  $C_3$  are the resistance and capacitance associated with the intergrain boundaries.

In real materials, a ‘perfect’ capacitance is seldom observed. Consequently, a constant phase element (CPE) is often used to model the inherent resistance within a capacitor. This is given by the relation

$$Z_Q = \frac{1}{(i\omega)^n Q_0} \quad (2.24)$$

where  $0 < n < 1$  is the additional constant phase (with  $n = 1$  being a perfect capacitor), and  $Q_0$  is the capacitance. Substituting this expression in Equation 2.22 gives

$$Z_T = R_1 + \frac{R_2}{1 + (i\omega)^{n_2} R_2 Q_2} + \frac{R_3}{1 + (i\omega)^{n_3} R_3 Q_3}. \quad (2.25)$$

The conductivity ( $\sigma$ , measured in  $\text{S cm}^{-1}$ ) is calculated by taking the inverse of the resistance and normalising by the surface area and length of the sample. Other relationships such as the activation energy of the ionic diffusion may be calculated using the Arrhenius equation

$$\sigma T = A \exp\left(\frac{E_a}{k_B T}\right) \quad (2.26)$$

where  $T$  is the absolute temperature (in K),  $A$  is a scaling factor,  $E_a$  is the activation energy (in J),  $k_B$  is the Boltzmann constant. Linearising Equation 2.26 gives

$$\ln(\sigma T) = \ln(A) - \frac{E_a}{k_B} \left(\frac{1}{T}\right) \quad (2.27)$$

which can be used to calculate the activation energy.

Ceramic samples, roughly 1.0–1.5 mm in thickness and 10 mm in diameter, were prepared for conductivity measurements by pressing pellets at 5 MPa using a uniaxial press. These were then sintered at high temperature for 12 hours before being cooled to room temperature at a rate of  $3\text{ }^{\circ}\text{ min}^{-1}$ . Before each measurement, pellets were coated in a conductive Pt paste and reheated to  $1000\text{ }^{\circ}\text{C}$  for two hours to cure the paste.

Samples were mounted into a Probostat set-up using a spring system to ensure good contact with two Pt grids acting as both current collectors and gas distributors. A gas flow rate of  $1\text{ L hour}^{-1}$  was selected for the measurements in air, Ar, wet Ar, and wet 5%  $\text{H}_2$  in Ar to assess the different carrier contributions ( $\text{H}^+$ ,  $\text{O}^{2-}$ , or  $e^-$ ). The set-up was then inserted into a vertical furnace to perform EIS measurements from  $850\text{--}600\text{ }^{\circ}\text{C}$  every  $25\text{ }^{\circ}\text{C}$  upon cooling. Spectra were recorded in the  $10^6\text{--}1\text{ Hz}$  frequency range to model different regions and phenomena in the sample. A Solartron 1260 potentiostat was used with an AC amplitude of 100 mV. The EIS spectra were fitted in the program ZView.

### 2.5.2 Solid State UV-Vis Spectroscopy for Band Gap Estimation

The band gap of a semiconductor describes the energy needed to excite an electron from its valence band to the conduction band. This is dependent on a number of structural factors of the material, such as its chemical composition and crystal symmetry. The band gap in semiconductor-based photocatalysts is an important tuneable property.

Photocatalysts absorb incoming radiation, exciting an electron from the valence band into the conduction band. This generates two mobile charge carriers: the photoexcited electron ( $e^-$ ) in the conduction band and a relatively positively-charged ‘hole’ ( $h^+$ ) in the valence band. These charge carriers are then free to participate in various photocatalytic reactions such as overall water splitting (by separating  $\text{H}_2\text{O}$  into its constituent  $\text{H}_2$  and  $\text{O}_2$  gases), dye degradation (by producing highly reactive hydroxyl radicals,  $\text{OH}\cdot$ ), and carbon dioxide conversion (by reducing  $\text{CO}_2$  to other fuels such as methane and ethanol using photoexcited electrons). The band gap of a photocatalyst determines the range of wavelengths of light the photocatalyst can absorb. Therefore, an accurate determination of the band gap energy is crucial in predicting its application and photochemical properties.

Band gaps can be investigated both computationally and experimentally. Computationally, the density of states (DoS) may be calculated using DFT as, for example, implemented in the Vienna *ab initio* simulation package (VASP). The electronic structure analysis provides information on which states dominate the valence and conduction bands specific to each element, allowing for predictions in how to tune the band gap of certain materials. Experimentally, the band gap is determined using diffuse reflectance spectroscopy (DRS). In DRS, a sample is illuminated with monochromatic light, with the reflected light analysed to determine at which wavelengths it is absorbed. However, several factors must be taken into account when performing DRS measurements. For example, sample inhomogeneities can cause an increase in background in the measurements. As light propagates through an inhomogeneous media, it can scatter off all points in its path causing errors in calculating the absorption coefficient from diffuse reflection data. To account for this, the Kubelka-Munk transform is used. The measured diffuse reflectance,  $R_{meas.}$ , is given as

$$R_{meas.} = 1 + \frac{k}{s} - \sqrt{\frac{k}{s} \left( 2 + \frac{k}{s} \right)} \quad (2.28)$$

where  $k$  is the absorption fraction associated with the sample and  $s$  is the scattering coefficient. This value is then formulated as a Kubelka-Munk transform by

$$\alpha = \frac{(1 - R_{meas.})^2}{2R_{meas.}} \quad (2.29)$$

where  $\alpha$  is the absorption coefficient.

The optical band gap of a material can be estimated using a Tauc plot, provided the material is a semiconductor. The Tauc method is based on the assumption that the energy-dependent absorption coefficient,  $\alpha$ , can be expressed as

$$(\alpha \cdot h\nu)^{1/\gamma} = B(h\nu - E_g) \quad (2.30)$$

where  $h$  is Planck's constant,  $\nu$  is the frequency of the incident photon (in Hz),  $\gamma$  accounts for the nature of the electron transition ( $\gamma = 1/2$  or  $2$  for direct or indirect transition band gaps respectively),  $B$  is a prefactor constant, and  $E_g$  is the band gap energy (in J). Plotting

the Tauc plot for a direct transition as  $h\nu$  vs.  $(\alpha \cdot h\nu)^2$ , an estimate of the direct band gap can be made by taking the  $x$ -axis intersection point of the linear fit.

Optical band gaps were measured using a Cary 5000 Solid State UV-Vis Spectrometer. The instrument was blanked using a sample of BaSO<sub>4</sub> and approximately 50 mg of sample was compacted, smoothed using a glass slide, and loaded into the instrument. UV-Vis DRS measurements were then taken over a range of 200–800 nm (1.55–6.20 eV) in 0.2 nm steps with five minute scans.

### 2.5.3 Physical Properties Measurement System for Magnetism

The study of magnetism in materials has led to many scientific advances in the field of superconductors,<sup>19</sup> giant magnetoresistance,<sup>46–48</sup> and the quantum Hall effect.<sup>49</sup> Key to these breakthroughs is understanding how materials (or, more specifically, how the unpaired electrons of its ions) interact to each other, and their response to external magnetic fields.

Ions with unpaired electrons can behave as small magnets which may show magnetic ordering within a crystal. At high temperatures, thermal fluctuations result in these spins being randomly orientated throughout the material, known as paramagnetism. As a sample is cooled, these thermal fluctuations reduce in energy allowing for the potential for long-range magnetic interactions to arise. This means that these spins may align to give a net magnetic susceptibility. This phenomena can produce magnetic interactions that are either ferromagnetic (all spins line up parallel to an external magnetic field) or antiferromagnetic (spins align antiparallel to each other such that the Pauli Exclusion Principle is obeyed).

To understand this behaviour, the magnetic susceptibility of some structures is often investigated to understand their response to an external magnetic field. This involves exposing a small sample to an external magnetic field and measuring its response with respect to temperature. This analysis is often undertaken to determine whether a material aligns either ferromagnetically or antiferromagnetically, as well as the temperature in which the onset of this ordering occurs.

This is achieved by using the Curie-Weiss law

$$\chi = \frac{C}{T - \theta} \quad (2.31)$$

where  $\chi$  is the magnetic susceptibility (in electromagnetic units  $\text{mol}^{-1}$ , or  $\text{emu mol}^{-1}$ ),  $C$  is the Curie constant (in  $\text{emu mol}^{-1} \text{K}^{-1}$ ),  $T$  is the temperature (in K), and  $\theta$  is a measure of the strength and sign of the local exchange interactions. When there are no competing interactions or frustration, this is equal to the magnetic ordering temperature (in K) which is positive for ferromagnetism and negative for antiferromagnetism in simple magnetic interactions. When these two values deviate, it signals a more complex picture of the magnetic interactions.

By fitting the paramagnetic region of the material, the Curie constant may be extracted, as well as the magnetic ordering temperature. The Curie constant is used to determine the spin only effective paramagnetic magnetic moment by

$$\mu_s = \sqrt{8C} \quad (2.32)$$

where  $\mu_s$  is the magnetic moment (in Bohr magnetons, or  $\mu_B$ ). This can also be compared to the ordered magnetic moment of the ion by

$$\mu = \sqrt{n(n+2)} \quad (2.33)$$

where  $n$  is the number of unpaired electrons in the ion.

Bulk magnetic susceptibility measurements were undertaken using a Quantum Design Physical Properties Measurement System (PPMS). Approximately 20 mg of sample was finely ground and placed in a tubular brass sample holder, held in place between two tightly fit plastic rods. The sample hold was then loaded into the PPMS. Data on the magnetic susceptibility of each sample was taken using the vibrating sample magnetometer (VSM) technique. Temperature-dependent DC magnetic susceptibility measurements were taken under zero field cooled (ZFC) upon heating, and field cooled (FC) upon cooling conditions over a range of 1.8–300 K, in an applied magnetic field of 1000 Oe (0.1 T). Isothermal field-dependent magnetisation data were collected to  $\pm 9$  T at constant temperatures.



# Bibliography

- (1) Huo, H.; Bartel, C. J.; He, T.; Trewartha, A.; Dunn, A.; Ouyang, B.; Jain, A.; Ceder, G. Machine-learning rationalization and prediction of solid-state synthesis conditions. *Chemistry of Materials* **2022**, *34*, 7323–7336.
- (2) Martins, M. A.; Pinho, S. P.; Coutinho, J. A. Insights into the nature of eutectic and deep eutectic mixtures. *Journal of Solution Chemistry* **2019**, *48*, 962–982.
- (3) Eckert, M. Disputed discovery: The beginnings of X-ray diffraction in crystals in 1912 and its repercussions. *Acta Crystallographica Section A: Foundations of Crystallography* **2012**, *68*, 30–39.
- (4) Jenkin, J. A unique partnership: William and Lawrence Bragg and the 1915 Nobel Prize in physics. *Minerva* **2001**, *39*, 373–392.
- (5) Kennedy, B. J.; Zhou, Q.; Avdeev, M. Neutron diffraction studies of  $\text{Gd}_2\text{Zr}_2\text{O}_7$  pyrochlore. *Journal of Solid State Chemistry* **2011**, *184*, 1695–1698.
- (6) Kennedy, B. J.; Injac, S.; Thorogood, G. J.; Brand, H. E.; Poineau, F. Structures and phase transitions in pertechnetates. *Inorganic Chemistry* **2019**, *58*, 10119–10128.
- (7) Knee, C. S.; Rainford, B. D.; Weller, M. T. Crystal structure of the ferromagnetic superconductor  $\text{RuSr}_2(\text{Gd}_{1.3}\text{Ce}_{0.7})\text{Cu}_2\text{O}_{10-\delta}$  by powder neutron diffraction. *Journal of Materials Chemistry* **2000**, *10*, 2445–2447.
- (8) Matsuda, M.; Kikkawa, A.; Katsumata, K.; Ebisu, S.; Nagata, S. Neutron diffraction study of  $\alpha\text{-Gd}_2\text{S}_3$ . *Journal of the Physical Society of Japan* **2005**, *74*, 1412–1415.

- (9) Wallwork, K. S.; Kennedy, B. J.; Wang, D. In *AIP Conference Proceedings*, 2007; Vol. 879, pp 879–882.
- (10) Liss, K.-D.; Hunter, B.; Hagen, M.; Noakes, T.; Kennedy, S. Echidna — The new high-resolution powder diffractometer being built at OPAL. *Physica B: Condensed Matter* **2006**, *385*, 1010–1012.
- (11) Studer, A. J.; Hagen, M. E.; Noakes, T. J. Wombat: The high-intensity powder diffractometer at the OPAL reactor. *Physica B: Condensed Matter* **2006**, *385*, 1013–1015.
- (12) Pawley, G. Unit-cell refinement from powder diffraction scans. *Journal of Applied Crystallography* **1981**, *14*, 357–361.
- (13) Le Bail, A. Whole powder pattern decomposition methods and applications: A retrospection. *Powder Diffraction* **2005**, *20*, 316–326.
- (14) Rietveld, H. M. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography* **1969**, *2*, 65–71.
- (15) Thompson, P.; Cox, D.; Hastings, J. Rietveld refinement of Debye–Scherrer synchrotron X-ray data from  $\text{Al}_2\text{O}_3$ . *Journal of Applied Crystallography* **1987**, *20*, 79–83.
- (16) Young, R. A., *The rietveld method*; International Union of Crystallography: 1993; Vol. 5.
- (17) Coelho, A. A. TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++. *Journal of Applied Crystallography* **2018**, *51*, 210–218.
- (18) Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* **2011**, *44*, 1272–1276.
- (19) Izumi, F.; Takekawa, S.; Matsui, Y.; Iyi, N.; Asano, H.; Ishigaki, T.; Watanabe, N. Crystal structure of the superconductor  $\text{Ba}_{1.8}\text{Nd}_{1.2}\text{Cu}_3\text{O}_{7-y}$ . *Japanese Journal of Applied Physics* **1987**, *26*, L1616.

## BIBLIOGRAPHY

---

- (20) Senyshyn, A.; Mühlbauer, M.; Nikolowski, K.; Pirling, T.; Ehrenberg, H. “*In-operando*” neutron scattering studies on Li-ion batteries. *Journal of Power Sources* **2012**, *203*, 126–129.
- (21) Lampis, N.; Sciau, P.; Lehmann, A. G. Rietveld refinements of the paraelectric and ferroelectric structures of  $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ . *Journal of Physics: Condensed Matter* **1999**, *11*, 3489.
- (22) Agostini, G.; Lamberti, C.; Palin, L.; Milanesio, M.; Danilina, N.; Xu, B.; Janousch, M.; Van Bokhoven, J. A. *In situ* XAS and XRPD parametric Rietveld refinement to understand dealumination of Y zeolite catalyst. *Journal of the American Chemical Society* **2010**, *132*, 667–678.
- (23) Németh, Z.; Sajó, I.; Demeter, Á. Rietveld refinement in the routine quantitative analysis of famotidine polymorphs. *Journal of Pharmaceutical and Biomedical Analysis* **2010**, *51*, 572–576.
- (24) Terban, M. W.; Billinge, S. J. Structural analysis of molecular materials using the pair distribution function. *Chemical Reviews* **2021**, *122*, 1208–1272.
- (25) Ladouceur, S.; Paillet, S.; Vijh, A.; Guerfi, A.; Dontigny, M.; Zaghib, K. Synthesis and characterization of a new family of aryl-trifluoromethanesulfonylimide Li-Salts for Li-ion batteries and beyond. *Journal of Power Sources* **2015**, *293*, 78–88.
- (26) Chupas, P. J.; Chapman, K. W.; Jennings, G.; Lee, P. L.; Grey, C. P. Watching nanoparticles grow: The mechanism and kinetics for the formation of  $\text{TiO}_2$ -supported platinum nanoparticles. *Journal of the American Chemical Society* **2007**, *129*, 13822–13824.
- (27) Beauvais, M. L.; Chupas, P. J.; O’Nolan, D.; Parise, J. B.; Chapman, K. W. Resolving single-layer nanosheets as short-lived intermediates in the solution synthesis of FeS. *ACS Materials Letters* **2021**, *3*, 698–703.
- (28) Chen, Z.; Strosio, G. D.; Liu, J.; Lu, Z.; Hupp, J. T.; Gagliardi, L.; Chapman, K. W. Node distortion as a tunable mechanism for negative thermal expansion in metal–organic frameworks. *Journal of the American Chemical Society* **2022**.

- (29) Benmore, C. J.; Benmore, S. R.; Edwards, A.; Shrader, C. D.; Bhat, M.; Cherry, B. R.; Smith, P.; Gozzo, F.; Shi, C.; Smith, D. A high energy X-ray diffraction study of amorphous indomethacin. *Journal of Pharmaceutical Sciences* **2022**, *111*, 818–824.
- (30) Smith, M. B.; Page, K.; Siegrist, T.; Redmond, P. L.; Walter, E. C.; Seshadri, R.; Brus, L. E.; Steigerwald, M. L. Crystal structure and the paraelectric-to-ferroelectric phase transition of nanoscale BaTiO<sub>3</sub>. *Journal of the American Chemical Society* **2008**, *130*, 6955–6963.
- (31) Petkov, V.; Jeong, I.-K.; Chung, J.; Thorpe, M.; Kycia, S.; Billinge, S. J. High real-space resolution measurement of the local structure of Ga<sub>1-x</sub>In<sub>x</sub>As using X-ray diffraction. *Physical Review Letters* **1999**, *83*, 4089.
- (32) Mikkelsen Jr, J.; Boyce, J. Atomic-scale structure of random solid solutions: Extended X-ray-absorption fine-structure study of Ga<sub>1-x</sub>In<sub>x</sub>As. *Physical Review Letters* **1982**, *49*, 1412.
- (33) Mikkelsen Jr, J.; Boyce, J. Extended X-ray-absorption fine-structure study of Ga<sub>1-x</sub>In<sub>x</sub>As random solid solutions. *Physical Review B* **1983**, *28*, 7130.
- (34) Cai, Y.; Thorpe, M. Length mismatch in random semiconductor alloys. II. Structural characterization of pseudobinaries. *Physical Review B* **1992**, *46*, 15879.
- (35) Ramesha, K.; Llobet, A.; Proffen, T.; Serrao, C.; Rao, C. Observation of local non-centrosymmetry in weakly biferroic YCrO<sub>3</sub>. *Journal of Physics: Condensed Matter* **2007**, *19*, 102202.
- (36) Liz-Marzán, L. M.; Artzi, N.; Bals, S.; Buriak, J. M.; Chan, W. C.; Chen, X.; Hersam, M. C.; Kim, I.-D.; Millstone, J. E.; Mulvaney, P., et al. Celebrating a Nobel Prize to the “Discovery of Quantum Dots, an Essential Milestone in Nanoscience”, 2023.
- (37) Chupas, P. J.; Qiu, X.; Hanson, J. C.; Lee, P. L.; Grey, C. P.; Billinge, S. J. Rapid-acquisition pair distribution function (RA-PDF) analysis. *Journal of Applied Crystallography* **2003**, *36*, 1342–1347.

## BIBLIOGRAPHY

---

- (38) Chupas, P. J.; Chapman, K. W.; Kurtz, C.; Hanson, J. C.; Lee, P. L.; Grey, C. P. A versatile sample-environment cell for non-ambient X-ray scattering experiments. *Journal of Applied Crystallography* **2008**, *41*, 822–824.
- (39) Basham, M.; Filik, J.; Wharmby, M. T.; Chang, P. C.; El Kassaby, B.; Gerring, M.; Aishima, J.; Levik, K.; Pulford, B. C.; Sikharulidze, I. Data analysis workbench (DAWN). *Journal of Synchrotron Radiation* **2015**, *22*, 853–858.
- (40) Toby, B. H.; Von Dreele, R. B. GSAS-II: The genesis of a modern open-source all purpose crystallography software package. *Journal of Applied Crystallography* **2013**, *46*, 544–549.
- (41) Juhás, P.; Davis, T.; Farrow, C. L.; Billinge, S. J. PDFgetX3: A rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions. *Journal of Applied Crystallography* **2013**, *46*, 560–566.
- (42) Yang, X.; Juhas, P.; Farrow, C. L.; Billinge, S. J. xPDFsuite: An end-to-end software solution for high throughput pair distribution function transformation, visualization and analysis. *arXiv preprint arXiv:1402.3163* **2014**.
- (43) Neufeind, J.; Feygenson, M.; Carruth, J.; Hoffmann, R.; Chipley, K. K. The nanoscale ordered materials diffractometer NOMAD at the spallation neutron source SNS. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **2012**, *287*, 68–75.
- (44) Huq, A.; Kirkham, M.; Peterson, P. F.; Hodges, J. P.; Whitfield, P. S.; Page, K.; Hügler, T.; Iverson, E. B.; Parizzi, A.; Rennich, G. POWGEN: Rebuild of a third-generation powder diffractometer at the Spallation Neutron Source. *Journal of Applied Crystallography* **2019**, *52*, 1189–1201.
- (45) Juhás, P.; Louwen, J. N.; Eijck, L. v.; Vogt, E. T.; Billinge, S. J. PDFgetN3: Atomic pair distribution functions from neutron powder diffraction data using ad hoc corrections. *Journal of Applied Crystallography* **2018**, *51*, 1492–1497.
- (46) Binasch, G.; Grünberg, P.; Saurenbach, F.; Zinn, W. Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange. *Physical Review B* **1989**, *39*, 4828.

- (47) Barnaś, J.; Fuss, A.; Camley, R.; Grünberg, P.; Zinn, W. Novel magnetoresistance effect in layered magnetic structures: Theory and experiment. *Physical Review B* **1990**, *42*, 8110.
- (48) Reig, C.; Cubells-Beltrán, M.-D.; Muñoz, D. R. Magnetic field sensors based on giant magnetoresistance (GMR) technology: Applications in electrical current sensing. *Sensors* **2009**, *9*, 7919–7942.
- (49) He, M.; Sun, H.; He, Q. L. Topological insulator: Spintronics and quantum computations. *Frontiers of Physics* **2019**, *14*, 1–16.

---

**Part II:**  
**Deducing Structure-Property**  
**Relationships in Functional Energy**  
**Materials**

---





# Chapter 3

## Ceramic Electrolytes for Solid Oxide Fuel Cells

*This chapter is adapted from the following manuscripts:*

- Mullens, B.G.; Avdeev, M.; Brand, H.E.A.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B.J.; Insights into the Structural Variations in  $\text{Sm}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  and  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  Combined Experimental and Computational Studies. *Dalton Transactions*, **2021**, 50, 9103-9117.<sup>1</sup>
- Mullens, B.G.; Saura-Múzquiz, M.; Marlton, F.P.; Avdeev, M.; Brand, H.E.A.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B.J.; Beyond the Ionic Radii: A Multifaceted Approach to Understand Differences Between the Structures of  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  Fergusonites. *Journal of Alloys and Compounds*, **2023**, 930, 167399.<sup>2</sup>
- Saura-Múzquiz, M.; Mullens, B.G.; Maynard-Casely, H.E.; Kennedy, B.J.; Neutron Diffraction Study of the Monoclinic–Tetragonal Phase Transition in  $\text{NdNbO}_4$  and  $\text{NdTaO}_4$ . *Dalton Transactions*, **2021**, 50, 11485-11497.<sup>3</sup>
- Mullens, B.G.; Saura-Múzquiz, M.; Cordaro, G.; Marlton, F.P.; Maynard-Casely, H.E.; Zhang, Z.; Baldinozzi, G.; Kennedy, B.J.; Understanding the Ionic Conductivity of  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$  Through Variable Temperature *In Situ* Neutron Powder Diffraction Studies.  
*Under Revision for Chemistry of Materials.*



### 3.1 Introduction: $\text{LaNbO}_4$ as a Solid Electrolyte

Materials with high ionic conductivity have been intensively studied as a source of efficient and carbon-neutral energy generation using SOFCs. Such research has mainly focused on metal oxides, with high ionic conductivities reported in perovskites ( $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$  with  $1.34 \times 10^{-2} \text{ S cm}^{-1}$  at  $700^\circ\text{C}$  in wet  $\text{H}_2$ ),<sup>4</sup> pyrochlores ( $\text{Gd}_{1.8}\text{La}_{0.2}\text{Zr}_2\text{O}_7$  with  $0.5 \times 10^{-2} \text{ S cm}^{-1}$  at  $800^\circ\text{C}$  in air),<sup>5,6</sup> and defect fluorites ( $\text{Y}_{0.16}\text{Zr}_{0.92}\text{O}_{2.08}$  with  $10.5 \times 10^{-2} \text{ S cm}^{-1}$  at  $1000^\circ\text{C}$  in air).<sup>7</sup> A limiting factor of these materials is their instability in carbon dioxide-containing atmospheres leading to degradation in their performance.<sup>8</sup> Therefore, a considerable amount of research has focused on ion-conducting materials, such as  $\text{LaNbO}_4$ , that are stable in harsh and acidic environments.

Despite its success as a solid electrolyte for SOFC applications, a detailed structure-functionality relationship of  $\text{LaNbO}_4$  has not been reported in the literature. For example,  $\text{LaNbO}_4$  undergoes a monoclinic-to-tetragonal ( $I2/a \rightarrow I4_1/a$ ) phase transition at  $\sim 500^\circ\text{C}$ . However, the nature of this phase transition has been recently contested. Early studies indicated this phase transition was ferroelastic and second order in nature.<sup>9–13</sup> However, high resolution synchrotron X-ray diffraction work by Sarin *et al.* identified the coexistence of both the  $I2/a$  and  $I4_1/a$  phases close to the phase transition temperature; an effect explained due to the differences in particle size within the sample.<sup>14</sup> More recent high resolution diffraction studies of other  $\text{LnNbO}_4$  materials have further confirmed the coexistence of both the monoclinic  $I2/a$  and tetragonal  $I4_1/a$  phases at high temperatures, as well as a small thermal hysteresis in the phase transition upon heating and cooling.<sup>3,15</sup> Such behaviour is inconsistent with a second order phase transition, suggesting it may, in fact, be first order and detrimental to its performance as a SOFC component.

#### 3.1.1 Expansion into $\text{LnNbO}_4$ and $\text{LnTaO}_4$

Attempts have been made to understand the role of chemical substitution within the  $\text{LaNbO}_4$  structure. By substituting  $\text{La}^{3+}$  for different lanthanoid cations ( $\text{Ln}^{3+}$ ) on the *A* site of the structure, the monoclinic  $I2/a$  space group structure is preserved.<sup>15</sup> However,

this causes a change in the temperature of the  $I2/a \rightarrow I4_1/a$  phase transition, with a relationship observed between the size of the  $A$ -site cation and the temperature of the phase transition ( $\text{LaNbO}_4$   $T_c \sim 500$  °C,  $\text{HoNbO}_4$   $T_c \sim 800$  °C).<sup>16,17</sup> It is believed that this increase in phase transition temperature is related to the strength of the long  $\text{Nb-O}_l$  bond within the  $\text{NbO}_6$  distorted octahedra. This distance decreases as the size of the  $\text{Ln}^{3+}$  cation decreases, implying a stronger bond that is more difficult to break.<sup>15</sup>

The exact role of this  $\text{Nb-O}_l$  bond with respect to ionic conductivity remains ambiguous. Previous studies have highlighted the high-temperature  $I4_1/a$  phase to be preferable for ionic conductivity due to the presence of more interstitial sites allowing for the facilitation of ionic mobility.<sup>18-20</sup> It is also believed that the long  $\text{Nb-O}_l$  bond needs to be broken to facilitate anion mobility, as it could ‘block’ oxygen interstitial sites and potentially increase the activation energy.<sup>15</sup> However, oxygen tracer diffusion measurements performed by Packer *et al.* show a decrease in diffusion coefficient for  $\text{CeNbO}_{4+\delta}$  above the  $I2/a \rightarrow I4_1/a$  phase transition temperature.<sup>21</sup> Therefore, a full structure-functionality relationship relating the influence of the  $\text{Ln}^{3+}$  cation and the ionic conductivity of the material remains elusive.

Ionic conductivity has not been extensively studied in the analogous  $\text{LnTaO}_4$  materials. These materials display complex crystallography, being synthesised with different symmetries depending on the size of the  $\text{Ln}^{3+}$  cation.<sup>22,23</sup> This is particularly remarkable, considering  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  have the same IR, and are therefore expected to exhibit similar crystal chemistry (IR = 0.64 Å in octahedra geometry).<sup>24</sup> Furthermore, the structure of some  $\text{LnTaO}_4$  materials appear to be dependent on the synthesis conditions,<sup>25</sup> which adds complexity when predicting the preferred crystal structure. The Errandonea *et al.* phase diagram (Figure 1.3) is based on the IR ratios of  $r_A/r_X$  and  $r_B/r_X$ , and does not consider complexities such as the thermal history of the sample.<sup>26</sup> The substitution of  $\text{Nb}^{5+}$  for  $\text{Ta}^{5+}$  also increases the observed  $I2/a \rightarrow I4_1/a$  phase transition temperature, with the phase transition in the orthotantalates occurring at a much higher temperature ( $\text{NdNbO}_4$   $T_c \sim 660$  °C,  $\text{NdTaO}_4$   $T_c \sim 1220$  °C).<sup>3,9,16</sup> A full understanding as to why the  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  materials behave so differently with temperature has not yet been determined.

This chapter is separated into three sections. Room temperature structural studies of  $LnNbO_4$  and  $LnTaO_4$  materials and the effect of gradually substituting  $Nb^{5+}$  with  $Ta^{5+}$  in the  $Ln(Nb_{1-x}Ta_x)O_4$  solid solution series are studied using SXRD. This will allow for an understanding of the structures of each material, and the effects of differently sized  $Ln^{3+}$  and  $B$ -site cations. This is followed up by analysing the differences in the response of  $HoNbO_4$  and  $HoTaO_4$  to temperature. This is complimented by an *in situ* study to determine the optimal synthesis conditions of each polymorph of  $HoTaO_4$ . Finally, the ionic conductivity of  $HoNbO_4$  and  $HoTaO_4$  will be analysed under a variety of different gaseous environments. These analyses will be combined with the earlier structural studies, concluding with a future outlook on designing and synthesising optimal  $ABO_4$  materials as solid electrolytes for SOFCs.

## 3.2 Synthesis Procedure and Experimental Methods

### 3.2.1 Sample Synthesis

Samples with the  $LnNbO_4$  and  $LnTaO_4$  composition ( $Ln^{3+}$  = lanthanoids La–Lu, excluding Ce and Pm) were prepared using a conventional solid state synthesis route. Reagent metal oxides of high purity  $Ln_2O_3$ ,  $Pr_6O_{11}$ ,  $Tb_4O_7$ ,  $Nb_2O_5$ , and  $Ta_2O_5$  (Aithaca Chemicals, 99.9–99.99 %), sufficient to prepare 2 g of each sample, were dried at 1000 °C for 15 hours in a muffle furnace to remove adsorbed water and carbon dioxide. This was with the exception of  $Pr_6O_{11}$  and  $Tb_4O_7$ , which were dried at 200 °C for 15 hours to ensure no change to their stoichiometry. The metal oxides were then weighed out in their appropriate stoichiometry and hand mixed using an agate mortar and pestle. A small amount ( $\sim 10$  mL) of acetone was added as a mixing medium and the mixture was ground as a slurry until the acetone evaporated. The powdered samples were then transferred to alumina crucibles and heated at 1000 °C for 24 hours. After hand-mixing again in an agate mortar and pestle, the samples were pressed into rods using a hydrostatic press at 200 bar for 10 minutes. The rods were then transferred to alumina crucibles and heated in air at 1200 °C for 24 hours, and 1400 °C for 48 hours, with intermittent grinding and repressing.

The same process was used to prepare the solid solution series of  $Ln(Nb_{1-x}Ta_x)O_4$  with  $x = 0.0$ – $1.0$  and  $\Delta x = 0.2$  for  $Ln^{3+} = \text{Pr, Nd, Gd, Tb, Dy, Yb, and Lu}$ ; and  $\Delta x = 0.1$  for  $Ln^{3+} = \text{Sm and Ho}$ . Initial X-ray diffraction measurements were taken at room temperature using a PANalytical X'Pert Pro diffractometer with Cu  $K_\alpha$  radiation to monitor the progress of the reactions.

Variable heating experiments were performed on  $LnTaO_4$  ( $Ln^{3+} = \text{Gd, Tb, Dy, Ho, and Er}$ ). After heating to  $1200^\circ\text{C}$ , each sample was reground in an agate mortar and pestle, repressed as a rod using a hydrostatic press, and heated in  $50^\circ\text{C}$  steps from  $1250$  to  $1550^\circ\text{C}$  for 24 hours each. A small amount of sample was set aside after each heating step, with the reactions monitored using X-ray diffraction.

### 3.2.2 Synchrotron X-ray and Neutron Powder Diffraction

SXRD data were collected for each  $Ln(Nb_{1-x}Ta_x)O_4$  sample at the Powder Diffraction beamline BL-10 at the Australian Synchrotron.<sup>27</sup> A small amount of each sample was ground and loaded into a 0.2 mm diameter borosilicate glass capillary. Data were collected over the angular range  $5 < 2\theta < 85^\circ$  using 18 keV ( $\lambda = 0.68751 \text{ \AA}$ ) X-rays, as determined by structural refinement of a diluted NIST SRM660b  $\text{LaB}_6$  standard. Each sample was rotated throughout the course of the measurement to minimise preferred orientation effects.

NPD measurements were performed on the high resolution powder diffractometer Echidna at the OPAL reactor, operated by ANSTO.<sup>28</sup> Powdered samples of the  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  series were loaded into 6 mm vanadium cans, with data collected over the angular range  $5 < 2\theta < 162^\circ$  at a wavelength of  $1.62 \text{ \AA}$ . The *in situ* heating NPD measurements were performed using  $1.54 \text{ \AA}$  neutrons on the high intensity powder diffractometer Wombat at the OPAL reactor, also operated by ANSTO.<sup>29</sup> A polycrystalline sample of  $\text{HoNbO}_4$  was housed in a 6 mm vanadium can and heated in an ILL-type high-vacuum furnace fitted with niobium heating elements, and heated to  $1000^\circ\text{C}$  with patterns collected every four minutes. Samples of  $\text{HoTaO}_4$  and the  $\text{Ho}_2\text{O}_3 + \text{Ta}_2\text{O}_5$  green powder were housed in open niobium cans with a niobium wire mesh

used to secure the samples. These were run in the same ILL-type furnace to 1500 °C with data collected upon heating and cooling. Each sample was pressed as a rod using the hydrostatic press to ensure minimal reaction or cation exchange between the Ta-containing samples and the Nb can.

Structure refinements were carried out using the Rietveld method as implemented in the program TOPAS6.<sup>30</sup> The peak shapes were modelled using a pseudo-Voigt function, with the Thompson-Cox-Hastings model used to account for the asymmetry.<sup>31</sup> The background of each pattern was estimated using a Chebyshev polynomial. The scale factor, lattice parameters, atomic coordinates, and ADPs were refined simultaneously with the peak profile parameters. ADPs were taken to be isotropic and equal across each Wyckoff position (regardless of Nb:Ta cation mixing). For the SXRD data of  $Ln(Nb_{1-x}Ta_x)O_4$ , the Stephens phenomenological model of anisotropic peak broadening was used.<sup>32</sup> In the final refinement cycle, all refined parameters were fully relaxed for the final cycle. The crystal structures were then drawn in VESTA.<sup>33</sup>

### 3.2.3 Physical Property Measurements

Optical band gaps were measured using a Cary 5000 solid state UV-Vis spectrometer. The instrument background was measured using a sample of  $BaSO_4$  and ~50 mg of sample was compacted, smoothed, and loaded into the instrument. UV-Vis DRS was then taken over a range of  $200 < \lambda < 800$  nm in 0.2 nm steps with five minute scans. A Tauc plot was then generated by plotting the direct-allowed Kubelka-Munk transformation (Equation 2.30) and extrapolating a linear region to determine the band gap.

For the conductivity measurements, the samples were pressed into pellets at 5 MPa for 15 minutes using an isostatic press. These were then sintered at either 1550 °C ( $HoNbO_4$  or  $HoTaO_4$   $I2/a$ ) or 1350 °C ( $HoTaO_4$   $P2/c$ ) before being cooled to room temperature at a rate of 3 ° min<sup>-1</sup>. Two or more discs of each sample were sintered until a disc of 1.0–1.5 mm thickness was obtained that had a sufficient relative density for the electrochemical measurements. The experimental density of each sample was obtained using electronic calipers for the geometrical parameters of the pellets, and a

high precision electronic balance for the mass, with the relative density calculated as the ratio of the experimental and theoretical density of the sample obtained from the SXRD measurements. Before each measurement, pellets were coated in a conductive Pt paste and reheated to 1000 °C for two hours to cure the paste.

Samples were mounted into a Probostat setup using a spring system to ensure good contact with two Pt grids acting as both current collectors and gas distributors. A gas flow rate of 1 L hour<sup>-1</sup> was selected for the measurements in air, Ar, wet Ar, and wet 5% H<sub>2</sub> in Ar. The setup was inserted into a vertical furnace to perform the EIS measurements between 850–600 °C at 25 °C intervals while cooling. Spectra were recorded in the 10<sup>6</sup>–1 Hz frequency range using an impedance spectrometer Solartron 1260 model potentiostat with an AC amplitude of 100 mV. The EIS spectra were fitted in ZView and the obtained resistance values were normalised over the pellet thickness and the active surface area to calculate the conductivity.

### 3.3 Structural Studies

Structural models for each sample of the *LnNbO<sub>4</sub>* and *LnTaO<sub>4</sub>* series were determined using Rietveld refinements against SXRD data. It was found that *LnNbO<sub>4</sub>* crystallised in the monoclinic *I2/a* space group, whereas *LnTaO<sub>4</sub>* crystallised in the monoclinic space groups *P2<sub>1</sub>/c*, *I2/a*, or *P2/c* depending on the size of the *Ln*<sup>3+</sup> cation and the synthesis conditions used. Furthermore, the *Ln(Nb<sub>1-x</sub>Ta<sub>x</sub>)O<sub>4</sub>* solid solutions were analysed by substituting Nb<sup>5+</sup> for Ta<sup>5+</sup>, where it was found the transformation from *P2<sub>1</sub>/c* → *I2/a* occurs suddenly, whereas the *P2/c* → *I2/a* appears much ‘sluggish’ with a two-phase region detected. A combined SXRD and NPD dataset was then refined for Ho(Nb<sub>1-x</sub>Ta<sub>x</sub>)O<sub>4</sub> to determine differences between the two structures with high precision. These structural studies were then supplemented by DFT calculations.



### 3.3.1 Structural Studies of $Ln\text{NbO}_4$

The synthesis of crystalline single-phase samples of the lanthanoid orthoniobates ( $Ln\text{NbO}_4$ ) was achieved using solid state reactions with a maximum annealing temperature of 1400 °C. Rietveld refinements were performed using the starting parameters of  $\text{LaNbO}_4$  by Sarin *et al.* as a model.<sup>14</sup> The  $Ln\text{NbO}_4$  materials were all isostructural, as evidenced by their SXRD patterns (Figure 3.1, Table 3.1). Each structure was indexed to the monoclinic space group  $I2/a$  (a non-standard setting of  $C2/c$  used to highlight its relation to the high-temperature tetragonal  $I4_1/a$  structure). The lattice parameters and atomic coordinates all showed good agreement with previous literature.<sup>14,15,34</sup>

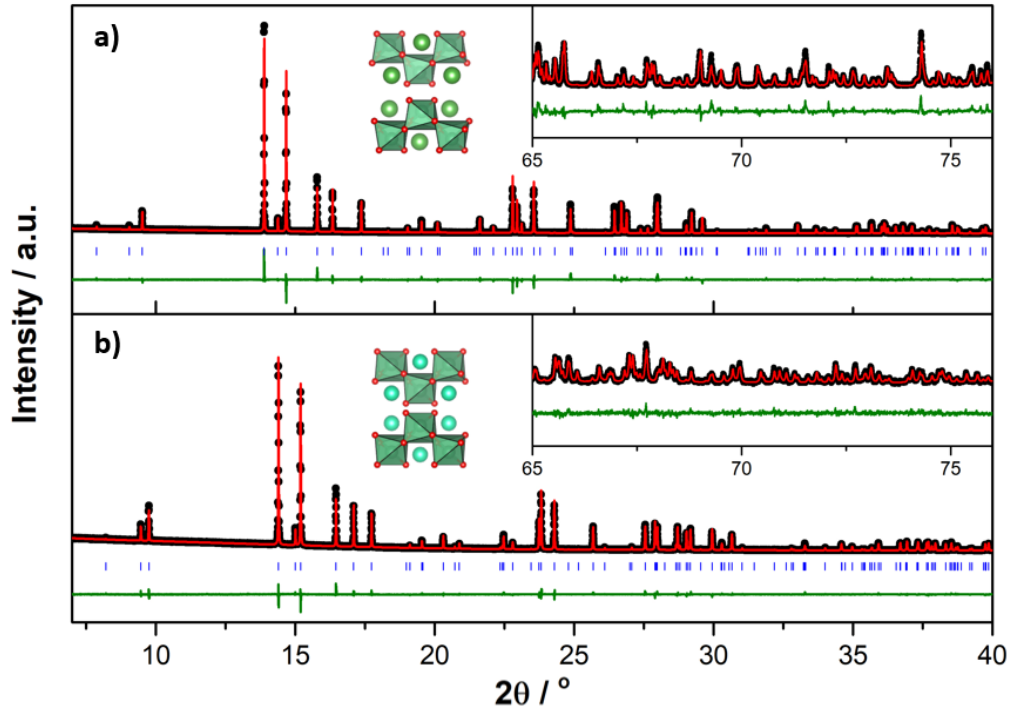


Figure 3.1: Representative Rietveld refinements against the synchrotron X-ray diffraction patterns of (a)  $\text{LaNbO}_4$  and (b)  $\text{LuNbO}_4$ . Each structure was refined to the monoclinic  $I2/a$  fergusonite-type structure. Data was collected to  $\sim 80^\circ 2\theta$ , with the insets highlighting the quality of the fit to the data. The black circles represent the data, the red line represents the calculated profile, the green line is the difference between the data and the calculated profile, and the blue ticks are the space group-allowed reflections.

Rietveld refinements were successfully performed on all 13 structures (Figure A.1). The lattice parameters and volume increase linearly as the IR of the  $Ln^{3+}$  cation increases (Figure 3.2). Although mixed valence states were present in the reagents used to prepare  $\text{PrNbO}_4$  ( $\text{Pr}_6\text{O}_{11}$  being  $\text{Pr}^{3+/4+}$ ) and  $\text{TbNbO}_4$  ( $\text{Tb}_4\text{O}_7$  being  $\text{Tb}^{3+/4+}$ ), a linear trend

across the  $Ln^{3+}$  series indicates both Pr and Tb exist in their trivalent state. Interestingly, there appears to be a stochastic relationship between the size of the  $Ln^{3+}$  cation and the size of the monoclinic  $\beta$  angle. This potentially suggests that the temperature of the  $I2/a \rightarrow I4_1/a$  phase transition and the magnitude of the monoclinic  $\beta$  angle may only be weakly correlated at room temperature.

Table 3.1: Selected Rietveld refinement structural parameters, bond distances, and bond valence sums for  $LnNbO_4$  ( $Ln^{3+} = La, Lu$ ) against synchrotron X-ray diffraction data.

| $Ln^{3+}$                             | <b>LaNbO<sub>4</sub></b> | <b>LuNbO<sub>4</sub></b> |
|---------------------------------------|--------------------------|--------------------------|
| <b>Radii (Å)</b>                      | 1.16                     | 0.977                    |
| <b>Space Group</b>                    | $I2/a$                   | $I2/a$                   |
| $a$ (Å)                               | 5.63469(5)               | 5.29225(3)               |
| $b$ (Å)                               | 11.66597(9)              | 10.95583(5)              |
| $c$ (Å)                               | 5.26748(4)               | 5.10235(3)               |
| $\beta$ (°)                           | 94.082(1)                | 94.421(1)                |
| <b>Vol. (Å<sup>3</sup>)</b>           | 345.375(8)               | 294.959(4)               |
| $Ln^{3+}$ $y$                         | 0.12033(6)               | 0.12136(8)               |
| <b>Nb<sup>5+</sup> <math>y</math></b> | 0.64604(5)               | 0.64232(9)               |
| <b>O(1) <math>x</math></b>            | 0.0111(6)                | -0.0049(8)               |
| <b>O(1) <math>y</math></b>            | 0.7158(2)                | 0.7150(3)                |
| <b>O(1) <math>z</math></b>            | 0.1915(6)                | 0.2028(8)                |
| <b>O(2) <math>x</math></b>            | 0.8930(5)                | 0.9057(8)                |
| <b>O(2) <math>y</math></b>            | 0.4479(2)                | 0.4576(4)                |
| <b>O(2) <math>z</math></b>            | 0.2378(5)                | 0.2644(8)                |
| $Ln-O(2)$ (Å)                         | 2.599(3)                 | 2.400(4)                 |
| $Ln-O(1)$ (Å)                         | 2.574(3)                 | 2.344(4)                 |
| $Ln-O(2)$ (Å)                         | 2.527(3)                 | 2.311(4)                 |
| $Ln-O(1)$ (Å)                         | 2.488(3)                 | 2.275(4)                 |
| $Ln-O_{av.}$ (Å)                      | 2.547(3)                 | 2.333(4)                 |
| <b>Nb-O(2) (Å)</b>                    | 2.596(3)                 | 2.499(4)                 |
| <b>Nb-O(2) (Å)</b>                    | 1.920(3)                 | 1.934(4)                 |
| <b>Nb-O(1) (Å)</b>                    | 1.810(3)                 | 1.878(4)                 |
| <b>Nb-O<sub>av.</sub> (Å)</b>         | 2.109(3)                 | 2.104(4)                 |
| <b>BVS (NbO<sub>4</sub>)</b>          | 4.58                     | 4.27                     |
| <b>BVS (NbO<sub>6</sub>)</b>          | 4.89                     | 4.67                     |
| $R_{wp}$ (%)                          | 3.35                     | 3.49                     |

Although SXRD was used for these measurements, the high energy and low  $d_{min}$  ( $<0.60$  Å) probed means that very precise values of both the cation and anion atomic coordinates were obtained. As a result, accurate  $Ln-O$  and  $Nb-O$  bond distances were also extracted from the refinements. Where available, these showed excellent agreement with previous work using NPD.<sup>13,35</sup> Although NPD measurements are expected to improve

the accuracy of the refined structures, this is nontrivial across the  $Ln^{3+}$  series as it includes examples with strong neutron-absorbing elements such as Sm, Eu, and Gd. This will be returned to later in the dissertation with an in-depth analysis of  $Ho(Nb_{1-x}Ta_x)O_4$ .

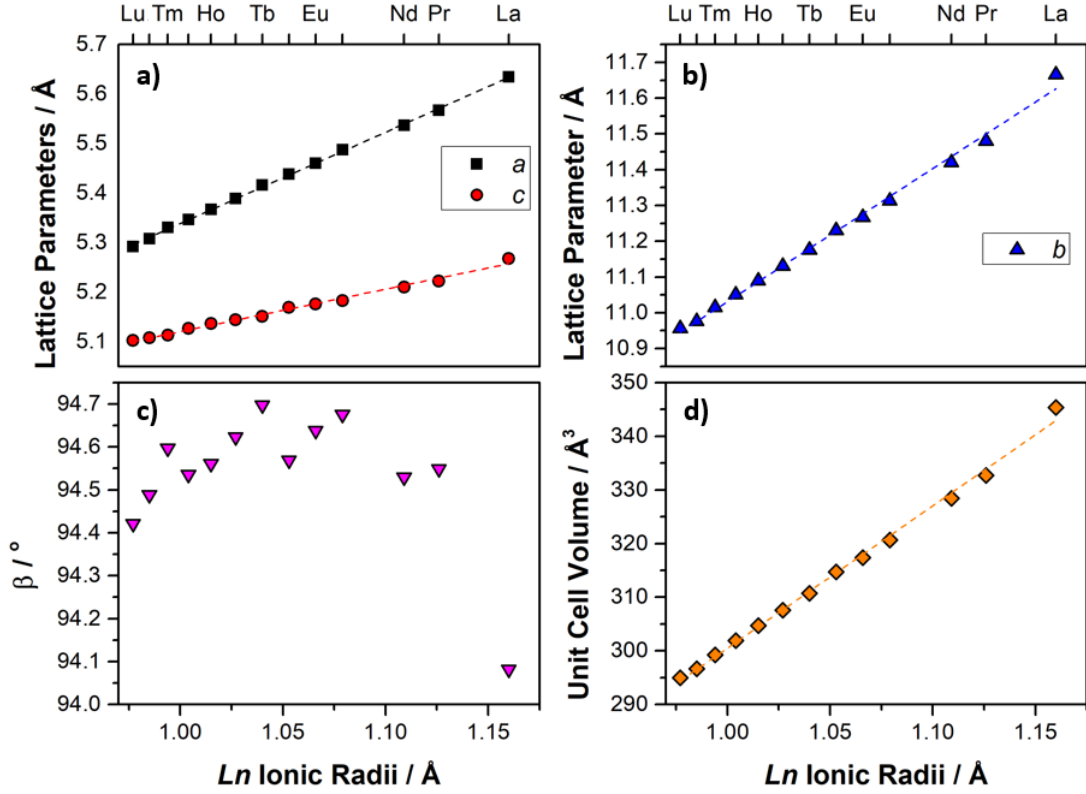


Figure 3.2: The refined lattice parameters for the  $LnNbO_4$  series, with (a) the  $a$  and  $c$  lattice parameters, (b) the  $b$  lattice parameter, (c) the monoclinic  $\beta$  angle, and (d) the unit cell volume. The error bars are smaller than the symbols, and the dashed lines have been drawn to guide the eyes. Note: For clarity, not all  $Ln^{3+}$  cations are listed on the top axes.

In the literature, the monoclinic  $I2/a$  fergusonite-type structure is often described as a network of  $LnO_8$  polyhedra and  $NbO_4$  tetrahedra (Figure 3.3a). This is done to highlight its close structural relationship to the high temperature tetragonal  $I4_1/a$  scheelite-type structure consisting of a similar network. However, this description is somewhat misleading, with  $Nb^{5+}$  cations often being cited as ‘too large’ to adopt a tetrahedra geometry. This has been seen in other studies where  $Nb^{5+}$ -containing oxides readily adopt octahedral geometry, such as the  $NaNbO_3$  perovskite,<sup>36</sup>  $Li_3NbO_4$  rock salt-type structure,<sup>37</sup> and layered structures such as the mixed-metal phosphate  $BaTeNbO_4(PO_4)$ ,<sup>38</sup> and the Aurivillius phase  $SrBi_2Nb_2O_9$ .<sup>39</sup> In the case of the fergusonite-type structures, several studies have noted the presence of longer  $Nb-O_l$  contacts that could potentially contribute to the coordination of the  $Nb^{5+}$  cation. A single crystal study by Bayliss

*et al.* noted the presence of these longer Nb–O<sub>*l*</sub> contacts, however did not consider their structural consequence.<sup>40</sup> Similarly, Fulle *et al.* considered these longer bonds, describing the Nb<sup>5+</sup> cations as having a distorted NbO<sub>6</sub> environment.<sup>41</sup> To investigate this further, bond valence sums (BVSs) were calculated for the Nb<sup>5+</sup> cation coordinated as both tetrahedra (NbO<sub>4</sub>) and octahedra (NbO<sub>6</sub>) to determine its optimal coordination environment. The bond valence sum is calculated by considering the valences of the individual bonds using

$$S_{ij} = \sum \exp \left[ \frac{R_0 - R_{ij}}{b} \right] \quad (3.1)$$

where  $R_0$  is a tabulated parameter of the ‘ideal’ bond length,  $R_{ij}$  is the observed bond length, and  $b$  is an empirical constant.<sup>42</sup>

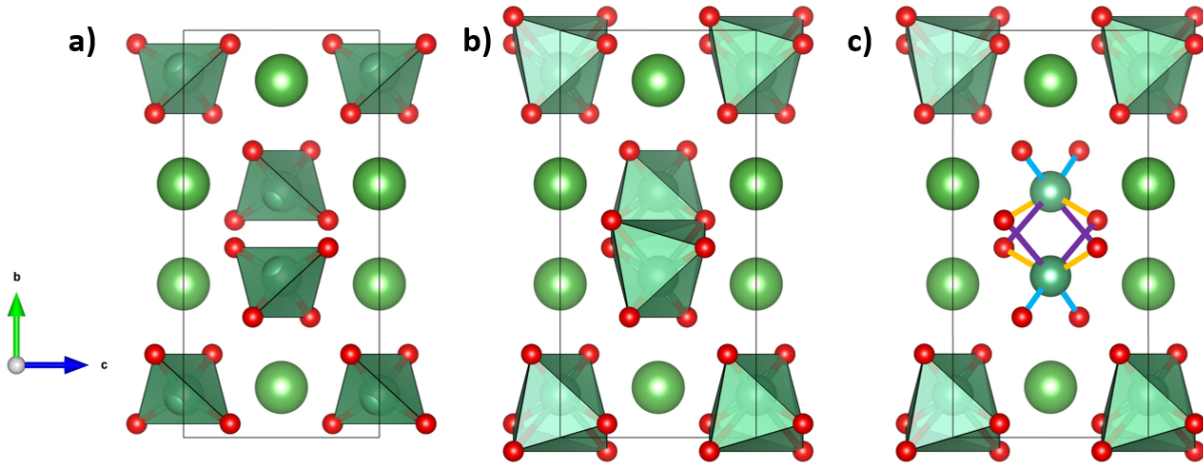


Figure 3.3: The refined structure for the  $Ln\text{NbO}_4$  series, with (a) NbO<sub>4</sub> tetrahedra, (b) NbO<sub>6</sub> distorted octahedra, and (c) NbO<sub>6</sub> distorted octahedra with individual Nb–O bonds labelled. The light green spheres are the La<sup>3+</sup> ions and the dark green polyhedra are the Nb<sup>5+</sup> environments. The blue and gold bonds are the regular NbO<sub>4</sub> bonds, whereas the purple bonds are the Nb–O<sub>*l*</sub> bonds.

Considering NbO<sub>4</sub> tetrahedra in the  $Ln\text{NbO}_4$  structure (Figure 3.3a) yields  $S_{ij} \sim 4.14\text{--}4.58$ , which is significantly smaller than the expected value of 5.0 for the Nb<sup>5+</sup> cation. However, considering the longer Nb–O<sub>*l*</sub> bond contacts at  $\sim 2.5$  Å yields  $S_{ij} \sim 4.55\text{--}4.89$  (Figure 3.3b). Therefore, it is considered more accurate to describe the Nb<sup>5+</sup> coordination environment as distorted NbO<sub>6</sub> octahedra as opposed to NbO<sub>4</sub> tetrahedra, as these longer bonds help alleviate the strain of the Nb<sup>5+</sup> coordination.

These longer Nb–O<sub>*l*</sub> bonds appear to strongly influence the overall structure of the *Ln*NbO<sub>4</sub> materials. Considering the *Ln*–O and Nb–O bond distances (Figure 3.4), the length of the *Ln*–O bonds (and, by extension, the volume of the *Ln*O<sub>8</sub> polyhedra) appear to increase as the size of the *Ln*<sup>3+</sup> cation increases. As expected, the Nb–O bond distances appear to be mostly consistent across the *Ln*NbO<sub>4</sub> series, with a small increase observed in the Nb–O<sub>*l*</sub> bond distance. This increase in bond distance correlates with a decrease in the *I*2/*a* → *I*4<sub>1</sub>/*a* phase transition temperature, implying that this longer contact may be important to the phase transition.

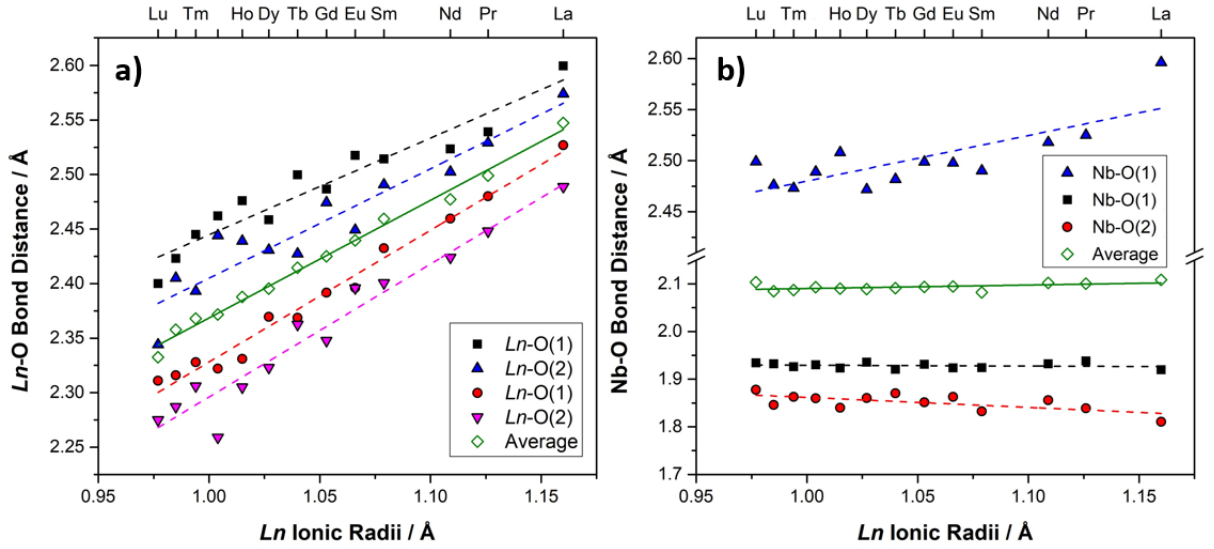


Figure 3.4: Composition dependence of the room temperature (a) *Ln*–O bond distances, and (b) Nb–O bond distances of the *Ln*NbO<sub>4</sub> structures. The dashed lines have been drawn to guide the eye, with the averages drawn with a solid line. Note: For clarity, not all *Ln*<sup>3+</sup> cations are listed on the top axes.

In summary, SXRD measurements have shown that the *Ln*NbO<sub>4</sub> materials crystallise in the fergusonite-type monoclinic *I*2/*a* structure, regardless of the size of the *Ln*<sup>3+</sup> cation. The lattice parameters and unit cell volume increase linearly with the size of the *Ln*<sup>3+</sup> cation in the structure. In considering parameters important to the *I*2/*a* → *I*4<sub>1</sub>/*a* phase transition, there appears to be a weak relationship between the size of the *Ln*<sup>3+</sup> cation and the monoclinic  $\beta$  angle. However, the Nb–O<sub>*l*</sub> bond distance increases as the size of the *Ln*<sup>3+</sup> cation increases. This implies that the increasing *Ln*O<sub>8</sub> polyhedra volume changes the atomic coordinates of the oxygen anions, potentially increasing (and weakening) the Nb–O<sub>*l*</sub> bond distance and lowering the phase transition temperature.

### 3.3.2 Structural Studies of $LnTaO_4$

The synthesis of crystalline single-phase samples of the lanthanoid orthotantalates ( $LnTaO_4$ ) was achieved using a similar solid state reaction to the  $LnNbO_4$  materials. However, in contrast to the  $LnNbO_4$  materials,  $LnTaO_4$  crystallises in different structures depending on the size of the  $Ln^{3+}$  cation (Figure 3.5).<sup>43,44</sup> For  $LnTaO_4$  ( $Ln^{3+} = La, Pr$ ), the SXRD patterns were successfully indexed to the monoclinic  $P2_1/c$  structure, with lattice parameters in good agreement with previous literature.<sup>34,44,45</sup> There was no indication of other phases present, such as the high temperature orthorhombic  $Cmc2_1$  phase seen at elevated temperatures.<sup>46</sup> For  $Ln^{3+} = Nd-Tb$ , the patterns were indexed to the monoclinic  $I2/a$  structure, similar to the  $LnNbO_4$  analogues. For  $Ln^{3+} = Dy-Lu$ , the monoclinic  $P2/c$  structure was appropriate. These structures are shown in Figure 3.5, with representative Rietveld refinements shown in Figure 3.6 and full parameters in Table A.2.

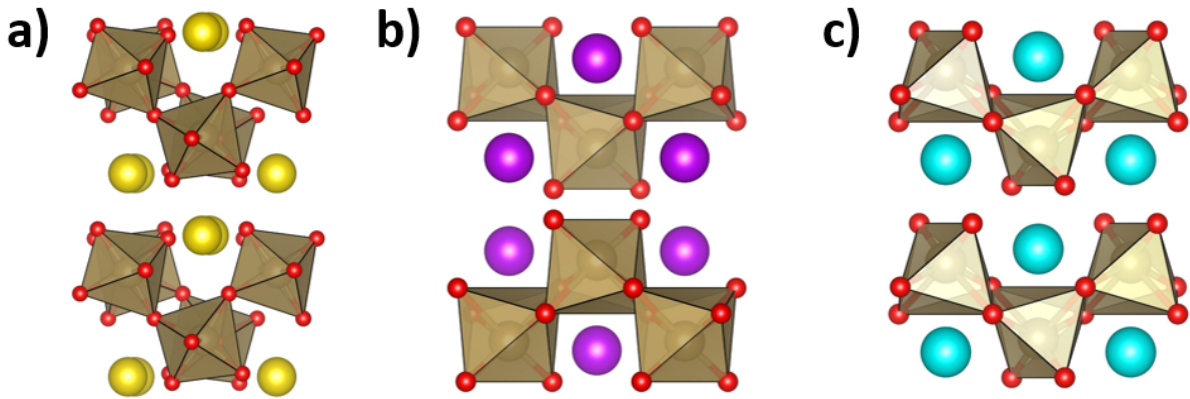


Figure 3.5: The (a) monoclinic  $P2_1/c$  structure, (b) monoclinic  $I2/a$  structure, and (c) monoclinic  $P2/c$  structure. The  $Ln^{3+}$  cations are drawn as coloured spheres, and the  $TaO_6$  polyhedra are drawn in brown.

As noted previously, it is possible to prepare certain  $LnTaO_4$  materials with different monoclinic structures depending on the synthesis conditions used. This can occur by changing the final annealing temperature,<sup>47</sup> as well as using a synthesis aid such as a chemical flux (a crystalline substance with a low melting point, such as  $LiSO_4$  or  $LiCl$ ).<sup>44</sup> This was observed in this study, where a sample of  $TbTaO_4$  was synthesised in the  $P2/c$  structure after being heated to 1350 °C, however this transformed to the  $I2/a$  structure after being heated to 1400 °C for 24 hours. This indicates that the  $P2/c$  structure is formed at lower temperatures than that of the  $I2/a$  structure. This phenomenon was

investigated further, where the  $LnTaO_4$  samples with intermediate sized  $Ln^{3+}$  cations ( $Ln^{3+} = \text{Gd–Er}$ ) were heated in 50 °C steps between 1200–1450 °C to determine any changes in symmetry. Attempts to synthesise  $GdTaO_4$  in the  $P2/c$  space group were unsuccessful. However, the synthesis of the  $P2/c$  and  $I2/a$  polymorphs was successfully achieved for  $Ln^{3+} = \text{Tb, Dy, Ho}$ . Similar to  $TbTaO_4$ , both  $DyTaO_4$  and  $HoTaO_4$  could be synthesised in the  $P2/c$  space group by annealing at 1400 °C, or in the  $I2/a$  space group by annealing at a higher temperature of 1450 °C. Efforts to recover the  $I2/a$  structure of  $ErTaO_4$  were partially successful. After annealing at 1550 °C (the temperature limit of the muffle furnace) for 12 hours, the X-ray diffraction pattern measured on the laboratory Cu-source diffractometer for  $ErTaO_4$  could be successfully fit to the  $I2/a$  structure (Figure A.5). However, subsequent SXRD data showed the sample contained a mixture of both  $I2/a$  and  $P2/c$  polymorphs. Not only does this suggest that the transformation between the  $P2/c$  and  $I2/a$  phases is slow and sluggish, but it also implies that annealing  $ErTaO_4$  at a higher temperature could have yielded a phase-pure sample of  $I2/a$ . This has been previously seen in a study by Wang *et al.*, where the  $I2/a$  polymorph of  $ErTaO_4$  was prepared by annealing at 1700 °C.<sup>48</sup>

Interestingly, and unique to this work, there appears to be a correlation between the preferred monoclinic structure, the heating temperature, and the temperature of the reversible  $I2/a \rightarrow I4_1/a$  phase transition (Table 3.2). This phase transition occurs at  $(1410 \pm 15)$  °C, which is around the annealing temperatures used to transform the  $P2/c$  polymorph to the  $I2/a$  polymorph upon heating. Limiting the maximum temperature to below the  $I2/a \rightarrow I4_1/a$  phase transition temperature invariably resulted in recovery of the  $P2/c$  phase, whereas heating through this (and presumably creating the high-temperature  $I4_1/a$  phase) results in recovery of the  $I2/a$  phase. These results are summarised in Table 3.2. A detailed *in situ* study of this transformation has not yet been performed, and will be focused on later in the dissertation.

The lattice parameters and unit cell volume of the  $LnTaO_4$  ( $Ln^{3+} = \text{Nd–Lu}$ ) series are plotted in Figure 3.7. In these figures, the monoclinic  $P2_1/c$  structures observed in  $LaTaO_4$  and  $PrTaO_4$  were excluded as their structural motifs are sufficiently different to the monoclinic  $I2/a$  and  $P2/c$  structures (consisting of corner-sharing as opposed to edge-



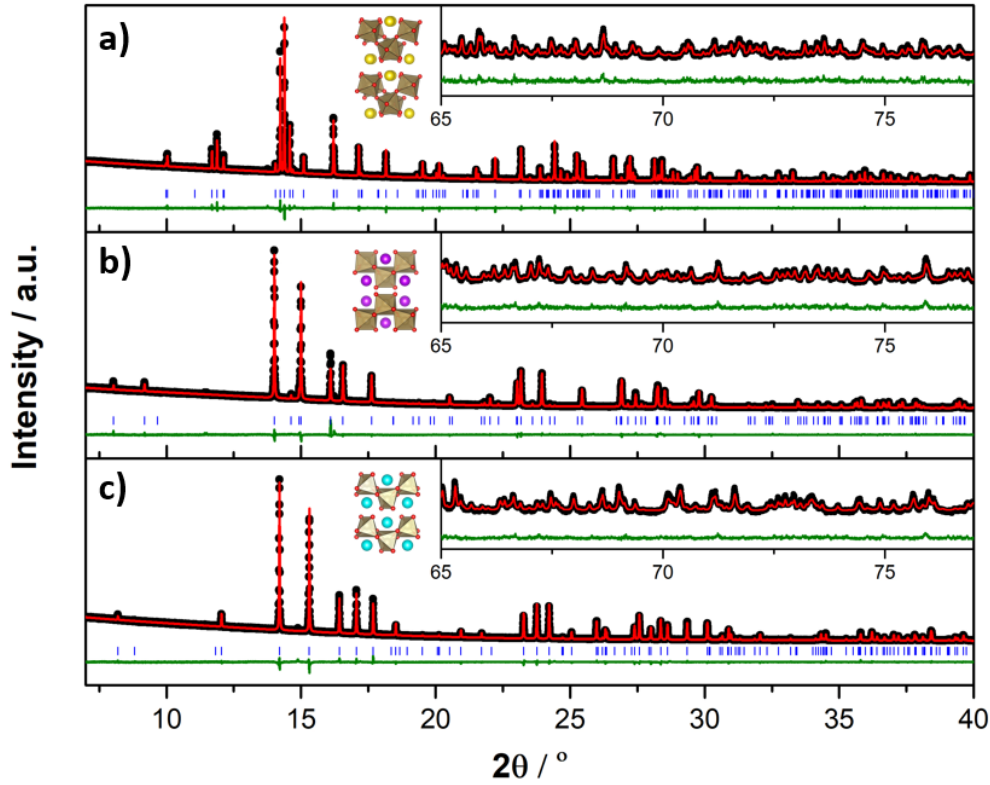


Figure 3.6: Representative Rietveld plots for (a)  $\text{PrTaO}_4$  fitted to the monoclinic  $P2_1/c$  space group, (b)  $\text{GdTaO}_4$  fitted to the monoclinic  $I2/a$  space group, and (c)  $\text{YbTaO}_4$  fitted to the monoclinic  $P2/c$  space group. The black circles represent the data, the solid red lines are the calculated profile, the solid green lines are the difference between the observed and calculated intensities, and the blue ticks are the space group-allowed reflections. The insets highlight the quality of the data and fits at high  $2\theta$ .

sharing  $\text{TaO}_6$  octahedra, see Figure 3.5). As previously seen in the  $\text{LnNbO}_4$  materials, the lattice parameters and unit cell volumes increase linearly as the IR of the  $A$  site  $\text{Ln}^{3+}$  cation increase. The atomic coordinates of the cations refined in this work are in excellent agreement with the values reported previously.<sup>23,44,50</sup> In contrast to the  $\text{LnNbO}_4$  structures, a linear relationship is observed between the monoclinic  $\beta$  angle and the IR of the  $\text{Ln}^{3+}$  cation, with the monoclinic  $\beta$  angle appearing to be higher in the  $P2/c$  phase compared to  $I2/a$ .

As for the  $\text{LnNbO}_4$  materials, accurate  $\text{Ln-O}$  and  $\text{Ta-O}$  bond distances were also determined from the refinement data.<sup>15</sup> BVS analysis of the  $I2/a$  and  $P2/c$  structures revealed the contribution of two additional  $\text{Ta-O}_l$  longer bonds, demonstrating the  $\text{Ta}^{5+}$  cations are best described in a six-coordinate distorted octahedra geometry. Including these two additional longer bonds in the BVS calculations gives a more reasonable value in each structure ( $S_{ij} \sim 4.8\text{--}5.5$  for  $\text{TaO}_6$  compared to  $\sim 4.2\text{--}4.8$  for  $\text{TaO}_4$ ).



Table 3.2: Final heating temperatures of the  $LnTaO_4$  samples with the space group of the recovered product. The sample marked with \* was found to be a mixture of  $P2/c + I2/a$  using SXRD data.

|                    | $P2/c$<br>Synthesis Temp.<br>(°C) | $I2/a$<br>Synthesis Temp.<br>(°C) | $I2/a \rightarrow I4_1/a$<br>Transition Temp.<br>(°C) |
|--------------------|-----------------------------------|-----------------------------------|-------------------------------------------------------|
| TbTaO <sub>4</sub> | 1350                              | 1400                              | $1410 \pm 15^{16}$                                    |
| DyTaO <sub>4</sub> | 1400                              | 1450                              | $1410 \pm 15^{16}$                                    |
| HoTaO <sub>4</sub> | 1400                              | 1450                              | $1410 \pm 15^{16}$                                    |
| ErTaO <sub>4</sub> | 1400                              | 1550*                             | $1410 \pm 15^{49}$                                    |

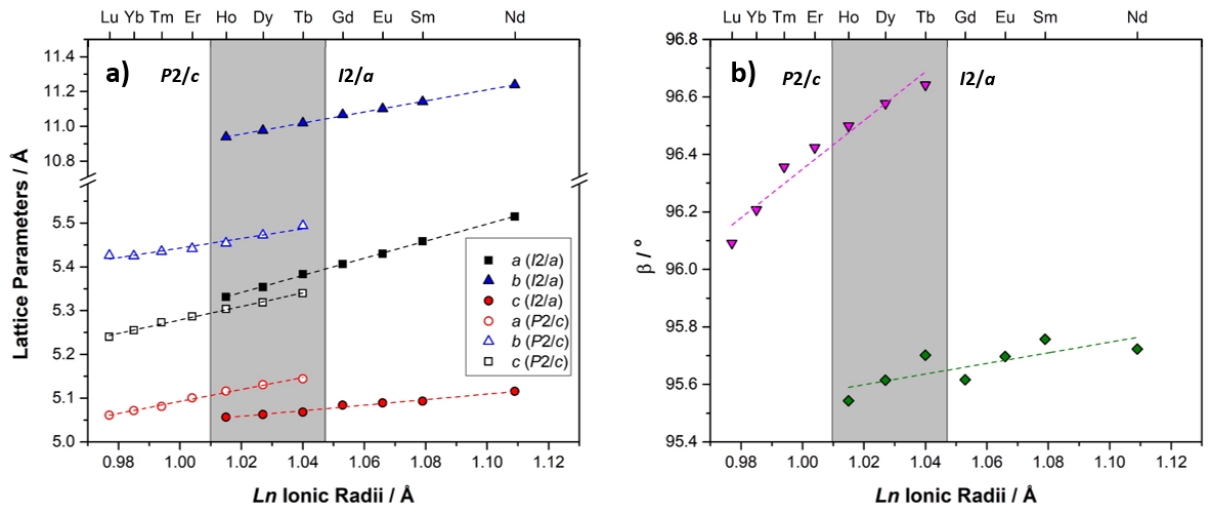


Figure 3.7: Composition dependence of the room temperature (a) lattice parameters and (b) monoclinic  $\beta$  angle of the  $LnTaO_4$  series. Where not apparent, the error bars are smaller than the symbols. For the samples inside the grey area ( $Ln^{3+} = Ho, Dy, \text{ and } Tb$ ) single-phase samples of both the  $P2/c$  and  $I2/a$  polymorphs were recovered and studied. The dashed lines have been drawn the guide the eyes.

Figure 3.8 illustrates the changes in the  $Ln-O$  and  $Ta-O$  bond lengths for both the  $P2/c$  and  $I2/a$  structure types, as well as changes in their polyhedra volume. Across each of the  $P2/c$  and  $I2/a$  series, the average  $Ln-O$  bond distances and the  $LnO_8$  polyhedra volume increases as the size of the  $Ln^{3+}$  cation increases. As expected, the average  $Ta-O$  bond distance remains essentially independent of the size of the  $Ln^{3+}$  cation, although a small volume decrease is observed across the series. This implies that the  $LnO_8$  polyhedra are much more flexible than their  $TaO_6$  counterparts, allowing for distortions within the structure. The average  $Ta-O$  bond length and  $TaO_6$  polyhedra volume appear to be larger in the  $I2/a$  structures compared to the  $P2/c$  polymorph.

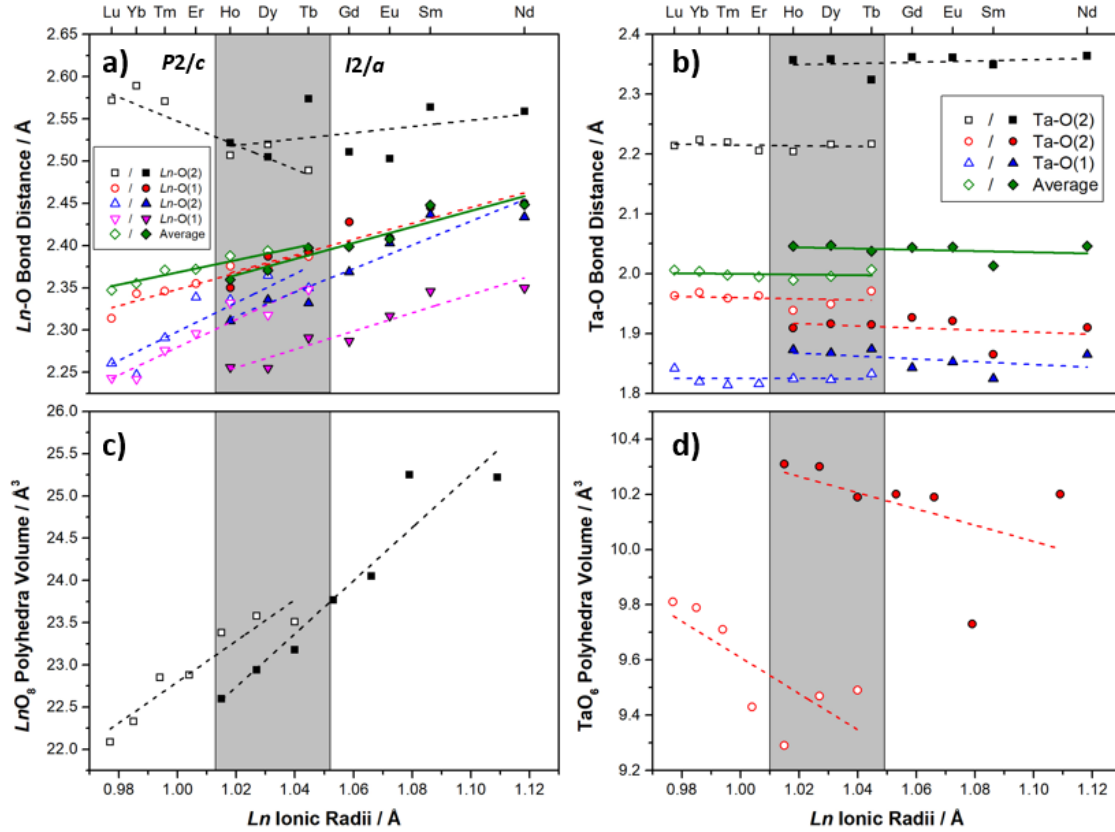


Figure 3.8: Composition dependence of the room temperature (a)  $Ln-O$  bond distances, (b)  $Ta-O$  bond distances, (c)  $LnO_8$  polyhedra volume, and (d)  $TaO_6$  polyhedra volume. The error bars are smaller than the symbols. For the samples inside the grey area ( $Ln^{3+} = Ho, Dy, \text{ and } Tb$ ) single-phase samples of both the  $P2/c$  and  $I2/a$  polymorphs were recovered and studied. The dashed lines have been drawn to guide the eyes, with the averages drawn with a solid line.

Comparing the  $LnNbO_4$  and  $LnTaO_4$  materials reveals a number of similarities. Both structures (regardless of their space group) consist of a network of  $LnO_8$  polyhedra and  $BO_6$  octahedra ( $B^{5+} = Nb, Ta$ ). The  $BO_6$  octahedra are essentially rigid, whereas the  $LnO_8$  polyhedra exhibit much more flexibility. However, a number of differences are also noted across each series. The size of the  $Ta-O_l$  bond appears essentially constant across the  $LnTaO_4$  series. These are consistently shorter than the similar  $Nb-O_l$  bonds observed in the  $LnNbO_4$  structures. This reflects the strength of the respective bonds, with the  $Nb-O_l$  bond being longer (and therefore weaker) than the  $Ta-O_l$  counterpart. This potentially explains why the  $LnTaO_4$  materials undergo the  $I2/a \rightarrow I4_1/a$  phase transition at much higher temperatures, as this longer bond is important to the  $I2/a \rightarrow I4_1/a$  phase transition. Furthermore, the monoclinic  $\beta$  angles are larger in  $LnTaO_4$  than the respective  $LnNbO_4$  materials. This could also explain the higher phase transition temperature observed.

SXRD measurements have shown that  $LnTaO_4$  materials crystallise in different monoclinic structures depending on the size of the  $Ln^{3+}$  cation and the synthesis conditions used. The Ta–O<sub>l</sub> bond distance is consistently smaller, and the monoclinic  $\beta$  angle is consistently larger, than those observed in the  $LnNbO_4$  counterparts. Whilst increasing the size of the  $Ln^{3+}$  cation potentially weakens the strength of the Nb–O<sub>l</sub> bond, no such trend is observed in  $LnTaO_4$  with the Ta–O<sub>l</sub> bond length consistent across the series.

### 3.3.3 Structural Studies of $Ln(Nb_{1-x}Ta_x)O_4$

Given that all three structures observed in the  $LnNbO_4$  and  $LnTaO_4$  studies are monoclinic with similar structural motifs, solid solution series were synthesised that gradually substituted Nb<sup>5+</sup> for Ta<sup>5+</sup>. Several oxides with mixed *B*-site cations of the type  $Ln(Nb_{1-x}Ta_x)O_4$  were prepared using the same solid state reaction method for the  $LnNbO_4$  and  $LnTaO_4$  materials.  $Ln^{3+}$  cations were selected such that the three composition-dependent structural phases could be probed in the different solid-solutions series:  $I2/a \rightarrow P2_1/c$  ( $Ln^{3+} = Pr$ ),  $I2/a \rightarrow I2/a$  ( $Ln^{3+} = Nd, Sm, Gd, Tb$ ), and  $I2/a \rightarrow P2/c$  ( $Ln^{3+} = Dy, Ho, Yb, Lu$ ). The behaviour observed in substituting Nb<sup>5+</sup> for Ta<sup>5+</sup> (increasing  $x$ ) was different depending on the size of the  $Ln^{3+}$  cation (Figure 3.9). In the  $Pr(Nb_{1-x}Ta_x)O_4$  solid solution series, all samples with  $x \leq 0.8$  were refined to the monoclinic  $I2/a$  structure, with  $x = 1.0$  refined to the monoclinic  $P2_1/c$  structure. This suggests that the solid solution series changes very abruptly from  $I2/a \rightarrow P2_1/c$ , possibly reflecting the change in connectivity between the TaO<sub>6</sub> octahedra within the structure. For the intermediate-sized lanthanoids ( $Ln^{3+} = Nd-Tb$ ), all structures were refined to the  $I2/a$  space group with a small change in unit cell volume detected across the series. For the smaller lanthanoids ( $Ln^{3+} = Ho-Lu$ ), the structures with  $x \leq 0.6$  were refined to the monoclinic  $I2/a$  space group. At higher levels of Ta<sup>5+</sup> substitution, either a  $I2/a + P2/c$  mix was observed, or a single phase monoclinic  $P2/c$  sample was recovered. This implies that the  $I2/a \rightarrow P2/c$  transformation along the solid solution series is more ‘sluggish’, with a two-phase region observed over a range of compositions.

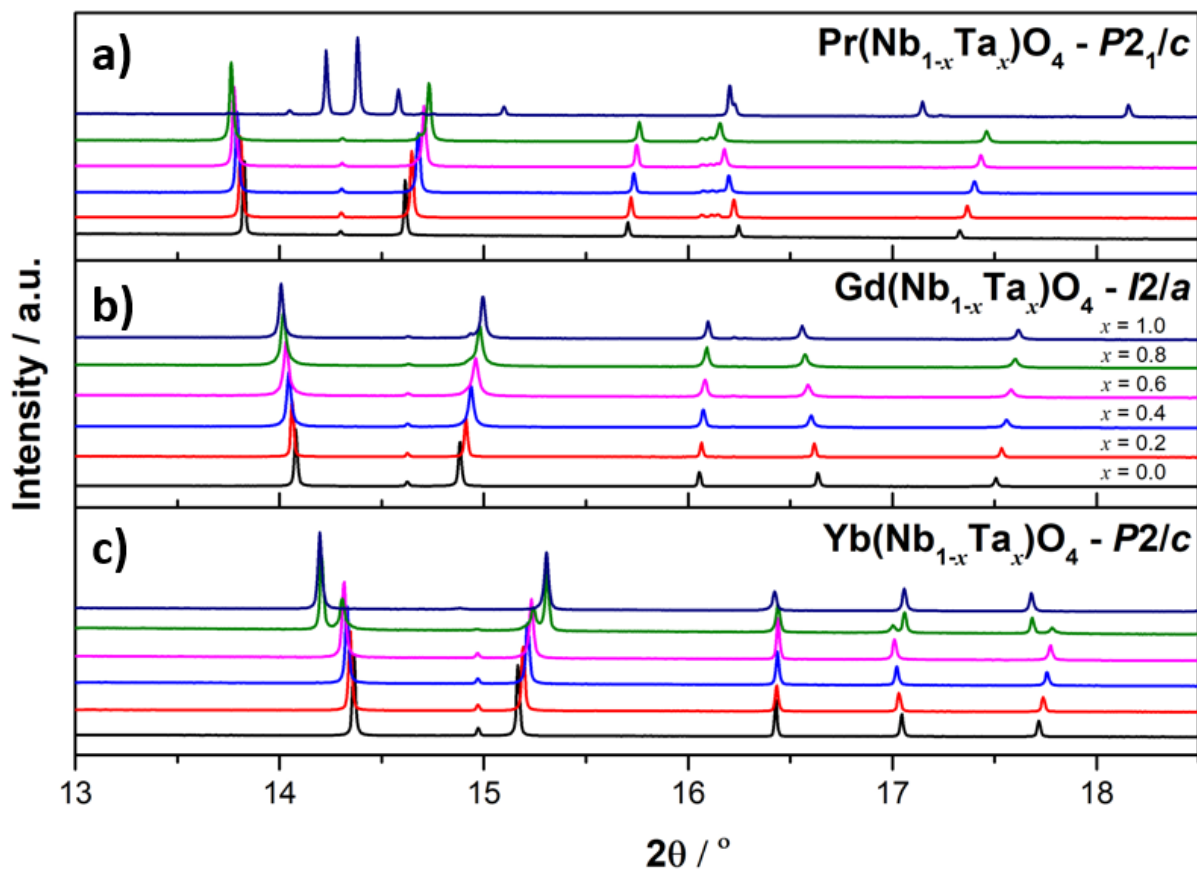


Figure 3.9: The synchrotron X-ray diffraction data for (a)  $\text{Pr}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  probing the  $P2_1/c \rightarrow I2/a$ , (b)  $\text{Gd}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  probing the  $I2/a \rightarrow I2/a$ , and (c)  $\text{Yb}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  probing the  $P2/c \rightarrow I2/a$  solid solution series.

$\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  are often expected to exhibit near-identical crystal chemistry based on the identical value of their IR reported by Shannon.<sup>24</sup> This is despite  $\text{Ta}^{5+}$  having an additional  $5d$  valence shell compared to the  $4d$  shell of  $\text{Nb}^{5+}$ , as the size of  $\text{Ta}^{5+}$  is strongly influenced by the lanthanoid contraction. However, work by Whittaker *et al.* contrarily concluded that  $\text{Ta}^{5+}$  is slightly smaller than  $\text{Nb}^{5+}$ .<sup>51</sup> This conclusion is supported by several examples of oxides where the tantalate is smaller than the isostructural niobate.<sup>52</sup> This phenomenon was tested against several of the  $\text{Ln}(\text{Nb,Ta})\text{O}_4$  materials synthesised in this work, and the  $\text{LnTaO}_4$  material was consistently observed to have a smaller unit cell volume than its isostructural  $\text{LnNbO}_4$  counterpart.

The normalised unit cell volumes of the  $\text{Ln}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  structures in the  $I2/a$  space group are plotted in Figure 3.10. In each case, the volume of the orthoniobate ( $\text{LnNbO}_4$ , or  $x = 0$ ) was taken as unity (Table A.3). Two features of this plot are remarkable. Firstly, the unit cell volume of the orthoniobate is consistently larger than

the corresponding orthotantalate. The second is that the size of  $Ln^{3+}$  appears to play a role in the contraction of the unit cell volume. The largest  $Ln^{3+}$  cation used,  $Ln^{3+} = Nd$ , has a volume difference of 0.39% between  $NdNbO_4$  and  $NdTaO_4$ , whereas the smallest  $Ln^{3+}$  cation used,  $Ln^{3+} = Ho$ , has a volume difference of 0.14%. This implies that the effective IR of  $Nb^{5+}$  and  $Ta^{5+}$  are dependent on their bonding environments. To determine whether this phenomena is unique to the fergusonite-type oxides, similar studies were performed on other metal oxides consisting of a weakly-interacting network of  $LnO_8$  and  $BO_6$  polyhedra, such as the  $A_2B_2O_7$  pyrochlore oxides. However, no such change in the effective IR of the  $B$ -site cation was observed (Figure A.6).<sup>2</sup> It appears that both the  $LnO_8$  and  $BO_6$  polyhedra in the fergusonite-type structures display an additional type of flexibility, with the size of the  $Ln^{3+}$  cation on the  $A$  site influencing the effective IR of the  $B$ -site cation in the  $BO_6$  distorted octahedra.

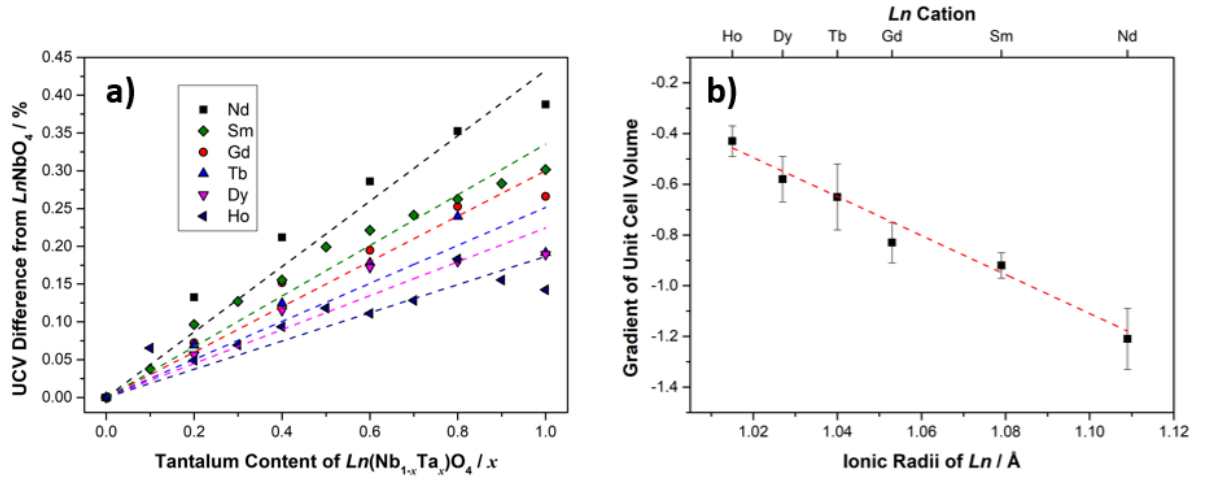


Figure 3.10: The  $Ln(Nb_{1-x}Ta_x)O_4$  solid solution series in the  $I2/a$  space group, with (a) the compositional dependence of the normalised unit cell volume. The values are normalised to the values of the corresponding  $LnNbO_4$  structure. (b) The linear dependence of the change in gradient of the unit cell volume between  $LnNbO_4$  and  $LnTaO_4$  in the  $I2/a$  space group. The dashed lines are linear fits to the data.

To further probe what influences the structural flexibility of both the  $LnO_8$  and  $BO_6$  polyhedra in the fergusonite-type structure, the  $Ho(Nb_{1-x}Ta_x)O_4$  solid solution series ( $\Delta x = 0.1$ ) were refined against a combined SXR and NPD dataset (Table A.4). This approach exploits the very precise lattice parameters afforded by the high peak-shape resolution of the SXR measurements, as well as increased sensitivity to the atomic coordinates of the oxygen atoms from the NPD measurements. Figure 3.11 displays the refined  $Ho-O$  and  $B-O$  bond lengths across the  $Ho(Nb_{1-x}Ta_x)O_4$  series. Although the

average Ho–O and  $B$ –O bond lengths remain almost constant, the individual bond lengths behave differently across the series. For the Ho–O bond distances (Figure 3.11a), the three pairs of shortest bonds slightly decrease in length with the substitution of  $\text{Nb}^{5+}$  for  $\text{Ta}^{5+}$ , whereas the longest Ho–O(2) bond length increases. The contrary effect is observed for the  $B$ –O bond distances, with the pairs of shortest  $B$ –O bonds slightly increasing whilst  $B$ –O(2) bond length (corresponding to  $B$ –O<sub>l</sub>) decreases. This was similarly observed by Shimakawa *et al.* in the  $\text{SrBi}_2(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_9$  Aurivillius phases, where changes in the Nb–O and Ta–O bonds were observed despite keeping the average bond distance constant.<sup>53</sup> This supports the hypothesis that interactions between the  $\text{LnO}_8$  and  $\text{BO}_6$  polyhedra in the  $I2/a$  fergusonite-type structure lead to changes in the unit cell volume.

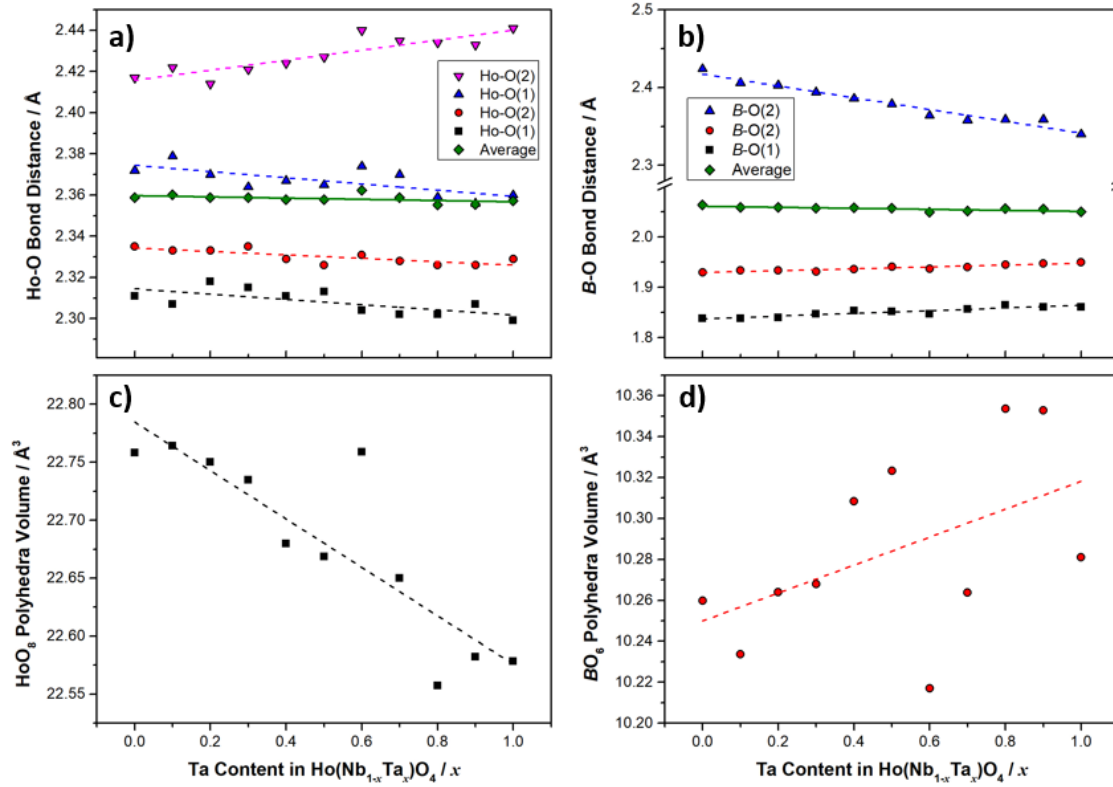


Figure 3.11: Composition dependence at room temperature of the solid solution series  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  for (a) Ho–O bond distances, (b)  $B$ –O bond distances, (c)  $\text{HoO}_8$  polyhedra volume, and (d)  $\text{BO}_6$  polyhedra volume. The dashed lines have been drawn the guide the eyes, with the averages drawn with a solid line.

Structural refinements using combined SXRD and NPD datasets reveal a movement of the  $B$ -site cation within the polyhedra. As observed in Figure 3.11, there is a systematic increase in the  $y$  atomic coordinate of the  $B$ -site cation. This shift shortens the  $B$ –O<sub>l</sub> distance, resulting in a stronger bonding interaction. Similar effects have also been

observed by Lufaso *et al.*, with an out-of-centre distortion present in the (Nb,Ta)O<sub>6</sub> octahedra of some perovskites as a consequence of the second order Jahn-Teller effect.<sup>54</sup> It has been suggested that the atomic coordinate of Nb<sup>5+</sup> in the NbO<sub>6</sub> distorted octahedra is closer to the ideal position in the NbO<sub>4</sub> tetrahedra of the *I*4<sub>1</sub>/*a* structure.<sup>17</sup> Hence, there is less of an energy barrier in the orthoniobates than the corresponding orthotantalates to undergo the *I*2/*a* → *I*4<sub>1</sub>/*a* phase transition.

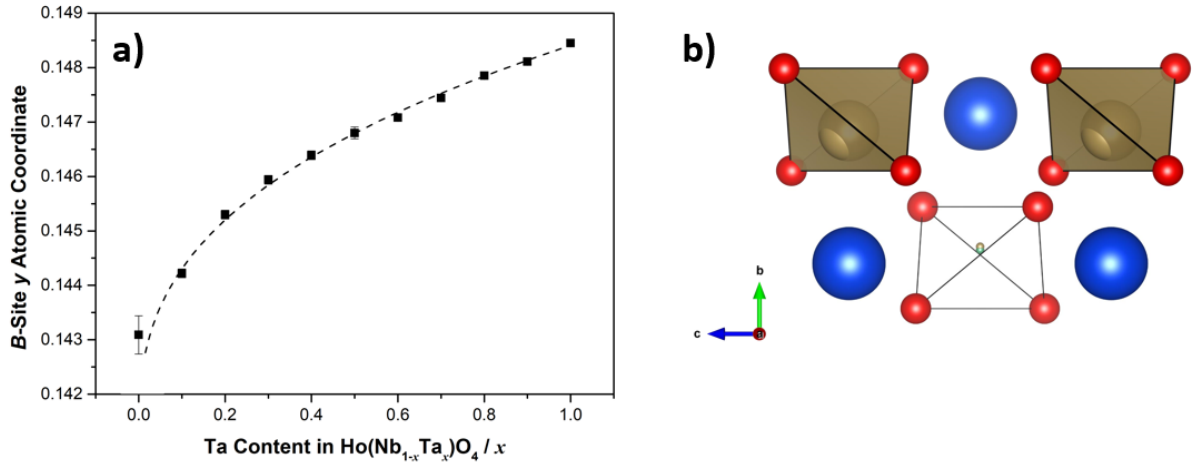


Figure 3.12: (a) The compositional dependence of the *B* site *y* atomic coordinate in the Ho(Nb<sub>1-x</sub>Ta<sub>x</sub>)O<sub>4</sub> series. Where not apparent, the error bars are smaller than the symbols. (b) The Ho(Nb,Ta)O<sub>4</sub> monoclinic *I*2/*a* fergusonite-type structure, drawn with (Nb,Ta)O<sub>4</sub> tetrahedra for clarity. The Ho<sup>3+</sup> cations are drawn as blue spheres, the Nb<sup>5+</sup> cations as green spheres, the Ta<sup>5+</sup> cations as brown spheres, and O<sup>2-</sup> anions as red spheres. The unshaded tetrahedra shows the difference in position between the Nb<sup>5+</sup> and Ta<sup>5+</sup> coordinates in the tetrahedra environment.

It should be noted that the substitution of Nb<sup>5+</sup> for Ta<sup>5+</sup> is only one possible route to prepare solid solution series. Whereas the substitution of Nb<sup>5+</sup> for Ta<sup>5+</sup> leads to an increase in the phase transition temperature,<sup>16</sup> substitution of Nb<sup>5+</sup> (IR = 0.64 Å) for smaller cations such as V<sup>5+</sup> (IR = 0.54 Å) and Sb<sup>5+</sup> (IR = 0.60 Å) leads to a decrease in the *I*2/*a* → *I*4<sub>1</sub>/*a* phase transition temperature.<sup>55,56</sup> This has been investigated as an additional way of stabilising the tetragonal *I*4<sub>1</sub>/*a* structure at room temperature. Wachowski *et al.* have identified samples in the La(Nb<sub>1-x</sub>Sb<sub>x</sub>)O<sub>4</sub> solid solution series (*x* = 0.1, 0.3) that are promising *p*-type/proton conductors.<sup>56,57</sup> Further studies by Guo *et al.* have highlighted the potential for La(Nb<sub>1-x</sub>V<sub>x</sub>)O<sub>4</sub> materials to be used in microwave devices due to their excellent microwave dielectric properties.<sup>58</sup>

As an extension of this, cations of different oxidation states can also be substituted onto the  $B$  site, leading to either an excess or absence of oxygen within the structure. However, this often leads to a complicated relationship between the structure, its conductivity, and the phase transitions observed. Substitution of  $\text{Nb}^{5+}$  for either  $\text{Mo}^{6+}$  or  $\text{W}^{6+}$  leads to a decrease in the  $I2/a \rightarrow I4_1/a$  phase transition temperature, but gives more complex crystallography with a variety of modulated structures observed.<sup>20,59-62</sup> Cations of lower oxidation states appear to have low solubilities ( $x \leq 0.03$ ), as demonstrated by Brandão *et al.* in their investigation of  $\text{La}(\text{Nb}_{1-x}\text{B}_x)\text{O}_{4-\delta}$  ( $\text{B}^{4+} = \text{Ti, Ge, and Si}$ ).<sup>55</sup> It should be noted these materials were not measured for ionic conductivity. Other attempts have included keeping the material stoichiometric by substituting equal parts of pentavalent and hexavalent cations, such as in  $\text{Sm}(\text{Nb}_{0.31}\text{Si}_{0.355}\text{Mo}_{0.355})\text{O}_4$ .<sup>63</sup> A large body of literature also exists in substituting onto the  $A$  site, such as  $(\text{Ca}_x\text{La}_{1-x})\text{NbO}_{4-\delta}$ , leading to other complex crystallographic relationships.<sup>19,22,43,50,64,65</sup>

### 3.3.4 Computational Studies of $\text{HoNbO}_4$ and $\text{HoTaO}_4$

Although not the focus of this dissertation, various DFT calculations have been performed by collaborators of the author's research group to further understand the substitution of  $\text{Nb}^{5+}$  for  $\text{Ta}^{5+}$  in the  $\text{Ln}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  solid solution series. The lattice parameters of some  $\text{LnBO}_4$  ( $\text{Ln}^{3+} = \text{Sm, Ho}$ ;  $\text{B}^{5+} = \text{Nb, Ta}$ ) structures were calculated using the Perdew-Burke-Ernzerhof (PBE) and PBEsol functionals and compared to the refined crystal structures. For  $\text{SmNbO}_4$  and  $\text{SmTaO}_4$ , the PBEsol functional was found to reproduce the lattice parameters well, within 2% of the experimental values. This was similarly seen for  $\text{HoNbO}_4$ . However, the PBE functional provides better agreement for both the  $I2/a$  and  $P2/c$  polymorphs of  $\text{HoTaO}_4$ . This suggests there is no unique universal exchange correlation functional appropriate for these types of oxides. The total energy per formula unit of the  $P2/c$  phase is less compared to  $I2/a$ , with the energy difference nearly 30 meV per formula unit. This potentially indicates that the  $P2/c$  phase is more energetically stable than the  $I2/a$  structure.



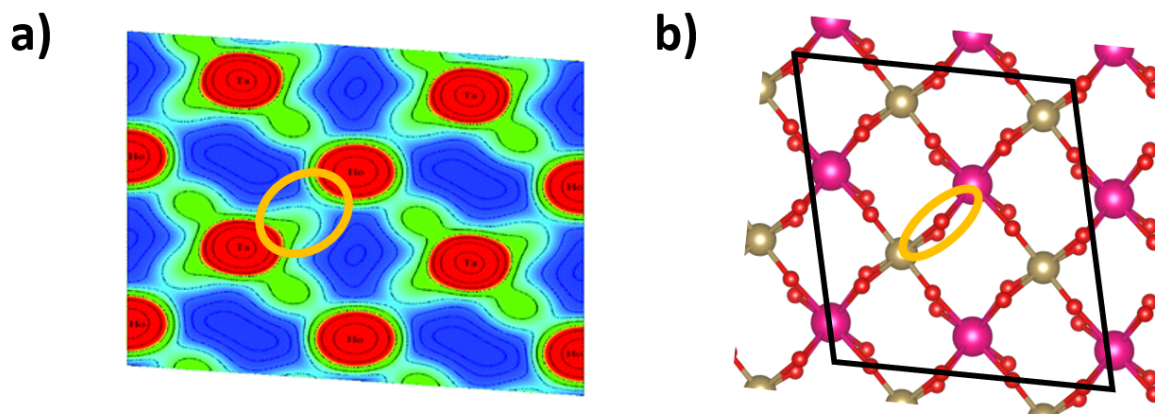


Figure 3.13: (a) Electron charge density distribution plot of the  $I2/a$  phase of  $\text{HoTaO}_4$  in the (010) plane. The gold circle highlights the significant electron density between the  $\text{Ho}^{3+}$  and  $\text{Ta}^{5+}$  cations. (b) A skeletal crystal structure of the  $I2/a$  phase of  $\text{HoTaO}_4$  in the (010) plane, with the same area highlighted in the gold circle. This demonstrates there is significant covalent character associated with the longer  $\text{Ta}-\text{O}_l$  bond.

The difference between the Nb–O and Ta–O bonding environments can be probed by observing the Born effective charge (BEC) tensors, defined as the coupling of the electrostatic field with the lattice displacement. In all cases, the BEC tensors  $Z_{11}$ ,  $Z_{22}$ , and  $Z_{33}$  show anisotropy, with  $Z_{33}$  being appreciably larger. This reflects the mixed ionic-covalent characteristics of the Nb–O and Ta–O bonds, with a considerable covalent contribution observed in the (Nb,Ta)– $\text{O}_l$  bonds. This is observed in Figure 3.13, with electron charge density in the same place as the Ta– $\text{O}_l$  bonds along the (010) plane.

The DoS of  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$  were examined using DFT. In both compounds, the electronic structure analysis shows that the O  $p$  states dominate the valence bands, and the Nb/Ta  $d$  states dominate the conduction bands. This calculation also highlights a difference in band gap between  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$ , which could also be experimentally observed using UV-Vis DRS (Figure A.7). A further calculation was performed whereby the calculations for  $\text{HoNbO}_4$  were repeated, but with  $\text{Nb}^{5+}$  artificially substituted by  $\text{Ta}^{5+}$  – that is, the  $\text{HoNbO}_4$  structure was imposed on  $\text{HoTaO}_4$ . These calculations resulted in an increase in the band gap, revealing significant differences between the electronics of  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$ .

As stated previously,  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  are expected to display almost identical crystal chemistry due to their identical IR.<sup>24</sup> This is due to the lanthanoid contraction, with the additional  $4f$  electrons being ‘core-like’ and not participating in bonding interactions.

However, the DFT results show that the differences between the electronic properties of  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  can lead to differences in the response of the material to external stimuli. Firstly, the empty  $4d$  orbitals of  $\text{Nb}^{5+}$  are expected to extend radially, allowing for a covalent contribution to the  $\text{Nb}-\text{O}_l$  bond. However, the empty  $5d$  orbitals of  $\text{Ta}^{5+}$  extends out further than the corresponding  $4d$  orbitals, allowing for greater orbital overlap and a larger covalent contribution. This, in turn, leads to a stronger  $\text{Ta}-\text{O}_l$  bond, as reflected in the structural refinements that show  $\text{Ta}-\text{O}_l$  to be consistently shorter than  $\text{Nb}-\text{O}_l$ . Similar differences have been seen with other  $4d$  and  $5d$  cations, leading to different spin-orbit coupling contributions,<sup>66</sup> different reduction-oxidation potentials,<sup>67</sup> and different thermal expansion behaviour.<sup>68</sup> The case of  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$  adds to this library, where differences between  $4d$  and  $5d$  orbitals can directly impact the bonding environment, phase transition temperature, and direct band gap of the material, leading to tunability in its use as an ion conductor and photocatalyst.

### 3.4 Heating and *In Situ* Studies

Let us review briefly what was observed in the systematic study of the  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  structures at room temperature. Each of the  $\text{LnNbO}_4$  materials crystallised in the monoclinic  $I2/a$  structure, whereas the  $\text{LnTaO}_4$  materials crystallised in the monoclinic  $P2_1/c$ ,  $I2/a$ , or  $P2/c$  structures depending on the size of the  $\text{Ln}^{3+}$  cation and the synthesis conditions used. Based on BVS calculations, the coordination environments of the  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  cations were determined to be distorted  $(\text{Nb,Ta})\text{O}_6$  octahedra, with the longer  $(\text{Nb,Ta})-\text{O}_l$  bonds predicted to play a significant role in the  $I2/a \rightarrow I4_1/a$  phase transition. This also leads to differences between the two structures, such as different atomic coordinates for the  $B$  site. These observations were further supplemented by DFT calculations. The response of the  $(\text{Nb,Ta})-\text{O}_l$  and  $B$  site atomic coordinates to heat is of interest. Neutron diffraction was therefore used to determine whether the strength of the longer bond is significant to the  $I2/a \rightarrow I4_1/a$  phase transition. An additional gap in the literature is understanding how it is possible to transform between the two  $\text{HoTaO}_4$  polymorphs ( $P2/c$  and  $I2/a$ ) upon heating. This has only been observed *ex situ* using a muffle furnace, and *in situ* measurements are likely to be beneficial.

### 3.4.1 Response of $Ln\text{NbO}_4$ to Heat

The structure of  $\text{HoNbO}_4$  at 50 and 1000 °C were established using Rietveld refinement against the NPD datasets (Figure 3.14). The 50 °C data were successfully indexed to the monoclinic  $I2/a$  space group, consistent with previous studies.<sup>69</sup> In the monoclinic structure, the  $\text{Nb}^{5+}$  cations are surrounded by four close oxygen ions at 1.847(4) and 1.970(4) Å, as well as two longer Nb–O<sub>*l*</sub> contacts at 2.437(4) Å. Including the two Nb–O<sub>*l*</sub> contacts in the BVS calculations increases the  $\text{Nb}^{5+}$  BVS from 4.29 to 4.77, supporting the previous conclusion that  $\text{Nb}^{5+}$  exists in heavily distorted  $\text{NbO}_6$  octahedra. The profile measured at 1000 °C was successfully indexed to a tetragonal cell and the structure was refined to the tetragonal scheelite model in the space group  $I4_1/a$ . The  $\text{Nb}^{5+}$  cations are surrounded by four close oxygen ions with identical Nb–O bond distances of 1.888(3) Å. However, due to the slight difference in the O–Nb–O bond angles (O–Nb–O = 105.9 and 116.9 °), it is appropriate to describe the  $\text{NbO}_4$  tetrahedra as distorted. The BVS of  $\text{NbO}_4$  is 4.25, meaning  $\text{Nb}^{5+}$  is significantly underbonded. This has been hypothesised to facilitate the occupancy of a nearby interstitial site, enhancing ionic conductivity.

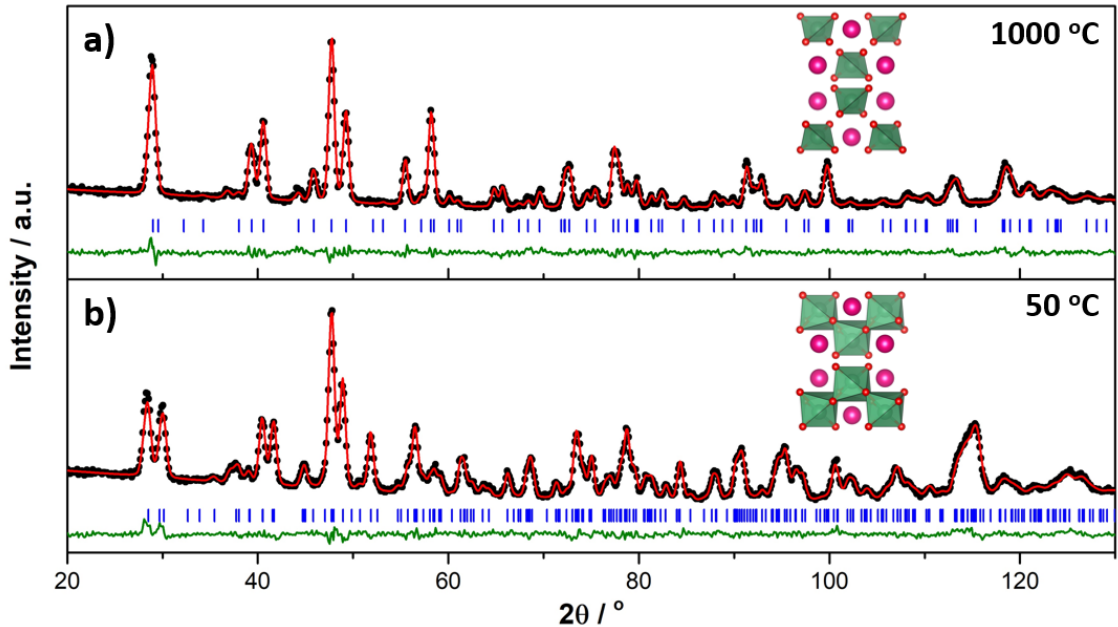


Figure 3.14: Representative Rietveld refinements for the neutron powder diffraction data for  $\text{HoNbO}_4$ , measured at 1.54 Å. At low temperature, the structures were refined using a monoclinic  $I2/a$  model. At high temperature, the structures were refined using a tetragonal  $I4_1/a$  model. In both cases, the black circles represent the observed data, the solid red line represents the fit to the measured profile, the lower green line represents the differences between the observed and calculated profiles, and the blue tick marks show the positions of the space group-allowed reflections.

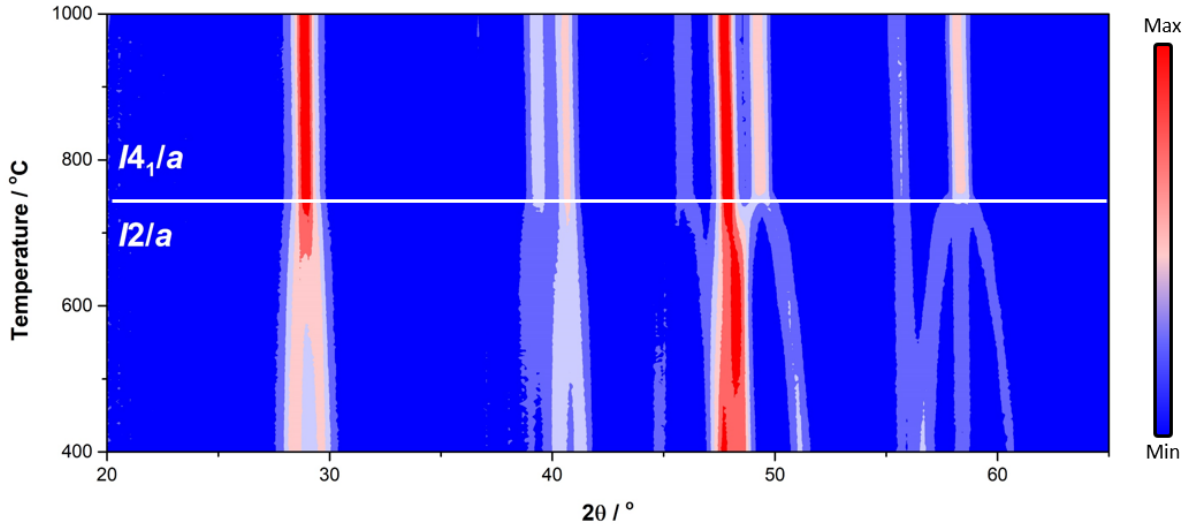


Figure 3.15: Portions of the temperature dependent neutron powder diffraction patterns of  $\text{HoNbO}_4$  measured on heating to 1000 °C. The  $I2/a \rightarrow I4_1/a$  phase transition at  $\sim 775$  °C is indicated by the solid line. The data were collected at 1.54 Å.

The temperature dependence of the NPD profiles (Figure 3.15) and the refined lattice parameters (Figure 3.16) for  $\text{HoNbO}_4$  are shown. Upon heating, the monoclinic cell undergoes anisotropic expansion, with the monoclinic  $a$  lattice parameter decreasing while the  $c$  lattice parameter increases. A phase transition is observed at  $\sim 775$  °C, where the  $a$  and  $c$  lattice parameters become equal, indicating an increase in symmetry (Figure 3.16a). The unit cell volume also increases linearly in both the monoclinic and tetragonal phases, with a small change in the rate of expansion at the phase transition (Figure 3.16b). This is accompanied by a decrease in the monoclinic  $\beta$  angle which approaches 90 °, as expected for the monoclinic-to-tetragonal  $I2/a \rightarrow I4_1/a$  phase transition (Figure 3.16c). The  $y$  atomic coordinates of  $\text{Ho}^{3+}$  and  $\text{Nb}^{5+}$  also change upon heating, with the cations moving from the general  $(1/4, y, 0)$  and  $(1/4, y', 0)$  positions in the monoclinic structure to the symmetrically constrained  $(0, 1/4, 5/8)$  and  $(0, 1/4, 1/8)$  positions in the tetragonal structure. Plotting the monoclinic  $\beta$  angle against the  $y$  atomic coordinate of  $\text{Nb}^{5+}$  reveals a linear relationship, demonstrating a strong coupling between the atomic structure and the lattice parameters (Figure 3.16d).

The nature of the  $I2/a \rightarrow I4_1/a$  phase transition has been investigated previously. This has been described as being continuous and second order, with studies suggesting the transition is purely ferroelastic in nature.<sup>9–12</sup> However, a more recent body of evidence

Table 3.3: Rietveld refinement structural parameters, bond distances, and bond valence sums for  $\text{HoNbO}_4$  at 50 and 1000 °C against neutron powder diffraction data.

| Temperature ( °C)       | 50         | 1000       |
|-------------------------|------------|------------|
| Space Group             | $I2/a$     | $I4_1/a$   |
| $a$ (Å)                 | 5.3074(3)  | 5.2339(2)  |
| $b$ (Å)                 | 10.9756(8) | $= a$      |
| $c$ (Å)                 | 5.0813(3)  | 11.1193(9) |
| $\beta$ (°)             | 94.444(6)  | $= 90$     |
| Vol. (Å <sup>3</sup> )  | 295.11(3)  | 304.60(4)  |
| Ho $y$                  | 0.6202(3)  | $= 5/8$    |
| Nb $y$                  | 0.1430(3)  | $= 1/8$    |
| Ho–O(2) (Å)             | 2.420(4)   | 2.393(3)   |
| Ho–O(1) (Å)             | 2.367(5)   | –          |
| Ho–O(2) (Å)             | 2.338(4)   | 2.354(3)   |
| Ho–O(1) (Å)             | 2.307(4)   | –          |
| Ho–O <sub>av.</sub> (Å) | 2.358(4)   | 2.374(3)   |
| Nb–O(2) (Å)             | 2.437(4)   | 2.803(3)   |
| Nb–O(2) (Å)             | 1.930(4)   | –          |
| Nb–O(1) (Å)             | 1.847(4)   | 1.888(3)   |
| Nb–O <sub>av.</sub> (Å) | 1.970(4)   | 2.193(3)   |
| BVS (NbO <sub>4</sub> ) | 4.29       | 4.25       |
| BVS (NbO <sub>6</sub> ) | 4.77       | 4.61       |
| $R_{wp}$ (%)            | 3.45       | 3.19       |

shows that the two phases can coexist at elevated temperatures.<sup>13,14,70</sup> Such behaviour is inconsistent with a continuous phase transition, suggesting that the  $I2/a \rightarrow I4_1/a$  transformation may, in fact, be first order. First order phase transitions are characterised by a sudden change in the thermodynamic properties of the material, meaning it is possible, but not required, for the two phases to coexist around the phase transition temperature. This was noted previously by Arulnesan *et al.*, where two-phase regions of  $I2/a + I4_1/a$  were observed in the  $Ln\text{NbO}_4$  materials with larger  $Ln^{3+}$  cations, such as  $\text{PrNbO}_4$  and  $\text{SmNbO}_4$ .<sup>15</sup>

As noted above, the monoclinic  $I2/a$  fergusonite-type structure is typically described as a distorted and compressed version of the tetragonal  $I4_1/a$  scheelite-type structure. This means it can be derived from the high symmetry aristotype by well-defined displacements of the cations and anions. Landau mean-field theory has previously been used to analyse the  $I2/a \rightarrow I4_1/a$  transition, including the (opposite,  $I4_1/a \rightarrow I2/b$ ) pressure-induced transition in the original  $\text{CaWO}_4$  scheelite structure itself.<sup>71</sup> The

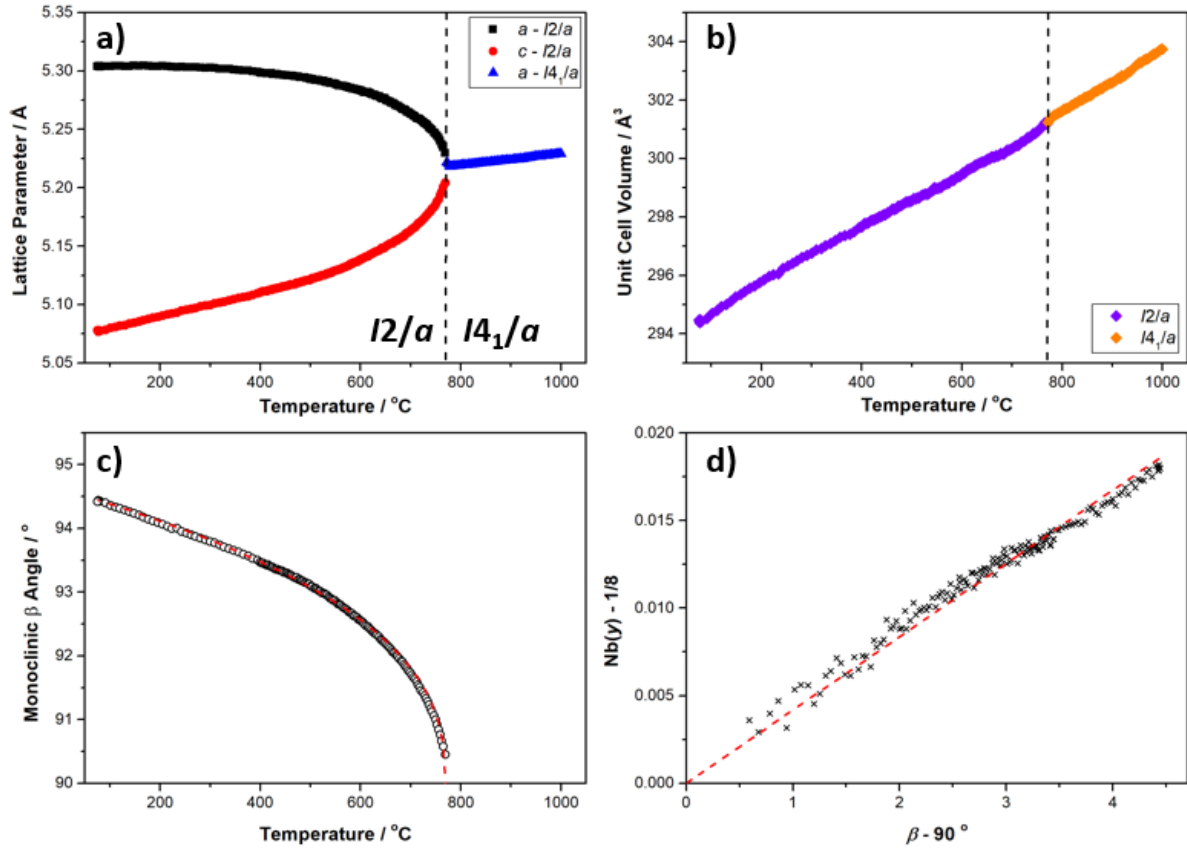


Figure 3.16: Rietveld refinements for the variable temperature neutron diffraction of  $\text{HoNbO}_4$ , with (a) the  $a$  and  $c$  lattice parameters, (b) the unit cell volume, (c) the monoclinic  $\beta$  angle, and (d) the  $y$  atomic coordinate of  $\text{Nb}^{5+}$  plotted against the monoclinic  $\beta$  angle. The black dashed line represents the temperature of the  $I2/a \rightarrow I4_1/a$  phase transition, and the red dashed lines are fits described in the text.

existence of a soft acoustic mode belonging to the  $B_g$  irreducible representation (*irrep*) was identified by Gu *et al.*, which is the primary order parameter of this phase transition and corresponds to both the  $(\epsilon_1 - \epsilon_2)$  and  $\epsilon_6$  strain components.<sup>72</sup> Further work by Wada *et al.* identified that  $\epsilon_6$  is soft using Brillouin scattering.<sup>73</sup> In this case, Landau mean-field theory was used to set up a series expansion of the Gibbs free energy difference between the low temperature monoclinic  $I2/a$  and high temperature tetragonal  $I4_1/a$  phases. The Gibbs free energy difference consists of three contributions:  $G_\epsilon$  from the ferroelastic order parameters describing the strains of  $B_g$  symmetry,  $G_\eta$  describing the atomic displacements of  $B_g$  symmetry, and  $G_c$  describing the coupling between the strains and the atomic displacements.

Using the framework of Landau mean-field theory, an order parameter of amplitude  $\eta$  is used to describe the distortions of the  $I2/a$  structure relative to the high-temperature  $I4_1/a$  structure by the optical phonon of  $B_g$  symmetry. This is such that  $\eta > 0$  for the (strained) monoclinic  $I2/a$  phase, and  $\eta = 0$  for the (strain-free) tetragonal  $I4_1/a$  phase. The symmetrised elastic contribution may be approximated as

$$G_\epsilon(\eta) = \frac{A}{2}(T - T_c)\eta^2 + \frac{B}{4}\eta^4 \quad (3.2)$$

where  $A$  and  $B$  are (positive) constant coefficients,  $T$  is the temperature (in °C), and  $T_c$  is the temperature of the phase transition (in °C). As there are only two potential phases, the expansion is limited to the fourth order with respect to  $\eta$ . If the phase transition is driven by this strain component, the  $B$  coefficient may be taken as sufficiently small (relative to  $A$ ) such that it may be neglected. This leads to a proportionality of

$$\eta \propto (T - T_c)^\beta \quad (3.3)$$

where  $\beta = 0.5$  for second order behaviour.

The coupling term ( $G_c$ ) in the Gibbs free energy difference expansion accounts for the interactions between the acoustic and optical modes of  $B_g$  symmetry. These were solved using the ISODISTORT software,<sup>74</sup> and are given as

$$G_c(\eta) = -c_1\eta(\epsilon_1 - \epsilon_2) - c_2\epsilon_6\eta - c_3\eta_6^2(\epsilon_1 + \epsilon_2 + \epsilon_3) \quad (3.4)$$

where  $c_1$ ,  $c_2$ , and  $c_3$  are (positive) constants, and the  $(\epsilon_1 + \epsilon_2 + \epsilon_3)$  term is the temperature dependent variation in volume.

The effect of the coupling term means there are several possible choices for the order parameter. Two specific choices are outlined below:

Method 1 – Strain Component Analysis: As previously outlined by Schlenker *et al.*, the spontaneous strains calculated from the lattice parameter values can be used as an order parameter since the displacement of the atoms from the equivalent positions of the high-temperature tetragonal scheelite-type  $I4_1/a$  phase gives rise to spontaneous strains.<sup>75,76</sup> The strain components are calculated as

$$\begin{aligned} (\epsilon_1 - \epsilon_2) &= \frac{2(a_m - c_m)}{a_0 + c_0} \\ \epsilon_6 &= \frac{(a_m + c_m) \cos \beta_m}{\sqrt{2}(a_0 + c_0)} \end{aligned} \quad (3.5)$$

where  $a_m$ ,  $c_m$ ,  $\beta_m$  are the lattice parameters associated with the monoclinic  $I2/a$  phase, and  $a_0$ ,  $c_0$  are the extrapolated lattice parameters associated with the tetragonal  $I4_1/a$  phase.

The temperature dependent fits to the strain components are displayed in Figure 3.17 over two different temperature ranges. Taking the spontaneous strains as the order parameter over the entire measured temperature range, attempts to fit Equation 3.6 with  $\beta = 0.5$  were unsuccessful. Instead, least squares fits to the general expression

$$\eta = A(T_c - T)^\beta \quad (3.6)$$

were performed, where the prefactor  $A$ , the phase transition temperature  $T_c$ , and the critical exponent  $\beta$  were allowed to freely refine. For  $\text{HoNbO}_4$  in plotting  $\epsilon_6$ , as suggested by Wada *et al.*,<sup>73</sup> this was calculated to be  $\beta = 0.441$  with  $T_c = 788$  °C. By fitting the data over a shorter temperature range (within 50 °C of the phase transition temperature), fits with  $\beta = 0.5$  were successful. This indicates the transformation obeys Landau mean-field theory close to the phase transition.

Method 2 – Analysis of the Monoclinic  $\beta$  Angle: Another consideration for choosing an appropriate order parameter is that it is sensitive to Rietveld refinement and easily traceable. In the case of the  $I2/a \rightarrow I4_1/a$  phase transition, the monoclinic  $\beta$  angle can also be chosen, as  $\beta > 90$  ° in the monoclinic  $I2/a$  phase, and  $\beta = 90$  ° in the tetragonal phase. This provides a sensitive variable for describing the phase transition. Furthermore,



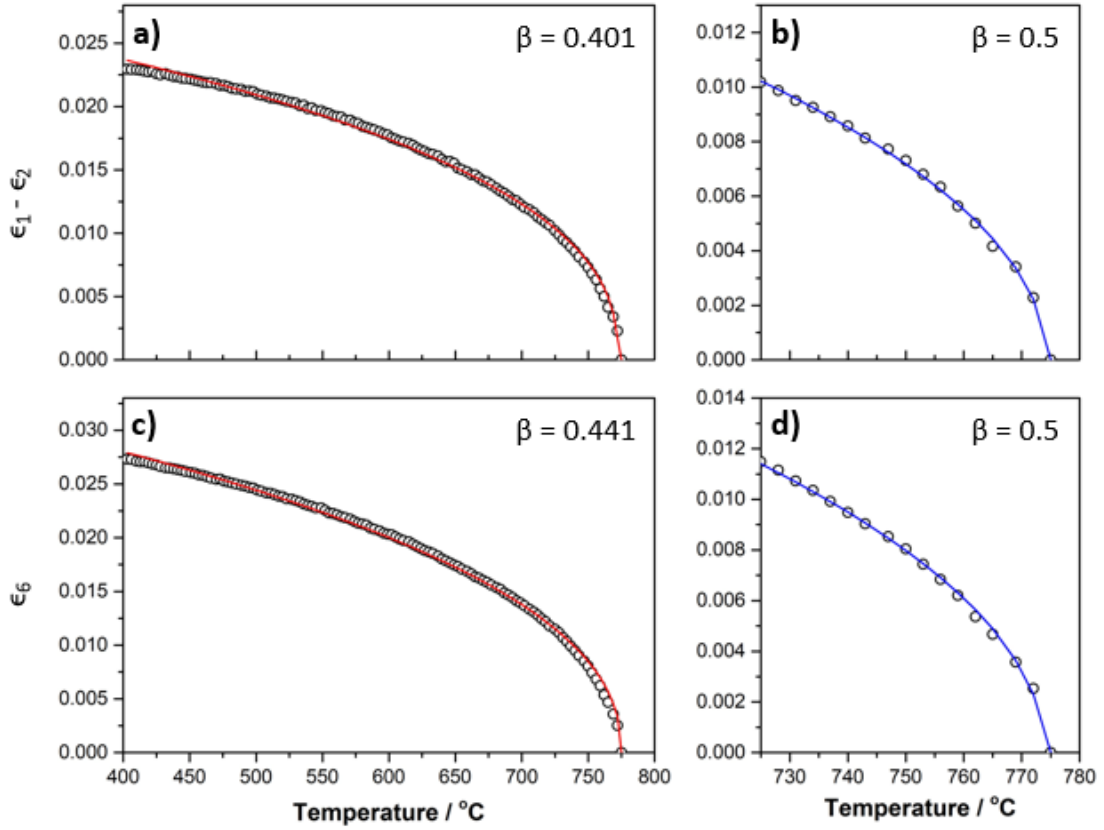


Figure 3.17: Strain analysis based on the lattice parameters from the variable temperature Rietveld refinements of  $\text{HoNbO}_4$ . (a) The  $(\epsilon_1 - \epsilon_2)$  strain component, as calculated using the expressions from Equation 3.5, fitted over the whole measured temperature range, and (b) the fit performed in a range 50 °C below  $T_c$ , with  $\beta = 0.5$ . The same are shown for (c) and (d) with the  $\epsilon_6$  strain component. Although the data was fit down to 100 °C, the plots show from 400–800 °C for clarity.

the monoclinic  $\beta$  angle also models the displacement of the atomic contents within the unit cell associated with the *irrep*  $B_g$ , as seen by the linear relationship between  $\text{Nb}(y)$  and the monoclinic  $\beta$  angle (Figure 3.16d).

Attempts to fit the dependence of the monoclinic  $\beta$  angle using the general expression in Equation 3.6 and fixing  $\beta = 0.5$  were also unsuccessful. Rather, allowing the value of the critical exponent  $\beta$  to vary resulted in  $\beta = 0.390$  and  $T_c = 768$  °C. This value is similar to previous studies that fit the monoclinic  $\beta$  angle, with Sarin *et al.* reporting  $0.350 \leq \beta \leq 0.405$  for other  $\text{ANbO}_4$  materials ( $A^{3+} = \text{La}, \text{Dy}, \text{Y}$ ), and  $\beta = 0.398$  reported by Saura-Múzquiz *et al.* for  $\text{NdNbO}_4$ .<sup>3,14</sup> Similar to the strain analysis, as the value for  $\beta \neq 0.5$  across the entire temperature range, it is evident that Landau mean-field theory does not capture the full nature of the phase transition, suggesting more complex behaviour. If the fitting temperature range is reduced to within 50 °C of the phase

transition, as seen in both Figures 3.17b,d and 3.18b, a fit with  $\beta = 0.5$  is achieved. This implies the phase transition undergoes Landau mean-field theory-type behaviour close to the phase transition, and a departure from mean-field theory behaviour far from the phase transition.

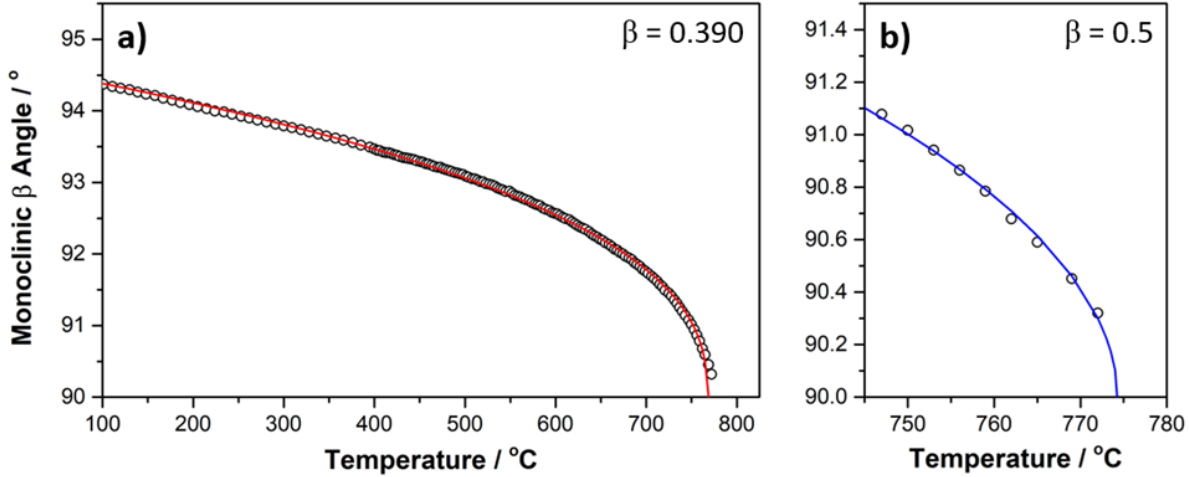


Figure 3.18: The monoclinic  $\beta$  angle from the variable temperature Rietveld refinements of  $\text{HoNbO}_4$ . (a) The monoclinic  $\beta$  angle fitted over the whole measured temperature range, and (b) the fit performed in a range 50 °C below  $T_c$ , with  $\beta = 0.5$ .

Although not performed in this dissertation, it is also possible to consider the amplitude of the displacement modes of the lower symmetry  $I2/a$  structure allowed by the *irreps* of the higher symmetry  $I4_1/a$  structure. A full analysis of this has previously been performed using the software AMPLIMODES,<sup>77</sup> and is seen in the publication on the variable temperature behaviour of  $\text{NdNbO}_4$  and  $\text{NdTaO}_4$  from the author's research group.<sup>3</sup> Saura-Múzquiz *et al.* identified two modes, designated by the *irreps*  $\Gamma_1^+$  and  $\Gamma_2^+$  with the latter identified as the primary mode, that act as an order parameter for the  $I2/a \rightarrow I4_1/a$  phase transition. These were also identified by Auckett *et al.*, who highlighted that the  $\Gamma_2^+$  mode causes in-plane displacement of the oxygen atoms, resulting in twisting of the  $\text{BO}_4$  tetrahedra about the  $c$ -axis, as well as displacements of the cations from their equivalent high-symmetry positions.<sup>59</sup>

That both methods of analysis show  $\beta \neq 0.5$  across the whole temperature range implies that the phase transition behaviour is complex. This could be a result of possible couplings between the second order ferroelastic movements of the  $\text{NbO}_6$  groups, as well as the first order breaking of the long Nb–O<sub>l</sub> bond. Therefore, it is concluded that it is

more appropriate to describe the  $I2/a \rightarrow I4_1/a$  phase transition as a reconstructive first order, as the characteristics of a continuous second order phase transition do not quite capture all of the features.

### 3.4.2 Response of $LnTaO_4$ to Heat

The structures of  $HoTaO_4$  at 50, 1500, and 50 °C upon cooling were established by Rietveld refinements against the NPD datasets (Figure 3.19 and Table A.5). The 50 °C data were successfully refined to the monoclinic  $P2/c$  space group consistent with previous studies.<sup>1,47</sup> As previously mentioned, it is unexpected for  $HoNbO_4$  and  $HoTaO_4$  to adopt different space groups, given the similar IR of  $Nb^{5+}$  and  $Ta^{5+}$ .<sup>24</sup> Similar to the monoclinic  $I2/a$  structure observed for  $HoNbO_4$ , the  $Ta^{5+}$  cations are surrounded by four close oxygens at 1.882(5) Å and 2.015(5) Å. However, like the  $HoNbO_4$  structure, there are an additional two Ta–O<sub>l</sub> bonds at 2.222(5) Å. These are much closer than the additional Nb–O<sub>l</sub> bonds seen in  $HoNbO_4$ , as evidenced by the significant covalent character of the bond (Figure 3.13). Inclusion of these additional contacts raises the BVS from 3.80 for  $TaO_4$  to 4.72 for  $TaO_6$ , which indicates a better model of its coordination environment.

The profile measured at 1500 °C was successfully refined to the tetragonal  $I4_1/a$  scheelite-type space group. In the tetragonal scheelite-type structure, the  $Ta^{5+}$  cations are surrounded by four close oxygen ions with identical Ta–O bond distances of 1.918(4) Å, with a similar distortion in bond angles to the high temperature scheelite-type  $HoNbO_4$  structure (O–Ta–O = 105.9 and 116.8 °). The BVS of  $TaO_4$  is 4.72, meaning that  $Ta^{5+}$  is underbonded like the corresponding  $Nb^{5+}$  in the  $HoNbO_4$  structure.

Upon cooling,  $HoTaO_4$  crystallises into a different space group and the reflections indicative of the primitive monoclinic cell were absent. The NPD dataset could be successfully indexed to the monoclinic  $I2/a$  fergusonite-type structure. Therefore, as deduced from the *ex situ* furnace experiments, heating the  $P2/c$  phase of  $HoTaO_4$  through the high temperature  $I4_1/a$  phase causes it to recrystallise in the  $I2/a$  phase isostructural to  $HoNbO_4$ . This is the first *in situ* analysis of this phase transformation. Comparison of isostructural  $HoNbO_4$  and  $HoTaO_4$  at similar temperatures reveal different bond lengths

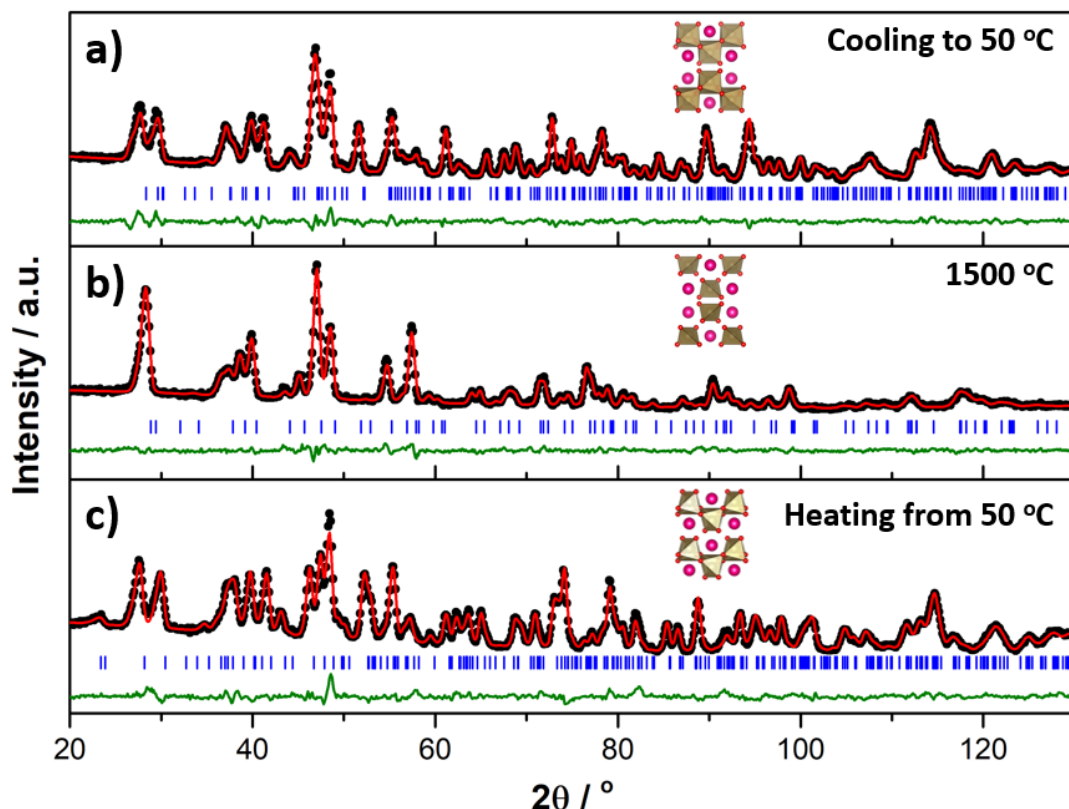


Figure 3.19: Representative Rietveld refinements for the neutron powder diffraction data, measured at 1.54 Å. (c) At low temperature, the structure was refined using the monoclinic  $P2_1/c$  model. (b) At high temperature, the structure was refined using a tetragonal  $I4_1/a$  model. (a) Upon cooling, the structure was refined to the monoclinic  $I2/a$  model. In each case, the black circles represent the observed data, the solid red line represents the fit to the measured profile, the solid green line represents the differences between the observed and calculated profiles, and the blue tick marks show the positions of the space group-allowed reflections.

and atomic coordinates, as previously seen in the room temperature structural analysis of the  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  solid-solution series.

The temperature profiles (Figure 3.20) and the appropriately scaled lattice parameters (Figure 3.21) are shown. Upon heating, the  $P2_1/c$  phase undergoes expansion in all three lattice directions. This is accompanied by a decrease in the monoclinic  $\beta$  angle and an increase in unit cell volume. At  $\sim 1423^\circ\text{C}$ , an additional reflection was observed between the  $(11\bar{1})$  and  $(111)$  reflections of the  $P2_1/c$  phase at  $\sim 28^\circ 2\theta$ . This reflection was fitted with the introduction of the  $I4_1/a$  scheelite-type phase. Upon further heating, additional reflections between  $40$ – $60^\circ 2\theta$  were observed which were also fitted to the  $I4_1/a$  phase. These  $I4_1/a$  reflections continued to grow in intensity as the  $P2_1/c$  reflections decreased, indicating that a first order phase transition was occurring. The two-phase model was

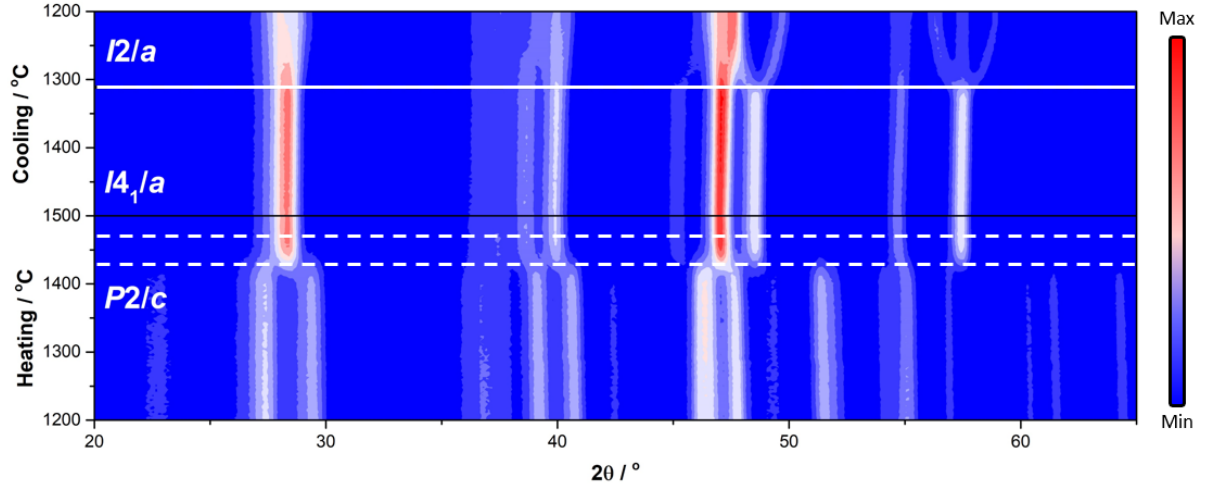


Figure 3.20: Portions of the temperature dependent neutron diffraction patterns of  $\text{HoTaO}_4$  measured on heating to 1500 °C. The  $P2/c$  and  $I4_1/a$  two-phase region is indicated by the dashed lines, whereas the  $I4_1/a \rightarrow I2/a$  phase transition upon cooling at  $\sim 1300$  °C is indicated by the solid line. The data were collected at 1.54 Å.

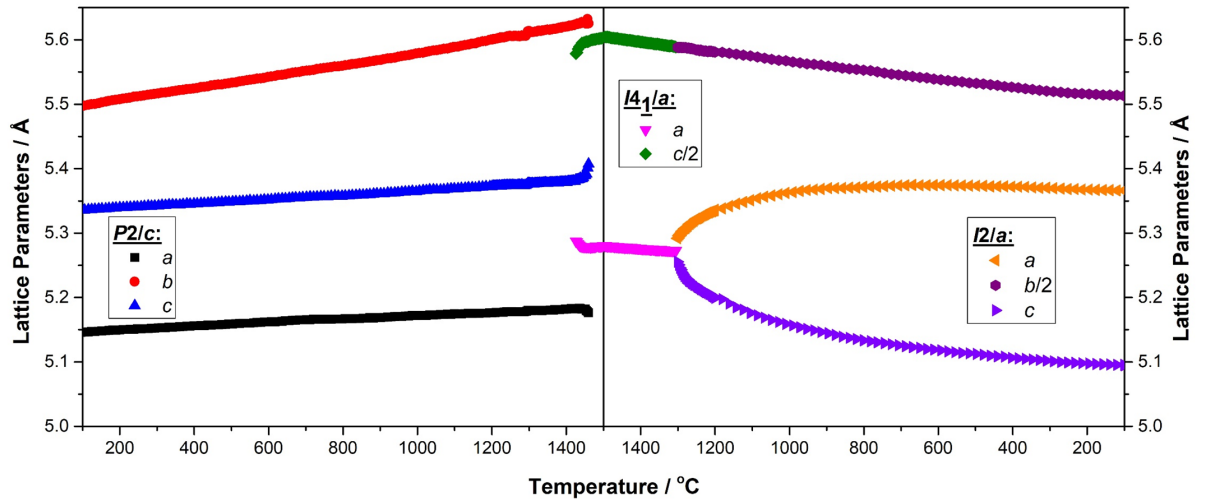


Figure 3.21: Temperature dependence of the lattice parameters for  $\text{HoTaO}_4$  obtained by Rietveld refinements against neutron powder diffraction data. The data were collected as the sample was heated from room temperature to 1500 °C, and then as the sample was cooled to room temperature. For ease of comparison, the lattice parameters of the  $I$ -centred cells have been appropriately rescaled. The error bars are smaller than the symbols.

refined until the peaks around  $26\text{--}30^\circ$  and the intense peak between  $50\text{--}53^\circ 2\theta$  were indistinguishable from the background. This was observed to be  $\sim 1464^\circ\text{C}$ , after which the tetragonal  $I4_1/a$  model was refined until  $1500^\circ\text{C}$ . The phase fraction of the  $P2/c$  and  $I4_1/a$  phases is plotted in Figure 3.22.

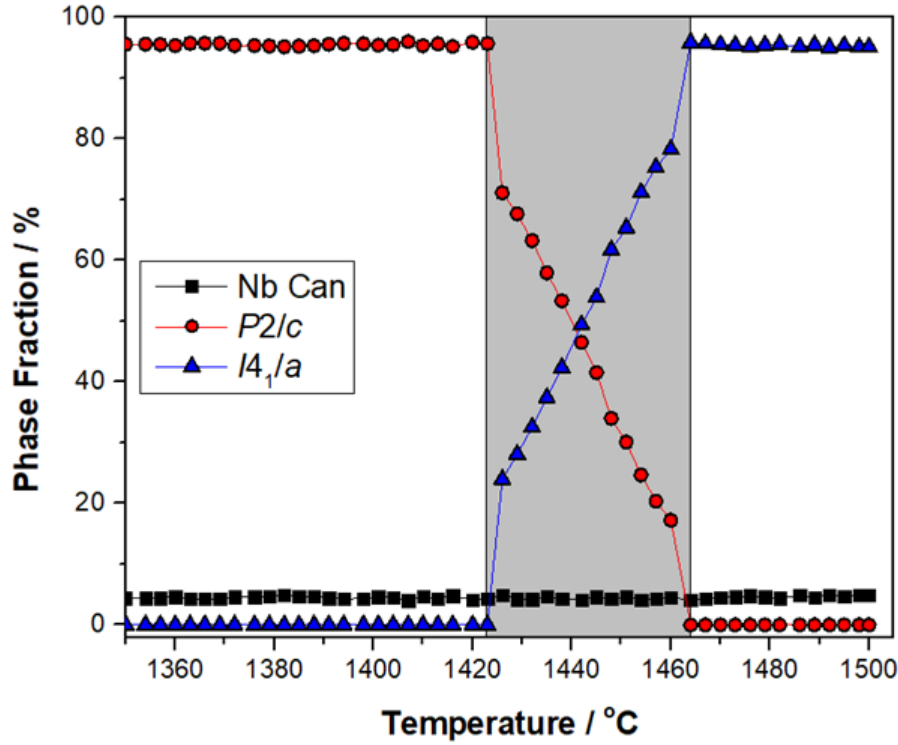


Figure 3.22: Phase fraction the two phase first order phase transition in  $\text{HoTaO}_4$  upon heating. The two-phase region is highlighted in grey.

Upon cooling, the tetragonal  $I4_1/a$  phase displayed unsurprising lattice contraction. At  $\sim 1300^\circ\text{C}$ , additional reflections began to emerge around  $45\text{--}50^\circ 2\theta$ . These reflections emerged in different ranges to those that were observed for the  $P2/c$  phase, indicating that  $\text{HoTaO}_4$  was transforming to a different phase upon cooling. The additional reflections were fitted with the introduction of a monoclinic  $I2/a$  phase to the refinement model. This phase transition occurred without a two-phase region, indicating it is possibly continuous in nature. A similar Landau mean-field theory analysis to that for  $\text{HoNbO}_4$  described above demonstrated the phase transition was not strictly second order, with plotted of the strain components and the monoclinic  $\beta$  angle modelled with the critical exponent  $\beta \neq 0.5$  (Figures A.8–10). Similar to that of  $\text{HoNbO}_4$ , fitting a reduced temperature region of within  $50^\circ\text{C}$  of the phase transition returns a good fit with a critical exponent  $\beta = 0.5$ . The  $P2/c$  phase was not detected upon cooling, indicating that the  $P2/c \rightarrow I4_1/a$  phase

transition is irreversible. The  $I4_1/a \rightarrow I2/a$  phase transition that occurred upon cooling followed the behaviour observed in  $\text{HoNbO}_4$  very closely, despite occurring at almost double the temperature ( $\text{HoNbO}_4$   $T_c \sim 775^\circ\text{C}$ ,  $\text{HoTaO}_4$   $T_c \sim 1300^\circ\text{C}$ ).

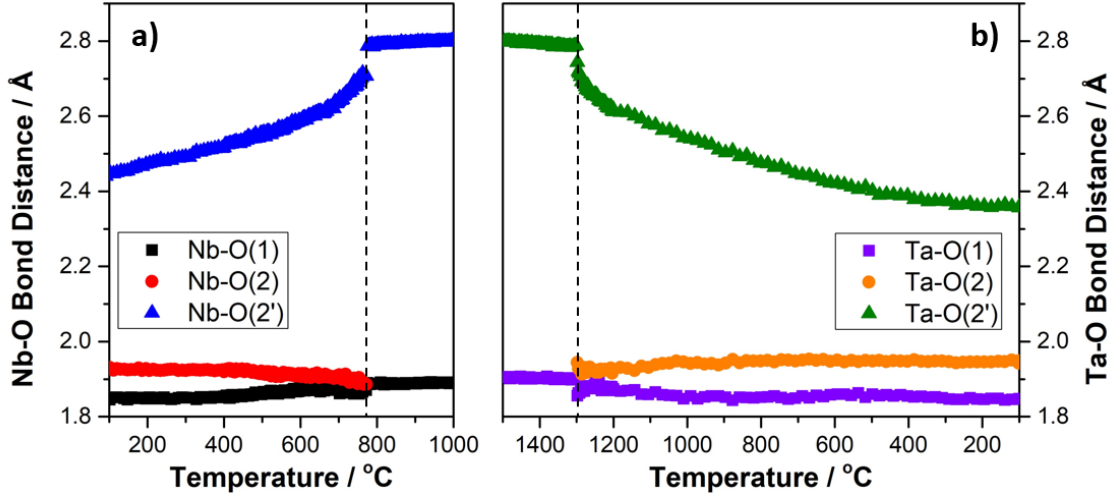


Figure 3.23: Temperature dependence of the (a) Nb–O bond distances calculated for  $\text{HoNbO}_4$  upon heating, and (b) Ta–O bond distances calculated for  $\text{HoTaO}_4$  upon cooling. The dotted line indicates the  $I2/a \rightarrow I4_1/a$  phase transition in both samples. Note the difference in the  $x$ -axis between the two plots.

It is hypothesised that the  $B\text{--}O_l$  ( $B^{5+} = \text{Nb}, \text{Ta}$ ) bond is critical to the  $I2/a \rightarrow I4_1/a$  phase transition. The  $B\text{--}O$  bond distances from the Rietveld refinements are plotted (Figure 3.23). As this is a NPD study, this will provide the greatest accuracy of the atomic coordinates of the oxygen atoms amongst the heavier  $\text{Ho}^{3+}$ ,  $\text{Nb}^{5+}$ , and  $\text{Ta}^{5+}$  cations. The similarity between the two results is striking. In the low temperature  $I2/a$  phase of  $\text{HoNbO}_4$ , the  $\text{Nb}\text{--}O_l$  bond shows an exponential-like increase with temperature that abruptly stops at the transition to the tetragonal structure. In the tetragonal structure, the  $\text{Nb}\text{--}O_l$  contacts are considered to be effectively nonbonding, indicating a change from distorted  $\text{NbO}_6$  octahedra to  $\text{NbO}_4$  tetrahedra. Upon cooling  $\text{HoTaO}_4$  through the  $I4_1/a \rightarrow I2/a$  phase transition, the  $\text{Ta}\text{--}O_l$  bond shows an exponential-like decrease over a much larger temperature range reflecting its stronger interaction. This provides further evidence that the  $I2/a \rightarrow I4_1/a$  phase transition is driven by the breaking of the longer  $B\text{--}O_l$  bond.

### 3.4.3 Determining Optimal Synthesis Conditions using *In Situ* Techniques

From the above work, it is clear that the  $P2/c$  phase in the  $LnTaO_4$  materials only forms if the material is heated at moderate temperatures. That is, it is heated for prolonged periods of time *below* the  $I2/a \rightarrow I4_1/a$  phase transition temperature (Table 3.2). This was observed *ex situ* with  $HoTaO_4$ , where the  $P2/c$  structure was synthesised when annealing for 48 hours at 1400 °C, and the  $I2/a$  structure was synthesised when annealing for 48 hours at 1450 °C.<sup>2</sup> Furthermore, the *in situ* heating study of  $HoTaO_4$  revealed a first order phase transition between  $P2/c$  and  $I4_1/a$  between 1423–1464 °C. Therefore, heating the  $LnTaO_4$  material through the  $P2/c$  phase to the high temperature  $I4_1/a$  phase results in formation of the  $I2/a$  phase upon cooling.

In order to further test this hypothesis, an experiment was conducted where a stoichiometric mixture of the starting  $Ho_2O_3$  and  $Ta_2O_5$  reagents was heated and monitored using NPD as an *in situ* synthesis study. Before the starting reagents were mixed, Rietveld analysis of the NPD profiles confirmed both reagents were crystalline and single phase. At room temperature,  $Ho_2O_3$  has a cubic structure (space group  $Ia\bar{3}$ ) with a lattice parameter  $a = 10.623(4)$  Å, as reported previously.<sup>78,79</sup> The structure of  $Ta_2O_5$  is more complex. Previous X-ray studies of  $Ta_2O_5$  have reported a reversible phase transition around 1360 °C, and earlier studies suggested that the structure is sensitive to the heat treatment of the material.<sup>80</sup> It has subsequently been established that at room temperature,  $Ta_2O_5$  has an incommensurate modulated structure with distortion planes. Stephenson and Roth proposed that this could be adequately described by an ‘average’ orthorhombic unit cell in space group  $P2mm$  with dimensions  $6.198 \times 40.29 \times 3.888$  Å that contains 11 formula units with 12 unique  $Ta^{5+}$  and 33 unique  $O^{2-}$  positions.<sup>80</sup> As the present experiment used a medium resolution, high intensity neutron diffractometer, it was elected to use the average structure developed by Stephenson and Roth in the Rietveld refinements of the NPD data.<sup>80</sup> In these refinements, the ADPs of the 12 unique  $Ta^{5+}$  positions were constrained to be equal, as were those of the 33 unique  $O^{2-}$  atoms. This resulted in an acceptable fit to the profile measured at room temperature and was employed in the subsequent variable temperature study.



Analysis of the NPD profiles of the green powder measured as the temperature was increased from room temperature to 1500 °C revealed a series of transformations. To avoid overparameterisation, several constraints were placed on the refinement process. A single  $B_{eq.}$  was used for the cations of each phase, with a second value used for the oxygens in the same phase. No constraints were placed on the relative size of the ADPs between the phases, with each phase allowed to refine freely. Due to the modest peak-shape resolution of the diffractometer, size and strain parameters were not refined. The fits were first performed by refining the atomic coordinates of each phase. This led to a large amount of ‘noise’ in the refined parameters, which was improved by fixing the atomic coordinates of each phase. Despite the smaller amount of refined parameters, this did not change the overall trends observed in the data.

The thermal evolution of the NPD data can be separated into five stages upon heating, with an additional process evident upon cooling. These stages are depicted in Figure 3.24, and are summarised as follows:

Stage 1: Thermal expansion of  $\text{Ho}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  from room temperature to 1145 °C.

Upon heating to 1145 °C, little change was initially seen in the profiles. The only crystalline phases identified were the cubic  $\text{Ho}_2\text{O}_3$  and orthorhombic  $\text{Ta}_2\text{O}_5$  phases, together with reflections from the Nb can used to house the sample. Both oxides showed conventional positive thermal expansion. Rietveld refinements demonstrate that both  $\text{Ho}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  remain unreacted below 1145 °C.

Stage 2: Emergence of a  $\text{HoTaO}_4$   $P2/c$  phase from  $\sim 1145$  °C.

Heating above 1145 °C resulted in changes to the relative intensities of a number of reflections that could not be fitted using the three-phase model ( $\text{Ho}_2\text{O}_3 + \text{Ta}_2\text{O}_5 + \text{Nb}$ ) employed in Stage 1. This was most apparent in the region  $20\text{--}50^\circ 2\theta$ , where the relatively strong reflection at  $\sim 22^\circ 2\theta$  from the  $\text{Ta}_2\text{O}_5$  phase begins to lose intensity, and additional reflections emerge at  $\sim 29^\circ$  and  $\sim 52^\circ 2\theta$ . These additional reflections were sharp, indicating the formation of a new crystalline phase. These reflections could be fitted using a  $P2/c$  monoclinic phase, corresponding to  $\text{HoTaO}_4$ , and inclusion of this in the Rietveld refinements lowered the  $R_{wp}$  value (from 4.92% to 4.39% at 1145 °C), indicating a better fit to the data. The phase fractions of  $\text{Ho}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  were observed to decrease

whilst the phase fraction of  $\text{HoTaO}_4$  increased. This indicated reaction between the two metal oxides began around 1145 °C.

Stage 3: Emergence of the weberite-type  $\text{Ho}_3\text{TaO}_7$  at 1200 °C.

Further heating to  $\sim 1200$  °C resulted in more reflections emerging that could not be indexed to the four-phase model ( $\text{Ho}_2\text{O}_3 + \text{Ta}_2\text{O}_5 + \text{HoTaO}_4$   $P2/c + \text{Nb}$ ). The appearance of these new reflections was accompanied by a noticeable reduction in the intensity of the most prominent reflections from  $\text{Ho}_2\text{O}_3$ , indicating a reaction to form an additional phase. Examination of the ICSD for other materials in the  $\text{Ho}_2\text{O}_3$ – $\text{Ta}_2\text{O}_5$  phase diagram suggested the possibility of a weberite-type  $\text{Ho}_3\text{TaO}_7$  structure. Three different space groups have been reported for weberite-type tantalates depending on the size of the *A*-site cation and synthesis conditions. The larger lanthanoids ( $A^{3+} = \text{La–Nd}$ ) are reported to adopt an orthorhombic structure in the space group  $Cmcm$ , whereas the  $C222_1$  space group is favoured for yttrium and the remainder of the lanthanoids (noting that a cubic structure in  $Fm\bar{3}m$  has also been described for  $A^{3+} = \text{Ho}$ ).<sup>81</sup> Both structures were tested and were found to give similar quality of fits. As previous work by Gussev *et al.* has shown the need for neutron total scattering measurements to differentiate between these closely-related structures, the  $C222_1$  space group was adopted in this work in keeping with their suggestion.<sup>82,83</sup>

The addition of this phase to the refinement model successfully accounted for the additional reflections, and at  $\sim 1234$  °C the sample was a mixture of  $\text{HoTaO}_4$  ( $P2/c$ ),  $\text{Ho}_3\text{TaO}_7$ , and unreacted  $\text{Ta}_2\text{O}_5$ . Further heating resulted in a gradual decrease in the intensity of the reflections from  $\text{Ta}_2\text{O}_5$  and these became indistinguishable from the background around  $\sim 1340$  °C.

The formation of  $\text{Ho}_3\text{TaO}_7$  is unusual, but not without precedent. The orthorhombic weberite-type structure is an ordered  $A_3\text{BO}_7$  superstructure of fluorite, formed by a combination of cation ordering and the presence of anion vacancies.<sup>82</sup> Previous studies have suggested final annealing temperatures of between 1200–1350 °C to successfully synthesise these materials.<sup>81,82</sup> This is in line with our *in situ* measurements, as the formation of  $\text{Ho}_3\text{TaO}_7$  from  $\text{Ho}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  reagents occurs within this temperature range. These *in situ* measurements show that the weberite-type structures can be

synthesised easily with a minimal heating and dwell time. This provides a potential avenue to explore them as thermal barrier coatings for gas turbines and aeroplane engines.<sup>84–87</sup> The *in situ* synthesis of metal oxides with minimal dwell time will be revisited in Chapter 5.

Stage 4: Two-phase region of  $\text{HoTaO}_4$  ( $P2/c$ ) and  $\text{Ho}_3\text{TaO}_7$  from 1340–1390 °C

With continued heating, the phase fraction of  $\text{Ho}_3\text{TaO}_7$  decreased whilst that of  $\text{HoTaO}_4$  ( $P2/c$ ) increased until  $\sim 1390$  °C, where peaks diagnostic of  $\text{Ho}_3\text{TaO}_7$  became indistinguishable from the background. That neither the initial metal oxides, nor  $\text{Ho}_3\text{TaO}_7$  are detected *in situ* above 1390 °C matches with previous *ex situ* studies that observed a pure  $\text{HoTaO}_4$  ( $P2/c$ ) structure upon cooling after annealing at 1400 °C for 48 hours.<sup>1</sup>

Stage 5: Conversion to the high temperature  $\text{HoTaO}_4$  ( $I4_1/a$ ) phase from 1390 °C

Heating the sample above 1390 °C resulted in the appearance of weak reflections diagnostic of the tetragonal scheelite-type structure. There was a wide temperature window from 1390–1450 °C in which the two phases ( $P2/c$  and  $I4_1/a$ ) coexisted, similar to that described in the heating study of  $\text{HoTaO}_4$ . The large two-phase region provides further evidence that this transformation is sluggish, suggesting incomplete conversion of  $P2/c \rightarrow I4_1/a$  is possible. This was seen earlier in the *ex situ* heating experiments with  $\text{ErTaO}_4$ , where a mixed  $I2/a + P2/c$  sample was recovered upon cooling to room temperature.<sup>2</sup> Further heating of the sample results in the complete conversion to the  $I4_1/a$  scheelite-type structure around  $\sim 1450$  °C and Rietveld refinement showed this to be phase pure up to 1500 °C (with the exception of the Nb can housing the sample).

Stage 6: Cooling the high temperature  $\text{HoTaO}_4$  phase back to room temperature

After heating the green powder to 1500 °C, the sample was maintained at this temperature for four hours before being cooled to near room temperature. NPD data was collected during the cooling, and the profiles displayed very similar characteristics to that of the cooling behaviour of  $\text{HoTaO}_4$  described earlier. The sample transformed from the high-temperature  $I4_1/a$  structure to the low-temperature  $I2/a$  phase at  $\sim 1300$  °C. By fitting the temperature dependence of the monoclinic  $\beta$  angle using Landau mean-field theory, similar values of the critical exponent  $\beta = 0.343$  and  $T_c = 1290$  °C were obtained.

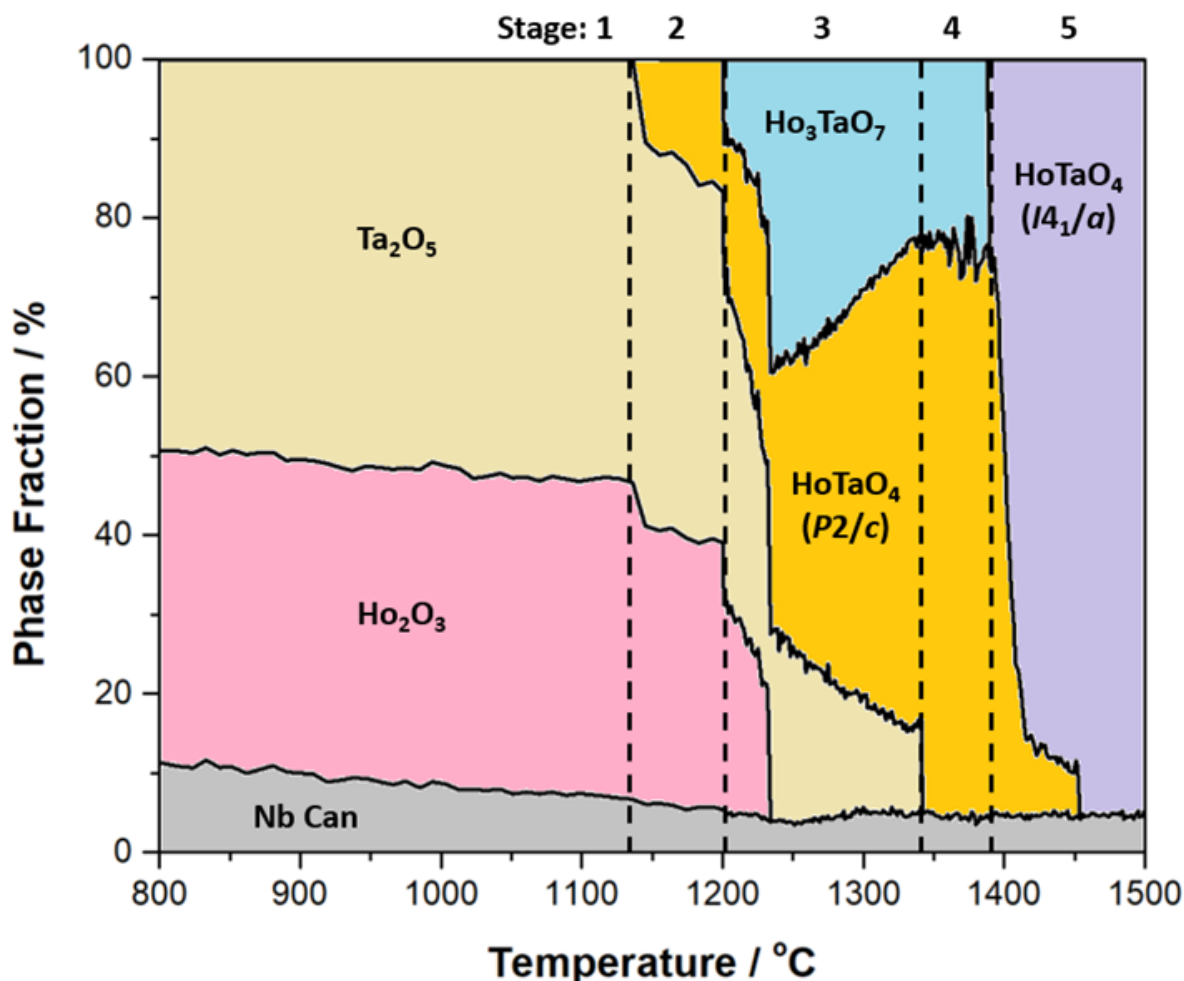


Figure 3.24: Refined phase fraction values extracted from *in situ* neutron powder diffraction study of the  $\text{Ho}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  green powder, as a function of temperature. For clarity, data below 800 °C is not shown. Samples were rapidly heated ( $180\text{ }^\circ\text{C hr}^{-1}$ ) to 1200 °C before being slowly heated ( $30\text{ }^\circ\text{C hr}^{-1}$ ) to 1500 °C. The data were collected at  $1.54\text{ \AA}$ .

It is interesting to note that, as described above, the  $I2/a$  phase was only observed upon cooling from the  $I4_1/a$  structure and was not evident at any stage during the heating of the  $\text{Ho}_2\text{O}_3 + \text{Ta}_2\text{O}_5$  green powder. The inability of the  $I4_1/a$  structure to cool back into the  $P2/c$  structure was described by Graham, where a rotational twinning between the two structures was identified.<sup>88</sup> Graham went on further to state that there is no simple mechanism to facilitate this transformation, meaning the metastable  $I2/a$  state is preferentially formed upon cooling. This data supports these findings.

This comprehensive study of the response of  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$  to heat establishes a number of important facts. Firstly, it identifies that the  $I2/a \rightarrow I4_1/a$  phase transition is pseudo-first order in both oxides. Neither oxide exhibits classical Landau mean-field

theory-type behaviour far from the phase transition, regardless of the order parameter chosen as evidenced by the intermediate values of the critical exponent  $\beta$ . Secondly, it reports the first *in situ* observation of the  $P2/c \rightarrow I4_1/a$  phase transition upon heating. HoTaO<sub>4</sub> was shown to undergo a first order phase transition, with both the  $P2/c$  and  $I4_1/a$  phases coexisting over an extended temperature range. This transition was also found to be irreversible, with cooling the sample resulting in the  $I2/a$  structure without reforming the  $P2/c$  structure. Finally, heating a green powder mixture of Ho<sub>2</sub>O<sub>3</sub> + Ta<sub>2</sub>O<sub>5</sub> results in a complex set of reactions and provides the first direct evidence for the formation of a weberite-type Ho<sub>3</sub>TaO<sub>7</sub> intermediate. That this intermediate phase is fast forming and only exists between 1200–1390 °C suggests a possible synthetic strategy for the isolation of this phase. This phase was also not detected upon cooling.

## 3.5 Ionic Conductivity Studies of HoNbO<sub>4</sub> and HoTaO<sub>4</sub>

### 3.5.1 Ionic Conductivity as a Function of Gas Environment

The conductivities of HoNbO<sub>4</sub> and HoTaO<sub>4</sub> were measured using EIS in the temperature range of 850–600 °C under different atmospheres (air, Ar, wet Ar, and wet 5% H<sub>2</sub> in Ar). After collecting the data in wet hydrogen, measurements in air were systematically repeated to verify the sample stability and regenerate the platinum cables and electrodes. Comparing the two measurements in air showed good data reproducibility and, therefore, excellent reliability. The total conductivity of each sample was calculated by the equivalence circuit method using the Nyquist plot. The results are reported in Figure 3.25 as Arrhenius plots (Equation 2.26). The conductivity values obtained were between 10<sup>-5</sup>–10<sup>-8</sup> S cm<sup>-1</sup>, showing an exponential reduction with a decrease in temperature typical of thermally-activated processes such as ionic diffusivity. The activation energies were calculated from linear fits to the Arrhenius plots.

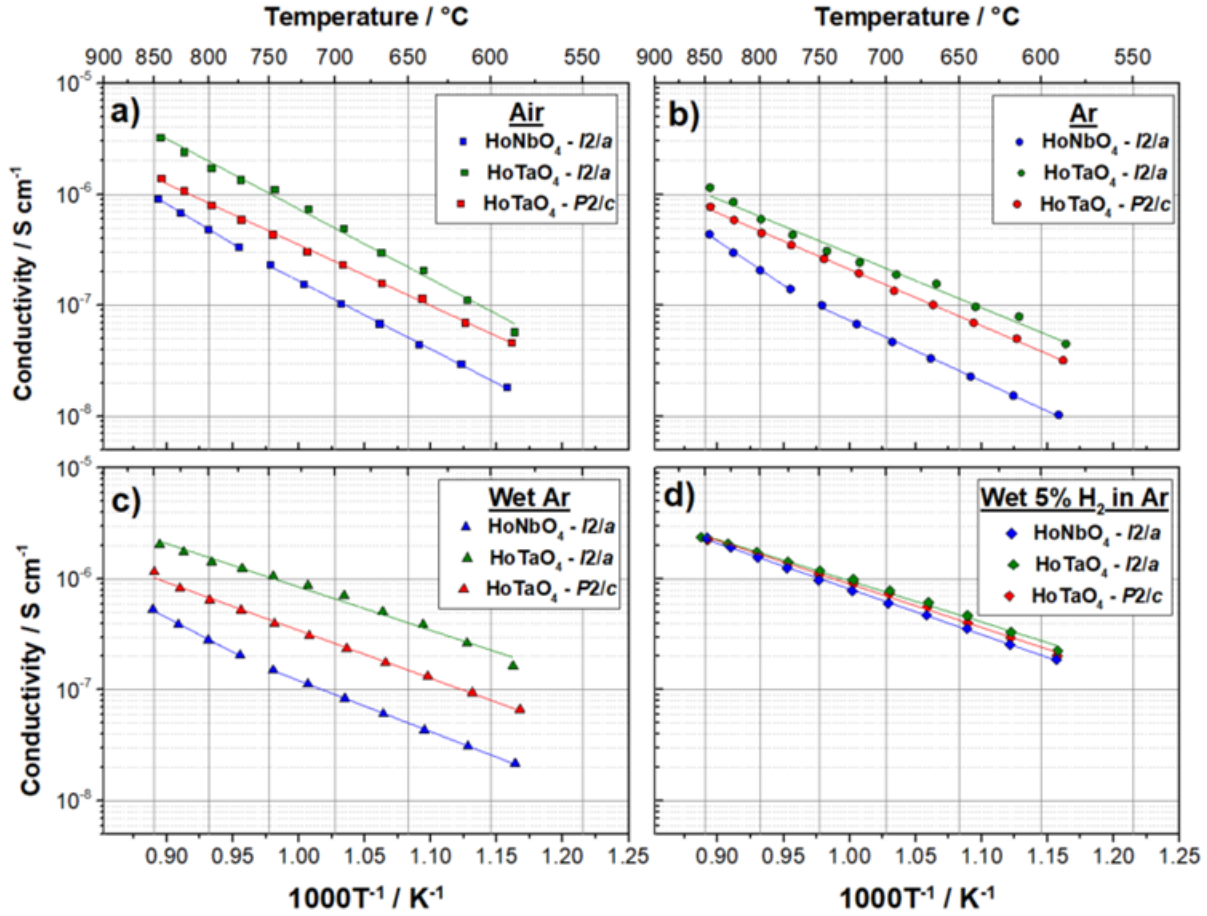


Figure 3.25: Conductivity results of  $\text{HoNbO}_4$  -  $I2/a$  (filled blue symbols),  $\text{HoTaO}_4$  -  $I2/a$  (filled green symbols), and  $\text{HoTaO}_4$  -  $P2/c$  (filled red symbols) in Arrhenius plots with logarithmic scale as a function of the inverse of the temperature measured at 850–600 °C in (a) air, (b) Ar, (c) wet Ar, and (d) wet 5%  $\text{H}_2$  in Ar.

The conductivity values are in line with results for similar  $\text{LnNbO}_4$  compounds.<sup>19,61,62</sup> Under dry conditions, the highest conductivities were obtained for  $\text{HoTaO}_4$  ( $I2/a$ ), followed by  $\text{HoTaO}_4$  ( $P2/c$ ), and  $\text{HoNbO}_4$  ( $I2/a$ ). Evidently, changing the  $B$ -site cation from  $\text{Nb}^{5+}$  to  $\text{Ta}^{5+}$  increases the conductivity of the  $I2/a$  phase. The conductivities in wet 5%  $\text{H}_2$  in Ar were essentially identical for the three samples. Both  $\text{HoTaO}_4$  phases show linear Arrhenius plots under all atmospheres. A change in the slope of the Arrhenius plot was observed in  $\text{HoNbO}_4$  for the measurements conducted in air, Ar, and wet Ar at  $\sim 775$  °C. This is associated with the  $I2/a \rightarrow I4_1/a$  phase transition. The high temperature scheelite-type phase has a higher activation energy, in contrast with the original hypothesis that the conductivity would be enhanced in the high-temperature phase because of the  $\text{Nb}^{5+}$  underbonding. In addition, the increase of the activation energy ( $E_{act}$ ) above the phase transition is also in contrast to the literature results obtained for

pure and *A* site-doped LaNbO<sub>4</sub> materials, suggesting the size of the *A*-site cation may play a role.<sup>19,61</sup> The related slope change in the HoTaO<sub>4</sub> materials is not observed, as the phase transition occurs at a much higher temperature than the measured ionic conductivity range.

The atmosphere-dependent  $E_{act}$  values are illustrated in Figure 3.26. Figure 3.26a contains an additional curve for HoNbO<sub>4</sub> for both the monoclinic *I2/a* and tetragonal *I4<sub>1</sub>/a* phases. A remarkable increase in  $E_{act}$  is observed for the tetragonal phase under all gaseous environments. The lowest value for HoNbO<sub>4</sub> is found in wet 5% H<sub>2</sub> in Ar (0.82 eV), which is similar to the trend observed for both HoTaO<sub>4</sub> phases (0.74 and 0.78 eV for *I2/a* and *P2/c*, respectively). A slight increase in  $E_{act}$  is observed for all samples in wet Ar, with the values increasing under Ar, and finally air. That adding water to the gases systematically reduces the  $E_{act}$  is a clear indication of protonic conductivity. The  $E_{act}$  values in air are quite large, which suggests that the resistance is dominated by transfer at the grain boundaries.<sup>89</sup> The addition of proton conduction lowers the estimated activation energy, but the grain boundary limitation is still present as pure bulk proton conductivity has  $E_{act} \sim 0.5$  eV.<sup>90</sup> Figure 3.26 also presents the conductivity values as a function of the gas environment that highlights the variation of conductivity between reducing and oxidising conditions.

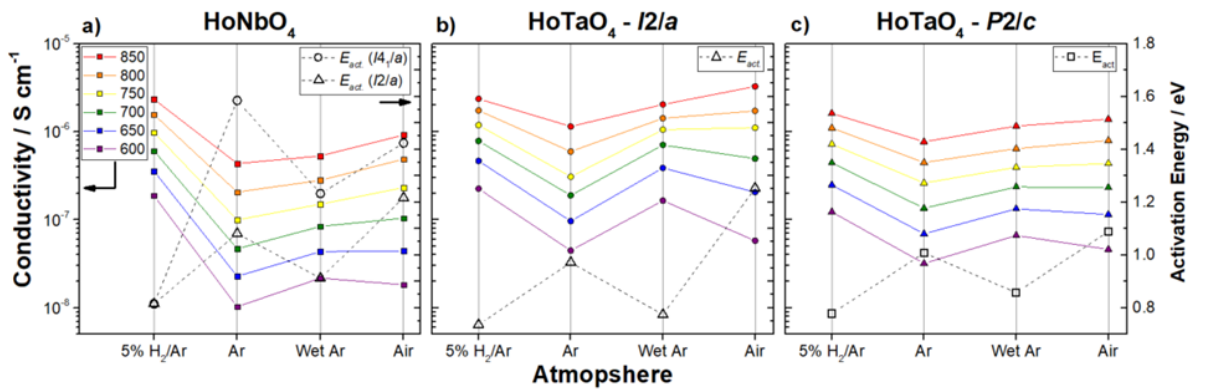


Figure 3.26: Conductivity results on a logarithmic scale (left axis) and activation energy (right scale) as a function of the atmosphere measured from 850–600 °C for (a) HoNbO<sub>4</sub>, (b) HoTaO<sub>4</sub> - *I2/a*, and (c) HoTaO<sub>4</sub> - *P2/c*. As HoNbO<sub>4</sub> exhibits a *I2/a* → *I4<sub>1</sub>/a* phase transition, the activation energy of both the monoclinic *I2/a* and tetragonal *I4<sub>1</sub>/a* phases are plotted.

### 3.5.2 Structural Studies of Ion Conduction Pathways

Given the highly accurate structures of  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$  obtained by NPD, an analysis of the potential conduction pathways was performed. Previous studies have highlighted the potential for oxygen ions to move *via* interstitial sites within  $\text{ABO}_4$ -type materials.<sup>20,91,92</sup> Huse *et al.* identified a correlation between ionic conductivity and the O–O distances separating the different  $\text{NbO}_6$  polyhedra in  $\text{LaNbO}_4$ .<sup>13</sup> A similar analysis was conducted with the O(1)–O(1) and O(1)–O(2) distances, determined from the analysis of the NPD datasets, to estimate the size of the conduction pathways (Figure 3.27). These values show a correlation between the average O–O distances and  $E_{act}$  in air (Figure A.11). Evidently, the conclusions drawn by Huse *et al.* extend to other  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  oxides.

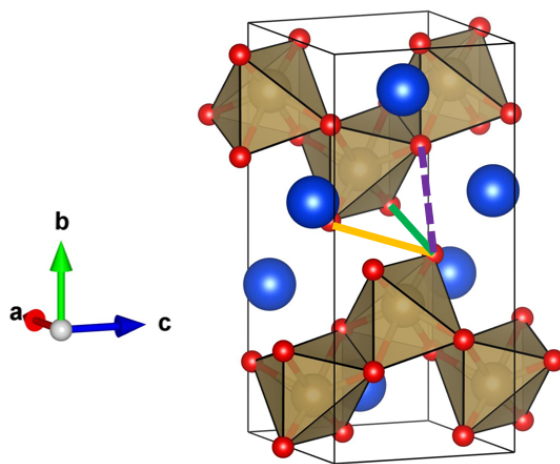


Figure 3.27: Refined structure of  $\text{HoTaO}_4$  ( $I2/a$ ) at room temperature. The solid green and orange lines represent the O(1)–O(1) distances, whilst the dashed purple line represents the O(1)–O(2) distance.

Further conclusions may be drawn based on the structural studies outlined in this dissertation. Firstly, larger *A*-site cations such as  $\text{La}^{3+}$  and  $\text{Nd}^{3+}$  have been identified as displaying higher ionic conductivity than their smaller  $\text{Ln}^{3+}$  counterparts.<sup>93</sup> The structural studies performed on  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  materials using SXRD supports this conclusion, with the cation–cation distances larger with larger *A*-site cations. Secondly, the high resolution combined SXRD and NPD study of  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  identified that  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  have slightly different atomic coordinates within the isostructural  $I2/a$  structures due to the difference in bonding requirements between the two cations. Calculating the *B*–*B* distances in these structures shows that Ta–Ta has a larger



separation than Nb–Nb, potentially contributing to the higher ionic conductivity exhibited in the  $\text{HoTaO}_4$  structures. Therefore, the combination of a large  $A$ -site cation, coupled with  $\text{Ta}^{5+}$  on the  $B$ -site is expected to yield a much better ion conductor that is stable in a large temperature range and to a variety of different gaseous environments.

As a final note, the  $I2/a$  and  $P2/c$  structures in  $\text{LnTaO}_4$  are different, as highlighted previously (Figure 3.5). The main difference is with the arrangement of the  $\text{TaO}_6$  octahedra chains, which are either ‘in-phase’ (in the  $P2/c$  structure) or ‘out-of-phase’ (in the  $I2/a$  structure). As this arrangement changes the potential ion conduction pathways within the material, this is worth further investigation using a combination of MD and *ab initio* techniques to determine whether the ionic conductivity could be enhanced in this phase.

## 3.6 Conclusions and Towards the Future Design of Solid Electrolytes

The present work provides accurate structures of the  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  materials at room temperature from Rietveld refinements of SXRD data. The data shows that while the  $\text{LnNbO}_4$  materials crystallise in the monoclinic  $I2/a$  space group, the  $\text{LnTaO}_4$  materials crystallise in the monoclinic  $P2_1/c$ ,  $I2/a$ , or  $P2/c$  space groups depending on the size of the  $\text{Ln}^{3+}$  cation. Furthermore, these samples appear to be sensitive to their thermal history, with some  $\text{LnTaO}_4$  materials ( $\text{Ln}^{3+} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$ ) synthesised in either the  $P2/c$  or  $I2/a$  space group depending on their final annealing temperature. Critically, this shows that the stability of the structures is not simply driven by the  $r_A/r_X$  and  $r_B/r_X$  IR ratios and steric effects, as suggested by the Errandonea *et al.*  $\text{ABX}_4$  phase diagram (Figure 1.3).<sup>26</sup>

For both  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$ , increasing the size of the  $\text{Ln}^{3+}$  cation results in an increase in the lattice parameters and unit cell volume. Bond valence sum calculations show that the  $\text{Nb}^{5+}$  cations are best described as six-coordinate distorted octahedra rather than four-coordinate tetrahedra, with four short Nb–O bonds ( $\sim 1.9$  Å) and two longer

Nb–O<sub>l</sub> bonds ( $\sim 2.5$  Å). Similar calculations confirm that the Ta<sup>5+</sup> cations are also best described as six-coordinate distorted octahedra in all three monoclinic structure types, with a similar distortion to the NbO<sub>6</sub> polyhedra found in *Ln*NbO<sub>4</sub>. Structural studies also highlighted the importance of these longer B–O<sub>l</sub> bonds, with a correlation found between the size of the *Ln*<sup>3+</sup> cation and the length of the Nb–O<sub>l</sub> and Ta–O<sub>l</sub> bonds. This correlation matches well with the predicted phase transition behaviour in these materials, with smaller *Ln*<sup>3+</sup> cations (and, by extension, shorter and stronger Nb–O<sub>l</sub> and Ta–O<sub>l</sub> bonds) leading to a higher temperature for the *I*2/*a* → *I*4<sub>1</sub>/*a* phase transition.

A comparison between the Nb<sup>5+</sup> and Ta<sup>5+</sup> cations was investigated by analysing solid solution series of the form *Ln*(Nb<sub>1–*x*</sub>Ta<sub>*x*</sub>)O<sub>4</sub>. For the Pr(Nb<sub>1–*x*</sub>Ta<sub>*x*</sub>)O<sub>4</sub> series, the *I*2/*a* → *P*2<sub>1</sub>/*c* phase transition occurred suddenly, potentially reflecting the different connectivity of the TaO<sub>6</sub> octahedra between the two phases. For Yb(Nb<sub>1–*x*</sub>Ta<sub>*x*</sub>)O<sub>4</sub>, the *I*2/*a* → *P*2/*c* phase transition is much more sluggish, with a two-phase region detected. For *Ln*(Nb<sub>1–*x*</sub>Ta<sub>*x*</sub>)O<sub>4</sub> (*Ln*<sup>3+</sup> = Nd–Ho), the orthotantalates were consistently observed to be smaller than their isostructural orthoniobate counterparts, in contrast to what is predicted by Shannon’s IR.<sup>24</sup> Further analysis revealed that the magnitude of this difference was dependent on the size of the *Ln*<sup>3+</sup> cation, suggesting an interaction between the *Ln*O<sub>8</sub> and BO<sub>6</sub> polyhedra in the fergusonite-type structures not seen in other similar metal oxides.

Analysis of a combined SXRD and NPD dataset of Ho(Nb<sub>1–*x*</sub>Ta<sub>*x*</sub>)O<sub>4</sub> revealed slight differences across the series. The average Ho–O and B–O bond distances were invariant of the Ta<sup>5+</sup> content. However, inspection of the individual bond lengths revealed shortening of the B–O<sub>l</sub> bonds, presumably due to the greater hybridisation between O 2*p* and the more radially extended Ta 5*d* compared to Nb 4*d*. This was verified using DFT, demonstrating that these longer contacts possess significant covalent character based on the BEC. DFT calculations also predict an increase in the band gap energy for *Ln*TaO<sub>4</sub> materials compared to *Ln*NbO<sub>4</sub>; a prediction that was verified experimentally using UV-Vis DRS.

Variable temperature NPD measurements of  $\text{HoNbO}_4$  reveal a reversible  $I2/a \rightarrow I4_1/a$  phase transition at  $\sim 775^\circ\text{C}$ , that involved breaking of the longer Nb–O<sub>l</sub> to form NbO<sub>4</sub> tetrahedra from NbO<sub>6</sub> octahedra. Landau mean-field theory revealed that neither the spontaneous strains, nor the monoclinic  $\beta$  angle were well modelled across the entire temperature range. Therefore, it was deduced that the  $I2/a \rightarrow I4_1/a$  phase transition is pseudo-first order, with potential coupling between the breaking of the Nb–O<sub>l</sub> bond and rotation of the NbO<sub>6</sub>/NbO<sub>4</sub> polyhedra governed by the  $\Gamma_2^+$  mode.  $\text{HoTaO}_4$  can be isolated as either the  $P2/c$  or  $I2/a$  phase based on its thermal history, with *in situ* diffraction measurements revealing the necessity of the high temperature  $P2/c \rightarrow I4_1/a$  phase transition before cooling and forming the  $I2/a$  structure. Heating a green powder mixture of  $\text{Ho}_2\text{O}_3 + \text{Ta}_2\text{O}_5$  results in a complex series of reactions and provides the first direct evidence for the formation of a weberite-type  $\text{Ho}_3\text{TaO}_7$  intermediate.

Both  $\text{HoTaO}_4$  and  $\text{HoNbO}_4$  can act as mixed oxide/proton conductors, with slightly higher conductivities observed in the more distorted orthotantalates. It is postulated this is a consequence of the subtle differences in the electronic properties of the Nb<sup>5+</sup> and Ta<sup>5+</sup> cations leading to more open channels for ionic conductivity in  $\text{HoTaO}_4$ . Structural analysis also highlights the significant role of the A-site cation to increase the size of the O–O channels in the structure, and hence, improving the overall conductivity of these materials.

Based on the structure-functionality relationships outlined for  $\text{ABO}_4$  materials as solid electrolytes, the following conclusions can be drawn regarding the requirements of engineering potential ion conductors:

- Large A-site cations: The size of the A-site cation clearly plays a role in the overall conductivity of the material. While  $\text{Ho}^{3+}$  was chosen to compare the  $I2/a$  and  $P2/c$  phases, larger cations such as  $\text{La}^{3+}$  can be incorporated to ‘open up’ the structure, increase the distance between the O–O anions, and allowing for greater conductivity. Further studies should be performed with larger cations to compare the  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  materials, such as  $\text{NdNbO}_4$  and  $\text{NdTaO}_4$  (both isostructural in  $I2/a$ ), as well as  $\text{TbTaO}_4$  (which can be synthesised in either  $P2/c$  or  $I2/a$  depending on its annealing temperature).

- Large separation between  $B$ -site cations: The interaction between the  $B$ -site cations also plays a role in the overall conductivity. As determined by the room temperature structure analysis,  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  cations sit at slightly different atomic positions in the  $I2/a$  structure as a result of subtle differences in their electronic structures. These different positions also contribute to ‘opening up’ the O–O channels in the structure, allowing for greater ionic movement and conductivity.
- Potential for oxygen vacancies: Based on the ionic conductivity studies of  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$ , the highest ionic conductivities and lowest activation energies were, in general, recorded in a 5%  $\text{H}_2$  atmosphere in wet Ar; a clear indication of  $p$ -type conductivity. In order to enhance this further, doping onto the  $B$  site should be investigated that could potentially lead to oxygen vacancies, such as substituting pentavalent cations for quadravalent cations like  $\text{Ge}^{4+}$  or  $\text{Si}^{4+}$ . Although limited solubility was noted by Brandão *et al.*, their ionic conductivity properties are still worth further investigation.<sup>55</sup> One potential substitution is  $\text{Fe}^{4+}$ , which is smaller than both  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$ , allowing for the tuning of the  $I2/a \rightarrow I4_1/a$  phase transition. This has been similarly investigated for other applications, such as Fe-doped  $\text{SrWO}_4$  as a hydrogen evolution catalyst,<sup>94</sup>
- No change in oxidation states in the cations: Attempts were made to determine the ionic conductivity of mixed  $B$ -site cations, such as  $\text{La}(\text{Nb}_{0.65}\text{V}_{0.3}\text{Mo}_{0.05})\text{O}_{4+\delta}$ . Although these materials showed a substantial increase in ionic conductivity (almost three orders of magnitude greater than  $\text{LaNbO}_4$  in dry air, see Figure A.12), the data were nonreproducible between runs. Specifically, the dry air data at the beginning and end of the experiment (after exposing the sample to harsh conditions, such as 5%  $\text{H}_2$  in Ar) showed a large degradation in performance. This was presumably due to the possible reduction of  $\text{V}^{5+}$  and  $\text{Mo}^{6+}$ , although was never quantified experimentally using X-ray absorption spectroscopy. An increase in activation energy was also determined for  $\text{La}(\text{Nb}_{0.65}\text{V}_{0.3}\text{Mo}_{0.05})\text{O}_{4+\delta}$  compared to  $\text{LaNbO}_4$  (increasing from 0.902(14) eV to 1.010(7) eV), implying that a complex  $B$ -site environment can lead to detrimental ion-trapping effects.<sup>59,95</sup>

- Lack of phase transition: Although not unique to this work, the presence of a first order phase transition can lead to material swelling and straining, potentially having a detrimental effect on the performance of the solid electrolyte after thermal cycling. For  $ABO_4$  structures,  $B^{5+} = \text{Ta}$  looms as a promising candidate for ionic conductors due to their lack of phase transitions within the operational temperature of SOFCs.



# Bibliography

- (1) Mullens, B. G.; Avdeev, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Insights into the structural variations in  $\text{Sm}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  and  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  combined experimental and computational studies. *Dalton Transactions* **2021**, 50, 9103–9117.
- (2) Mullens, B. G.; Saura-Múzquiz, M.; Marlton, F. P.; Avdeev, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Beyond the ionic radii: A multifaceted approach to understand differences between the structures of  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  fergusonites. *Journal of Alloys and Compounds* **2023**, 930, 167399.
- (3) Saura-Múzquiz, M.; Mullens, B. G.; Maynard-Casely, H. E.; Kennedy, B. J. Neutron diffraction study of the monoclinic–tetragonal phase transition in  $\text{NdNbO}_4$  and  $\text{NdTaO}_4$ . *Dalton Transactions* **2021**, 50, 11485–11497.
- (4) Radojković, A.; Žunić, M.; Savić, S. M.; Perać, S.; Golić, D. L.; Branković, Z.; Branković, G. Co-doping as a strategy for tailoring the electrolyte properties of  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ . *Ceramics International* **2019**, 45, 8279–8285.
- (5) Díaz-Guillén, J.; Díaz-Guillén, M.; Padmasree, K.; Fuentes, A.; Santamaría, J.; León, C. High ionic conductivity in the pyrochlore-type  $\text{Gd}_{2-y}\text{La}_y\text{Zr}_2\text{O}_7$  solid solution ( $0 \leq y \leq 1$ ). *Solid State Ionics* **2008**, 179, 2160–2164.
- (6) Anantharaman, A. P.; Dasari, H. P. Potential of pyrochlore structure materials in solid oxide fuel cell applications. *Ceramics International* **2021**, 47, 4367–4388.

- (7) Chen, X.; Khor, K.; Chan, S.; Yu, L. Influence of microstructure on the ionic conductivity of yttria-stabilized zirconia electrolyte. *Materials Science and Engineering: A* **2002**, *335*, 246–252.
- (8) Kreuer, K. On the development of proton conducting materials for technological applications. *Solid State Ionics* **1997**, *97*, 1–15.
- (9) David, W. The high-temperature paraelastic structure of  $\text{LaNbO}_4$ . *Materials Research Bulletin* **1983**, *18*, 749–756.
- (10) Kuroiwa, Y.; Muramoto, H.; Shobu, T.; Tokumichi, H.; Yamada, Y. Pretransitional phenomena at the first-order phase transition in  $\text{LaNbO}_4$ . *Journal of the Physical Society of Japan* **1995**, *64*, 3798–3803.
- (11) Fjeld, H.; Toyoura, K.; Haugrud, R.; Norby, T. Proton mobility through a second order phase transition: Theoretical and experimental study of  $\text{LaNbO}_4$ . *Physical Chemistry Chemical Physics* **2010**, *12*, 10313–10319.
- (12) Hara, K.; Sakai, A.; Tsunekawa, S.; Sawada, A.; Ishibashi, Y.; Yagi, T. A soft acoustic mode in the ferroelastic phase transition of  $\text{LaNbO}_4$ . *Journal of the Physical Society of Japan* **1985**, *54*, 1168–1172.
- (13) Huse, M.; Skilbred, A.; Karlsson, M.; Eriksson, S. G.; Norby, T.; Haugrud, R.; Knee, C. S. Neutron diffraction study of the monoclinic to tetragonal structural transition in  $\text{LaNbO}_4$  and its relation to proton mobility. *Journal of Solid State Chemistry* **2012**, *187*, 27–34.
- (14) Sarin, P.; Hughes, R. W.; Lowry, D. R.; Apostolov, Z. D.; Kriven, W. M. High-temperature properties and ferroelastic phase transitions in rare-earth niobates ( $\text{LnNbO}_4$ ). *Journal of the American Ceramic Society* **2014**, *97*, 3307–3319.
- (15) Arulnesan, S. W.; Kayser, P.; Kimpton, J. A.; Kennedy, B. J. Studies of the fergusonite to scheelite phase transition in  $\text{LnNbO}_4$  orthoniobates. *Journal of Solid State Chemistry* **2019**, *277*, 229–239.
- (16) Stubičan, V. High-temperature transitions in rare-earth niobates and tantalates. *Journal of the American Ceramic Society* **1964**, *47*, 55–58.
- (17) David, W. Transition temperature — Spontaneous strain — Atomic displacement relationships in ferroelastics. *Materials Research Bulletin* **1983**, *18*, 809–816.



## BIBLIOGRAPHY

---

- (18) Packer, R.; Tsipis, E.; Munnings, C.; Kharton, V.; Skinner, S.; Frade, J. Diffusion and conductivity properties of cerium niobate. *Solid State Ionics* **2006**, *177*, 2059–2064.
- (19) Bi, Z.; Peña-Martínez, J.; Kim, J.-H.; Bridges, C. A.; Huq, A.; Hodges, J. P.; Paranthaman, M. P. Effect of Ca doping on the electrical conductivity of the high temperature proton conductor  $\text{LaNbO}_4$ . *International Journal of Hydrogen Energy* **2012**, *37*, 12751–12759.
- (20) Ferrara, C.; Mancini, A.; Ritter, C.; Malavasi, L.; Tealdi, C. Interstitial oxide ion migration in scheelite-type electrolytes: A combined neutron diffraction and computational study. *Journal of Materials Chemistry A* **2015**, *3*, 22258–22265.
- (21) Packer, R.; Skinner, S. Remarkable oxide ion conductivity observed at low temperatures in a complex superstructured oxide. *Advanced Materials* **2010**, *22*, 1613–1616.
- (22) Haugsrud, R.; Norby, T. Proton conduction in rare-earth ortho-niobates and ortho-tantalates. *Nature Materials* **2006**, *5*, 193–196.
- (23) Machida, M.; Murakami, S.; Kijima, T.; Matsushima, S.; Arai, M. Photocatalytic property and electronic structure of lanthanide tantalates,  $\text{LnTaO}_4$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{and Sm}$ ). *The Journal of Physical Chemistry B* **2001**, *105*, 3289–3294.
- (24) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **1976**, *32*, 751–767.
- (25) Siqueira, K. P.; Dias, A. Effect of the processing parameters on the crystalline structure of lanthanide orthotantalates. *Materials Research* **2014**, *17*, 167–173.
- (26) Errandonea, D.; Manjon, F. J. Pressure effects on the structural and electronic properties of  $\text{ABX}_4$  scintillating crystals. *Progress in Materials Science* **2008**, *53*, 711–773.
- (27) Wallwork, K. S.; Kennedy, B. J.; Wang, D. In *AIP Conference Proceedings*, 2007; Vol. 879, pp 879–882.

- (28) Liss, K.-D.; Hunter, B.; Hagen, M.; Noakes, T.; Kennedy, S. Echidna — The new high-resolution powder diffractometer being built at OPAL. *Physica B: Condensed Matter* **2006**, *385*, 1010–1012.
- (29) Studer, A. J.; Hagen, M. E.; Noakes, T. J. Wombat: The high-intensity powder diffractometer at the OPAL reactor. *Physica B: Condensed Matter* **2006**, *385*, 1013–1015.
- (30) Coelho, A. A. TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++. *Journal of Applied Crystallography* **2018**, *51*, 210–218.
- (31) Thompson, P.; Cox, D.; Hastings, J. Rietveld refinement of Debye–Scherrer synchrotron X-ray data from Al<sub>2</sub>O<sub>3</sub>. *Journal of Applied Crystallography* **1987**, *20*, 79–83.
- (32) Stephens, P. W. Phenomenological model of anisotropic peak broadening in powder diffraction. *Journal of Applied Crystallography* **1999**, *32*, 281–289.
- (33) Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* **2011**, *44*, 1272–1276.
- (34) Rooksby, H.; White, E. The structures of 1:1 compounds of rare earth oxides with niobia and tantala. *Acta Crystallographica* **1963**, *16*, 888–890.
- (35) David, W. High resolution neutron powder diffraction studies of the ferroelastic phase transition in LaNbO<sub>4</sub>. *MRS Online Proceedings Library (OPL)* **1989**, *166*.
- (36) Sakowski-Cowley, A.; Łukaszewicz, K.; Megaw, H. D. The structure of sodium niobate at room temperature, and the problem of reliability in pseudosymmetric structures. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* **1969**, *25*, 851–865.
- (37) Jacquet, Q.; Rousse, G.; Iadecola, A.; Saubanère, M.; Doublet, M.-L.; Tarascon, J.-M. Electrostatic interactions versus second order Jahn–Teller distortion as the source of structural diversity in Li<sub>3</sub>MO<sub>4</sub> compounds (*M* = Ru, Nb, Sb and Ta). *Chemistry of Materials* **2018**, *30*, 392–402.

## BIBLIOGRAPHY

---

- (38) Ok, K. M.; Orzechowski, J.; Halasyamani, P. S. Synthesis, structure, and characterization of two new layered mixed-metal phosphates,  $\text{BaTeMO}_4(\text{PO}_4)$  ( $M = \text{Nb}^{5+}$  or  $\text{Ta}^{5+}$ ). *Inorganic Chemistry* **2004**, *43*, 964–968.
- (39) Kennedy, B. J. Structure of  $\text{ABi}_2\text{Nb}_2\text{O}_9$  ( $A = \text{Sr}, \text{Ba}$ ): Refinement of powder neutron diffraction data. *Journal of Solid State Chemistry* **1996**, *126*, 135–141.
- (40) Bayliss, R. D.; Pramana, S. S.; An, T.; Wei, F.; Kloc, C. L.; White, A. J.; Skinner, S. J.; White, T. J.; Baikie, T. Fergusonite-type  $\text{CeNbO}_{4+\delta}$ : Single crystal growth, symmetry revision and conductivity. *Journal of Solid State Chemistry* **2013**, *204*, 291–297.
- (41) Fulle, K.; McMillen, C. D.; Sanjeeva, L. D.; Kolis, J. W. Hydrothermal chemistry and growth of fergusonite-type  $\text{RENbO}_4$  ( $RE = \text{La-Lu}, \text{Y}$ ) single crystals and new niobate hydroxides. *Crystal Growth & Design* **2016**, *16*, 4910–4917.
- (42) Brese, N.; O’Keeffe, M. Bond-valence parameters for solids. *Acta Crystallographica Section B: Structural Science* **1991**, *47*, 192–197.
- (43) Haugsrud, R.; Norby, T. High-temperature proton conductivity in acceptor-doped  $\text{LaNbO}_4$ . *Solid State Ionics* **2006**, *177*, 1129–1135.
- (44) Brixner, L. On the structural and luminescent properties of the  $M'$   $\text{LnTaO}_4$  rare earth tantalates. *Journal of the Electrochemical Society* **1983**, *130*, 2435.
- (45) Roth, R. S.; Negas, T.; Parker, H.; Minor, D.; Jones, C. Crystal chemistry of cerium titanates, tantalates and niobates. *Materials Research Bulletin* **1977**, *12*, 1173–1182.
- (46) Howieson, G. W.; Wu, S.; Gibbs, A. S.; Zhou, W.; Scott, J. F.; Morrison, F. D. Incommensurate–commensurate transition in the geometric ferroelectric  $\text{LaTaO}_4$ . *Advanced Functional Materials* **2020**, *30*, 2004667.
- (47) Hartenbach, I.; Lissner, F.; Nikelski, T.; Meier, S. F.; Müller-Bunz, H.; Schleid, T. Über oxotantalate der lanthanide des formeltyps  $\text{MTaO}_4$  ( $M = \text{La-Nd}, \text{Sm-Lu}$ ). *Zeitschrift für Anorganische und Allgemeine Chemie* **2005**, *631*, 2377–2382.
- (48) Wang, J.; Chong, X.; Zhou, R.; Feng, J. Microstructure and thermal properties of  $\text{RETaO}_4$  ( $RE = \text{Nd}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Er}, \text{Yb}, \text{Lu}$ ) as promising thermal barrier coating materials. *Scripta Materialia* **2017**, *126*, 24–28.

- (49) Guskov, V.; Gavrichev, K. Thermal expansion, heat capacity, and thermodynamic properties of monoclinic lanthanide orthotantalates: A review. *Russian Journal of Inorganic Chemistry* **2021**, *66*, 1947–1972.
- (50) Haugrud, R.; Norby, T. High-temperature proton conductivity in acceptor-substituted rare-earth ortho-tantalates,  $LnTaO_4$ . *Journal of the American Ceramic Society* **2007**, *90*, 1116–1121.
- (51) Whittaker, E.; Muntus, R. Ionic radii for use in geochemistry. *Geochimica et Cosmochimica Acta* **1970**, *34*, 945–956.
- (52) Barnes, P. W.; Lufaso, M. W.; Woodward, P. M. Structure determination of  $A_2M^{3+}TaO_6$  and  $A_2M^{3+}NbO_6$  ordered perovskites: Octahedral tilting and pseudosymmetry. *Acta Crystallographica Section B: Structural Science* **2006**, *62*, 384–396.
- (53) Shimakawa, Y.; Kubo, Y.; Tauchi, Y.; Kamiyama, T.; Asano, H.; Izumi, F. Structural distortion and ferroelectric properties of  $SrBi_2(Ta_{1-x}Nb_x)_2O_9$ . *Applied Physics Letters* **2000**, *77*, 2749–2751.
- (54) Lufaso, M. W. Crystal structures, modeling, and dielectric property relationships of 2:1 ordered  $Ba_3MM'_2O_9$  ( $M = Mg, Ni, Zn$ ;  $M' = Nb, Ta$ ) perovskites. *Chemistry of Materials* **2004**, *16*, 2148–2156.
- (55) Brandão, A.; Gracio, J.; Mather, G.; Kharton, V.; Fagg, D. B-site substitutions in  $LaNb_{1-x}M_xO_{4-\delta}$  materials in the search for potential proton conductors ( $M = Ga, Ge, Si, B, Ti, Zr, P, Al$ ). *Journal of Solid State Chemistry* **2011**, *184*, 863–870.
- (56) Wachowski, S.; Mielewczyk-Gryn, A.; Gazda, M. Effect of isovalent substitution on microstructure and phase transition of  $LaNb_{1-x}M_xO_4$  ( $M = Sb, V$  or  $Ta$ ;  $x = 0.05$ – $0.3$ ). *Journal of Solid State Chemistry* **2014**, *219*, 201–209.
- (57) Wachowski, S.; Mielewczyk-Gryn, A.; Zagórski, K.; Li, C.; Jasiński, P.; Skinner, S. J.; Haugrud, R.; Gazda, M. Influence of Sb-substitution on ionic transport in lanthanum orthoniobates. *Journal of Materials Chemistry A* **2016**, *4*, 11696–11707.

## BIBLIOGRAPHY

---

- (58) Guo, D.; Zhou, D.; Li, W.-B.; Pang, L.-X.; Dai, Y.-Z.; Qi, Z.-M. Phase evolution, crystal structure, and microwave dielectric properties of water-insoluble  $(1-x)\text{LaNbO}_4-x\text{LaVO}_4$  ( $0 \leq x \leq 0.9$ ) ceramics. *Inorganic Chemistry* **2017**, *56*, 9321–9329.
- (59) Auckett, J. E.; Lopez-Odriozola, L.; Clark, S. J.; Evans, I. R. Exploring the nature of the fergusonite–scheelite phase transition and ionic conductivity enhancement by  $\text{Mo}^{6+}$  doping in  $\text{LaNbO}_4$ . *Journal of Materials Chemistry A* **2021**, *9*, 4091–4102.
- (60) Canu, G.; Giannici, F.; Chiara, A.; Confalonieri, G.; Longo, A.; Buscaglia, M. T.; Dapiaggi, M.; Buscaglia, V.; Martorana, A. Characterisation of scheelite  $\text{LaW}_{0.16}\text{Nb}_{0.84}\text{O}_{4.08}$  ion conductor by combined synchrotron techniques: Structure, W oxidation state and interdiffusion. *Journal of Alloys and Compounds* **2021**, *857*, 157532.
- (61) Li, C.; Bayliss, R. D.; Skinner, S. J. Crystal structure and potential interstitial oxide ion conductivity of  $\text{LnNbO}_4$  and  $\text{LnNb}_{0.92}\text{W}_{0.08}\text{O}_{4.04}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$ ). *Solid State Ionics* **2014**, *262*, 530–535.
- (62) Cao, Y.; Duan, N.; Wang, X.; Chi, B.; Jian, L. Enhanced electrical conductivity of Mo-doped  $\text{LaNbO}_4$ . *Journal of the European Ceramic Society* **2015**, *35*, 1979–1983.
- (63) Ramarao, S.; Murthy, V. Structural phase transformation and microwave dielectric studies of  $\text{SmNb}_{1-x}(\text{Si}_{1/2}\text{Mo}_{1/2})_x\text{O}_4$  compounds with fergusonite structure. *Physical Chemistry Chemical Physics* **2015**, *17*, 12623–12633.
- (64) Norby, T.; Magrasó, A. On the development of proton ceramic fuel cells based on Ca-doped  $\text{LaNbO}_4$  as electrolyte. *Journal of Power Sources* **2015**, *282*, 28–33.
- (65) Mather, G. C.; Fisher, C. A.; Islam, M. S. Defects, dopants, and protons in  $\text{LaNbO}_4$ . *Chemistry of Materials* **2010**, *22*, 5912–5917.
- (66) Injac, S.; Yuen, A. K.; Avdeev, M.; Wang, C.-H.; Turner, P.; Brand, H. E.; Kennedy, B. J. Structural and magnetic studies of  $\text{ABO}_4$ -type ruthenium and osmium oxides. *Inorganic Chemistry* **2020**, *59*, 2791–2802.

- (67) Lukens, W. W.; McKeown, D. A.; Buechele, A. C.; Muller, I. S.; Shuh, D. K.; Pegg, I. L. Dissimilar behavior of technetium and rhenium in borosilicate waste glass as determined by X-ray absorption spectroscopy. *Chemistry of Materials* **2007**, *19*, 559–566.
- (68) Reynolds, E. M.; Yu, M.; Thorogood, G. J.; Brand, H. E.; Poineau, F.; Kennedy, B. J. Thermal expansion of ammonium pertechnetate and ammonium perrhenate. *Journal of Solid State Chemistry* **2019**, *274*, 64–68.
- (69) Garg, A.; Errandonea, D.; Rodríguez-Hernández, P.; Muñoz, A. High-pressure monoclinic–monoclinic transition in fergusonite-type  $\text{HoNbO}_4$ . *Journal of Physics: Condensed Matter* **2021**, *33*, 195401.
- (70) Brunckova, H.; Mudra, E.; Medvecký, L.; Kovalčíková, A.; Durisin, J.; Sebek, M.; Girman, V. Effect of lanthanides on phase transformation and structural properties of  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  thin films. *Materials & Design* **2017**, *134*, 455–468.
- (71) Errandonea, D. Landau theory applied to phase transitions in calcium orthotungstate and isostructural compounds. *Europhysics Letters* **2007**, *77*, 56001.
- (72) Gu, B.; Cummins, H.; Qiu, S.; Copic, M. Acoustic soft modes and the ferroelastic phase transition in  $\text{BiVO}_4$  and  $\text{LaNbO}_4$ . *Ferroelectrics* **1983**, *52*, 45–57.
- (73) Wada, M.; Nakayama, Y.; Sawada, A.; Tsunekawa, S.; Ishibashi, Y. Raman scattering and fluorescence spectra of  $\text{LaNbO}_4$ . *Journal of the Physical Society of Japan* **1979**, *47*, 1575–1580.
- (74) Stokes, H. T.; Orden, S. v.; Campbell, B. J. ISOSUBGROUP: An internet tool for generating isotropy subgroups of crystallographic space groups. *Journal of Applied Crystallography* **2016**, *49*, 1849–1853.
- (75) Aizu, K. Determination of the state parameters and formulation of spontaneous strain for ferroelastics. *Journal of the Physical Society of Japan* **1970**, *28*, 706–716.
- (76) Schlenker, J. L.; Gibbs, G.; Boisen, M. Strain-tensor components expressed in terms of lattice parameters. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **1978**, *34*, 52–54.

## BIBLIOGRAPHY

---

- (77) Perez-Mato, J.; Orobengoa, D.; Aroyo, M. Mode crystallography of distorted structures. *Acta Crystallographica Section A: Foundations of Crystallography* **2010**, *66*, 558–590.
- (78) Antic, B.; Mitric, M.; Rodic, D. Structure properties and magnetic susceptibility of diluted magnetic semiconductor  $Y_{2-x}Ho_xO_3$ . *Journal of Magnetism and Magnetic Materials* **1995**, *145*, 349–356.
- (79) Maslen, E.; Streltsov, V.; Ishizawa, N. A synchrotron X-ray study of the electron density in *C*-type rare earth oxides. *Acta Crystallographica Section B: Structural Science* **1996**, *52*, 414–422.
- (80) Stephenson, N.; Roth, R. Structural systematics in the binary system  $Ta_2O_5-WO_3$ . V. The structure of the low-temperature form of tantalum oxide *L-Ta\_2O\_5*. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* **1971**, *27*, 1037–1044.
- (81) Subramani, T.; Navrotsky, A. Energetics of formation and disordering in rare earth weberite  $RE_3TaO_7$  materials. *Inorganic chemistry* **2019**, *58*, 16126–16133.
- (82) Gushev, I. M.; O’Quinn, E. C.; Baldinozzi, G.; Neuefeind, J.; Ewing, R. C.; Zhang, F.; Lang, M. Local order of orthorhombic weberite-type  $Y_3TaO_7$  as determined by neutron total scattering and density functional theory calculations. *Acta Materialia* **2020**, *196*, 704–709.
- (83) Gushev, I. M.; O’Quinn, E. C.; Tucker, M.; Ewing, R. C.; Overstreet, C.; Neuefeind, J.; Everett, M.; Zhang, Q.; Sprouster, D.; Olds, D. Systematic study of short-and long-range correlations in  $RE_3TaO_7$  weberite-type compounds by neutron total scattering and X-ray diffraction. *Journal of Materials Chemistry A* **2023**, *11*, 8886–8903.
- (84) Shi, D.; Cao, Z.; Huang, Y.; Wu, W.; Gong, Y.; Wan, C.; Yang, J. Highly efficient thermal insulation in crystalline weberites  $RE_3NbO_7$  ( $RE = La, Nd, Sm, Eu, Gd$ ) with glass-like thermal conductivity. *Ceramics International* **2022**, *48*, 2686–2692.
- (85) Wu, F.; Wu, P.; Chen, L.; Feng, J. Structure and thermal properties of  $Al_2O_3$ -doped  $Gd_3TaO_7$  as potential thermal barrier coating. *Journal of the European Ceramic Society* **2019**, *39*, 2210–2214.

- (86) Qian, Z.; Kui, L.; Shi-Huai, W.; Hongsong, Z.; Xianfeng, Y.; Weiwei, S.; Yongtao, Z.; An, T. Synthesis and thermophysical performances of  $(\text{Nd}_{1-x}\text{Yb}_x)_2\text{AlTaO}_7$  oxides for heat-insulation coating applications. *Ceramics International* **2020**, *46*, 26754–26759.
- (87) Chen, L.; Wu, P.; Song, P.; Feng, J. Potential thermal barrier coating materials:  $\text{RE}_3\text{NbO}_7$  ( $\text{RE} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$ ) ceramics. *Journal of the American Ceramic Society* **2018**, *101*, 4503–4508.
- (88) Graham, J. Crystal chemistry of complex niobium and tantalum oxides III. Relationship between  $M$ ,  $T$ , and  $M'$  fergusonite structure. *American Mineralogist: Journal of Earth and Planetary Materials* **1974**, *59*, 1045–1046.
- (89) Peters, A.; Korte, C.; Hesse, D.; Zakharov, N.; Janek, J. Ionic conductivity and activation energy for oxygen ion transport in superlattices — The multilayer system CSZ ( $\text{ZrO}_2 + \text{CaO}$ )/ $\text{Al}_2\text{O}_3$ . *Solid State Ionics* **2007**, *178*, 67–76.
- (90) Fjeld, H.; Kepaptsoglou, D. M.; Haugsrud, R.; Norby, T. Charge carriers in grain boundaries of 0.5% Sr-doped  $\text{LaNbO}_4$ . *Solid State Ionics* **2010**, *181*, 104–109.
- (91) Takai, S.; Kaji, S.; Yabutsuka, T.; Yao, T. In *Electrochemical Society Meeting Abstracts 232*, 2017, pp 1751–1751.
- (92) Takai, S.; Sano, T.; Yabutsuka, T.; Yao, T. In *Electrochemical Society Meeting Abstracts 236*, 2019, pp 1854–1854.
- (93) Shan, Y. J.; Kawaguchi, R.; Akizawa, R.; Tezuka, K. Crystal structure and ionic conductivity of novel rare-earth niobates  $\text{LnNbO}_4$  ( $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ ) by substituting Nb with W. *Ionics* **2023**, 1–7.
- (94) Swathi, S.; Yuvakkumar, R.; Kumar, P. S.; Ravi, G.; Manigandan, A.; Velauthapillai, D. Scheelite-type Fe substituted  $\text{SrWO}_4$  for hydrogen evolution reaction under alkaline conditions. *Fuel* **2022**, *316*, 123309.
- (95) Toyoura, K.; Sakakibara, Y.; Yokoi, T.; Nakamura, A.; Matsunaga, K. Oxide-ion conduction *via* interstitials in scheelite-type  $\text{LaNbO}_4$ : A first-principles study. *Journal of Materials Chemistry A* **2018**, *6*, 12004–12011.



## Chapter 4

# Rare-Earth Ion Matrices for Solid State Lasers

*This chapter is adapted from the following manuscript:*

- Mullens, B.G.; Nicholas, M.K.; Marlton, F.P.; Brand, H.E.A.; Gu, Q.; Maynard-Casely, H.E.; Kennedy, B.J.; Long-Range A-Site Cation Disorder in  $\text{NaA}(\text{MO}_4)_2$  ( $M = \text{Mo}, \text{W}$ ) Double Scheelite Oxides. *Journal of Solid State Chemistry*, **2023**, *321*, 123871.<sup>1</sup>



## 4.1 Introduction: Solid State Lasers

Lasers (an acronym of ‘light amplification by stimulated emission of radiation’) are devices that emit coherent and focused light, leading to applications in printing, semiconductor chip manufacturing, and medical procedures. There are five main types of lasers: gas, fiber, liquid, semiconductor, and solid state. Of these, solid state lasers have gained a lot of attention due to their low beam divergence, high peak power, and extreme stability.<sup>2</sup>

Solid state lasers use an optically-transparent solid as their active medium, such as a single crystal, glass, or ceramic. One of the most common crystals used for solid state lasing is neodymium-doped yttrium aluminium garnet:  $\text{Nd}:\text{Y}_3\text{Al}_5\text{O}_{12}$ , or Nd:YAG (Figure 4.1a).<sup>3</sup> In this structure,  $\text{Nd}^{3+}$  replaces a small fraction ( $\sim 1\%$ ) of  $\text{Y}^{3+}$  ions in the host crystal structure due to its similar ionic radii ( $\text{Nd}^{3+} = 1.109$  *vs.*  $\text{Y}^{3+} = 1.019$  Å in eight-coordinate geometry).<sup>4</sup> The crystal field splitting in the  $5d$  and  $4f$  energy levels of  $\text{Nd}^{3+}$  then provide the lasing activity in the crystal,<sup>5</sup> where the  ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$  transition emits a photon with a wavelength of 1064 nm in the infrared region.<sup>6</sup> This has found applications in medical procedures, such as cataract surgery and the removal of skin cancers.<sup>7,8</sup>

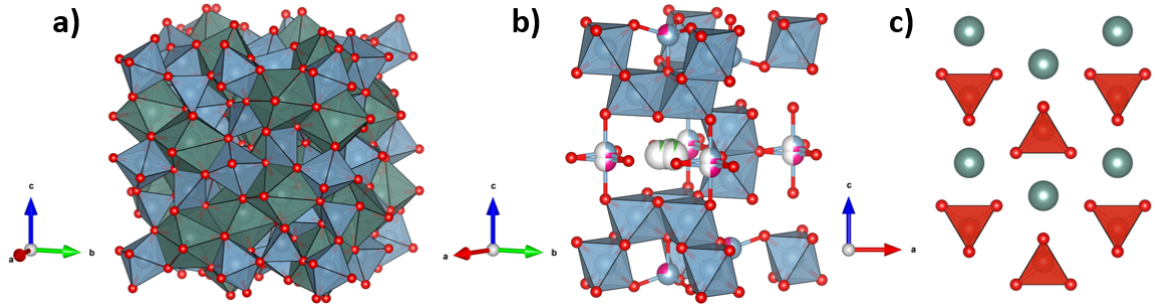


Figure 4.1: The crystal structures of some well known solid state lasing materials. (a)  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , (b)  $\text{LaMgAl}_{11}\text{O}_{19}$ , and (c)  $\text{YVO}_4$ . The teal environments are  $\text{Y}^{3+}$ , blue environments are  $\text{Al}^{3+}$ , and orange environments are  $\text{V}^{5+}$ . The disordered environments in (b) are shown as  $\text{La}^{3+}$  green and  $\text{Mg}^{2+}$  pink partially-filled spheres, with vacancies shown in white.

In solid state lasing materials, there is a delicate balance between structural properties and operation. Highly ordered structures, such as Nd:YAG, exhibit a narrow absorption bandwidth which requires a consistent temperature for operation.<sup>9</sup> By inducing disorder in these crystals, such as site vacancies in Nd:LaMgAl<sub>11</sub>O<sub>19</sub> (Figure 4.1b), the absorption and emission bands are broadened to allow for easier operation and less temperature dependence. However, this broadening also results in a decrease in the stimulation

emission and the performance of the laser.<sup>10,11</sup> A compromise is necessary between these two structural features to allow a weak sensitivity to temperature, whilst also ensuring good lasing efficiency and performance. Such a compromise was found in the zircon-type Nd:YVO<sub>4</sub> (Figure 4.1c), however its crystal growth is very difficult, preventing its use industrially.<sup>12–14</sup>

The zircon-type structure consists of a network of edge-sharing  $AO_8$  polyhedra and isolated  $BO_4$  tetrahedra.<sup>15</sup> However, zircon-type structures are seldom-observed in nature. According to the Errandonea *et al.* phase diagram of  $ABX_4$  structures (Figure 1.3),<sup>16</sup> very small  $B$ -site cations (such as  $Si^{4+}$  or  $V^{5+}$ ) are required to stabilise these structures. In the case of YVO<sub>4</sub>, vanadium is often reduced under single crystal synthesis conditions, leading to the formation of crystal defects that can darken the crystal and inhibit its lasing performance.<sup>17,18</sup> This has led to the investigation of similar structures for lasing applications that possess the same structural motifs that are easier to synthesise, such as CaWO<sub>4</sub>-based scheelite-type oxides.<sup>19</sup> These materials are easily grown as single crystals, exhibit excellent thermal and hydrolytic stability, and contain cations less prone to reduction such as  $Mo^{6+}$  and  $W^{6+}$ .<sup>20–22</sup>

#### 4.1.1 Scheelite-Type Oxides as Solid State Lasing Materials

Scheelite-type structures consist of a network of  $AO_8$  polyhedra and  $BO_4$  tetrahedra, with the  $A$ - and  $B$ -site cations at the  $4b$  and  $4a$  Wyckoff positions respectively.<sup>23,24</sup> As first proposed by Bastide, and later by Errandonea *et al.*,<sup>16,25</sup> it is possible to predict the structure of a given  $ABO_4$  compound based on the IR ratios  $r_A/r_O$  and  $r_B/r_O$ . Bastide's analysis provides a rationale for the observation that both RbTcO<sub>4</sub> and RbReO<sub>4</sub> exhibit the tetragonal  $I4_1/a$  scheelite-type structure, whereas CsTcO<sub>4</sub> and CsReO<sub>4</sub> exhibit the orthorhombic  $Pnma$  structure at room temperature.<sup>26,27</sup>

The scheelite archetype, CaWO<sub>4</sub>, has been extensively investigated as a potential medium for solid state lasing. It is able to host rare-earth cations (such as  $Ln^{3+} = La-Lu$ ) on the  $A$  site, similar to Nd:YAG, Nd:LaMgAl<sub>11</sub>O<sub>19</sub>, and Nd:YVO<sub>4</sub>. Several studies have looked at the lasing properties of these rare-earth substituted variants, such

as  $\text{Yb:CaWO}_4$ ,<sup>28,29</sup>  $\text{Eu:CaWO}_4$ ,<sup>30,31</sup> and  $\text{Er:CaWO}_4$ .<sup>32</sup> In some applications, increased levels of doping have led to scheelite-type compounds competing with traditional laser hosts.<sup>33,34</sup> This is due to the substitution of rare-earth ions distorting the  $\text{AO}_8$  polyhedra environment, leading to broadened absorption bands whilst maintaining excellent thermal stability.<sup>35</sup>

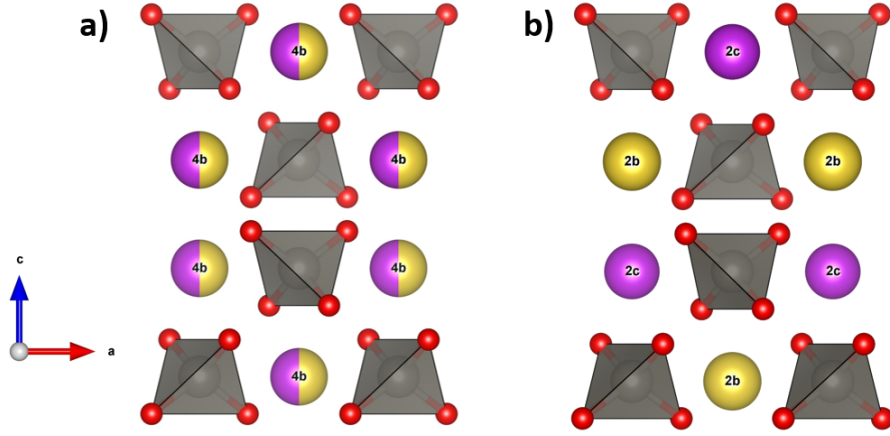


Figure 4.2: The  $AA'B_2O_8$  scheelite-type structure consisting of  $(A, A')O_8$  polyhedra (not drawn) and  $\text{BO}_4$  tetrahedra. (a) The  $I4_1/a$  space group, showing a random arrangement of two different cations across the 4b Wyckoff position. (b) The  $I\bar{4}$  space group, showing a fully ordered arrangement of A-site cations with A on the 2b and A' at the 2c Wyckoff position.

Increasing the amount of  $\text{Ln}^{3+}$  substituted for  $\text{Ca}^{2+}$  on the A site of  $\text{CaWO}_4$  requires the additional substitution of a monovalent  $A^+$  cation for charge compensation. At its extreme, the scheelite-type structures may be extended to include ‘double scheelites’ of the form  $(A_{0.5}A'_{0.5})\text{BO}_4$  [or  $AA'(\text{BO}_4)_2$ ], where two different cations occupy the A site of the  $\text{ABO}_4$  structure in a 50:50 ratio.<sup>36</sup> The two cations on the A site may order, lowering the symmetry of the structure from  $I4_1/a$  to  $I\bar{4}$ . This splits the A site from the 4b Wyckoff position in  $I4_1/a$  to two distinct 2b and 2c Wyckoff positions in  $I\bar{4}$ . This is similar to the cation ordering observed in perovskites, where substitution of  $\text{Ti}^{4+}$  in the  $\text{BaTiO}_3$  perovskite for  $\text{Mn}^{2+}$  and  $\text{W}^{6+}$  forms a  $\text{Ba}_2(\text{MnW})\text{O}_6$  double perovskite. Ordering between the  $\text{Mn}^{2+}$  and  $\text{W}^{6+}$  cations changes the symmetry from  $Pm\bar{3}m$  to  $Fm\bar{3}m$  with a doubling of the unit cell lengths.<sup>37</sup> This ordering is driven by the difference in size and oxidation state of the cations, which invariably results in a change in crystallographic symmetry. Furthermore, symmetry lowering may also occur due to the presence of cations with stereochemically active lone pair electrons. This is observed in  $\text{TlReO}_4$  and  $\text{BiVO}_4$  scheelites,<sup>38,39</sup> and  $\text{PbZrO}_3$  perovskites,<sup>40</sup> where the electron density of the  $6s^2$  lone pair

causes the  $A$ -site cation to move away from its centrosymmetric position, leading to distortions in the  $A$ -site polyhedra.

The potential of  $A$ -site cation ordering in the double scheelites  $A^+A^{3+}(BO_4)_2$  remains controversial. Perera *et al.* reported the synthesis of  $NaLn(BO_4)_2$  ( $Ln^{3+} = La, Pr, Eu, Dy$ ;  $B^{6+} = Mo, W$ ) using a microwave-assisted solid state synthesis method and concluded, based on XRD, that the  $I4_1/a$  structure in which the  $Na^+$  and  $Ln^{3+}$  cations are disordered across a single  $4b$  Wyckoff site was observed.<sup>41</sup> Other authors have reported the same disordered  $I4_1/a$  model was appropriate for a wide variety of  $A^+A^{3+}(BO_4)_2$  oxides ( $A^+ = Li, K, Ag$ ;  $A^{3+} = Ln^{3+}$ ;  $B^{6+} = Mo, W$ ).<sup>21,42-47</sup> However, Hanuza *et al.* observed vibrational states in  $NaBi(BO_4)_2$  single crystals using polarized infrared and Raman spectroscopy that were inconsistent with the disordered structure.<sup>48</sup> These were postulated to be the result of short-range ordering of the  $Na^+$  and  $Bi^{3+}$  cations and a lowering of symmetry from  $I4_1/a$  to  $I\bar{4}$ .<sup>49</sup> Furthermore, Rico *et al.* related the large spectroscopic broadening observed in some  $Na^+$  and  $Ln^{3+}/Bi^{3+}$ -containing double scheelites to a partial ordering of the cations across the  $2b$  and  $2c$  crystallographic sites in the  $I\bar{4}$  space group.<sup>50</sup> Volkov *et al.* attributed the optical absorption and photoluminescent properties of  $LiYb(MoO_4)_2$  single crystals to local ordering between  $Yb$ - $Yb$  pairs, whereas Cascales *et al.* identified in  $NaGd(WO_4)_2$  that  $Na^+$  and  $Gd^{3+}$  preferentially occupied the  $2c$  and  $2b$  Wyckoff positions respectively. The above suggests that an incomplete or partial ordering of the two  $A$ -site cations in the  $A^+A^{3+}(BO_4)_2$  double scheelites can impact their optical lasing properties, as the  $5d$  and  $4f$  energy level transitions associated with lasing are determined by the relationship between their crystal field splitting and local environment.<sup>5</sup>

This chapter is separated into three main sections: a long-range average structure study, a short-range local structure study, and a variable temperature study. Using a combination of SXRD and NPD, analysis of  $NaA(BO_4)_2$  ( $A^{3+} = Ln^{3+}, Bi$ ;  $B^{6+} = Mo, W$ ) were undertaken to determine whether long-range ordering of the  $A$ -site cations is present and, if so, how this is influenced by the difference in the IR of the two cations. Shannon reported that the IR of eight-coordinate  $Na^+$  and  $La^{3+}$  are very similar (1.18 *vs.* 1.16 Å) allowing for a straightforward cationic substitution.<sup>4</sup> As the atomic number increases, the

IR of  $Ln^{3+}$  decrease such that when  $Ln^{3+} = Lu^{3+}$  (0.977 Å), a considerable difference between the  $Na^+$  and  $Lu^{3+}$  IR occurs ( $\sim 17\%$ ) that may facilitate cation ordering. In double perovskites, differences as small as  $\sim 6\%$ , such as in  $La_2CuSnO_6$ , have led to cation ordering.<sup>51,52</sup> This is complemented with a comparative study of  $NaBi(BO_4)_2$ , where  $Bi^{3+}$  has the same oxidation state and similar IR (1.17 Å) to  $La^{3+}$ , however possesses a  $6s^2$  lone pair which may enhance cation ordering. Neutron total scattering was used to determine the presence of local scale ordering. The thermal expansion of double scheelites is also investigated to model their response to heat.

## 4.2 Synthesis Procedure and Experimental Methods

### 4.2.1 Sample Synthesis

Samples with the composition  $NaA(BO_4)_2$  ( $A^{3+} = Ln^{3+}$ , Bi;  $B^{6+} = Mo, W$ ) were prepared using a conventional solid state chemistry route. The reagents  $Ln_2O_3$  (Aithaca Chemicals, 99.999%),  $Pr_6O_{11}$  (Aithaca Chemicals, 99.999%),  $Bi_2O_3$  (Sigma-Aldrich, 99.9%),  $Na_2CO_3$  (Merck, 99.9%),  $MoO_3$  (Sigma-Aldrich, 99.5%), and  $WO_3$  (Aithaca Chemicals, 99.998%) were dried at 1000 °C ( $Ln_2O_3$ ), 600 °C ( $Bi_2O_3$ ), or 200 °C ( $Na_2CO_3$ ,  $Pr_6O_{11}$ ,  $MoO_3$ , and  $WO_3$ ) for 15 hours to remove adsorbed water and carbon dioxide before use. Appropriate stoichiometric mixtures, sufficient to prepare 4 g of each sample, were finely mixed by hand in an agate mortar using an acetone slurry. The resulting powders with  $A^{3+} = Ln^{3+}$  were pressed into rods using a hydrostatic press at 200 bar for 10 minutes. These were placed in alumina crucibles and heated in air at 800 °C (for  $B^{6+} = Mo$ ) or 850 °C (for  $B^{6+} = W$ ) for 12 hours. All samples were cooled at 3 ° min<sup>-1</sup> to room temperature to enhance the possibility of cation ordering. For  $A^{3+} = Bi$ , the samples were heated as a loose powder to 600 °C for 12 hours to assist in the decomposition of  $Na_2CO_3$ , then further heated to 800 °C (for Mo-containing samples) or 850 °C (for W-containing samples) for 12 hours without regrinding.

### 4.2.2 Synchrotron X-Ray and Neutron Powder Diffraction

SXRD data were collected for the  $\text{NaA}(\text{BO}_4)_2$  series over an angular range of  $3 < 2\theta < 85^\circ$  at 16.0 keV ( $\lambda = 0.77481 \text{ \AA}$  for  $B^{6+} = \text{Mo}$ ) or 21.0 keV ( $\lambda = 0.58879 \text{ \AA}$  for  $B^{6+} = \text{W}$ ). Due to the potential for fluorescence from the Mo K-edge and Bi L-edge, data for  $\text{NaBi}(\text{MoO}_4)_2$  were collected at 12.4 keV ( $\lambda = 0.99980 \text{ \AA}$ ). The precise wavelengths were determined by the structural refinement against a NIST SRM660b  $\text{LaB}_6$  standard on the Powder Diffraction beamline BL-10 at the Australian Synchrotron.<sup>53</sup> The samples were housed in 0.2 mm diameter borosilicate glass capillaries that were rotated during the measurements to minimise preferred orientation effects. The resulting datasets were then merged using PDViPeR. Variable temperature measurements of  $\text{NaBi}(\text{WO}_4)_2$  were collected using a sample housed in a 0.2 mm quartz capillary over a temperature range of 100–480 °C using a hot air blower.

NPD measurements were performed on Echidna, the high resolution powder diffractometer at the OPAL reactor operated by ANSTO.<sup>54</sup> Powder samples were loaded into 6 mm diameter vanadium cans, with data collected over the range  $5 < 2\theta < 162^\circ$  at a wavelength of 1.62 Å.

Neutron total scattering data for  $\text{NaA}(\text{WO}_4)_2$  ( $A^{3+} = \text{La, Lu, and Bi}$ ) were collected at 100 and 300 K using NOMAD at the SNS located at ORNL.<sup>55</sup> The samples were loaded into 6 mm vanadium cans and run using a sample changer environment. Data were collected under ambient conditions for the empty instrument, an empty sample holder, and three calibration standards (diamond, silicon, and vanadium) to calibrate the instrument. Software available at the beamline was used to calculate the NPDFs with a  $Q_{\text{max}}$  of  $31.4 \text{ \AA}^{-1}$ .

Structures were refined using the Rietveld method implemented in the program TOPAS6 using a combined SXRD and NPD dataset.<sup>56</sup> The peak shapes were modelled using the Thompson-Cox-Hastings profile function.<sup>57</sup> The background of each pattern was estimated using a Chebyshev polynomial, with a 12<sup>th</sup> order polynomial found to be sufficient to model the capillary in the SXRD data, whereas a 6<sup>th</sup> order polynomial was sufficient to model the background in the NPD. The scale factor, lattice parameters,



atomic coordinates, and ADPs were refined simultaneously with the peak profile parameters. The ADPs were taken to be isotropic and constrained to be equal across the  $A$  site of each structure, regardless of the cation occupancy. In the final refinement cycle, the parameters were fully relaxed with all free parameters refined. The crystal structures were drawn using VESTA.<sup>58</sup>

### 4.3 Structural Studies of $\text{NaA}(\text{BO}_4)_2$

The synthesis of crystalline single-phase  $\text{NaA}(\text{BO}_4)_2$  samples was achieved using solid state reactions. The Mo- and W-containing samples were heated to 800 and 850 °C respectively to ensure decomposition of  $\text{Na}_2\text{CO}_3$  and complete reaction of the metal oxides. SXRD and NPD data were used to refine the structures to the tetragonal  $I4_1/a$  space group, with slight differences between the  $\text{AO}_8$  polyhedra environments observed using NPDF in the  $I\bar{4}$  space group. Variable temperature measurements show these materials exhibit little thermal expansion.

#### 4.3.1 Synthesis and Space Group Determination

SXRD and NPD of the W-containing samples are presented in Figure 4.3. The incorporation of smaller  $\text{Ln}^{3+}$  cations causes a shift in peaks to higher  $Q$  due to the smaller lattice parameters. The near-instrumental peak widths and the absence of any unindexed peaks in the diffraction data demonstrates the samples to be highly crystalline and phase pure.

The synthesis of crystalline single-phase samples of the sodium bismuth double scheelites,  $\text{NaBi}(\text{BO}_4)_2$  ( $B^{6+} = \text{Mo}, \text{W}$ ), proved challenging using solid state reactions. The same synthesis procedure used to prepare the sodium lanthanoid double scheelites resulted in impure samples, with several prominent peaks that could not be indexed to a tetragonal cell in either the  $I4_1/a$  or  $I\bar{4}$  space groups. These reflections persisted when the synthesis was reattempted at either a lower or higher temperature. Eventually, the

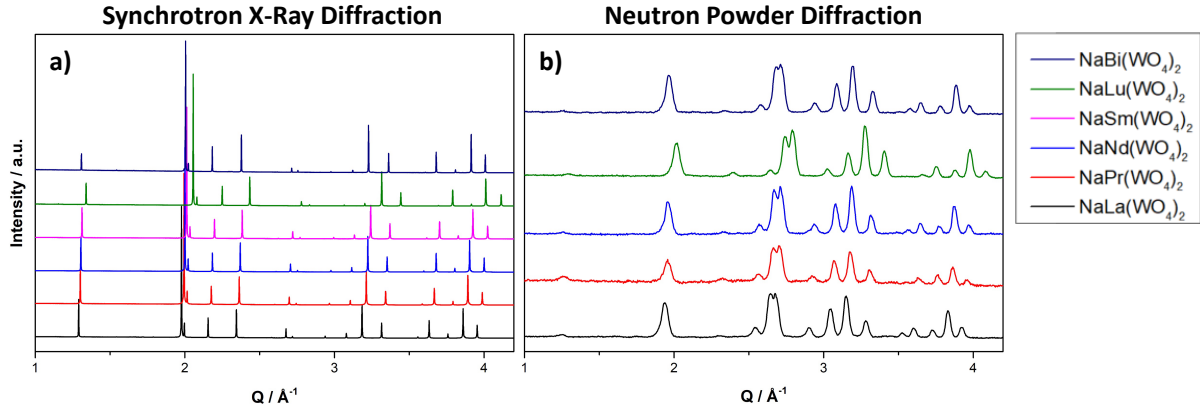


Figure 4.3: (a) Synchrotron X-ray and (b) neutron powder diffraction patterns of  $\text{NaA}(\text{WO}_4)_2$  ( $A^{3+} = \text{La, Pr, Nd, Sm, Lu, and Bi}$ ). The  $\text{NaSm}(\text{WO}_4)_2$  sample was not analysed using neutron powder diffraction due to the large neutron absorption cross section of Sm. Each diffraction pattern has been offset vertically for visibility.

synthesis conditions of Huang *et al.* were adopted where the samples were kept as loose powders, initially heated to 600 °C for 12 hours to assist in the decomposition of  $\text{Na}_2\text{CO}_3$ , then heated to 800 °C (for Mo-containing samples) or 850 °C (for W-containing samples) for 12 hours without regrinding.<sup>59</sup>

There is some uncertainty around the most appropriate space group for the  $A^+A^{3+}(\text{BO}_4)_2$  double scheelites, with structures in both the  $I4_1/a$  and  $I\bar{4}$  space groups reported in the literature. Ordering of the  $A^+$  and  $A^{3+}$  cations results in a loss of symmetry centres. This is reflected in the number of reflections observed in diffraction, with the  $00l$  ( $l = 2n$ ) and  $hk0$  ( $h + k = 2n$ ) reflections forbidden in  $I4_1/a$ , but allowed in  $I\bar{4}$ . Observation of the former would indicate violation of the  $4_1$  screw axis and, of the latter, the  $a$  glide plane of  $I4_1/a$ . Rietveld refinement of the combined SXRD and NPD datasets of  $\text{NaA}(\text{BO}_4)_2$  in both  $I4_1/a$  and  $I\bar{4}$  were apparently successful and there was little difference in their quality of fit [for  $\text{NaBi}(\text{WO}_4)_2$ :  $R_{wp} = 6.50\%$  vs.  $6.49\%$  for  $I4_1/a$  and  $I\bar{4}$  respectively]. To determine the presence of any superlattice reflections, the SXRD data was examined in closer detail. This is due to the large difference in electron counts between the two  $A$ -site cations ( $Z_{\text{Na}^+} = 10$ ,  $Z_{\text{Bi}^{3+}} = 80$ ), and the superior signal-to-noise ratio of the data compared to the NPD data ( $b_{\text{Na}} = 3.63$ ,  $b_{\text{Bi}} = 8.53$  fm).

Figure 4.3 demonstrates that there is no composition-induced change in the number of reflections for the various  $\text{NaA}(\text{WO}_4)_2$  oxides, demonstrating that the materials are isostructural. Critically, the (002) and (110) reflections, near  $Q = 1.09$  and  $1.68 \text{ \AA}^{-1}$

respectively, were not evident in any of the patterns, initially suggesting the  $I4_1/a$  space group. A series of pattern calculations were then undertaken to establish the sensitivity of the SXRD data to cation ordering. Initially the structure, including the anion positions and ADPs, was refined in the  $I\bar{4}$  space group whilst constraining the ADPs of the  $\text{Na}^+$  and  $\text{Bi}^{3+}$  cations to be equal across the  $2b$  and  $2c$  sites. The  $\text{Na}^+/\text{Bi}^{3+}$  occupancies of the  $2b$  and  $2c$  sites were then refined, constraining both sites to be fully occupied whilst maintaining the stoichiometry of the compound. This returned a  $\text{Na}^+:\text{Bi}^{3+}$  occupancy ratio across the two sites of 0.413(4):0.587(4) with  $B_{eq.} = 1.34(2) \text{ \AA}^2$ . Examination of the resulting profile revealed that the intensity of the unobserved (002) reflection was appreciably overestimated (around six times the noise in the background). The intensity of the (110) reflection was also underestimated, although for this reflection the calculated intensity was comparable to the noise in the data. The refinement was then repeated imposing a random distribution of the  $\text{Na}^+$  and  $\text{Bi}^{3+}$  cations over the two sites (that is, a 50:50 ratio on each site). As expected, this calculated zero intensity for both the (002) and (110) reflections, as this is comparable to the high-symmetry  $I4_1/a$  model.

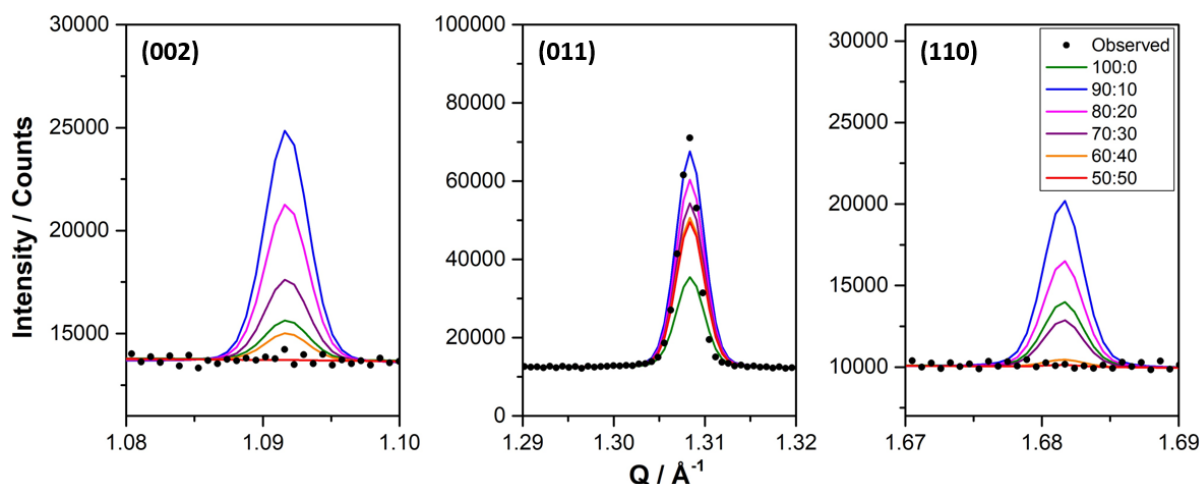


Figure 4.4: Influence of ordering of the  $\text{Na}^+$  and  $\text{Bi}^{3+}$  cations in  $\text{NaBi}(\text{WO}_4)_2$  across the  $2b$  and  $2c$  sites of  $I\bar{4}$  space group model. The black circles represent the observed synchrotron X-ray powder diffraction data, and the solid lines represent different extents of ordering, from 100:0  $\text{Na}^+$  to  $\text{Bi}^{3+}$  on the  $2c$  site (fully ordered) to 50:50  $\text{Na}^+$  to  $\text{Bi}^{3+}$  on the  $2c$  site (fully disordered). The fully disordered model is comparable to that of the fully disordered  $I4_1/a$  model.

The dependence of the calculated intensities of the (002) and (110) reflections on cation ordering are illustrated in Figure 4.4, where they are compared to that of the (011) reflection that is allowed in both the disordered  $I4_1/a$  and partially ordered  $I\bar{4}$  models. In these calculations, the anion positions and ADPs were fixed at the values obtained

from the refinement that imposed a random distribution of  $\text{Na}^+$  and  $\text{Bi}^{3+}$  cations. These calculations suggest an upper limit of disorder of less than 5% distribution, assuming that the superlattice reflections are not strain or size broadened. Similar observations were made for the other compositions studied in both the  $B^{6+} = \text{Mo}, \text{W}$  series. This indicates that although the SXRD has sufficient sensitivity to ordering of the two cations, it is not observed and hence it is reasonable to conclude that no long-range ordering is present. This demonstrates that the  $I4_1/a$  space group is appropriate.

### 4.3.2 Rietveld Refinements of Double Scheelites

Having established the absence of long-range ordering between the two  $A$ -site cations, combined SXRD and NPD datasets were used for Rietveld refinements of  $\text{NaA}(\text{BO}_4)_2$  ( $A^{3+} = \text{La}, \text{Pr}, \text{Nd}, \text{Lu}, \text{and Bi}$ ;  $B^{6+} = \text{W}, \text{Mo}$ ) to the disordered  $I4_1/a$  structural model proposed by the Perets *et al.* single crystal study.<sup>60</sup> For  $A^{3+} = \text{Sm}$ , only a SXRD dataset was acquired due to its large neutron absorption cross section. The exceptional peak-shape resolution of the SXRD data allows for accurate quantification of the lattice parameters. The patterns were successfully fitted using a  $I4_1/a$  structural model, with the lattice parameters and atomic coordinates in good agreement with previous literature where available (Table A.6).<sup>61,62</sup> Representative Rietveld refinements are displayed in Figure 4.5 and Table 4.1. The following discussion of  $\text{NaA}(\text{BO}_4)_2$  focuses on  $B^{6+} = \text{W}$ , with similar trends observed for  $B^{6+} = \text{Mo}$  and presented in the Appendix (Figures A.13–15, Table A.7).

The lattice parameters and unit cell volume of the  $\text{NaA}(\text{WO}_4)_2$  series are plotted in Figure 4.6 and show a linear increase as the IR of  $Ln^{3+}$  increases, with the exception of  $\text{Bi}^{3+}$  which will be discussed later. The absence of any discernible deviation from the linearity shows that Pr is present in its trivalent state, despite  $\text{Pr}_6\text{O}_{11}$  being used as a reagent. In all cases the BVS for W, calculated using Equation 3.1, was consistent with the oxidation state of  $\text{W}^{6+}$ . The ADPs were physically reasonable with greater displacements observed for the lighter oxygen anions than for the heavier  $A$ - or  $B$ -site cations.

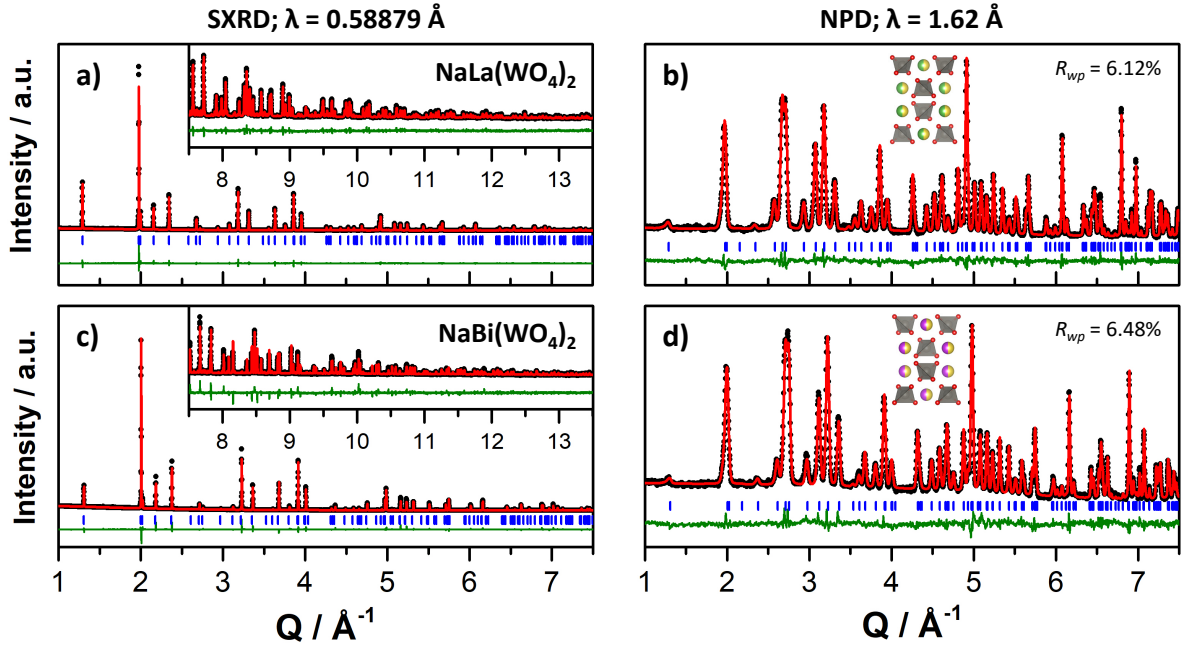


Figure 4.5: Rietveld refinement plots of (a,b)  $\text{NaLa}(\text{WO}_4)_2$  and (c,d)  $\text{NaBi}(\text{WO}_4)_2$  fitted in the tetragonal space group  $I4_1/a$ . The black circles are the observed data, the solid red line is the calculated profile, and the solid green line is the difference between the observed and calculated intensities. The blue vertical tick marks show the positions of the space group-allowed reflections. The synchrotron X-ray diffraction insets highlight the quality of the data.

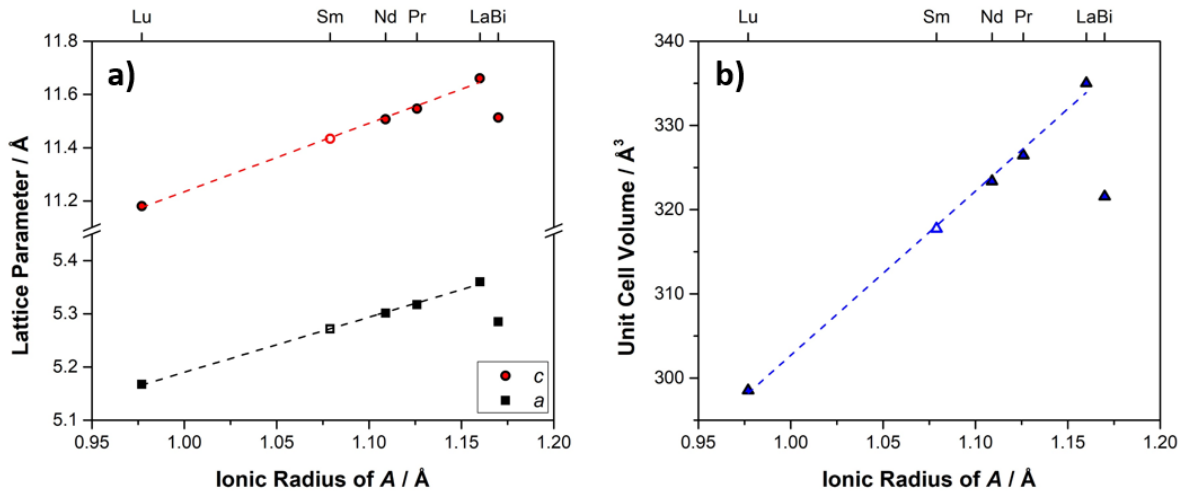


Figure 4.6: Composition dependence of the (a) lattice parameters and (b) unit cell volume for the  $\text{NaA}(\text{WO}_4)_2$  ( $A^{3+} = \text{La, Pr, Nd, Sm, Lu, and Bi}$ ) oxides. The values were obtained by Rietveld refinement against a combined synchrotron X-ray and neutron powder diffraction dataset to the  $I4_1/a$  structural model, except for  $A^{3+} = \text{Sm}$ , where only the X-ray dataset was used (indicated by hollow symbols) due to the large neutron absorption cross section of Sm. The error bars are smaller than the symbols, and the dashed lines have been drawn to guide the eyes.

Table 4.1: Selected Rietveld refinement structural parameters, bond distances, and bond valence sums for  $\text{Na}A(\text{WO}_4)_2$  ( $A^{3+} = \text{La}, \text{Bi}$ ) against combined synchrotron X-ray and neutron powder diffraction data.

|                                 | <b>NaLa(WO<sub>4</sub>)<sub>2</sub></b> | <b>NaBi(WO<sub>4</sub>)<sub>2</sub></b> |
|---------------------------------|-----------------------------------------|-----------------------------------------|
| $A^{3+}$ <b>Radii</b> (Å)       | 1.16                                    | 1.17                                    |
| $a$ (Å)                         | 5.360040(9)                             | 5.28487(1)                              |
| $c$ (Å)                         | 11.66093(3)                             | 11.51278(3)                             |
| <b>Vol.</b> (Å <sup>3</sup> )   | 335.019(1)                              | 321.551(1)                              |
| <b>O(1)</b> $x$                 | 0.1455(3)                               | 0.1519(3)                               |
| <b>O(1)</b> $y$                 | 0.0151(3)                               | 0.0127(4)                               |
| <b>O(1)</b> $z$                 | 0.2102(2)                               | 0.2103(2)                               |
| $B_{eq.}$ (A) (Å <sup>2</sup> ) | 0.787(12)                               | 0.793(15)                               |
| $B_{eq.}$ (W) (Å <sup>2</sup> ) | 0.535(5)                                | 0.66(7)                                 |
| $B_{eq.}$ (O) (Å <sup>2</sup> ) | 1.29(7)                                 | 0.96(3)                                 |
| $A\text{--O(1)}$ (Å)            | 2.5723(17)                              | 2.5052(19)                              |
| $A\text{--O(1)}$ (Å)            | 2.514(2)                                | 2.483(3)                                |
| <b>W–O</b> (Å)                  | 1.782(2)                                | 1.784(3)                                |
| <b>BVS (WO<sub>4</sub>)</b>     | 5.80                                    | 5.80                                    |
| $R_{wp}$ (%)                    | 6.12                                    | 6.48                                    |

Previous studies of  $ABO_4$  scheelite-type structures have reported that the  $BO_4$  tetrahedra are essentially rigid, with the  $B\text{--O}$  bond lengths reasonably invariant to changes in composition and temperature.<sup>63,64</sup> This is observed for the  $WO_4$  tetrahedra (and the  $MoO_4$  tetrahedra) in this study. The composition dependence of the bond distances in the  $\text{Na}A(\text{WO}_4)_2$  oxides are plotted in Figure 4.7a,b. There are two unique  $A\text{--O}$  bond distances within the  $AO_8$  polyhedra that are approximately equal in most tetragonal scheelite structures. As the size of the  $A$ -site cation increases, a linear increase in the average  $A\text{--O}$  bond length is observed. However, the two bond lengths do not increase at the same rate, with the difference increasing as the size of  $A^{3+}$  increases, reflecting greater distortion of the  $AO_8$  polyhedra. Amarsinghe *et al.* concluded that distortions in the flexible  $AO_8$  polyhedra are necessary to accommodate the very rigid  $BO_4$  tetrahedra in the scheelite-type structure.<sup>65</sup> It should be noted that  $\text{Sm}^{3+}$  is the outlier in this series. It is unclear if this is a consequence of the different data analysis strategy (the absence of NPD data) or if it is a result of local incoherent rotations of the  $WO_4$  tetrahedra, noted previously by Amarsinghe *et al.* and Marlton *et al.*, that are modelled in the refinements by an nonphysical shortening of the  $B\text{--O}$  bonds and a concurrent increase in the BVS.<sup>65,66</sup>

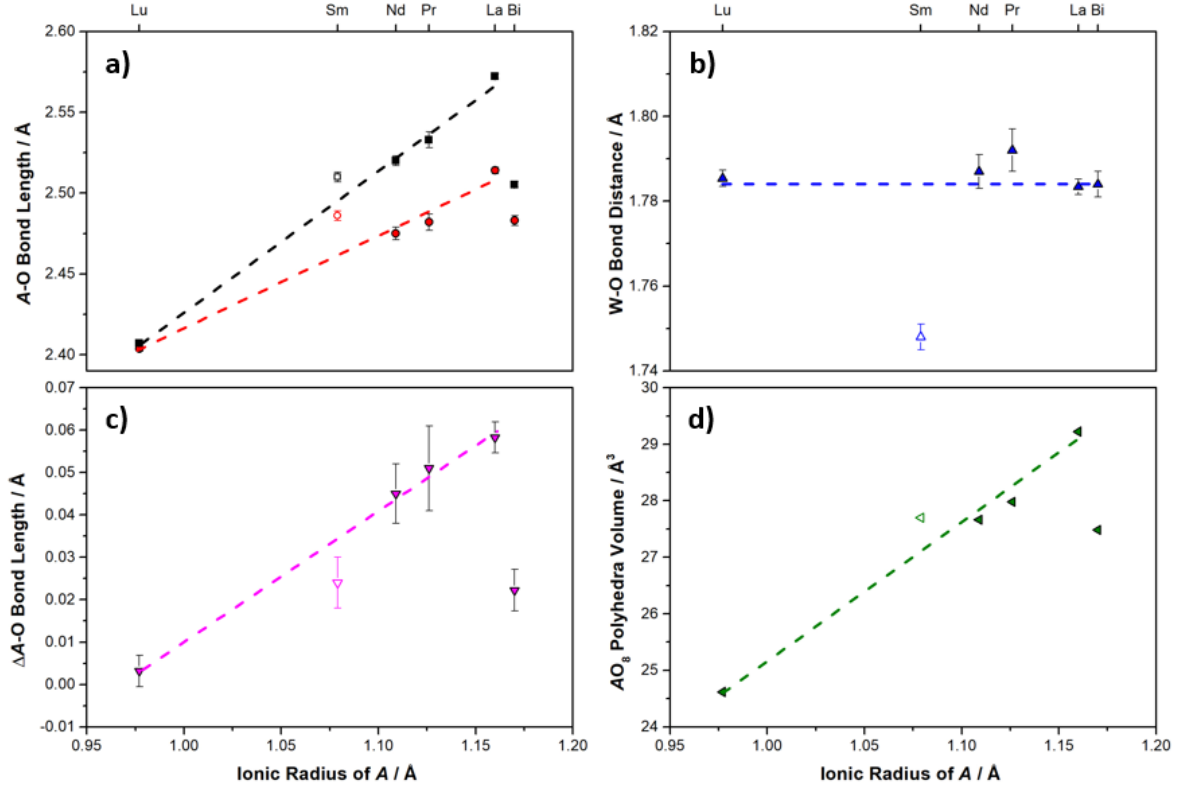


Figure 4.7: Composition dependence of the (a)  $\text{A-O}$  bond distances, (b)  $\text{W-O}$  bond distance, (c) difference between the two  $\text{A-O}$  distances, and (d) volume of the  $\text{AO}_8$  polyhedra of the  $\text{NaA}(\text{WO}_4)_2$  oxides derived from Rietveld refinements. Where not apparent, the error bars are smaller than the symbols. The dashed lines have been drawn to guide the eyes.

The deviation of  $\text{A}^{3+} = \text{Bi}$  from the linear trends seen in Figures 4.6 and 4.7 with  $\text{A}^{3+} = \text{Ln}^{3+}$  is remarkable. A key difference between  $\text{A}^{3+} = \text{Bi}$  and  $\text{Ln}^{3+}$  is the presence of a  $6s^2$  lone pair on  $\text{Bi}^{3+}$ . The smaller than expected, based on the Shannon  $\text{IR}^{4,4}$  unit cell volume of  $\text{NaBi}(\text{BO}_4)_2$  is correlated with the smaller volume of the  $\text{AO}_8$  polyhedra evident in Figure 4.7d. This suggests that the  $6s^2$  lone pair may cause more efficient packing of the polyhedra in  $\text{NaBi}(\text{BO}_4)_2$ , leading to an overall smaller unit cell volume. This has been observed in other scheelite-type oxides containing lone pair-bearing cations, such as  $\text{TlReO}_4$  and  $\text{Bi}_3\text{FeMO}_{12}\text{O}_{12}$ .<sup>38,67</sup>

The simplest signature for such long-range ordering of lone pair electrons would be an increase in the anisotropy of the  $\text{A-O}$  bond distances and/or increased ADPs, as observed in the similarly-structured  $\text{BiVO}_4$  scheelite.<sup>68</sup> However, the difference between the two  $\text{A-O}$  bond distances plotted in Figure 4.7c and the similarity of the ADPs demonstrate that neither of these signatures emerge from the Rietveld refinements.

Indeed, the difference between the two crystallographically distinct  $A(\text{Na,Bi})\text{-O}$  bond distances is less than that of the two  $(\text{Na,Lu})\text{-O}$  distances observed in  $\text{NaLa}(\text{WO}_4)_2$  (Figure 4.7a,c). Therefore, it appears that the lone pairs are not ordered in the long-range average structure of  $\text{NaBi}(\text{WO}_4)_2$ . Despite this, it is possible that short-range correlations contribute to the observed reduction in the unit cell volume. The local ordering between the  $6s^2$  lone pairs in  $\text{NaBi}(\text{WO}_4)_2$  may lead to a more densely-packed structure overall than its  $\text{NaLa}(\text{WO}_4)_2$  counterpart whilst maintaining the long-range  $I4_1/a$  symmetry.

### 4.3.3 Neutron Total Scattering Studies

To probe the possibility of local cation ordering in double scheelite oxides, neutron total scattering data were collected for  $\text{NaA}(\text{WO}_4)_2$  ( $A^{3+} = \text{La, Lu, and Bi}$ ). The NPDFs collected at 100 K are plotted in Figure 4.8. The NPDFs may be thought of as a weighted histogram of all atom–atom distances within a material, with each peak corresponding to a specific atom–atom pair. This gives a greater sensitivity to bond distances within the structure, as well as the observation of any differences between the long-range average (derived from Rietveld refinements of the Bragg diffraction) and the short-range local structure.

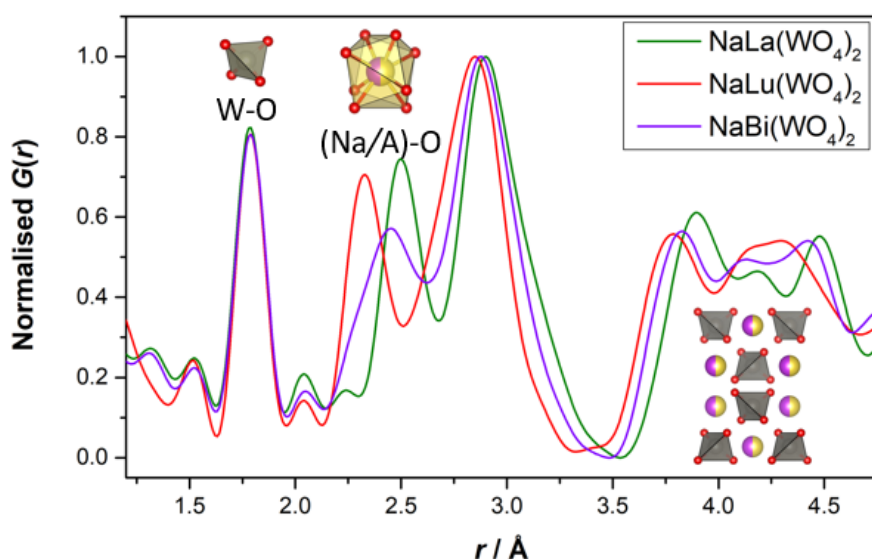


Figure 4.8: Neutron pair distribution function data of (green)  $\text{NaLa}(\text{WO}_4)_2$ , (red)  $\text{NaLu}(\text{WO}_4)_2$ , and (purple)  $\text{NaBi}(\text{WO}_4)_2$ .



In Figure 4.8, the first peak at  $\sim 1.76$  Å corresponds to the W–O distance within the  $\text{WO}_4$  tetrahedra. This peak remains unchanged regardless of the size of the *A*-site cation, reflecting the rigid nature of the  $\text{WO}_4$  tetrahedra observed in the Bragg diffraction study of the  $\text{NaA}(\text{BO}_4)_2$  oxides (Figure 4.7b).<sup>65</sup> The next peak observed between 2.3–2.5 Å corresponds to the Na–O and *A*–O distances within the (Na,*A*) $\text{O}_8$  polyhedra. This peak clearly moves from  $r \sim 2.5$  Å in  $\text{NaLa}(\text{WO}_4)_2$  to  $\sim 2.3$  Å in  $\text{NaLu}(\text{WO}_4)_2$ , consistent with the reduction in the size of the  $\text{Ln}^{3+}$  cation (Figure 4.6a). This indicates that the size of the  $\text{NaO}_8$  polyhedra change in accordance with the size of the  $\text{AO}_8$  polyhedra, as there are no common peaks shared between all three datasets in this region. This can be explained by the edge-sharing connectivity of the (Na,*A*) $\text{O}_8$  polyhedra influencing the size of their nearest neighbours. This peak in the  $\text{NaBi}(\text{WO}_4)_2$  dataset appears much broader than the similar peak in  $\text{NaLn}(\text{WO}_4)_2$ . This potentially reflects the stereochemical activity of the  $\text{Bi}^{3+}$   $6s^2$  lone pair, as off centring of the  $\text{Bi}^{3+}$  cation can lead to multiple different Bi–O bond lengths, and static disorder can cause peaks in the NPDF to broaden. As a result, this dataset will be modelled separately from  $\text{NaLn}(\text{WO}_4)_2$ . Finally, the peak between 2.7–3.0 Å corresponds to the O–O distances across the  $\text{WO}_4$  tetrahedra and (Na,*A*) $\text{O}_8$  polyhedra. That these peaks shift very slightly to lower  $r$  with smaller *A*-site cations reflects the dependence of the size of both the  $\text{NaO}_8$  and  $\text{AO}_8$  polyhedra on the size of the *A*-site cation.

For  $\text{NaLn}(\text{WO}_4)_2$  ( $\text{Ln}^{3+} = \text{La}, \text{Lu}$ ), two models were fitted to the data over a range of 1.2–30 Å (Figure 4.9, Table 4.2). The first model was the cation-disordered  $I4_1/a$  structure derived from the SXRD and NPD combined Rietveld refinements, whereas the second model was the cation-ordered  $I\bar{4}$  structure with 100% ordering of the cations (that is, 100:0  $\text{Na}^+$  to  $\text{Ln}^{3+}$  ratio at the Wyckoff  $2b$  site and 0:100  $\text{Na}^+$  to  $\text{Ln}^{3+}$  ratio at the Wyckoff  $2c$  site). Similar fits were performed for both  $\text{Ln}^{3+} = \text{La}, \text{Lu}$  and displayed similar trends. Therefore, the following discussion will focus on  $\text{NaLa}(\text{WO}_4)_2$ .

Fitting the NPDF of  $\text{NaLa}(\text{WO}_4)_2$  at 100 K to the cation-disordered  $I4_1/a$  model resulted in an acceptable fit at high  $r$ . However, this model struggled to account for many of the features at low  $r$ . The peak at  $\sim 1.76$  Å was well fitted, reflecting the rigid  $\text{WO}_4$  in the disordered  $I4_1/a$  structure. However, the (Na,La) $\text{O}_8$  polyhedra environments

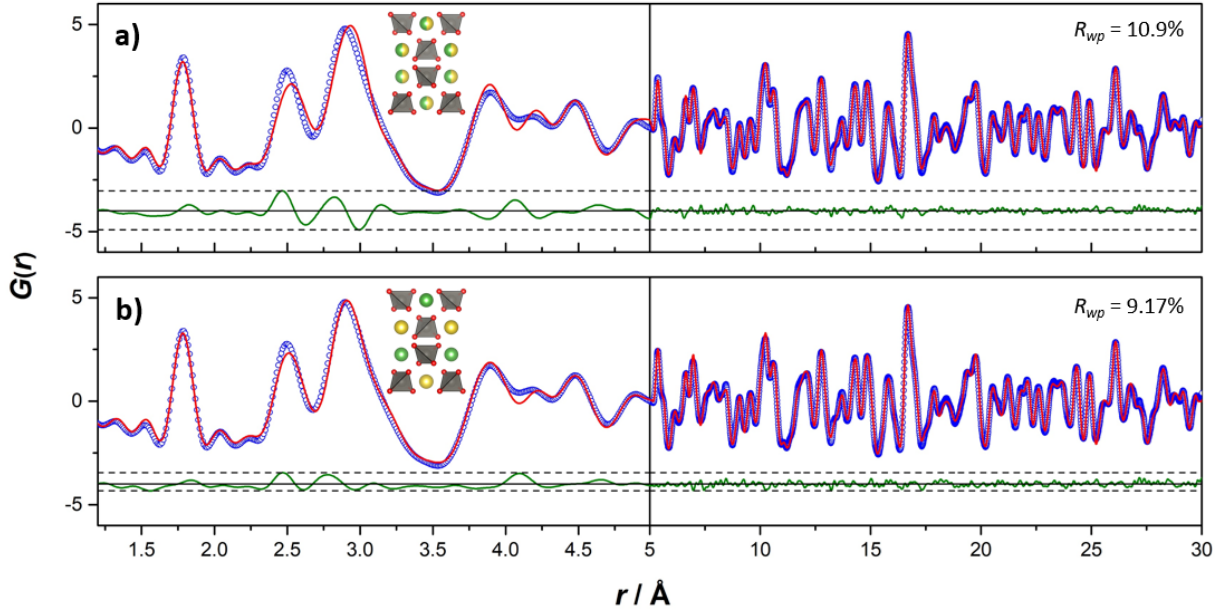


Figure 4.9: Fits to the neutron pair distribution function data at 100 K of  $\text{NaLa}(\text{WO}_4)_2$  over a range of 1.2–30 Å to the (a) disordered  $I4_1/a$  and (b) ordered  $I\bar{4}$  models. The blue circles represent the data, the red line represents the fit to the data, and the green line represents the difference between the two.

between 2.0–3.5 Å were poorly fit. This means that there are structural distortions in the (Na,La) $\text{O}_8$  polyhedra on the local scale within the  $\text{NaLa}(\text{WO}_4)_2$  material that are not captured in the modelling of the long-range average Bragg diffraction data. A second fit was undertaken where the fully ordered  $I\bar{4}$  model was used, and this produced a better fit to the data at both low and high  $r$ . This was similarly noted in a study of  $\text{NaCe}(\text{WO}_4)_2$ , where a lower-symmetry model was required to model the noncentrosymmetry of the local structure.<sup>5</sup>

Differences between the two models were further examined. Although  $\text{Na}^+$  and  $\text{La}^{3+}$  have similar IR (1.18 *vs.* 1.16 Å),<sup>4</sup> the difference in neutron scattering length ( $b_{\text{Na}} = 3.6$ ,  $b_{\text{La}} = 8.2$ ,  $b_{\text{O}} = 5.8$  fm) allows for a distinction between the Na–O and La–O bonds. In the disordered  $I4_1/a$  model, the (Na,La) $\text{O}_8$  polyhedra are averaged across a single  $4b$  cation site, leading to a small range of (Na,La)–O bond lengths [2.5112(6)–2.5573(6) Å] and a prominent peak at  $\sim 2.5$  Å in the fit. In the ordered  $I\bar{4}$  model, the polyhedra are split into two separate and unique  $\text{NaO}_8$  and  $\text{LaO}_8$  environments. The  $\text{NaO}_8$  polyhedra have a greater distribution of longer Na–O bond distances [2.520(2)–2.59(3) Å] and a larger polyhedra volume (29.8 Å<sup>3</sup>), whereas the  $\text{LaO}_8$  polyhedra have a narrower distribution of shorter [2.496(2)–2.514(2) Å] bonds and a smaller polyhedra volume (28.0 Å<sup>3</sup>), reflecting

Table 4.2: Selected Rietveld refinement structural parameters, bond distances, and bond valence sums for  $\text{NaA}(\text{WO}_4)_2$  ( $A^{3+} = \text{La, Bi}$ ) against combined synchrotron X-ray and neutron powder diffraction data.

| Space Group                       | NaLa(WO <sub>4</sub> ) <sub>2</sub> |                       |
|-----------------------------------|-------------------------------------|-----------------------|
|                                   | $I4_1/a$                            | $I\bar{4}$            |
| $a$ (Å)                           | 5.3516(8)                           | 5.3513(6)             |
| $c$ (Å)                           | 11.624(3)                           | 11.630(2)             |
| Vol. (Å <sup>3</sup> )            | 332.91(14)                          | 333.05(9)             |
| O(1) $x$                          | 0.1467(2)                           | 0.3523(4)             |
| O(1) $y$                          | 0.01338(14)                         | 0.2443(4)             |
| O(1) $z$                          | 0.20989(11)                         | 0.16875(12)           |
| O(2) $x$                          | –                                   | 0.8553(4)             |
| O(2) $y$                          | –                                   | 0.2299(4)             |
| O(2) $z$                          | –                                   | 0.08821(13)           |
| $B_{eq.} (A)$ (Å <sup>2</sup> )   | 0.55(2)                             | 0.71(2)               |
| $B_{eq.} (W)$ (Å <sup>2</sup> )   | 0.39(2)                             | 0.33(2)               |
| $B_{eq.} (O)$ (Å <sup>2</sup> )   | 0.65(2)                             | 0.65(2)               |
| A–O (Å)                           | 2.556(2)                            | (Na) 2.599(3)         |
| A–O (Å)                           | 2.507(2)                            | (Na) 2.520(2)         |
| A–O (Å)                           | –                                   | (La) 2.514(3)         |
| A–O (Å)                           | –                                   | (La) 2.496(2)         |
| AO <sub>8</sub> (Å <sup>3</sup> ) | 28.9                                | (Na) 29.8 / (La) 28.0 |
| W–O (Å)                           | 1.7871(11)                          | 1.796(2)              |
| BVS (WO <sub>4</sub> )            | 5.75                                | 5.60                  |
| $R_{wp}$ (%)                      | 10.9                                | 9.17                  |

the larger  $\text{La}^{3+}$  oxidation state (Figure 4.10). The two different polyhedra environments allow for a greater number of O–O distances, leading to a better fit of the features between 2.7–3.5 Å. These results are similar to studies of  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  ferroelectrics, where neutron total scattering was sensitive to differences between the Na–O and Bi–O environments in the structure.<sup>69–71</sup> A combination of the lower  $\text{Na}^+$  oxidation state, longer Na–O bond lengths, and larger  $\text{NaO}_8$  polyhedra leads to these polyhedra being easier to deform than their  $\text{LaO}_8$  counterparts.

To investigate how the cation ordering changes in real space  $r$ , fits were performed from  $12 \leq r \leq 40$  Å. This ensured at least two unit cells were captured in the fit to model the ordering at a longer length scale, whilst not being biased by the immediate local environments of the  $\text{NaO}_8$  and  $\text{LaO}_8$  polyhedra. The fits were performed using the  $I\bar{4}$  model with a fixed  $\text{Na}^+:\text{La}^{3+}$  ratio. The resulting  $R_{wp}$  values are plotted in Figure 4.11, and show that a better fit to the data is obtained with a more random distribution

of *A*-site cations. Despite the  $\text{NaA}(\text{WO}_4)_2$  double scheelites consisting of two unique  $(\text{Na},\text{A})\text{O}_8$  polyhedra environments, there is no ordering between these environments at longer length scales. This is consistent with the lack of long-range ordering observed in the SXRD and NPD diffraction studies.

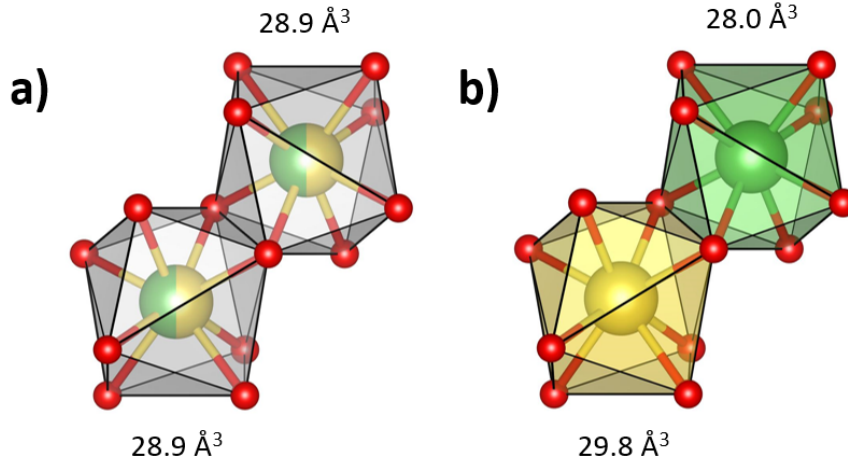


Figure 4.10: The refined  $\text{AO}_8$  polyhedra volumes of the  $\text{NaLa}(\text{WO}_4)_2$  in (a) disordered  $I4_1/a$  and (b) ordered  $I4$  over a range of 1.2–30  $\text{\AA}$ . The yellow spheres represent  $\text{Na}^+$ , whereas the green spheres represent  $\text{La}^{3+}$ .

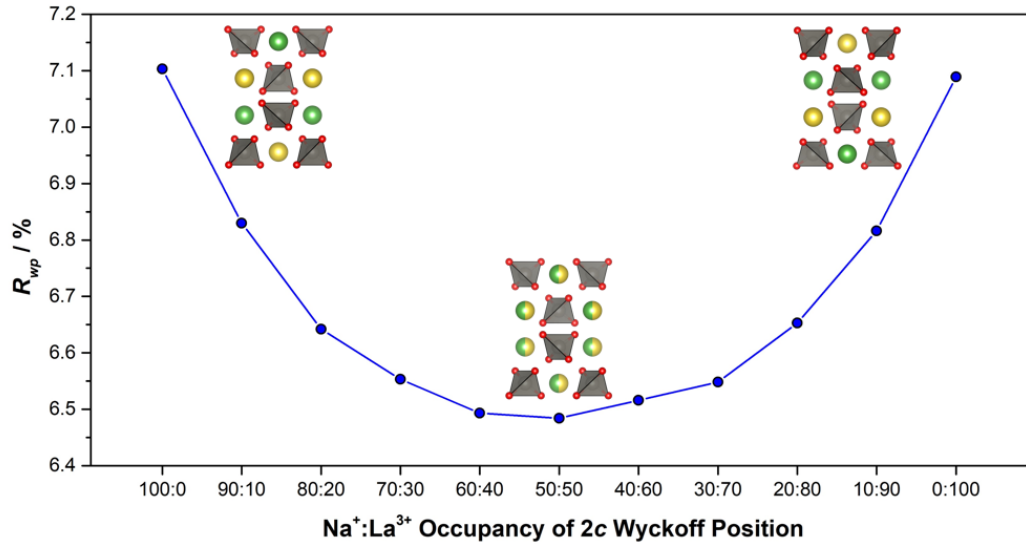


Figure 4.11: Neutron pair distribution function fits to  $\text{NaLa}(\text{WO}_4)_2$  conducted over the range of 12–40  $\text{\AA}$  to the  $I4$  model. A fixed distribution of  $\text{Na}^+$  and  $\text{La}^{3+}$  across the 2c Wyckoff position was modelled, and the  $R_{wp}$  value was used to assess the quality of the fits.

A similar analysis was performed on the NPDF data of  $\text{NaBi}(\text{WO}_4)_2$ . As stated previously, although  $\text{La}^{3+}$  and  $\text{Bi}^{3+}$  have similar IR (1.16 *vs.* 1.17 Å),<sup>4</sup>  $\text{Bi}^{3+}$  possesses  $6s^2$  lone pair electrons which can lead to distortions within its local environment. This is seen in the NPDF data of  $\text{NaA}(\text{WO}_4)_2$  in Figure 4.8, where the second peak at  $\sim 2.4$  Å was much broader in  $A^{3+} = \text{Bi}$  than the corresponding  $\text{Ln}^{3+}$  structures. This indicates that a broad range of Bi–O bond lengths may be present.

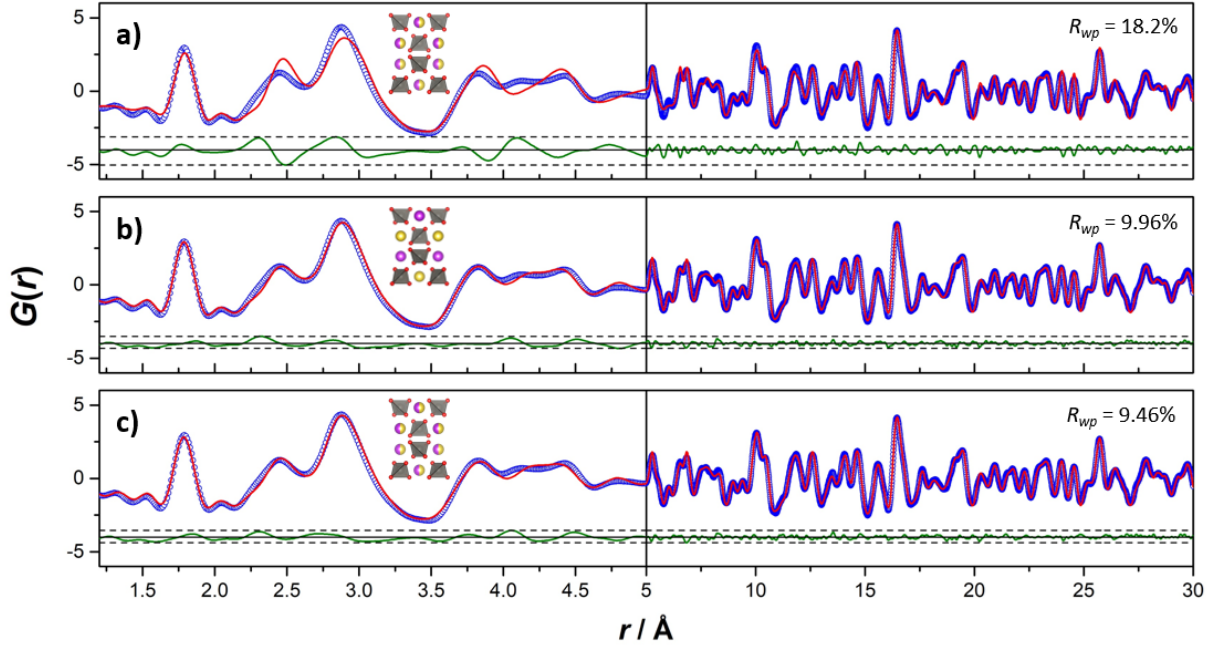


Figure 4.12: Fits to the neutron pair distribution function data at 100 K of  $\text{NaBi}(\text{WO}_4)_2$  over a range of 1.2–30 Å to the (a) disordered tetragonal  $I4_1/a$ , (b) ordered tetragonal  $I\bar{4}$  and (c) disordered monoclinic  $I2/b$  models. The blue circles represent the data, the red line represents the fit to the data, and the green line represents the difference between the two.

Initial fits to the NPDF data to the disordered  $I4_1/a$  model were unsuccessful, and the  $R_{wp}$  was significantly worse than for  $\text{NaLa}(\text{WO}_4)_2$  ( $R_{wp} = 18.2$  *vs.* 10.9%). The (Na,Bi)–O bonds between 2.2–3.2 Å were poorly fit, as well as the consistent noise in the difference curve at high  $r$ . Consistent with the study of the  $\text{NaLn}(\text{WO}_4)_2$  materials, dropping the symmetry from disordered  $I4_1/a$  to ordered  $I\bar{4}$  to allow for different  $\text{NaO}_8$  and  $\text{BiO}_8$  polyhedra environments substantially improved the fit (from  $R_{wp} = 18.2\%$  to  $R_{wp} = 9.96\%$ ), although the quality of fit was still not as good as for  $\text{NaLa}(\text{WO}_4)_2$ . This is associated with the fitting of the Bi–O bond lengths between 2.2–2.5 Å. Finally, a monoclinic  $I2/b$  model was used, and this resulted in the best fit to the data (Figure 4.12b and Table A.8). Although this model does not differentiate between the  $\text{NaO}_8$

and  $\text{BiO}_8$  polyhedra, the increase in the number of degrees of freedom allows for each  $\text{AO}_8$  polyhedra volume to consist of four unique  $A$ -O bond distances. This is also coupled with freedom in the  $z$ -axis direction of both the  $A$ - and  $B$ -site cations, which has been previously shown to account for the  $6s^2$  lone pair stereochemical activity in other  $\text{ABO}_4$  materials such as  $\text{BiVO}_4$ .<sup>68,72,73</sup> The atomic coordinates of the  $A$  and  $B$  sites were determined to be away from the symmetry constrained positions. The unit cell volumes of the tetragonal  $I4_1/a$  and monoclinic  $I2/b$  structures were determined to be the same within the refinement uncertainty [ $319.39(4)$  vs.  $319.36(4)$  Å<sup>3</sup>, respectively], indicating that there is not a sufficient amount of lone pair ordering to facilitate the more dense packing of the polyhedra, as observed in the related  $\text{TlReO}_4$  and  $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$  scheelite-type structures.<sup>38,67</sup> A local structure model that allows for the movement of cations away from their centrosymmetric positions to account for the stereochemical activity of the  $\text{Bi}^{3+}$   $6s^2$  lone pair is necessary to produce a good model for its local environment.

In observing the NPDFs in Figure 4.8, it is clear that the Bi-O and O-O bond distances across the  $\text{BiO}_8$  polyhedra are smaller than the corresponding La-O and O-O bond distances across the  $\text{LaO}_8$  polyhedra. Despite  $\text{Bi}^{3+}$  having a larger IR than  $\text{La}^{3+}$ , the  $\text{BiO}_8$  polyhedra are shown to be smaller than the  $\text{LaO}_8$  polyhedra in both the long-range average Bragg diffraction fits, and the short-range local NPDF fits. It is possible that these shorter Bi-O bond distances reflect the greater covalency of the Bi-O bonds compared to La-O due to strong hybridisation between the  $\text{Bi}^{3+}$   $6s$ ,  $\text{O}^{2-}$   $2p$ , and empty  $\text{W}^{6+}$   $5d$  orbitals. A similar effect has been noted in the photocatalytic material  $\text{BiVO}_4$ , where strong hybridisation between the  $\text{Bi}^{3+}$   $6s$  and  $\text{O}^{2-}$   $2p$  orbitals leads to enhanced photocatalytic activity.<sup>72</sup> Differences between Bi-O and La-O were also noted by Kazin *et al.* in their study of substituted apatites, where the Bi-O bond lengths were identified to be shorter than the corresponding La-O bond lengths.<sup>74</sup> This is an observation that is worth investigating further through DFT calculations on the partial density of states (pDoS).

### 4.3.4 Variable Temperature Study of $\text{NaBi}(\text{WO}_4)_2$

Given the unusual contraction in the unit cell volume observed in  $\text{NaBi}(\text{WO}_4)_2$  and the apparent absence of long-range lone pair correlations, variable temperature SXRD was undertaken to determine the response of the structure to temperature. Scheelite-type structures may undergo a  $I4_1/a \rightarrow I4_1/amd$  phase transition to the true scheelite-type aristotype upon heating by elimination of the rotation of the  $\text{BO}_4$  tetrahedra about the  $c$ -axis. This phase transition has been observed in the binary oxide scheelites such as  $\text{RbTcO}_4$ ,<sup>26</sup>  $\text{RbReO}_4$ ,<sup>27,66</sup>  $\text{RbOsO}_4$ ,<sup>75</sup> and  $\text{TlTcO}_4$ ,<sup>26</sup> but has not been reported in any of the double scheelites.

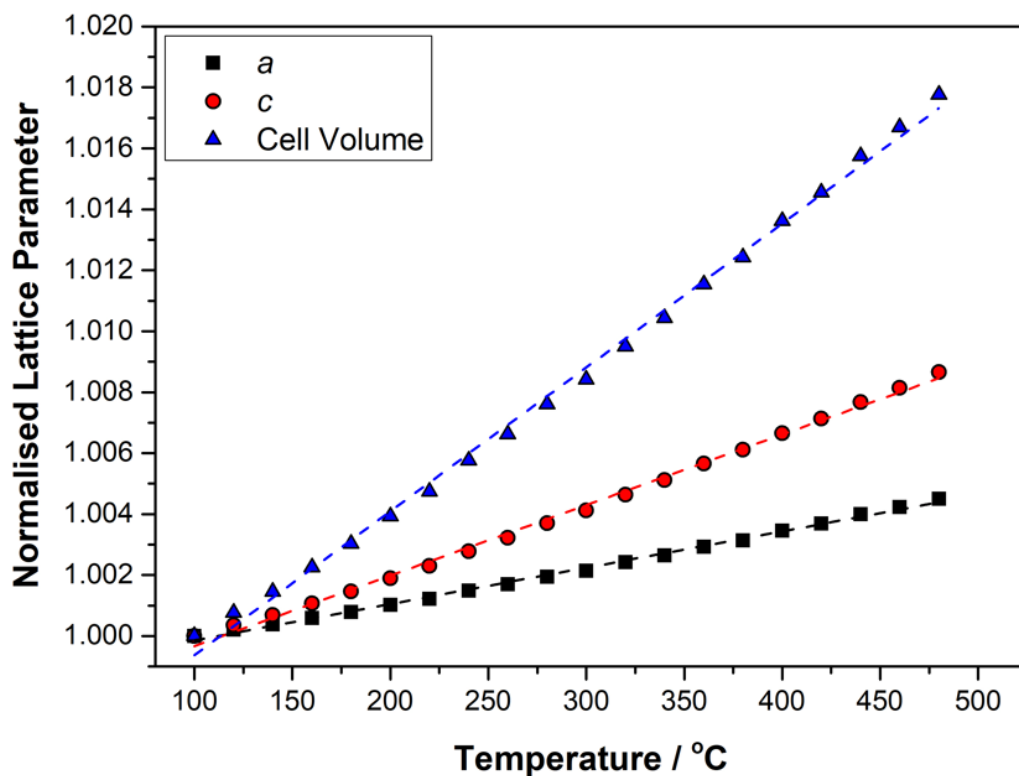


Figure 4.13: Normalised lattice parameters and unit cell volume for  $\text{NaBi}(\text{WO}_4)_2$  upon heating, obtained from Rietveld refinements of synchrotron X-ray diffraction data.

The temperature dependence of the normalised lattice parameters and unit cell volume of  $\text{NaBi}(\text{WO}_4)_2$  are presented in Figure 4.13 and show linear behaviour upon heating.  $\text{NaBi}(\text{WO}_4)_2$  displays anisotropic thermal expansion, with the  $c$ -axis expanding at a greater rate than the  $a$ -axis.

This can be quantified by using

$$\alpha_P = \frac{\Delta P}{P_i \Delta T} \quad (4.1)$$

where  $\alpha_P$  is the coefficient of thermal expansion,  $P$  denotes the parameter of interest (lattice parameters  $a$ ,  $b$ ,  $c$ , or unit cell volume  $V$ ),  $P_i$  is the initial value of the parameter of interest, and  $\Delta T$  is the change in temperature.

The corresponding linear thermal expansion coefficients are  $\alpha_a = 11.8 \times 10^{-6}$ ,  $\alpha_c = 22.7 \times 10^{-6}$ , and  $\alpha_V = 46.5 \times 10^{-6} \text{ K}^{-1}$ . This is similar to that seen in other scheelite-type oxides and reflects the layered-like arrangement of the cations in the structure.<sup>76</sup> There is no evidence for the formation of the true  $I4_1/amd$  scheelite aristotype structure in this temperature range. This also confirms the thermal stability of these structures, with less than a 1% increase observed in the (Na,Bi)O<sub>8</sub> polyhedra volume between 100–480 °C, making them suitable as solid state lasing materials.

## 4.4 Conclusions and Towards the Future Design of Lasing Materials

Series of double scheelites of the form  $\text{Na}A(\text{BO}_4)_2$  ( $A^{3+} = \text{Ln}^{3+}$ , Bi;  $B^{6+} = \text{Mo}$ , W) were synthesised using a conventional solid state synthesis technique.  $\text{NaLn}(\text{BO}_4)_2$  were prepared by pressing the samples as rods and by using a one-step synthesis process, whereas the  $\text{NaBi}(\text{BO}_4)_2$  samples were heated as loose powders with an additional lower temperature heating step to facilitate the decomposition of  $\text{Na}_2\text{CO}_3$ . The samples were confirmed as highly crystalline and phase pure using SXRD and NPD.

The structures of several  $\text{Na}A(\text{BO}_4)_2$  oxides were refined against combined SXRD and NPD datasets, and similar quality fits for both the disordered  $I4_1/a$  and partially-ordered  $I\bar{4}$  models were obtained. Ordering of the  $\text{Na}^+$  and  $A^{3+}$  cations on the  $A$  site breaks the  $I4_1/a$  symmetry, allowing for several additional reflections. The presence or absence of such reflections can be used to establish the presence of cation ordering.



Despite the appreciable difference in the atomic numbers of the two *A*-type cations in the studied oxides, such reflections are expected to be very weak. The most intense of these, calculated to occur between  $Q \sim 1.0\text{--}1.8 \text{ \AA}^{-1}$ , were not detected in the high-quality diffraction data. The exceptional signal-to-noise ratio of the SXRD data demonstrates the absence of long-range ordering of the cations on the *A* site. An alternate approach to break the  $I4_1/a$  symmetry is to introduce stereochemically active lone pair electrons into the system, such as the addition of  $\text{Bi}^{3+}$ . From the Rietveld refinements, the Bi-based double scheelites showed a denser packing, with smaller  $\text{AO}_8$  polyhedra and unit cell volumes than the isostructural  $\text{NaLn}(\text{BO}_4)_2$  counterparts with similar  $\text{Ln}^{3+}$  IR. Variable temperature SXRD measurements of  $\text{NaBi}(\text{WO}_4)_2$  showed little change in the structure upon heating. The structure did not undergo any phase transitions (such as  $I4_1/a \rightarrow I4_1/amd$ ) and showed very little change in the  $\text{AO}_8$  polyhedra volume between  $100\text{--}480 \text{ }^\circ\text{C}$ , demonstrating their thermal stability for solid state lasing applications.

Neutron total scattering data showed that disordering across the *A* site is dependent on the length scale investigated. Fits to the data between  $1.2\text{--}30 \text{ \AA}$  showed that the long-range average disordered  $I4_1/a$  structure could not account for the features corresponding to the  $(\text{Na},\text{A})\text{O}_8$  polyhedra. On the local scale, lowering the symmetry from the disordered  $I4_1/a$  to the ordered  $I\bar{4}$  structure was required to fit the individual  $(\text{Na},\text{A})\text{O}_8$  polyhedra environments. Fits to the data between  $12\text{--}40 \text{ \AA}$  showed that the long-range average structure is better fit with a disordering across the *A* site, with a minimum  $R_{wp}$  observed around the 50:50 ordering. This shows that whilst each *A*-site cation exhibits a unique polyhedra environment, there is no ordering of these environments on the long-range average scale. It is possible that further increasing the difference in the IR of the two cations may increase the tendency of these to order at a longer length scale, such as replacing  $\text{Na}^+$  ( $1.18 \text{ \AA}$ ) with either  $\text{K}^+$  ( $1.51 \text{ \AA}$ ) or  $\text{Li}^+$  ( $0.92 \text{ \AA}$ ).<sup>4</sup> This would also lead to symmetry lowering in the long-range average structure, as  $\text{KLu}(\text{WO}_4)_2$  reportedly crystallises in a monoclinic  $C2/c$  structure,<sup>77</sup> and  $\text{LiLu}(\text{WO}_4)_2$  crystallises in a monoclinic  $P2_1/n$  structure.<sup>42</sup> Neutron total scattering data also identified differences between the  $\text{NaLn}(\text{WO}_4)_2$  and  $\text{NaBi}(\text{WO}_4)_2$ , with a broader range of Bi–O bonds and cation off centring required to accurately model its local structure, consistent with the noncentrosymmetry expected from the  $\text{Bi}^{3+} 6s^2$  lone pairs.

With the identification of the different bonding environments around the  $\text{Na}^+$  and  $A^{3+}$  cations, further local scale modelling could be undertaken to more accurately determine element-specific polyhedra distortions within the structure. Combinations of neutron total scattering and EXAFS measurements have been used to decouple the different bonding requirements of similar cations sharing the same cation site, such as  $(\text{Sr},\text{La})\text{TiO}_3$  solid solutions.<sup>78</sup> This could also be achieved by modelling the NPDF data using a ‘large box’ model of many unit cells, such as using the reverse Monte Carlo method implemented in the program RMCProfile.<sup>79</sup> This would allow other structural studies to be undertaken, such as determining the presence of any incommensurate structuring like the  $\text{Ag}_{1/8}\text{Pr}_{5/8}(\text{MoO}_4)_2$  and  $\text{KNd}(\text{MoO}_4)_2$  double scheelites.<sup>80</sup> This analysis is worth pursuing further.

The substitution of  $A^+$  and  $A^{3+}$  cations into the  $\text{CaWO}_4$  structure induces local changes, such as creating two unique polyhedra environments with different bond lengths and volumes. Long-range average structure-determining techniques, such as SXRD and NPD, are insensitive to this information, and ‘average out’ the two environments to give a single  $(\text{Na},A)\text{O}_8$  environment. NPDF analysis was used to quantify the differences between the  $\text{NaO}_8$  and  $\text{AO}_8$  polyhedra environments, demonstrating the need for understanding the local structure to develop full structure-functionality relationships. In this case, the substitution of different  $A$ -site cations led to different  $\text{AO}_8$  polyhedra distortions that can effect the crystal field splitting of the lasing rare-earth ions. Where appropriate, it is important to consider discrepancies between the average (from diffraction) and local (from total scattering or spectroscopy) structures for such materials in order to better understand their applications.

# Bibliography

- (1) Mullens, B. G.; Nicholas, M. K.; Marlton, F. P.; Brand, H. E.; Gu, Q.; Maynard-Casely, H. E.; Kennedy, B. J. Long-range *A*-site cation disorder in  $\text{NaA}(\text{MO}_4)_2$  ( $M = \text{Mo}, \text{W}$ ) double scheelite oxides. *Journal of Solid State Chemistry* **2023**, *321*, 123871.
- (2) Šulc, J.; Jeřínková, H. In *Lasers for Medical Applications*; Elsevier: 2013, pp 127–176.
- (3) Dubey, A. K.; Yadava, V. Experimental study of Nd:YAG laser beam machining — An overview. *Journal of Materials Processing Technology* **2008**, *195*, 15–26.
- (4) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **1976**, *32*, 751–767.
- (5) Munirathnappa, A. K.; Neuefeind, J. C.; Yanda, P.; Sundaresan, A.; Kityk, I.; Ozga, K.; Jedryka, J.; Rao, A.; Sundaram, N. G. Average structure, local structure, photoluminescence, and NLO properties of scheelite type  $\text{NaCe}(\text{WO}_4)_2$ . *Crystal Growth & Design* **2019**, *19*, 6082–6091.
- (6) Bäumlér, W.; Ulrich, H.; Hartl, A.; Landthaler, M.; Shafirstein, G. Optimal parameters for the treatment of leg veins using Nd:YAG lasers at 1064 nm. *British Journal of Dermatology* **2006**, *155*, 364–371.
- (7) Javitt, J. C.; Tielsch, J. M.; Canner, J. K.; Kolb, M. M.; Sommer, A.; Steinberg, E. P.; Bergner, M.; Anderson, G. F.; Bass, E. B.; Canner, J. National outcomes of cataract extraction: Increased risk of retinal complications associated with Nd:YAG laser capsulotomy. *Ophthalmology* **1992**, *99*, 1487–1498.

- (8) Moskalik, K.; Kozlov, A.; Demin, E.; Boiko, E. The efficacy of facial skin cancer treatment with high-energy pulsed neodymium and Nd:YAG lasers. *Photomedicine and Laser Surgery* **2009**, *27*, 345–349.
- (9) Faure, N.; Borel, C.; Couchaud, M.; Basset, G.; Templier, R.; Wyon, C. Optical properties and laser performance of neodymium doped scheelites  $\text{CaWO}_4$  and  $\text{NaGd}(\text{WO}_4)_2$ . *Applied Physics B* **1996**, *63*, 593–598.
- (10) Sorokin, E.; Sorokina, I.; Unterhuber, A.; Wintner, E.; Zagumennyi, A.; Shcherbakov, I.; Carozza, V.; Toncelli, A.; Tonelli, M. In *Advanced Solid State Lasers*, 1998, p ML2.
- (11) Mann, K.; Weber, H. Surface heat transfer coefficient, heat efficiency, and temperature of pulsed solid-state lasers. *Journal of Applied Physics* **1988**, *64*, 1015–1021.
- (12) Huignard, A.; Gacoin, T.; Boilot, J.-P. Synthesis and luminescence properties of colloidal  $\text{YVO}_4\text{:Eu}$  phosphors. *Chemistry of Materials* **2000**, *12*, 1090–1094.
- (13) Erdei, S.; Johnson Jr, G.; Ainger, F. Growth studies of  $\text{YVO}_4$  crystals (II). Changes in Y-V-O stoichiometry. *Crystal Research and Technology* **1994**, *29*, 815–828.
- (14) Erdei, S.; Jin, B.; Ainger, F.; Keszei, B.; Vandlik, J.; Süveges, A. Possible trends for the growth of low scattering Nd:YVO<sub>4</sub> laser crystals; phase relations—growth techniques. *Journal of Crystal Growth* **1997**, *172*, 466–472.
- (15) Chakoumakos, B. C.; Abraham, M. M.; Boatner, L. A. Crystal structure refinements of zircon-type  $M\text{VO}_4$  ( $M = \text{Sc}, \text{Y}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Tb}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$ ). *Journal of Solid State Chemistry* **1994**, *109*, 197–202.
- (16) Errandonea, D.; Manjon, F. J. Pressure effects on the structural and electronic properties of  $ABX_4$  scintillating crystals. *Progress in Materials Science* **2008**, *53*, 711–773.
- (17) Ermeneux, F.; Goutaudier, C.; Moncorge, R.; Cohen-Adad, M.; Bettinelli, M.; Cavalli, E. Comparative optical characterization of various  $\text{Nd}^{3+}\text{:YVO}_4$  single crystals. *Optical Materials* **1999**, *13*, 193–204.

## BIBLIOGRAPHY

---

- (18) Forbes, A. R.; McMillen, C. D.; Giesber, H. G.; Kolis, J. W. The hydrothermal synthesis, solubility and crystal growth of  $\text{YVO}_4$  and  $\text{Nd:YVO}_4$ . *Journal of Crystal Growth* **2008**, *310*, 4472–4476.
- (19) Wang, A.; Wang, C.; Jia, G. Recent advances in strontium tungstate scheelite material. *Frontiers of Chemistry in China* **2010**, *5*, 61–70.
- (20) Stedman, N. J.; Cheetham, A. K.; Battle, P. D. Crystal structures of two sodium yttrium molybdates:  $\text{NaY}(\text{MoO}_4)_2$  and  $\text{Na}_5\text{Y}(\text{MoO}_4)_4$ . *Journal of Materials Chemistry* **1994**, *4*, 707–711.
- (21) Shi, F.; Meng, J.; Ren, Y. Structure and luminescent properties of three new silver lanthanide molybdates. *Journal of Solid State Chemistry* **1996**, *121*, 236–239.
- (22) Jiang, L.; Liu, G.; Li, D.; Dong, X.; Yu, W. Up/down conversion luminescence and energy transfer of  $\text{Er}^{3+}/\text{Tb}^{3+}$  activated  $\text{NaGd}(\text{WO}_4)_2$  green emitting phosphors. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2018**, *201*, 88–97.
- (23) Mullens, B. G.; Avdeev, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Insights into the structural variations in  $\text{Sm}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  and  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  combined experimental and computational studies. *Dalton Transactions* **2021**, *50*, 9103–9117.
- (24) Mullens, B. G.; Saura-Múzquiz, M.; Marlton, F. P.; Avdeev, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Beyond the ionic radii: A multifaceted approach to understand differences between the structures of  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  fergusonites. *Journal of Alloys and Compounds* **2023**, *930*, 167399.
- (25) Bastide, J. Systématique simplifiée des composés  $\text{ABX}_4$  ( $X = \text{O}^{2-}$ ,  $\text{F}^-$ ) et evolution possible de leurs structures cristallines sous pression. *Journal of Solid State Chemistry* **1987**, *71*, 115–120.
- (26) Kennedy, B. J.; Injac, S.; Thorogood, G. J.; Brand, H. E.; Poineau, F. Structures and phase transitions in pertechnetates. *Inorganic Chemistry* **2019**, *58*, 10119–10128.

- (27) Chay, C.; Avdeev, M.; Brand, H. E.; Injac, S.; Whittle, T. A.; Kennedy, B. J. Crystal structures and phase transition behaviour in the 5d transition metal oxides  $A\text{ReO}_4$  ( $A = \text{Ag, Na, K, Rb, Cs}$  and  $\text{Tl}$ ). *Dalton Transactions* **2019**, 48, 17524–17532.
- (28) Dong, L.; Zhou, Y.; Chen, J.; Han, W.; Zhang, Y.; Xu, H.; Liu, J. Lasing properties and their anisotropy of  $\text{Yb}:\text{CaWO}_4$  crystal. *Optics Communications* **2022**, 508, 127815.
- (29) Chen, J.; Dong, L.; Liu, F.; Xu, H.; Liu, J. Investigation of  $\text{Yb}:\text{CaWO}_4$  as a potential new self-Raman laser crystal. *CrystEngComm* **2021**, 23, 427–435.
- (30) Nayak, P.; Nanda, S. S.; Dash, S. Enhanced luminescence and Judd-Ofelt analysis in  $\text{SiO}_2$  encapsulated  $\text{CaWO}_4@\text{CaWO}_4:\text{Eu}:\text{Bi}$  for visualization of latent fingerprints and anti-counterfeiting. *Applied Surface Science* **2023**, 609, 155426.
- (31) Mattner, A.; Zimmermann, L.; Lienenklaus, S.; Weiss, S.; Wickleder, C. Tailoring long lasting luminescence of red-emitting  $\text{CaWO}_4:\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$  nanoparticles with enhanced crystallinity for improved bio-imaging. *Ceramics International* **2020**, 46, 26295–26298.
- (32) Xu, Y.-L.; Zhao, H.; Wang, R.; Zhang, C.-Y. Green upconversion luminescence in  $\text{Er}^{3+}/\text{Yb}^{3+}$  codoped  $\text{CaWO}_4$  polycrystals. *Chinese Physics Letters* **2011**, 28, 064210.
- (33) Kaminskii, A. A. In *Annales de Physique*, 1991; Vol. 16, pp 639–706.
- (34) Kuleshov, N.; Lagatsky, A.; Shcherbitsky, V.; Mikhailov, V.; Heumann, E.; Jensen, T.; Dening, A.; Huber, G. CW laser performance of Yb and Er, Yb doped tungstates. *Applied Physics B* **1997**, 64, 409–413.
- (35) Subbotin, K.; Zharikov, E.; Smirnov, V. Yb-and Er-Doped single crystals of double tungstates  $\text{NaGd}(\text{WO}_4)_2$ ,  $\text{NaLa}(\text{WO}_4)_2$ , and  $\text{NaBi}(\text{WO}_4)_2$  as active media for lasers operating in the 1.0 and 1.5  $\mu\text{m}$  ranges. *Optics and Spectroscopy* **2002**, 92, 601–608.
- (36) Wang, Z.; Liang, H.; Gong, M.; Su, Q. Luminescence investigation of  $\text{Eu}^{3+}$  activated double molybdates red phosphors with scheelite structure. *Journal of Alloys and Compounds* **2007**, 432, 308–312.

## BIBLIOGRAPHY

---

- (37) Azad, A.; Ivanov, S.; Eriksson, S.-G.; Eriksen, J.; Rundlöf, H.; Mathieu, R.; Svedlindh, P. Synthesis, crystal structure, and magnetic characterization of the double perovskite  $\text{Ba}_2\text{MnWO}_6$ . *Materials Research Bulletin* **2001**, *36*, 2215–2228.
- (38) Saura-Múzquiz, M.; Marlton, F. P.; Mullens, B. G.; Manjón-Sanz, A. M.; Neufeind, J. C.; Everett, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Understanding the re-entrant phase transition in a non-magnetic scheelite. *Journal of the American Chemical Society* **2022**, *144*, 15612–15621.
- (39) Tokunaga, S.; Kato, H.; Kudo, A. Selective preparation of monoclinic and tetragonal  $\text{BiVO}_4$  with scheelite structure and their photocatalytic properties. *Chemistry of Materials* **2001**, *13*, 4624–4628.
- (40) Teslic, S.; Egami, T. Atomic structure of  $\text{PbZrO}_3$  determined by pulsed neutron diffraction. *Acta Crystallographica Section B: Structural Science* **1998**, *54*, 750–765.
- (41) Perera, S. S.; Munasinghe, H. N.; Yatooma, E. N.; Rabuffetti, F. A. Microwave-assisted solid-state synthesis of  $\text{NaRE}(\text{MO}_4)_2$  phosphors ( $\text{RE} = \text{La, Pr, Eu, Dy}$ ;  $M = \text{Mo, W}$ ). *Dalton Transactions* **2020**, *49*, 7914–7919.
- (42) Postema, J.; Fu, W.; Ijdo, D. Crystal structure of  $\text{LiLnW}_2\text{O}_8$  ( $\text{Ln} = \text{lanthanides and Y}$ ): An X-ray powder diffraction study. *Journal of Solid State Chemistry* **2011**, *184*, 2004–2008.
- (43) Xue, Y.; Zhao, D.; Cui, X.; Han, X.; Liu, B.; Fan, Y. Crystal structure of scheelite-type  $\text{LiTb}(\text{WO}_4)_2$  and multi-color emitting properties doped by  $\text{Eu}^{3+}$ . *Chinese Journal of Structural Chemistry* **2020**, *39*, 310–320.
- (44) Han, X.; Lin, Z.; Hu, Z.; Wang, G. Structure of  $\text{KLa}(\text{WO}_4)_2$  with a novel isolated La polyhedron. *Materials Research Innovations* **2002**, *6*, 118–121.
- (45) Sotelo, P.; Moore, M.; Galante, M. T.; Longo, C.; Rajeshwar, K.; Suescun, L.; Macaluso, R. T. Structure and optical properties of a new  $\text{AgBiW}_2\text{O}_8$  polymorph. *Polyhedron* **2019**, *170*, 486–489.
- (46) Zhang, H.-J.; Fu, L.; Wang, C.-P.; Fu, H.-F.; Xie, W.-G. Crystal structure of scheelite-type potassium cerium bis(tetraoxomolybdate(VI)),  $\text{KCe}(\text{MoO}_4)_2$ . *Zeitschrift für Kristallographie - New Crystal Structures* **2014**, *229*, 191–192.

- (47) Terebilenko, K. V.; Bychkov, K. L.; Klymyshyna, K. E.; Baumer, V. N.; Slobodyanik, M. S.; Khomenko, E. V.; Dotsenko, V. P. Single crystals of  $KRE(\text{MoO}_4)_2$ , ( $RE = \text{Ce}, \text{Pr}$ ) obtained from fluorides: Scheelite-related structure and luminescence. *Crystal Research and Technology* **2017**, *52*, 1700222.
- (48) Hanuza, J.; Mączka, M.; Van der Maas, J. Polarized IR and Raman spectra of tetragonal  $\text{NaBi}(\text{WO}_4)_2$ ,  $\text{NaBi}(\text{MoO}_4)_2$  and  $\text{LiBi}(\text{MoO}_4)_2$  single crystals with scheelite structure. *Journal of Molecular Structure* **1995**, *348*, 349–352.
- (49) Hanuza, J.; Haznar, A.; Maczka, M.; Pietraszko, A.; Lemiec, A.; Van der Maas, J.; Lutz, E. Structure and vibrational properties of tetragonal scheelite  $\text{NaBi}(\text{MoO}_4)_2$ . *Journal of Raman Spectroscopy* **1997**, *28*, 953–963.
- (50) Rico, M.; Méndez-Blas, A.; Volkov, V.; Monge, M. Á.; Cascales, C.; Zaldo, C.; Kling, A.; Fernández-Díaz, M. T. Polarization and local disorder effects on the properties of  $\text{Er}^{3+}$ -doped  $X\text{Bi}(\text{YO}_4)_2$ ,  $X = \text{Li}$  or  $\text{Na}$  and  $Y = \text{W}$  or  $\text{Mo}$ , crystalline tunable laser hosts. *Journal of the Optical Society of America B* **2006**, *23*, 2066–2078.
- (51) Anderson, M. T.; Poeppelmeier, K. R. Lanthanum copper tin oxide ( $\text{La}_2\text{CuSnO}_6$ ): A new perovskite-related compound with an unusual arrangement of  $B$  cations. *Chemistry of Materials* **1991**, *3*, 476–482.
- (52) Anderson, M. T.; Greenwood, K. B.; Taylor, G. A.; Poeppelmeier, K. R.  $B$ -cation arrangements in double perovskites. *Progress in Solid State Chemistry* **1993**, *22*, 197–233.
- (53) Wallwork, K. S.; Kennedy, B. J.; Wang, D. In *AIP Conference Proceedings*, 2007; Vol. 879, pp 879–882.
- (54) Liss, K.-D.; Hunter, B.; Hagen, M.; Noakes, T.; Kennedy, S. Echidna — The new high-resolution powder diffractometer being built at OPAL. *Physica B: Condensed Matter* **2006**, *385*, 1010–1012.
- (55) Neuefeind, J.; Feygenson, M.; Carruth, J.; Hoffmann, R.; Chipley, K. K. The nanoscale ordered materials diffractometer NOMAD at the spallation neutron source SNS. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **2012**, *287*, 68–75.



## BIBLIOGRAPHY

---

- (56) Coelho, A. A. TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++. *Journal of Applied Crystallography* **2018**, *51*, 210–218.
- (57) Thompson, P.; Cox, D.; Hastings, J. Rietveld refinement of Debye–Scherrer synchrotron X-ray data from Al<sub>2</sub>O<sub>3</sub>. *Journal of Applied Crystallography* **1987**, *20*, 79–83.
- (58) Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* **2011**, *44*, 1272–1276.
- (59) Huang, J.; You, W.; Gong, G.; Liu, G.; Liu, P.; Wang, B. Electronic structure and photoluminescence of Dy<sup>3+</sup> single-doped and Dy<sup>3+</sup>/Tm<sup>3+</sup> co-doped NaBi(WO<sub>4</sub>)<sub>2</sub> phosphors. *Optical Materials* **2019**, *88*, 534–539.
- (60) Perets, S.; Tseitlin, M.; Shneck, R.; Mogilyanski, D.; Kimmel, G.; Burshtein, Z. Sodium gadolinium tungstate NaGd(WO<sub>4</sub>)<sub>2</sub>: Growth, crystallography, and some physical properties. *Journal of Crystal Growth* **2007**, *305*, 257–264.
- (61) Teller, R. G. Refinement of some Na<sub>0.5-x</sub>M'<sub>0.5+x/3</sub>□<sub>2x/3</sub>MoO<sub>4</sub>, M' = Bi, Ce, La, scheelite structures with powder neutron and X-ray diffraction data. *Acta Crystallographica Section C: Crystal Structure Communications* **1992**, *48*, 2101–2104.
- (62) Stevens, S.; Morrison, C.; Allik, T.; Rheingold, A.; Haggerty, B. NaLa(MoO<sub>4</sub>)<sub>2</sub> as a laser host material. *Physical Review B* **1991**, *43*, 7386.
- (63) Rabuffetti, F. A.; Culver, S. P.; Suescun, L.; Brutchey, R. L. Structural disorder in AMoO<sub>4</sub> (A = Ca, Sr, Ba) scheelite nanocrystals. *Inorganic Chemistry* **2014**, *53*, 1056–1061.
- (64) Culver, S. P.; Brutchey, R. L. Thermally activated rotational disorder in CaMoO<sub>4</sub> nanocrystals. *CrystEngComm* **2016**, *18*, 4485–4488.
- (65) Amarasinghe, D. K.; Perera, S. S.; Rabuffetti, F. A. Rotational disorder in scheelite-type NaRE(MO<sub>4</sub>)<sub>2</sub> (RE = Rare-Earth, Y; M = Mo, W). *Crystal Growth & Design* **2020**, *20*, 3442–3448.

- (66) Marlton, F. P.; Mullens, B. G.; Chater, P. A.; Kennedy, B. J. Tetrahedral displacive disorder in the scheelite-type oxide  $\text{RbReO}_4$ . *Inorganic Chemistry* **2022**, *61*, 15130–15137.
- (67) Saura-Múzquiz, M.; Marlton, F. P.; Mullens, B. G.; Liu, J.; Vogt, T.; Maynard-Casely, H. E.; Avdeev, M.; Blom, D. A.; Kennedy, B. J. Cation and lone pair order–disorder in the polymorphic mixed metal bismuth scheelite  $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$ . *Chemistry of Materials* **2022**, *35*, 123–135.
- (68) Sleight, A.; Chen, H.-Y.; Ferretti, A.; Cox, D. Crystal growth and structure of  $\text{BiVO}_4$ . *Materials Research Bulletin* **1979**, *14*, 1571–1581.
- (69) Aksel, E.; Forrester, J. S.; Nino, J. C.; Page, K.; Shoemaker, D. P.; Jones, J. L. Local atomic structure deviation from average structure of  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ : Combined X-ray and neutron total scattering study. *Physical Review B* **2013**, *87*, 104113.
- (70) Dawson, J. A.; Chen, H.; Tanaka, I. Crystal structure, defect chemistry and oxygen ion transport of the ferroelectric perovskite,  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ : Insights from first-principles calculations. *Journal of Materials Chemistry A* **2015**, *3*, 16574–16582.
- (71) Jeong, I.; Park, C. Y.; Kim, D. J.; Kim, S.-h.; Moon, B. K.; Kim, I. W.; Ahn, C. W. Neutron total scattering studies on A-site disorder in lead-free ferroelectric  $\text{Bi}_{0.5}(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{TiO}_3$ . **2011**.
- (72) Walsh, A.; Yan, Y.; Huda, M. N.; Al-Jassim, M. M.; Wei, S.-H. Band edge electronic structure of  $\text{BiVO}_4$ : Elucidating the role of the Bi *s* and V *d* orbitals. *Chemistry of Materials* **2009**, *21*, 547–551.
- (73) Malathi, A.; Madhavan, J.; Ashokkumar, M.; Arunachalam, P. A review on  $\text{BiVO}_4$  photocatalyst: Activity enhancement methods for solar photocatalytic applications. *Applied Catalysis A: General* **2018**, *555*, 47–74.
- (74) Kazin, P. E.; Pogosova, M. A.; Trusov, L. A.; Kolesnik, I. V.; Magdysyuk, O. V.; Dinnebier, R. E. Crystal structure details of La- and Bi-substituted hydroxyapatites: Evidence for  $\text{LaO}^+$  and  $\text{BiO}^+$  with a very short metal–oxygen bond. *Journal of Solid State Chemistry* **2016**, *237*, 349–357.

- (75) Injac, S.; Yuen, A. K.; Avdeev, M.; Wang, C.-H.; Turner, P.; Brand, H. E.; Kennedy, B. J. Structural and magnetic studies of  $ABO_4$ -type ruthenium and osmium oxides. *Inorganic Chemistry* **2020**, *59*, 2791–2802.
- (76) Saura-Múzquiz, M.; Mullens, B. G.; Maynard-Casely, H. E.; Kennedy, B. J. Neutron diffraction study of the monoclinic–tetragonal phase transition in  $NdNbO_4$  and  $NdTaO_4$ . *Dalton Transactions* **2021**, *50*, 11485–11497.
- (77) Zhang, J.; Wang, J.; Wang, K.; Yu, W.; Zhang, H.; Wang, Z.; Wang, X.; Ba, M. Growth and structure of monoclinic  $KLu(WO_4)_2$  crystals. *Journal of Crystal Growth* **2006**, *292*, 373–376.
- (78) Levin, I.; Krayzman, V.; Playford, H.; Woicik, J.; Maier, R.; Lu, Z.; Bruma, A.; Eremenko, M.; Tucker, M. The mediation of bond strain by vacancies and displacive disorder in  $A$ -site-deficient perovskites. *Acta Materialia* **2021**, *207*, 116678.
- (79) Tucker, M. G.; Keen, D. A.; Dove, M. T.; Goodwin, A. L.; Hui, Q. RMCProfile: Reverse Monte Carlo for polycrystalline materials. *Journal of Physics: Condensed Matter* **2007**, *19*, 335218.
- (80) Morozov, V. A.; Arakcheeva, A. V.; Chapuis, G.; Guiblin, N.; Rossell, M. D.; Van Tendeloo, G.  $KNd(MoO_4)_2$ : A new incommensurate modulated structure in the scheelite family. *Chemistry of Materials* **2006**, *18*, 4075–4082.



## Chapter 5

# Local Structure Studies of Photocatalysts

*This chapter is adapted from the following manuscripts:*

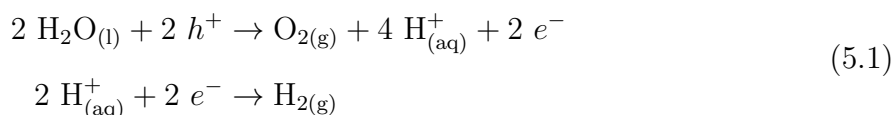
- Mullens, B.G.; Marlton, F.P.; Nicholas, M.K.; Permana, A.J.; Avdeev, M.; Vaitheeswaran, G.; Li, C.; Liu, J.; Chater, P.A.; Kennedy, B.J.; Seeing the Unseen: The Structural Influence of the Lone Pair Electrons in the Photocatalyst PbWO<sub>4</sub>. *Under Revision for Inorganic Chemistry*.
- Mullens, B.G.; Marlton, F.P.; Nicholas, M.K.; Permana, A.J.; Brand, H.E.A.; Maynard-Casely, H.E.; Zhang, Z.; Baldinozzi, G.; Kennedy, B.J.; A Multifaceted Approach to Understand the Monoclinic-Tetragonal Phase Transition in BiVO<sub>4</sub>. *Manuscript in Preparation*.
- Hu, D.; Beauvais, M.L.; Kamm, G.E.; Mullens, B.G.; Sanchez Monserrate, B.A.; Vornholt, S.M.; Chupas, P.J.; Chapman, K.W.; Resolving Fast Relative Kinetics in Inorganic Solid-State Synthesis. *Journal of the American Chemical Society*, **2023**, *145* (49), 26545-26549.<sup>1</sup>
- Hu, D.; Beauvais, M.L.; Mullens, B.G.; Sanchez Monserrate, B.A.; Vornholt, S.M.; Kamm, G.E.; Ferrari, J.J.; Chupas, P.J.; Chapman, K.W.; The RAPTR Furnace: A Rapid Heating and Cooling Sample Furnace for *In Situ* X-Ray Scattering Studies of Temperature-Induced Reactions. *Journal of Applied Crystallography*, **2024**, *57*, 88-93.<sup>2</sup>



## 5.1 Introduction: Photocatalytic Water Splitting

Photocatalytic water splitting is the acceleration of a reaction using a material (such as a semiconductor) able to split water into its constituent gases (oxygen and hydrogen) in the presence of sunlight. Photocatalytic water splitting has the potential to enable the utilisation of an abundant and clean energy source (such as sunlight) for the green processes of environmental remediation (water pollutant degradation) and clean energy production (the production of hydrogen and oxygen gas, or the reduction of carbon dioxide to organic carbon feed stocks).<sup>3</sup> Therefore, there is a collective research effort into the development and classification of novel photocatalytic materials for potential industrial use.

Semiconductor metal oxide photocatalysts operate by absorbing a photon of sunlight, leading to the excitation of an electron from the valence band into the conduction band of the material. This creates a photogenerated electron and ‘hole’ pair which are free to engage in oxidation-reduction reactions (provided they don’t recombine), such as the production of hydrogen and oxygen gas from water, by



where  $h^+$  and  $e^-$  are the photogenerated hole and electron respectively.

Despite its apparent simplicity, photocatalysts have not yet been commercialised due to their low efficiency using visible light. The two most heavily studied binary semiconductor photocatalysts –  $\text{TiO}_2$  and  $\text{ZnO}$  – have band gaps of 3.2 and 3.4 eV respectively.<sup>4,5</sup> This places their absorption range in the ultraviolet region of the electromagnetic spectrum that accounts for less than 10% of natural sunlight. Current research has focused on the controlled introduction of crystal defects such as vacancies, interstitials, antisites, and chemical doping to ‘tune’ the band gap to be more favourable for absorbing solar radiation. Of particular note are the use of ternary oxides, such as  $\text{Bi}_2\text{WO}_6$  as a novel photocatalytic degrader of phenols,<sup>6</sup>  $\text{Zn}_2\text{GeO}_4$  as a reducer of  $\text{CO}_2$ ,<sup>7</sup> and  $\text{InVO}_4$  and  $\text{SrTiO}_3$  as hydrogen evolution photocatalysts.<sup>8,9</sup>

### 5.1.1 BiVO<sub>4</sub> and PbWO<sub>4</sub> as Photocatalysts

Along with InVO<sub>4</sub>, several other  $ABO_4$  materials have been identified as materials for photocatalysis. In particular, BiVO<sub>4</sub> has been investigated as a promising visible light-driven semiconductor photocatalyst due to its low production cost, low toxicity, high stability, and narrow band gap.<sup>10</sup> BiVO<sub>4</sub> has already been investigated for degrading organic pollutants such as methylene blue and rhodamine B in the presence of sunlight.<sup>11,12</sup> However, despite its outstanding chemical and photostability, its narrow band gap of  $\sim 2.4$  eV allows for the fast recombination of photoinduced carriers, leading to a decrease in efficiency.<sup>13</sup> Similarly, PbWO<sub>4</sub> has been investigated for its ability to degrade organic pollutants.<sup>14–16</sup>

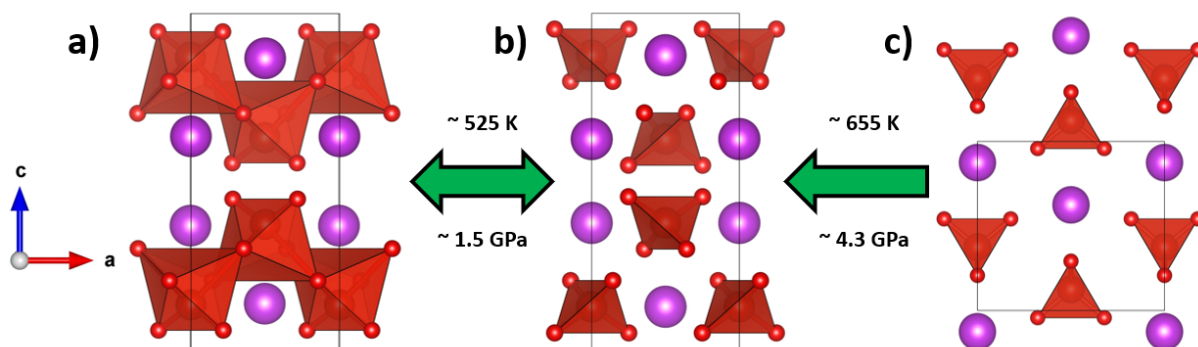


Figure 5.1: The three phases of BiVO<sub>4</sub>. (a) The monoclinic-fergusonite form of space group  $I2/b$ , (b) the tetragonal-scheelite form of space group  $I4_1/a$ , and (c) the tetragonal-zircon form of space group  $I4_1/amd$ . Note that the  $I2/b \rightarrow I4_1/a$  phase transition is reversible with both temperature and pressure, whereas the  $I4_1/amd \rightarrow I4_1/a$  is irreversible.

There are three crystalline structures of BiVO<sub>4</sub>: monoclinic-fergusonite ( $m-f$ , space group  $I2/b$ ), tetragonal-scheelite ( $t-s$ , space group  $I4_1/a$ ), and tetragonal-zircon ( $t-z$ , space group  $I4_1/amd$ ).<sup>17</sup> The  $m-f$  form (isostructural to the LaNbO<sub>4</sub>-type materials described in Chapter 3) consists of eight-coordinate BiO<sub>8</sub> polyhedra and four-coordinate VO<sub>4</sub> tetrahedra. The BiO<sub>8</sub> polyhedra consist of four pairs of different Bi–O bond lengths ranging from 2.3–2.8 Å, whereas the VO<sub>4</sub> tetrahedra are slightly distorted with two different V–O bond lengths (1.57 Å and 1.68 Å respectively).<sup>18</sup> Upon heating (or pressurising), the  $m-f$  form of BiVO<sub>4</sub> undergoes a  $I2/a \rightarrow I4_1/a$  phase transition to the  $t-s$  form.<sup>19–21</sup> This structure consists of two different Bi–O bond lengths (2.4–2.5 Å), as well as a single V–O bond length (1.7 Å).<sup>19</sup> Due to the second order nature of



this phase transition, the *t-s* structure cannot be quenched to room temperature, and only exists under high temperature or pressure environments.<sup>17</sup> The third form, the *t-z* form, must be prepared through a low temperature coprecipitation route.<sup>22,23</sup> It consists of similar structural motifs, with the BiO<sub>8</sub> polyhedra made up of two different Bi–O bonds (2.4–2.6 Å) and the VO<sub>4</sub> tetrahedra made up of a single unique V–O bond length (1.7 Å).<sup>17</sup> These three structures are related through the application of either heat or pressure, as illustrated in Figure 5.1.

Of the three phases of BiVO<sub>4</sub>, the *m-f* phase exhibits the greatest photocatalytic performance.<sup>24</sup> It has been hypothesised that this is due to the larger distortion of the BiO<sub>8</sub> polyhedra in the *m-f* phase. To quantify this distortion, the distortion index (*D*) can be calculated as

$$D = \frac{1}{n} \sum_{i=1}^n \frac{|l_i - l_\mu|}{l_\mu} \quad (5.2)$$

where *n* is the number of bonds in the polyhedra, *l<sub>i</sub>* is the bond length, and *l<sub>μ</sub>* is the average bond length in the polyhedra.<sup>25</sup>

In the case of the three BiVO<sub>4</sub> polymorphs, the *m-f* BiO<sub>8</sub> are regarded as the most distorted (*D* = 0.0452), followed by *t-z* (*D* = 0.0271), and finally *t-s* (*D* = 0.0152). The distortion of the BiO<sub>8</sub> polyhedra is identified as a consequence of the Bi<sup>3+</sup> cations possessing stereochemically active lone pair electrons.<sup>20,24</sup> Lone pair electrons play a central role in determining the structural and electronic properties of both chemically simple materials (such as the bent shape of H<sub>2</sub>O or the trigonal pyramidal shape of NH<sub>3</sub>) to more complex macromolecules such as proteins.<sup>26,27</sup> There are, however, numerous examples of condensed phases that apparently violate the valence shell electron pair repulsion (VSEPR) rules. Compounds with 6s<sup>2</sup> lone pair electrons (such as Bi<sup>3+</sup>, Pb<sup>2+</sup>, and Tl<sup>+</sup>) are well known for their unique polar properties, such as Bi-based semiconductors,<sup>28</sup> Pb-based perovskite ferroelectrics,<sup>29–31</sup> and the unusual magnetic ordering in Tl-based oxide materials.<sup>32</sup> The presence of lone pair electrons has also been identified as an approach to engineer new materials with low thermal conductivity and enhanced thermoelectric properties.<sup>33,34</sup> In the case of *m-f* BiVO<sub>4</sub>, the overlap of the O 2*p* and Bi 6*s* orbitals impacted by the Bi<sup>3+</sup> lone pair in the valence band allows for the

$\text{Bi}^{3+}$  lone pair to be ‘stereochemically active’, leading to structural distortions in the  $\text{BiO}_8$  polyhedra.<sup>35</sup> A coupling of the overlapping O  $2p$  and Bi  $6s$  orbitals allows for increased mobility for photogenerated charge carriers, along with the distorted  $\text{BiO}_8$  polyhedra preventing recombination, explains the high photocatalytic activity of the  $m$ - $f$  phase.<sup>10</sup>

The structural influence of lone pair electrons is of interest in other heavier  $p$ -block atoms.<sup>36</sup> It has recently been established that the stereochemical influence of the lone pair electrons in the compounds formed with  $ns^2$ -containing metals is influenced by the relative energy differences between the electronic states of the constituent atoms.<sup>36</sup> In some species, such as  $\alpha$ - $\text{PbO}$ , the structural influence of the lone pair is obvious; all four coordinated oxygens are found on one side of the  $\text{Pb}^{2+}$  cation with the lone pair projected in the opposite direction. In other species, such as  $\text{PbS}$ , the  $6s^2$  electrons do not appear to exert any influence on the long-range average structure, with  $\text{Pb}^{2+}$  at the centrosymmetric position of the  $\text{PbS}_6$  octahedra (Figure 5.2). For metal oxides, the energy separation between the cation  $ns$  and O  $2p$  levels determines the stereochemical activity of the lone pair, following the trend of:  $\text{Sn}^{2+} > \text{Pb}^{2+} > \text{Sb}^{3+} > \text{Bi}^{3+} > \text{Te}^{4+} > \text{Po}^{4+}$ . This atomic orbital trend has been used to explain why  $\text{SnO}$  crystallises in a distorted litharge structure, whereas  $\text{PoO}_2$  forms the centrosymmetric fluorite structure. As an extension, the implication is that the  $6s^2$  electrons are more likely to exert stereochemical influence in  $\text{Pb}^{2+}$  systems than in  $\text{Bi}^{3+}$  systems. However, this is not observed, with  $\text{BiVO}_4$  displaying monoclinic distortions that appear to be absent in the  $\text{PbWO}_4$  analogue.

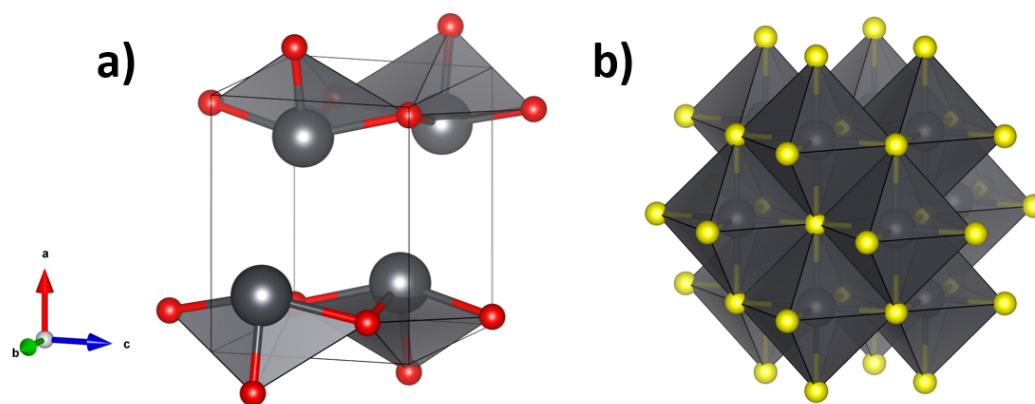


Figure 5.2: The structure of (a)  $\alpha$ - $\text{PbO}$  ( $Pbcm$ ). The four short Pb–O bonds reflect the projection of the lone pair electron density in the opposite direction (along the  $a$ -axis). (b) The structure of  $\text{PbS}$  ( $Fm\bar{3}m$ ). The centrosymmetry of  $\text{Pb}^{2+}$  in the  $\text{PbS}_6$  octahedra, and the six Pb–S bonds of identical length indicate limited lone pair stereoactivity.

Isostructural with the high temperature *t-s* form of  $\text{BiVO}_4$ ,  $\text{PbWO}_4$  has a tetragonal scheelite  $I4_1/a$  structure at ambient temperature and pressure.<sup>37</sup> The  $\text{Pb}^{2+}$  cations are bonded to eight oxygen atoms with two different Pb–O bond distances (2.5–2.7 Å). Neutron and X-ray diffraction studies show the  $\text{W}^{6+}$  cations are bonded to four oxygen atoms with a single W–O distance (1.7 Å).<sup>37–39</sup> Like  $\text{BiVO}_4$ ,  $\text{PbWO}_4$  has been identified as a promising photocatalyst for removing organic pollution in water.<sup>14,40–42</sup> However, this property is considered unusual for  $\text{PbWO}_4$ , as other isostructural materials (such as the ‘original’ scheelite  $\text{CaWO}_4$ ) have demonstrated no such photocatalytic activity.<sup>43</sup> This implies that the  $\text{Pb}^{2+}$   $6s^2$  lone pair electrons are active in terms of its photocatalytic activity, but not stereochemically active as observed in its lack of distorted  $\text{PbO}_8$  polyhedra ( $D = 0.0109$ ).<sup>39</sup>

Recent SXRD and NPD studies of two other  $\text{ABO}_4$  tetragonal scheelites with lone pair-containing cations on the *A* site –  $\text{TlReO}_4$  and  $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$  – showed the absence of any stereochemical influence of the lone pairs in their average structure using Bragg diffraction.<sup>44,45</sup> However, in both of these examples, neutron total scattering methods showed the structure to have lower local symmetry than the average structure of the material. This is a consequence of uncorrelated displacements associated with the  $6s^2$  lone pairs, where the lone pairs appear to be ‘active’ in the short-range structure, but ‘averaged out’ over the long-range structure. These two oxides display unusual *emphanitic*-like behaviour in their long-range structure, whereby they undergo symmetry lowering upon warming as a result of displacements of cations from their centrosymmetric positions.<sup>46,47</sup> This behaviour has been identified as a result of a change in correlation length of the  $6s^2$  lone pairs.

The observation of ‘hidden’ lone pair local ordering in the tetragonal polymorphs of  $\text{TlReO}_4$  and  $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$ , as well as the polyhedra distortions observed in  $\text{NaBi}(\text{WO}_4)_2$  in Chapter 4, was made possible using total scattering data in the form of NPDF analysis.<sup>44,45</sup> This has prompted a study of the high temperature *t-s* structure of  $\text{BiVO}_4$  to determine if similar cation displacements, as a result of the  $\text{Bi}^{3+}$  lone pair, can be observed. This will be complemented with a similar study of  $\text{PbWO}_4$  and  $\text{PbMoO}_4$ , which have also been determined (using diffraction studies) to be highly symmetric in the

tetragonal  $I4_1/a$  space group, despite the presence of the lone pair-bearing  $\text{Pb}^{2+}$  cation and photocatalytic activity.<sup>48</sup> The local structure of  $\text{PbWO}_4$  is compared to that of the isostructural compound  $\text{CaWO}_4$  which does not contain a lone pair-bearing cation.

This chapter is separated into two main sections. The first section details a SXRD and NPD study of  $\text{BiVO}_4$ , where the  $I2/b \rightarrow I4_1/a$  phase transition is investigated. This study is repeated using a combination of XPDF and NPDF to observe any symmetry-lowering phenomena on the local scale as a result of the  $\text{Bi}^{3+} 6s^2$  lone pair. The second section details a similar study of  $\text{PbWO}_4$  which, according to the revised lone pair model, should also exhibit structural distortions like its  $\text{BiVO}_4$  counterpart. A full study of this material is undertaken: including determining its optimal synthesis conditions, using NPD to determine any signatures of lone pair activity, and using neutron total scattering to compare and contrast with other scheelite-type oxides, such as the lone pair-bearing  $\text{TlReO}_4$  and non-lone pair-bearing  $\text{CaWO}_4$ . The chapter is then concluded with an outlook on the future design of photocatalysts.

## 5.2 Synthesis Procedure and Experimental Methods

### 5.2.1 Sample Synthesis

$\text{BiVO}_4$  was prepared using a conventional solid state synthesis technique.  $\text{Bi}_2\text{O}_3$  (Sigma-Aldrich, 99.9%) and  $\text{V}_2\text{O}_5$  (Sigma-Aldrich, 99.6%) were used as reagents.  $\text{Bi}_2\text{O}_3$  was dried at 600 °C for 16 hours to remove adsorbed carbon dioxide and water. Due to its low melting point ( $\sim 690$  °C),  $\text{V}_2\text{O}_5$  was dried at 200 °C for 16 hours. Stoichiometric amounts of  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  (enough to synthesise  $\sim 10$  g of sample) were weighed and finely ground in acetone using an agate mortar to obtain a homogeneous mixture. The dried powder was pressed into a rod using a hydrostatic press at 200 bar for 10 minutes, then heated in air in an alumina crucible at 750 °C for 24 hours.

A similar procedure was adopted for the synthesis of  $\text{PbMoO}_4$  and  $\text{PbWO}_4$ .  $\text{PbO}$  (May and Baker, 99%),  $\text{MoO}_3$  (Sigma-Aldrich,  $\geq 99.5\%$ ), and  $\text{WO}_3$  (Aithaca Chemicals, 99.998%) were used as reagents, with each metal oxide first dried at 200 °C for 24 hours to remove adsorbed carbon dioxide and water. Stoichiometric amounts of  $\text{PbO}$  and  $\text{WO}_3$  (enough to synthesise  $\sim 10$  g of sample), and  $\text{PbO}$  and  $\text{MoO}_3$  (enough to synthesise  $\sim 4$  g of sample) were weighed and finely ground in acetone using an agate mortar before being pressed into a rod using a hydrostatic press at 200 bar for 10 minutes. Each sample was then heated in air in an alumina crucible at 800 °C for 24 hours.

$\text{CaWO}_4$  (enough to prepare  $\sim 5$  g of sample) was also prepared using the solid state synthesis technique.  $\text{CaCO}_3$  (Sigma-Aldrich, 99.95%) was dried at 600 °C for 12 hours to ensure no partial decomposition of  $\text{CaCO}_{3(\text{s})} \rightleftharpoons \text{CaO}_{(\text{s})} + \text{CO}_{2(\text{g})}$  occurred.  $\text{WO}_3$  (Aithaca Chemicals, 99.998%) was dried at 200 °C to remove adsorbed carbon dioxide and water. Stoichiometric amounts were weighed and finely ground using an agate mortar before being pressed into a rod using a hydrostatic press at 200 bar for 10 minutes. Each sample was heated in air in an alumina crucible at 800 °C for 24 hours. All samples were ground to a fine powder for analysis.

### 5.2.2 Synchrotron X-Ray and Neutron Powder Diffraction

SXRD data were collected for  $\text{BiVO}_4$  and  $\text{PbWO}_4$  over an angular range  $5 \leq 2\theta \leq 85^\circ$  at 21.0 keV ( $\lambda = 0.59007 \text{ \AA}$ ), as determined by a structural refinement of a NIST SRM660b  $\text{LaB}_6$  standard, on the Powder Diffractometer beamline BL-10 of the Australian Synchrotron.<sup>49</sup> The  $\text{BiVO}_4$  sample was housed in a 0.5 mm diameter quartz capillary. Due to a potential reaction between  $\text{Bi}^{3+}$  and the quartz capillary, and the high attenuation of  $\text{Bi}^{3+}$ , each capillary was diluted in a 50:50 ratio with diamond powder. The  $\text{PbWO}_4$  sample was housed in a 0.2 mm diameter borosilicate glass capillary for room temperature measurements. Each sample was rotated during the measurements to minimise preferred orientation effects. Variable temperature SXRD data were collected for  $\text{BiVO}_4$  from 100–500 K using an Oxford cryostream, and from 400–750 K using a hot air blower.

*In situ* synthesis measurements of  $\text{PbWO}_4$  were collected within the rapidly-actuating pneumatic thermal reactor (RAPTR),<sup>2</sup> with data collected at beamline 11-ID-B of the APS at Argonne National Laboratory, USA ( $\lambda = 0.2115 \text{ \AA}$ , 58.62 keV). Following translation of a pressed, stoichiometric mixture of  $\text{PbO}$  and  $\text{WO}_3$  into the hot zone, data were collected with one second exposures during the first minute, then at increasing intervals at longer intervals: two second exposures (1–2 minutes), five second exposures (2–4 minutes), and finally ten second exposures (4–5 minutes) to match the data density of the anticipated rate of change for the reaction. Data were collected with the 2D area detector placed far from the sample (1000 mm). The 2D image data were corrected for the polarisation, detector transmission, and flat field, with badly performing pixels masked prior to integration to 1D using the program GSAS-II.<sup>50</sup>

High resolution NPD data were measured using Echidna at the OPAL reactor operated by ANSTO.<sup>51</sup> Powder samples were loaded into 6 mm diameter vanadium cans, with data collected over the range  $15 \leq 2\theta \leq 155^\circ$  with a step size of  $0.05^\circ$ . For  $\text{BiVO}_4$ , three patterns were collected using the cryofurnace at 3, 300, and 723 K using  $1.62 \text{ \AA}$  wavelength neutrons. For  $\text{PbWO}_4$  and  $\text{CaWO}_4$ , patterns were also measured in the cryofurnace at 300 K using  $1.30 \text{ \AA}$  wavelength neutrons, as well as at 3 K using both  $2.44$  and  $1.30 \text{ \AA}$  wavelength neutrons. High intensity variable temperature NPD data for  $\text{BiVO}_4$  were measured using Wombat, also at the OPAL reactor operated by ANSTO.<sup>52</sup> Powder samples were loaded into 6 mm vanadium cans, with data collected over the range  $15 \leq 2\theta \leq 135^\circ$  using  $1.62 \text{ \AA}$  wavelength neutrons. Data were collected upon heating from 50–750 K.

Structures were refined using the Rietveld method implemented in the program TOPAS6.<sup>53</sup> The peak shapes were modelled using the Thompson-Cox-Hastings profile function.<sup>54</sup> The background was modelled using a 12<sup>th</sup>-order Chebyshev polynomial for the SXRD, and a 6<sup>th</sup>-order Chebyshev polynomial for the NPD. The scale factor, lattice parameters, atomic coordinates, and ADPs were refined simultaneously with the peak profile and background parameters. In the SXRD data where  $\text{BiVO}_4$  was diluted with diamond powder, an additional Le Bail fit was undertaken to account for the reflections of the  $Fd\bar{3}m$  diamond structure. The crystal structures were drawn using VESTA.<sup>55</sup>

### 5.2.3 X-Ray and Neutron Total Scattering

X-ray total scattering measurements for  $\text{BiVO}_4$  were performed on beamline 11-ID-B of the APS at Argonne National Laboratory, USA ( $\lambda = 0.2115 \text{ \AA}$ , 58.62 keV). A small amount of finely ground sample was loaded into a borosilicate glass capillary (inner diameter 0.7 mm) to a height of 3 cm. Data were collected under ambient conditions for the sample, an empty capillary, and the empty sample environment. The sample was loaded into a flow-cell furnace and heated from 400–630 K before being cooled.<sup>56</sup> During heating, the 2D area detector was placed far from the sample (1000 mm) yielding data suitable for Rietveld refinement, whereas during cooling the detector was placed close to the sample (180 mm) for PDF data collection. The 2D image data were corrected for the polarisation, detector transmission, and flat field, with badly performing pixels masked prior to integration to 1D using the program GSAS-II.<sup>50</sup> The PDF  $G(r)$  were calculated using the PDFgetX3 software from the xPDFsuite.<sup>57,58</sup> Calculations were performed using a  $Q_{\text{max}}$  of  $14.2 \text{ \AA}^{-1}$ .

X-ray total scattering measurements for  $\text{PbMoO}_4$  were performed on beamline I15-1 of the Diamond Light Source, UK ( $\lambda = 0.161669 \text{ \AA}$ , 76.69 keV). A small amount of finely ground sample was loaded into a borosilicate glass capillary (inner diameter 0.78 mm) to a height of 3.5 cm. Data were collected under ambient conditions for the sample, an empty capillary, and the empty instrument. Diffraction data were collected using two 2D area detectors at different distances relative to the sample: 860 mm from the sample for Rietveld refinement and 200 mm from the sample for PDF analysis. The 2D diffraction data were corrected for the polarisation, detector transmission, and flat field, with badly performing pixels masked prior to integration to 1D using the program DAWN.<sup>59</sup> The PDF  $G(r)$  were calculated using the PDFgetX3 software from the xPDFsuite with a  $Q_{\text{max}}$  of  $18.0 \text{ \AA}^{-1}$ .<sup>57,58</sup>

Neutron total scattering data for  $\text{BiVO}_4$ ,  $\text{PbWO}_4$ , and  $\text{CaWO}_4$  were collected at 100 and 300 K using the NOMAD beamline at the SNS located at ORNL.<sup>60</sup> For  $\text{PbWO}_4$ , the sample was loaded into a 3 mm quartz capillary and run during mail-in operations. For  $\text{BiVO}_4$  and  $\text{CaWO}_4$ , samples were loaded into 6 mm vanadium cans. Data were collected under ambient conditions for the empty instrument, an empty sample holder, and three

calibration standards (diamond, silicon, and vanadium) to calibrate the instrument. For the variable temperature measurements of  $\text{BiVO}_4$ , the sample was run from 100–500 K in the sample changer environment before being run from 500–750 K in the furnace environment. Software available at the beamline was used to calculate the PDFs, with a  $Q_{max}$  of  $31.4 \text{ \AA}^{-1}$ . As TOPAS6 lacks the functions required for anisotropic ADPs in PDF fitting, these fits were performed using the program PDFgui.<sup>61</sup>

### 5.3 Structural Studies of $\text{BiVO}_4$

Structural studies of  $\text{BiVO}_4$  are challenging, owing to the strong X-ray scattering of  $\text{Bi}^{3+}$  compared to  $\text{V}^{5+}$  and  $\text{O}^{2-}$  ( $Z_{\text{Bi}^{3+}} = 80$ ,  $Z_{\text{V}^{5+}} = 18$ ,  $Z_{\text{O}^{2-}} = 10$ ), and the lack of scattering of  $\text{V}^{5+}$  from neutrons ( $b_{\text{V}} = -0.38 \text{ fm}$ ). Therefore, a combination of SXRD and NPD studies were undertaken in order to exploit the small sensitivity of  $\text{V}^{5+}$  to X-rays, as well as the sensitivity of  $\text{O}^{2-}$  to neutrons. This allowed for a precise structural model of  $\text{BiVO}_4$  to be obtained.

#### 5.3.1 Room Temperature Synchrotron X-Ray and Neutron Powder Diffraction

A polycrystalline sample of  $\text{BiVO}_4$  was prepared using solid state methods and the structure and phase purity were confirmed using SXRD and NPD. The two datasets show significant differences between them. SXRD has a superior signal-to-noise ratio and outstanding peak-shape resolution, allowing for the quantification of lattice parameters and atomic coordinates of the cations, whereas NPD provides additional sensitivity to the atomic coordinates of the oxygen anionic sublattice. Also evident in Figure 5.3 is the difference in the scattering interaction between the two radiation sources, with X-rays interacting with the electron cloud and the scattering factor dropping off with a Gaussian envelope (Equation 2.6), whereas neutrons interact with the point-like nucleus of atoms and have a constant scattering factor (Equation 2.8).



At room temperature, BiVO<sub>4</sub> was indexed to the  $m\text{-}f$  structure in the  $I2/b$  space group. Like the  $m\text{-}f$   $I2/a$  space group used in Chapter 3 of this dissertation for  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$ , the  $I2/b$  is a non-standard setting of  $C2/c$  that provides  $a \sim b$  and  $\gamma \neq 90^\circ$  rather than  $a \sim c$  and  $\beta \neq 90^\circ$  in  $I2/a$  (Table A.9). This choice is made for ease of comparison to the monoclinic  $P2_1/c$  structure of  $\text{TlReO}_4$ , for reasons that will become apparent later in this dissertation. A combined SXRD and NPD Rietveld refinement was performed using the starting parameters of BiVO<sub>4</sub> from the single crystal work performed by Sleight *et al.* as a model.<sup>18</sup> This was to complement the relative sensitivity of SXRD to  $\text{V}^{5+}$  with the sensitivity of NPD to  $\text{O}^{2-}$ . A combined Rietveld refinement was successfully performed, with the lattice parameters and atomic coordinates in good agreement with the Sleight *et al.* single crystal structural model.<sup>18</sup>

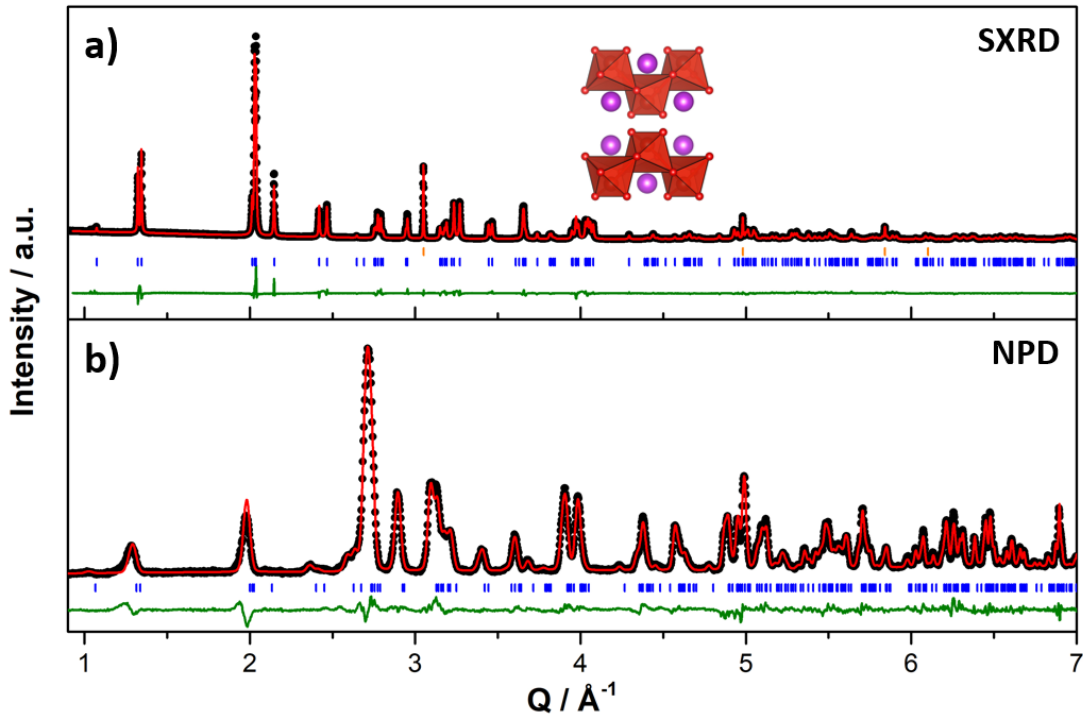


Figure 5.3: Rietveld refinements against the (a) synchrotron X-ray diffraction and (b) neutron powder diffraction data of BiVO<sub>4</sub> at room temperature. The black circles represent the data, the red line represents the calculate profile of the monoclinic fergusonite  $I2/b$  (and diamond in the synchrotron X-ray diffraction data), the green line represents the difference between the data and the calculated profile, and the blue ( $I2/b$ ) and orange ( $Fd\bar{3}m$ ) tick marks represent the space group-allowed reflections.

The BiO<sub>8</sub> polyhedra consist of four pairs of Bi–O distances ranging from 2.342(3)–2.637(3) Å, whilst the VO<sub>4</sub> polyhedra consist of two pairs of V–O bonds at 1.66(2) and 1.79(2) Å respectively. BVS analysis using Equation 3.1 indicates that both Bi<sup>3+</sup> and V<sup>5+</sup> are found in their ideal BiO<sub>8</sub> and VO<sub>4</sub> coordination environments, with

$S_{ij} = 3.07$  and  $4.95$  for  $\text{Bi}^{3+}$  and  $\text{V}^{5+}$  respectively. Similar to the  $\text{LnNbO}_4$  work discussed in Chapter 3, the possibility of a longer  $\text{V}-\text{O}_l$  bond was also explored. A  $\text{V}-\text{O}_l$  contact was identified at  $2.98(5)$  Å, which is considerably larger than the secondary  $\text{Nb}-\text{O}_l$  and  $\text{Ta}-\text{O}_l$  contacts observed in  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$  at  $2.437(4)$  and  $2.222(5)$  Å respectively. These are also further away than the longer  $\text{Nb}-\text{O}_l$  and  $\text{Ta}-\text{O}_l$  contacts in the high temperature scheelite-type structures that were identified as nonbonding (Figure 3.23). Further BVS analysis also revealed little contribution of the  $\text{V}-\text{O}_l$  bond to the BVS ( $0.044$ , compared to  $1.3$  and  $1.5$ ). Therefore, it was concluded that  $\text{BiVO}_4$  consists of  $\text{BiO}_8$  polyhedra and distorted  $\text{VO}_4$  tetrahedra, although in this dissertation they will be drawn as  $\text{VO}_6$  distorted octahedra to emphasise their identical symmetry to  $\text{LaNbO}_4$  and to distinguish between the  $m\text{-}f$   $I2/b$  and  $t\text{-}s$   $I4_1/a$  structures (Figure 5.1).

### 5.3.2 Variable Temperature Synchrotron X-Ray Diffraction

A sample of  $\text{BiVO}_4$  was cooled to  $100$  K using an Oxford cryostream, and diffraction patterns were measured upon heating from  $100$ – $500$  K on the Powder Diffraction beamline at the Australian Synchrotron. The Oxford cryostream was then swapped for a hot air blower, and diffraction data were collected from  $300$ – $900$  K. To calibrate the temperature between the two sample environments, the lattice parameter of the diamond diluent was compared and the hot air blower temperature was adjusted to match that of the cryostream. At temperatures above  $\sim 820$  K, additional reflections emerged that were not modelled by either the  $m\text{-}f$   $I2/b$  or the  $t\text{-}s$   $I4_1/a$  phases. After indexing the pattern, two additional phases were identified:  $\text{Bi}_4\text{V}_2\text{O}_{11}$  (space group  $I4/mmm$ ) and  $\text{Bi}_2\text{SiO}_5$  (space group  $Cmc2_1$ ). As the sample of  $\text{BiVO}_4$  decomposed, and these additional side products remained present upon cooling, diffraction data measured above  $\sim 800$  K and upon cooling were not analysed.

The refined unit cell parameters of  $\text{BiVO}_4$  are shown in Figure 5.4. Upon heating, the monoclinic unit cell undergoes anisotropic thermal expansion, with the  $a$  lattice parameter decreasing while the  $b$  lattice parameter increases. A phase transition is observed between  $512$ – $527$  K, in good agreement with the  $525$  K phase transition temperature reported in

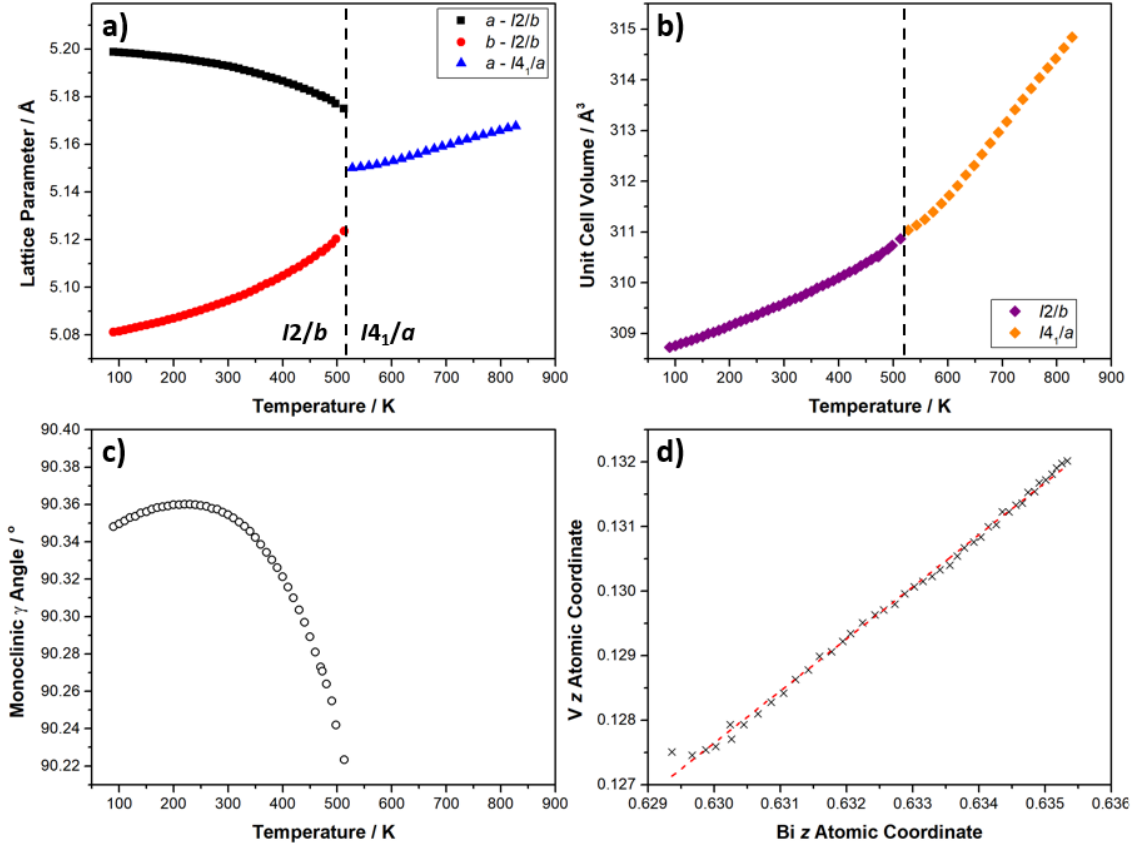


Figure 5.4: Rietveld refinements for the synchrotron X-ray diffraction variable temperature dataset of BiVO<sub>4</sub>, with (a) the  $a$  and  $c$  lattice parameters, (b) the unit cell volume, (c) the monoclinic  $\gamma$  angle, and (d) the  $z$  atomic coordinates of Bi<sup>3+</sup> and V<sup>5+</sup> plotted against each other. The black dashed line represents the temperature of the  $I2/b \rightarrow I4_1/a$  phase transition, and the red dashed line is a fit described in the text.

the literature.<sup>17,20,21,62</sup> However, the phase transition shows a discontinuity in the lattice parameters upon heating which are not indicative of a continuous phase transition, and will be discussed in detail later in this dissertation. The unit cell volume also increases linearly in both the monoclinic and tetragonal phases, with a change in the rate of thermal expansion observed between the two phases. The thermal expansion was quantified using Equation 4.1, with the  $c$ -axis expanding at a greater rate than the average of the  $a$ - and  $b$ -axes ( $\alpha_c = 7.2 \times 10^{-6} \text{ K}^{-1}$ ,  $\alpha_{a,b} = 4.1 \times 10^{-6} \text{ K}^{-1}$ ) reflecting the layered-like arrangement of the BiVO<sub>4</sub> structure.<sup>63–65</sup> The volume of the  $m$ - $f$  structure expands at a slower rate [ $\alpha_{V(m-f)} = 1.5 \times 10^{-5} \text{ K}^{-1}$ ] than the  $t$ - $s$  structure [ $\alpha_{V(t-s)} = 2.9 \times 10^{-5} \text{ K}^{-1}$ ], which is in line with other variable temperature studies of BiVO<sub>4</sub>, but interestingly contrasts with other fergusonite- and scheelite-type structures.<sup>66–68</sup>

Two features of the SXRD data are prominent, and worth discussing. The first is the apparent discontinuity in the lattice parameters when transitioning between the  $I2/b$  and  $I4_1/a$  phases. Such a discontinuity was not noted in the earlier work concerning the  $I2/a \rightarrow I4_1/a$  phase transitions of  $\text{HoNbO}_4$  or  $\text{HoTaO}_4$  in Chapter 3. To better observe the behaviour of the phase transition, the (200) and (020) Bragg reflections were inspected in more detail (Figure 5.5a). Upon heating from 300 K, each reflection displays an increase in full width at half maximum (FWHM) upon approaching the phase transition. This was modelled by fitting two Gaussian curves of equal FWHM at various temperatures, and is plotted in Figure 5.5b. That the FWHM increases through the phase transition provides further evidence that this is not purely a second order ferroelastic phase transition. There was also a considerable amount of scattering detected between the (200) and (020) reflections, which was presumably due to domain wall broadening between the ferroelastic  $I2/b$  and paraelastic  $I4_1/a$  phases. This point will be explored further below.

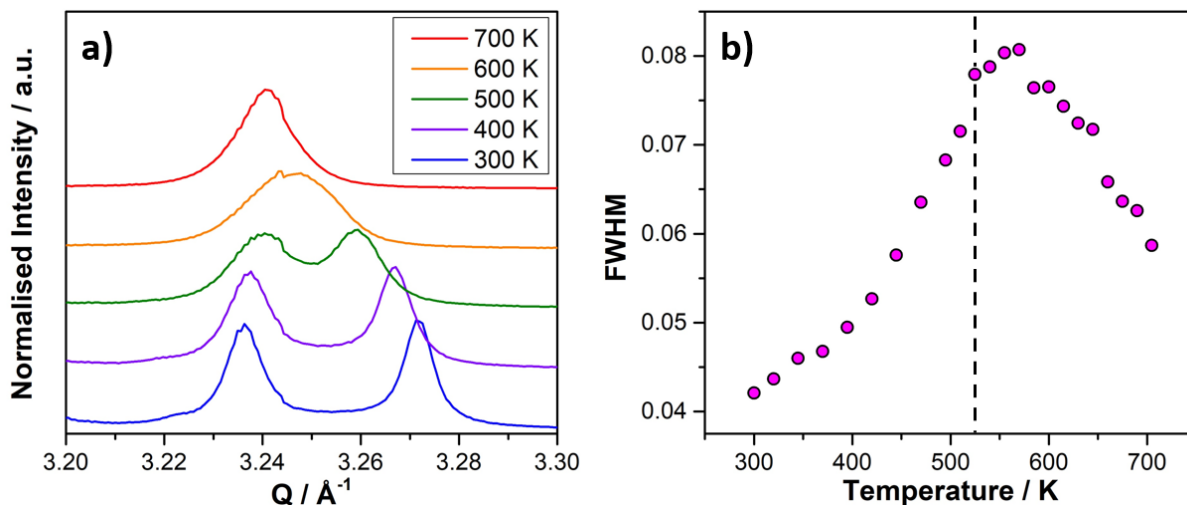


Figure 5.5: (a) Synchrotron X-ray diffraction data for  $\text{BiVO}_4$  heating from 300–700 K, highlighting the (200) and (020) reflections in the low temperature data, and (004) in the high temperature data. (b) The plotted full width at half maximum of the reflections across the temperature range, fitted using two Gaussians of equal width. The dotted line indicates the  $I2/b \rightarrow I4_1/a$  phase transition.

As described for  $\text{HoNbO}_4$  in Section 3.4.1, the modes that govern the observed  $I2/b \rightarrow I4_1/a$  phase transition,  $\Gamma_1^+$  and  $\Gamma_2^+$ , were identified using ISODISTORT.<sup>69</sup> These modes are capable of displacements or strain within the structure, with the atomic displacements allowed by each mode in the  $I2/b$  space group notated in Table 5.1. The atomic displacements of both  $\text{Bi}^{3+}$  and  $\text{V}^{5+}$  in the  $z$ -direction [henceforth, notated as  $\text{Bi}(z)$  and  $\text{V}(z)$  respectively] are only driven by the  $\Gamma_2^+$  mode, and hence are identified as the

primary order parameter for the  $I2/b \rightarrow I4_1/a$  phase transition, in line with previous work and as described for HoNbO<sub>4</sub> in Section 3.4.1.<sup>68,70</sup> It is also important to note that the  $\Gamma_2^+$  mode has the same symmetry as the  $B_g$  optical phonons, meaning this phase transition is governed by the condensation of a soft optical phonon rather than a soft acoustic phonon as seen in other ferroelastic studies. This means the  $I2/b \rightarrow I4_1/a$  transformation in BiVO<sub>4</sub> cannot be considered a true ferroelastic phase transition, as has been suggested in previous Raman spectroscopy studies.<sup>71–74</sup> Furthermore, Bi( $z$ ) and V( $z$ ) are both coupled with the  $\Gamma_2^+$  mode, meaning a linear relationship should be observed between the two. This is observed with the two atomic coordinates plotted against each other in Figure 5.4d. Therefore, this relationship can be used to effectively determine the atomic position of the near-zero scatterer vanadium in the NPD studies by relating it to the position of bismuth.

Table 5.1: Atomic displacements allowed by the  $\Gamma_1^+$  and  $\Gamma_2^+$  modes in the space group  $I2/b$ . In this case, the letters  $a$ – $h$  have been used to denote the magnitude of the atomic displacements, with the subscripts used to denote which are coupled.

| $\Gamma_1^+$ | $\delta x$ | $\delta y$ | $\delta z$ |
|--------------|------------|------------|------------|
| Bi(1)        | 0          | 0          | 0          |
| V(1)         | 0          | 0          | 0          |
| O(1)         | $a_1$      | $b_1$      | $c_1$      |
| O(2)         | $b_2$      | $a_2$      | $c_2$      |

| $\Gamma_2^+$ | $\delta x$ | $\delta y$ | $\delta z$ |
|--------------|------------|------------|------------|
| Bi(1)        | 0          | 0          | $d_1$      |
| V(1)         | 0          | 0          | $e_1$      |
| O(1)         | $f_1$      | $g_1$      | $h_1$      |
| O(2)         | $g_2$      | $f_2$      | $h_2$      |

The second feature worth discussing is the apparent anomalous behaviour of the monoclinic  $\gamma$  angle at low temperatures. The monoclinic  $\gamma$  angle decreases towards 90 ° as it approaches the  $I2/b \rightarrow I4_1/a$  phase transition temperature (Figure 5.4c). However, an inspection of the full temperature range revealed that upon heating from 100 K the angle undergoes an unexpected increase from 90.3482(5) to 90.3601(5) ° at 230 K, before decreasing towards 90 ° at the  $I2/b \rightarrow I4_1/a$  phase transition. This low-temperature behaviour is unusual, and is expected to saturate at lower temperatures based on the internal energy of the system.<sup>75</sup> Furthermore, this observation appears to be unique to this study, as it has not been reported previously in the literature. Attempts to model this using the Landau mean-field theory used for HoNbO<sub>4</sub> and HoTaO<sub>4</sub> in Chapter 3 will be performed later in this dissertation.

### 5.3.3 Variable Temperature Neutron Powder Diffraction

The same batch of  $\text{BiVO}_4$  sample analysed using SXRD was also analysed using variable temperature NPD. However, due to the near-zero scattering of vanadium by neutrons, several constraints were placed on the Rietveld refinements. Firstly, initial Rietveld refinements outputted large, negative ADPs for  $\text{V}^{5+}$  due to its near-zero neutron scattering length. In order to correct for this, the ADP value of  $\text{V}^{5+}$  was constrained to be equal to that of  $\text{Bi}^{3+}$ , with a separate value used to describe the ADP of the oxygen anions. The near-zero scattering of vanadium also resulted in a lack of change and large uncertainties for the atomic coordinates of  $\text{V}^{5+}$ . In order to overcome this issue, the linear coupling between  $\text{Bi}(z)$  and  $\text{V}(z)$ , as determined by the previous mode analysis and the SXRD data, was used such that the two atomic coordinates were linearly correlated with each other. Therefore, the large neutron scattering length of bismuth was used to account for the lack of scattering from vanadium.

In addition to the room temperature (300 K) dataset, two more patterns of  $\text{BiVO}_4$  were collected using the high resolution neutron powder diffractometer: one at 3 K, and another at 723 K. These two datasets were refined, with lattice parameters and atomic coordinates in good agreement with previous studies.<sup>17,18</sup> At 3 K,  $\text{BiVO}_4$  adopts the  $m\text{-}f$   $I2/b$  structure, whereas at 723 K it adopts the  $t\text{-}s$   $I4_1/a$  structure. Consistent with the variable temperature SXRD data, the monoclinic  $\gamma$  angle was smaller at 3 K than at 300 K, with the angle measured to be  $90.3606(14)$  and  $90.3791(15)^\circ$  respectively. The increase in FWHM of the (200) and (020) reflections identified in the SXRD data was unable to be investigated due to the limited peak-shape resolution afforded by NPD.

Variable temperature measurements were collected on the high intensity neutron powder diffractometer from 50–750 K in the cryofurnace. The results of these are shown in Figure 5.7. A majority of the phenomena observed in the SXRD variable temperature data (Figure 5.4) are also present in the NPD variable temperature data. The  $a$  and  $b$  lattice parameters show anisotropic thermal expansion, as well as a phase transition observed at a similar temperature of  $\sim 510$  K (Figure 5.7a). The  $\sim 15$  K difference between the SXRD and NPD phase transition temperatures is presumably due to the difference in

Table 5.2: Rietveld refinement structural parameters, bond distances, and bond valence sums for BiVO<sub>4</sub> against neutron powder diffraction data. The atomic coordinates of vanadium have been fixed as described in the text.

| Temperature (K)              | 3                    | 300                  | 723                   |
|------------------------------|----------------------|----------------------|-----------------------|
| Space Group                  | <i>I</i> 2/ <i>b</i> | <i>I</i> 2/ <i>b</i> | <i>I</i> 41/ <i>a</i> |
| <i>a</i> (Å)                 | 5.20043(7)           | 5.19018(7)           | 5.15764(6)            |
| <i>b</i> (Å)                 | 5.06904(8)           | 5.08576(9)           | = <i>a</i>            |
| <i>c</i> (Å)                 | 11.67197(14)         | 11.68862(17)         | 11.7581(4)            |
| $\gamma$ (°)                 | 90.3608(11)          | 90.3811(12)          | = 90                  |
| Vol. (Å <sup>3</sup> )       | 307.681(7)           | 308.526(8)           | 312.781(13)           |
| Bi <i>z</i>                  | 0.63708(10)          | 0.63431(11)          | = 5/8                 |
| V <i>z</i>                   | = 0.13346(8)         | 0.13117(10)          | = 1/8                 |
| O(1) <i>x</i>                | 0.1514(2)            | 0.1474(2)            | 0.1368(2)             |
| O(1) <i>y</i>                | 0.5117(2)            | 0.5092(2)            | -0.0002(3)            |
| O(1) <i>z</i>                | 0.21017(9)           | 0.20811(11)          | 0.20261(12)           |
| O(2) <i>x</i>                | 0.2637(2)            | 0.2601(2)            | –                     |
| O(2) <i>y</i>                | 0.3799(2)            | 0.3813(2)            | –                     |
| O(2) <i>z</i>                | 0.44818(9)           | 0.44906(11)          | –                     |
| Bi–O(2)                      | 2.6766(15)           | 2.6353(17)           | 2.5033(15)            |
| Bi–O(2)                      | 2.5343(12)           | 2.5143(12)           | –                     |
| Bi–O(1)                      | 2.3336(12)           | 2.3586(12)           | 2.4498(13)            |
| Bi–O(1)                      | 2.2956(14)           | 2.3431(16)           | –                     |
| BiO <sub>8</sub>             | 26.3                 | 26.5                 | 27.0                  |
| <i>D</i> (BiO <sub>8</sub> ) | 0.05912              | 0.04547              | 0.01079               |
| V–O(1)                       | 2.8996(12)           | 2.9408(14)           | 3.0468(14)            |
| V–O(1)                       | 1.7799(12)           | 1.7659(13)           | 1.7308(15)            |
| V–O(2)                       | 1.6917(12)           | 1.6990(13)           | –                     |
| O(1)–V–O(1)                  | 119.60(9)            | 118.77(11)           | 116.36(10)            |
| O(2)–V–O(2)                  | 111.43(9)            | 113.00(11)           | –                     |
| O(2)–V–O(1)                  | 104.74(5)            | 105.04(6)            | 106.14(5)             |
| O(1)–V–O(2)                  | 104.74(5)            | 105.04(6)            | –                     |
| VO <sub>4</sub>              | 2.65                 | 2.64                 | 2.63                  |
| <i>D</i> (VO <sub>4</sub> )  | 0.02542              | 0.01929              | = 0                   |
| BVS (VO <sub>6</sub> )       | 4.93                 | 4.95                 | –                     |
| BVS (VO <sub>4</sub> )       | 4.83                 | 4.86                 | 4.86                  |
| <i>R</i> <sub>wp</sub> (%)   | 5.00                 | 4.77                 | 5.12                  |

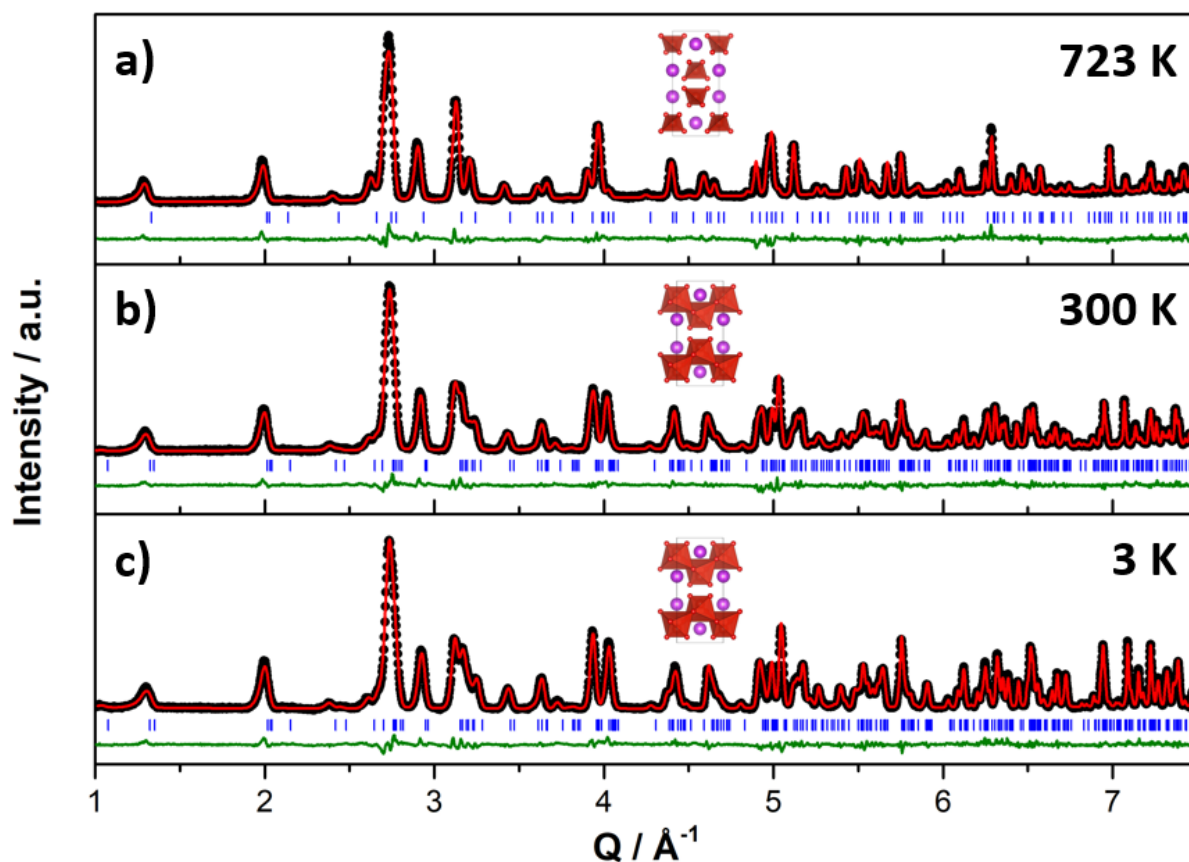


Figure 5.6: Rietveld refinements for  $\text{BiVO}_4$  using neutron powder diffraction at (a) 723 K refined to the  $I4_1/a$  space group, (b) 300 K refined to the  $I2/b$  space group, and (c) 3 K refined to the  $I2/b$  space group. The black circles represent the data, the red lines represent the calculated profile, and the green line represents the difference between the data and the calculated profile, and the blue tick marks represent the space group-allowed reflections.

thermometry between the two experiments. A similar increase in the rate of thermal expansion is observed in the unit cell volume (Figure 5.7b), as well as a decrease in the monoclinic  $\gamma$  angle towards  $90^\circ$  at the  $I2/b \rightarrow I4_1/a$  phase transition (Figure 5.7c). The same lack of saturation in the monoclinic  $\gamma$  angle, as observed in the SXR and Echidna data, is observed once more in the Wombat data, with the monoclinic  $\gamma$  angle achieving a maximum value at  $\sim 220$  K. The ADPs of  $\text{Bi}^{3+} + \text{V}^{5+}$ , as well as  $\text{O}^{2-}$  show an increase with temperature (Figure 5.7d).

Attempts to model the monoclinic  $\gamma$  angle using the Landau mean-field theory-type analysis used for  $\text{HoNbO}_4$  proved inconsistent. Recall that if the amplitude of the order parameter of a given phase transition follows the power law  $\eta = A(T_c - T)^\beta$ , it may be identified as second order if the critical exponent  $\beta = 0.5$ . Fitting the same expression to the variable temperature data of the monoclinic  $\gamma$  angle yields  $\beta = 0.414$  over a reduced



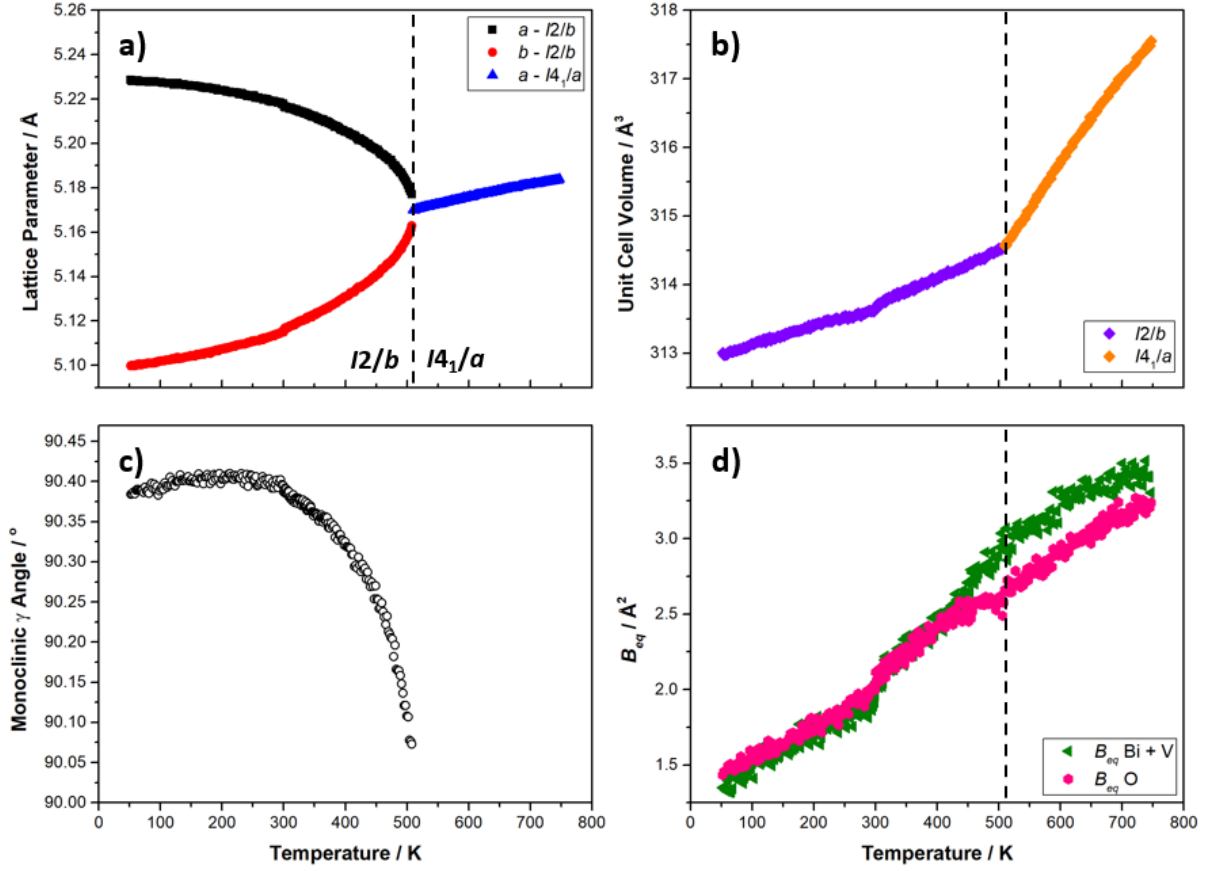


Figure 5.7: Rietveld refinements for the neutron powder diffraction variable temperature dataset of BiVO<sub>4</sub>, with (a) the  $a$  and  $c$  lattice parameters, (b) the unit cell volume, (c) the monoclinic  $\gamma$  angle, and (d) the atomic displacement parameters of Bi + V, as well as O. The black dashed line represents the temperature of the  $I2/b \rightarrow I4_1/a$  phase transition.

400–510 K range, and  $\beta = 0.5$  within 50 K of the phase transition (Figure A.16). Attempts were also made to introduce a ‘saturation term’ as seen in previous work,<sup>76–78</sup> which was also unsuccessful. Therefore, the  $I2/b \rightarrow I4_1/a$  phase transition observed in BiVO<sub>4</sub> does not appear to be a second order ferroelastic phase transition.

Due to the difference in scattering length between the three atoms ( $b_{\text{Bi}} = 8.53$ ,  $b_{\text{V}} = -0.38$ ,  $b_{\text{O}} = 5.80$  fm), the NPD data affords great sensitivity to the oxygen anionic sublattice. As a result, the Bi–O and V–O bond lengths are plotted (Figure 5.8). A change in the BiO<sub>8</sub> polyhedra is evident in undergoing the  $I2/b \rightarrow I4_1/a$  phase transition, with the number of different Bi–O bond distances decreasing from four to two. Similarly, changes in the VO<sub>4</sub> polyhedra are also observed, with the number of distinct V–O bond distances decreasing as the symmetry of the structure increases. The length of the V–O<sub>*l*</sub> distance also displays a discontinuity which was not present in the analysed HoNbO<sub>4</sub> and

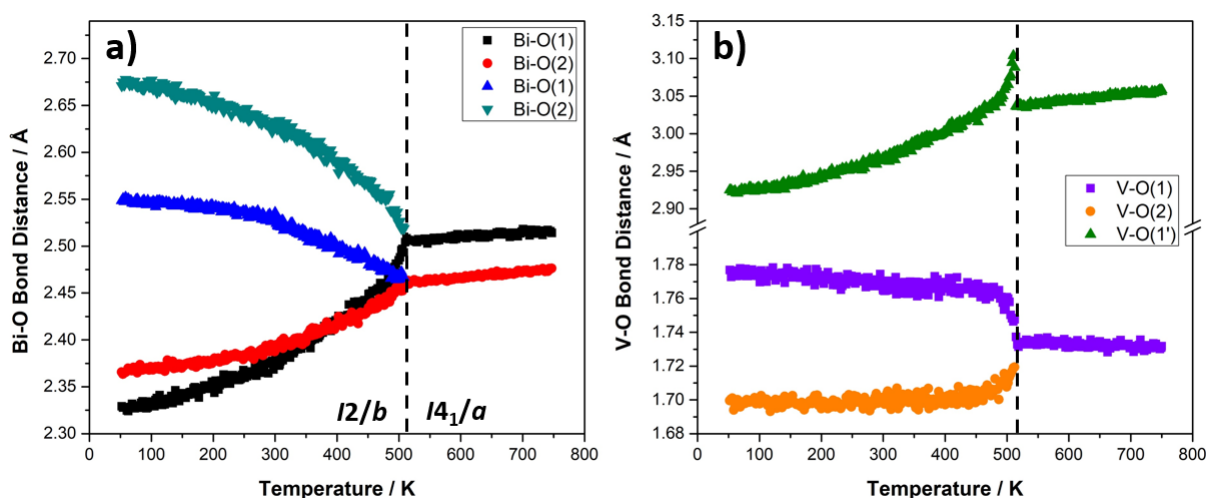


Figure 5.8: Temperature dependence of the (a) Bi–O bond distances and (b) V–O bond distances upon heating. The dotted lines indicate the *I*2/*b* → *I*4<sub>1</sub>/*a* phase transition.

HoTaO<sub>4</sub> oxides (Figure 3.23), accompanied with a small discontinuity in the other V–O bond distances. This is presumably an artefact due to the lack of sensitivity to the V atomic position.

The *I*2/*b* → *I*4<sub>1</sub>/*a* phase transition has been investigated previously in the literature. Bierlein *et al.* identified that BiVO<sub>4</sub> was ferroelastic, identifying a displacive and nonquenchable phase transition that was second order in nature.<sup>79</sup> However, this transition was re-examined by Pinczuk *et al.* later, who identified a soft optical phonon in the variable temperature Raman spectra of BiVO<sub>4</sub>.<sup>72</sup> A follow-up variable temperature Raman study then identified that the phase transition was not simple, with a secondary order parameter also present.<sup>73</sup> Further studies identified the large anisotropy for Bi<sup>3+</sup>, particularly along the [001] direction, possibly due to the 6s<sup>2</sup> lone pair.<sup>18,21,80</sup> This led David *et al.* to conclude that whilst the transition is continuous, it may not conform exactly to a second order phase transition.<sup>80</sup>

Finally, a brief comparison is made between the *I*2/*a* → *I*4<sub>1</sub>/*a* phase transition in HoNbO<sub>4</sub> in Chapter 3, and the *I*2/*b* → *I*4<sub>1</sub>/*a* phase transition observed in BiVO<sub>4</sub> in the current chapter. The normalised polyhedra volume are plotted in Figure 5.9. An interesting feature of these phase transitions is that they appear to be driven by changes occurring at different sites of the structure. The phase transition in HoNbO<sub>4</sub> was driven by a combination of a rotation of the NbO<sub>6</sub> polyhedra and a breaking of the longer

Nb–O<sub>l</sub> bonds at the *B* site, as governed by the  $\Gamma_2^+$  mode. This is seen in Figure 5.9, where the NbO<sub>4</sub> tetrahedra expand in volume before the rate of expansion decreases in the tetragonal *I*4<sub>1</sub>/*a* phase. This is also accompanied by a constant rate of change in the volume of the HoO<sub>8</sub> polyhedra, indicating they do not heavily contribute to the phase transition. However, the phase transition in BiVO<sub>4</sub> appears to be driven by a change at the *A* site, with the rate of expansion of the volume of the BiO<sub>8</sub> polyhedra increasing after undergoing the *I*2/*b* → *I*4<sub>1</sub>/*a* phase transition. Like the HoO<sub>8</sub> polyhedra, the VO<sub>4</sub> tetrahedra show a constant rate of change in their volume.

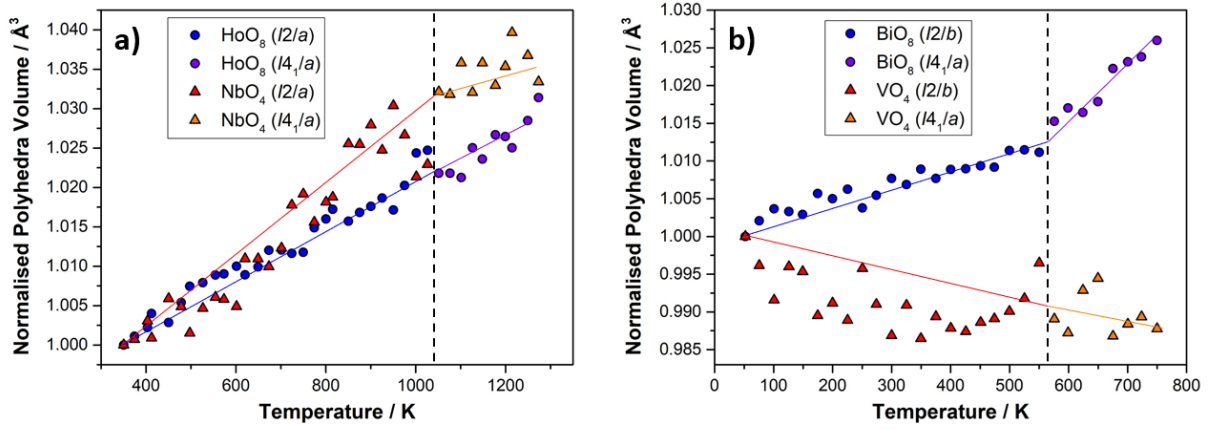


Figure 5.9: Temperature dependence of the normalised (a) HoO<sub>8</sub> and NbO<sub>4</sub>, and (b) BiO<sub>8</sub> and VO<sub>4</sub> polyhedra volumes. The dotted lines indicate the phase transition. The solid lines have been drawn to guide the eyes.

BiVO<sub>4</sub> is a rare example of a metal oxide that undergoes a *symmetry raising* phase transition upon pressurising.<sup>17</sup> In HoNbO<sub>4</sub>, heating the room temperature structure results in a *I*2/*a* → *I*4<sub>1</sub>/*a* phase transition at  $\sim 775$  °C,<sup>81</sup> whereas pressurising the room temperature structure results in a *I*2/*a* → *P*2<sub>1</sub>/*c* phase transition at  $\sim 19$  GPa.<sup>82</sup> Paradoxically, BiVO<sub>4</sub> shows the same *I*2/*b* → *I*4<sub>1</sub>/*a* upon both heating (at  $\sim 250$  °C) and pressurising (at  $\sim 1.5$  GPa).<sup>17</sup> It is postulated that the Bi<sup>3+</sup> 6s<sup>2</sup> lone pair electrons impact the compressibility of the polyhedra. However, the change in the AO<sub>8</sub> polyhedra and BO<sub>4</sub> tetrahedra volume as a function of pressure has not been looked at in detail for either HoNbO<sub>4</sub> or BiVO<sub>4</sub>. This is an observation worth further pursuing.

The SXRD and NPD diffraction data demonstrates a number of features that are worth recapping. Firstly, BiVO<sub>4</sub> represents a challenging diffraction study due to the comparatively large X-ray scattering of Bi<sup>3+</sup>, as well as the near-zero neutron scattering

of V. Using SXRD, a linear relationship between the atomic coordinates of  $\text{Bi}^{3+}$  and  $\text{V}^{5+}$  was identified. This relationship could then be used to identify the position of the  $\text{V}^{5+}$  cations in the NPD. Despite  $\text{BiVO}_4$  being previously referred to as a ferroelastic phase transition in the literature,<sup>79</sup> observation of the unit cell parameters obtained using Rietveld refinement demonstrate that this is not the case. A large discontinuity was observed in the lattice parameters across the  $I2/b \rightarrow I4_1/a$  phase transition, as well as in the V–O bond lengths. Furthermore, various features in the  $\text{BiVO}_4$  data are unusual, such as the increase in the FWHM of the (200) and (020) reflections on approaching the phase transition, the decrease in monoclinic  $\gamma$  angle upon cooling from 200 K to 50 K observed in both the SXRD and NPD data, and the increase in the rate of thermal expansion of the  $\text{BiO}_8$  polyhedra. These features may be the result of the stereochemical activity of the  $\text{Bi}^{3+} 6s^2$  lone pair, which is presumed to play a role in the structure of  $\text{BiVO}_4$  due to the anomaly high ADPs in the NPD Rietveld refinements. The influence of the  $6s^2$  lone pair on the local structure is not well accounted for in the long-range average diffraction data, and may provide clues as to the origin of these anomalous structural features.

### 5.3.4 X-Ray Total Scattering

X-ray Bragg diffraction data collected at the 11-ID-B at the APS at Argonne National Lab further confirm that the sample of  $\text{BiVO}_4$  was phase pure (Figure 5.10). Data were collected upon heating from 400–630 K, and reproduced all of the main features from the previous SXRD and NPD Rietveld refinements (Figure A.17).

Close attention was paid to the (200) and (020) Bragg reflections in the SXRD data. Rietveld refinements to each of the diffraction datasets are displayed in Figure 5.11, with an emphasis on the (200) and (020) Bragg reflections. The superior peak-shape resolution of the Australian Synchrotron data shows irregular peak shapes at the phase transition, which are not replicated in the APS data. This was identified to be the result of domain wall broadening between the ferroelastic  $I2/b$  and paraelastic  $I4_1/a$  phases of  $\text{BiVO}_4$ . Domain wall broadening occurs when a material undergoes an increase in symmetry from a ferroelastic to a paraelastic phase, resulting in different polarisation vectors within

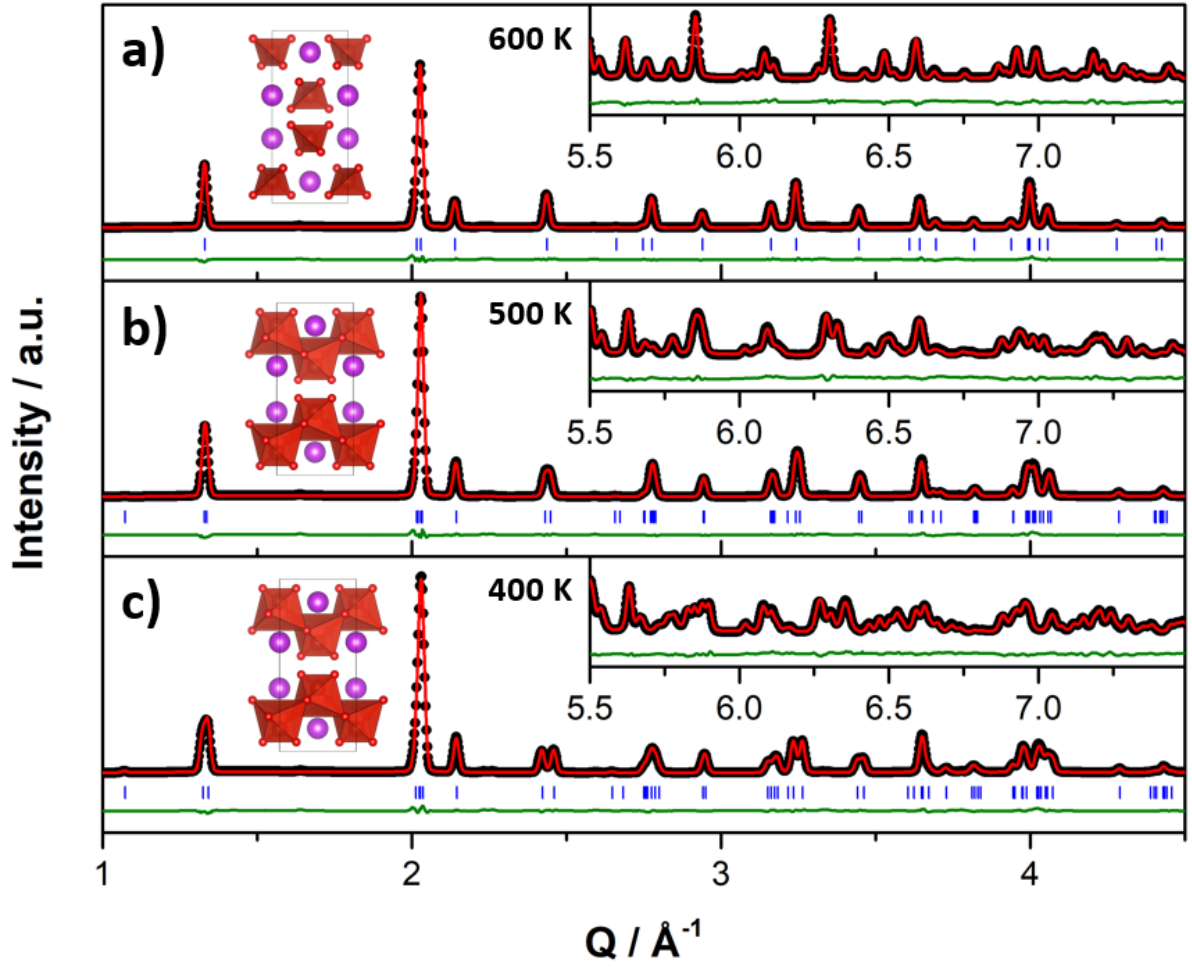


Figure 5.10: Rietveld refinements for BiVO<sub>4</sub> using synchrotron X-ray diffraction at (a) 600 K refined to the  $I4_1/a$  space group, (b) 500 K refined to the  $I2/b$  space group, and (c) 400 K refined to the  $I2/b$  space group. The black circles represent the data, the red lines represent the calculated profile, and the green line represents the difference between the data and the calculated profile, and the blue tick marks represent the space group-allowed reflections.

the material. This has been extensively studied in the literature,<sup>83</sup> where Lim *et al.* identified two different types of domains in ferroelastic crystals, such as BiVO<sub>4</sub>, based on the ferroelastic strains of the system.<sup>84</sup> These have previously been studied using solid state nuclear magnetic resonance (NMR) spectroscopy, with <sup>209</sup>Bi NMR used to differentiate between the two distinctive domains.<sup>84</sup> The superior peak-shape resolution of the Australian Synchrotron dataset allow for the detection of these broad features, and suggests the Bi<sup>3+</sup> 6s<sup>2</sup> electron lone pair is active across the phase transition.

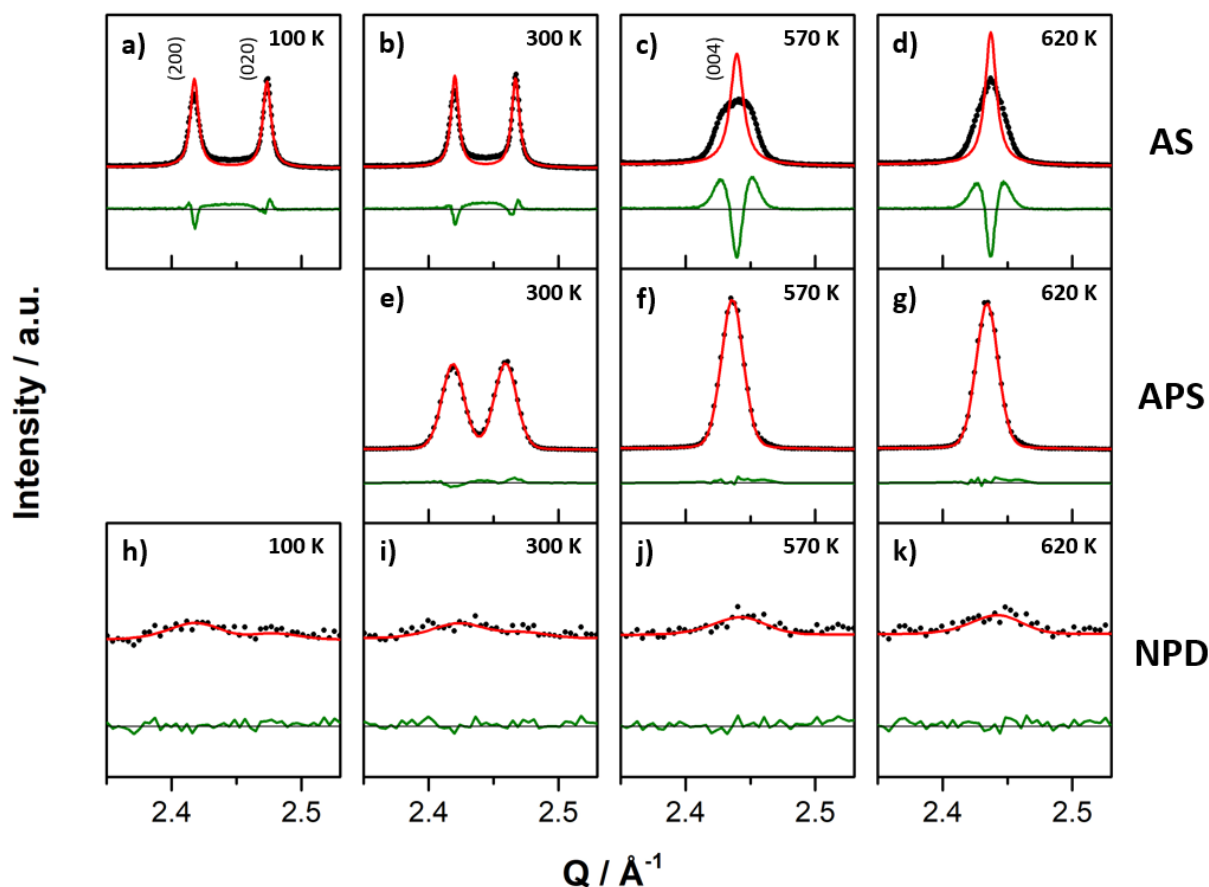


Figure 5.11: Rietveld refinements to the variable temperature datasets of  $\text{BiVO}_4$  collected using (a–d) the Australian Synchrotron, (e–g) the Advanced Photon Source, and (h–k) Wombat. The black circles represent the data, the red lines represent the calculated profile, and the green line represents the difference between the data and the calculated profile. The anomalous peak shapes identified in the Australian Synchrotron data are identified as the result of domain wall broadening within  $\text{BiVO}_4$ .

Upon cooling, the detector was moved closer to the sample and data suitable for X-ray total scattering analysis were collected. The XPDF data for  $\text{BiVO}_4$  upon cooling are plotted in Figure 5.12. Recall that in undergoing the  $I2/b \rightarrow I4_1/a$  phase transition, the number of different bond lengths in the  $\text{VO}_4$  tetrahedra reduces from two to a single unique distance. This is coupled with a reduction from four to two different Bi–O bonds in the  $\text{BiO}_8$  polyhedra. This is evident from the temperature dependence of the XPDFs, where the first peak at  $r \sim 1.67 \text{ \AA}$ , associated with the V–O bond distances, appears to sharpen upon heating. This indicates that the  $\text{VO}_4$  tetrahedra increase in symmetry; from two different V–O distances to a unique distance in the high temperature  $I4_1/a$  phase. However, the same is not observed in the Bi–O bond distances between 2.0–3.0  $\text{\AA}$ , where little broadening is observed across the phase transition. This suggests that the local polyhedra environments of the  $\text{VO}_4$  tetrahedra and  $\text{BiO}_8$  polyhedra are not captured

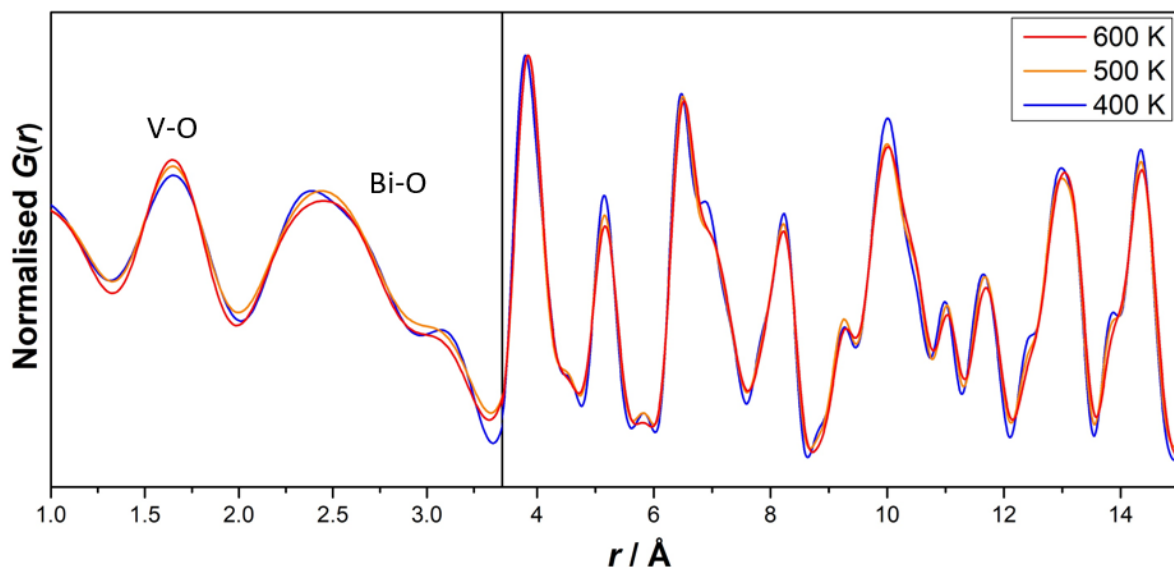


Figure 5.12: X-ray pair distribution function data for BiVO<sub>4</sub>. The data were taken at 400 K (blue), 500 K (orange), and 600 K (red).

by the long-range average models. The remaining peaks ( $r > 3.5$  Å) in the XPDF data, corresponding to various cation–cation distance pairs, show a noticeable shift to higher  $r$  with temperature, consistent with the thermal expansion of the material.

Fits to the XPDF data were conducted using the long-range  $m$ - $f$   $I2/b$  (400–510 K) and  $t$ - $s$   $I4_1/a$  (540–620 K) models, with example fits shown in Figure 5.13. When fitting the XPDF data, a spherical correlation function was used to model the change in  $B_{iso}$  with respect to  $r$ . This gives a local ADP (referred to as  $B_{local}$ , or  $B_l$ ) and a ‘high’ value at high  $r$  (referred to as  $B_{high}$ ). This accounts for local correlations, such as the correlated V–O bond distances in VO<sub>4</sub> tetrahedra, whilst allowing for a change in correlation for atom–atom pairs with longer interatomic distances.<sup>85</sup> Initially, a fitting range of 1.0–30 Å was attempted. However, these returned poor fits to the data. The V–O and Bi–O distances between 1.6–3.6 Å were poorly reproduced in all datasets, regardless of the long-range average model used. This is also seen at high  $r$ , with several peaks either misfit or overfit using the long-range average structural models.

Due to the lack of sensitivity of XPDF data to the V–O and Bi–O pairs, fits were performed from 3.3–30 Å to determine information on the cation–cation distances (Figure 5.14b). Interestingly, by reducing the fitting range from 1.0–30 to 3.3–30 Å, the peaks associated with either Bi–V or Bi–Bi distances (such as  $\sim 4.0$ ,  $\sim 6.4$ , and  $\sim 8.3$  Å) were



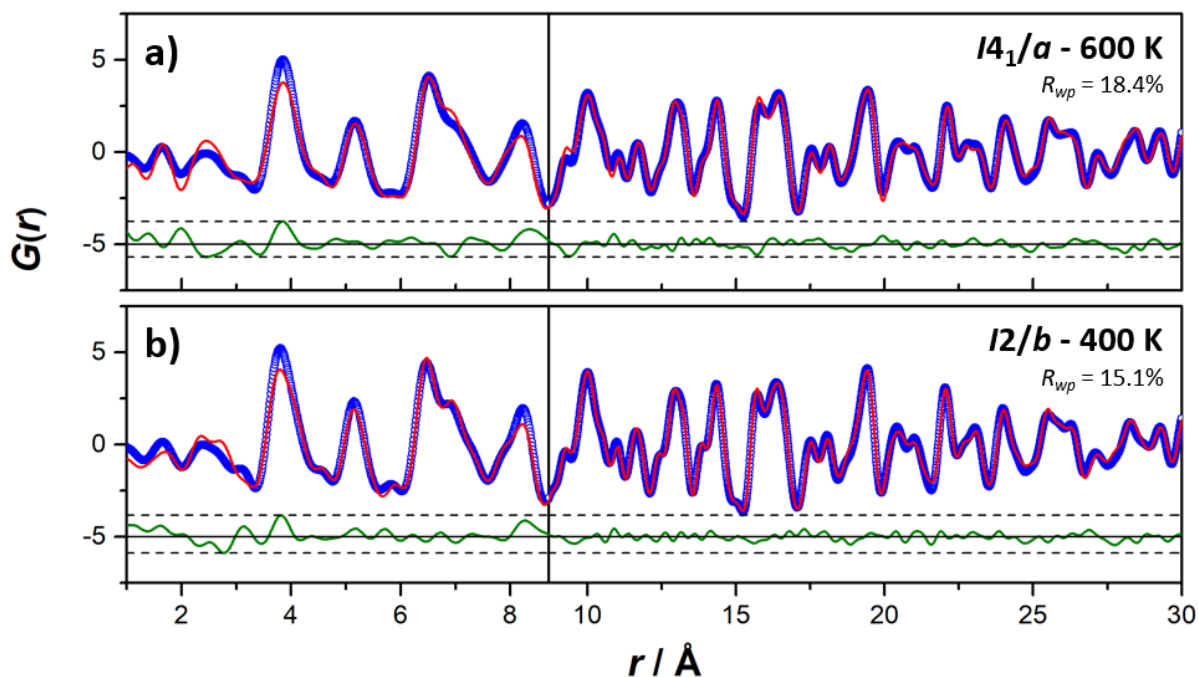


Figure 5.13: X-ray pair distribution function fits for the variable temperature dataset of  $\text{BiVO}_4$  over a range of 1.0–30 Å. Data taken at (a) 600 K and fit to the *t-s*  $I4_1/a$  model, and at (b) 400 K and fit to the *m-f*  $I2/b$  model.

better fit, whereas little change occurs in fitting the peaks associated with the V–V distances (such as  $\sim 5.2$ ,  $\sim 6.9$ , and  $\sim 7.3$  Å). This improvement in the fit with a shorter fitting range was coupled with an increase in the local ADP of the  $\text{Bi}^{3+}$  site [ $B_l(\text{Bi}^{3+}) = 0.84$  vs.  $1.3$  Å<sup>2</sup>]. This could potentially correspond to local static disorder at the  $\text{Bi}^{3+}$  site not captured by the *m-f*  $I2/b$  structural model, potentially as the result of the  $6s^2$  lone pair electrons.

By observing the fits to the XPDF data in Figure 5.13, there appear to be significant misfitting to the local V–O and Bi–O distances between 1.2–3.5 Å, as well as a substantial amount of features in the difference curve across the remaining 3.5–30 Å. By shortening the fitting range, a better fit to the XPDF data is obtained, indicating the long-range average structure does not capture the local environment of the  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra. As seen in the study of the  $\text{NaBi}(\text{WO}_4)_2$  local structure using NPDF in Chapter 4, displacement of  $\text{Bi}^{3+}$  from its centrosymmetric position, due to its  $6s^2$  lone pair electrons, can cause distortions in the  $\text{BiO}_8$  polyhedra. These increase the distribution of Bi–O bond distances. As XPDF data is insensitive to modelling these local environments, NPDF was used to determine the Bi–O bond distances within the system.



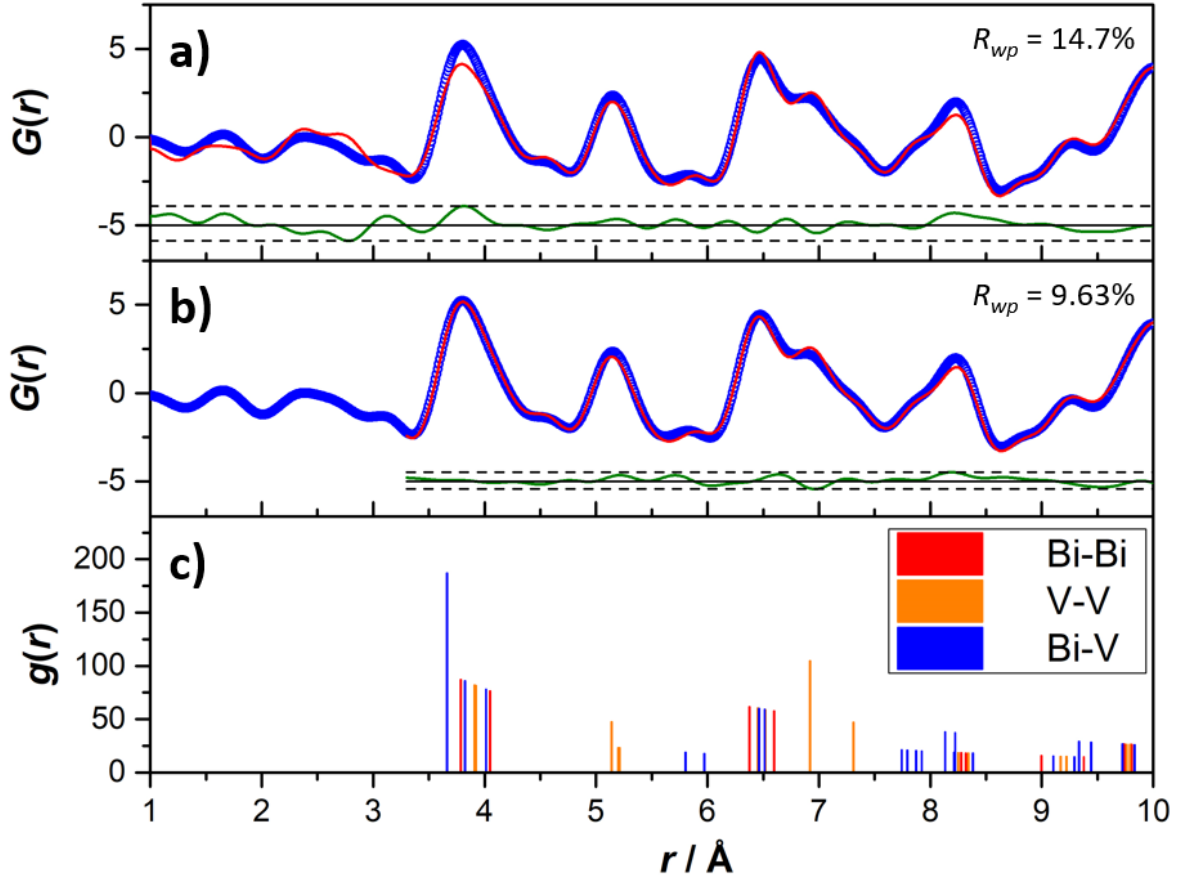


Figure 5.14: XPDF data for BiVO<sub>4</sub> at 400 K fitted over a range of (a) 1.0–30 Å and (b) 3.3–30 Å. (c) The calculated partial fits, with focus placed on the cation–cation distances. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles.

### 5.3.5 Neutron Total Scattering

NPD data suitable for total scattering analysis were collected using two different sample environments: a cryostream from 100–500 K, and a furnace capable of heating from 500–750 K. A measurement was taken at 500 K in each environment to confirm the accuracy between the two. There are two main advantages of NPDF over XPDF. Firstly, neutron diffraction is sensitive to the oxygen atomic coordinates, which will allow for a thorough understanding of the BiO<sub>8</sub> polyhedra within the BiVO<sub>4</sub> structure. Secondly, the data is Fourier transformed from a structure function  $S(Q)$  with a larger  $Q$ , providing better short-range resolution for the cation–oxygen and oxygen–oxygen distances that are not visible in the XPDF due to a combination of the weak scattering of X-rays and the limited short-range real-space resolution.

The data at 100 K were fitted first due to the reduced thermal motion, allowing for greater sensitivity to static disorder. Three distinct crystallographic models were tested: the high temperature *t-s*  $I4_1/a$  structure derived from the Bragg fits of  $\text{BiVO}_4$ , the room-temperature *m-f*  $I2/b$  structure also derived from the Bragg fits of  $\text{BiVO}_4$ , and the monoclinic  $P2_1/c$  structure modelled from the  $\text{TlReO}_4$  structure.<sup>44</sup> The  $I4_1/a$  structure has the  $\text{Bi}^{3+}$  and  $\text{V}^{5+}$  cations occupying special symmetry-constrained Wyckoff positions, where only a single  $\text{O}^{2-}$  site is not constrained and can be refined. This general oxygen position, as previously stated, allows for rotations of the  $\text{BO}_4$  polyhedra in the  $I4_1/a$  model.<sup>86,87</sup> In the  $I2/b$  structure, there are two general  $\text{O}^{2-}$  sites and the  $\text{Bi}(z)$  and  $\text{V}(z)$  atomic coordinates are free to move for a total of eight variable position parameters. The  $P2_1/c$  structure is still metrically tetragonal, however has been tripled along the *a*-axis to capture the different arrangements of the  $\text{BO}_4$  tetrahedra. This allows for even more degrees of freedom, with six cation and 12 anion sites, each at general *x*, *y*, and *z* positions. This model has previously been shown to successfully account for distortions present in  $\text{ABO}_4$  materials containing  $6s^2$  A-site cations.<sup>44</sup> When modelling the  $P2_1/c$  structure, fitting was done with restraints placed such that the V–O bond distances were equal, and the O–V–O bond angles were fixed to the ideal  $\sim 109.5^\circ$  tetrahedra value predicted by VESPR theory.<sup>26,27</sup> This keeps the  $\text{VO}_4$  tetrahedra ‘rigid’ to prevent any distortions, while still allowing the tetrahedra to rotate. Each of these structural models are illustrated in Figure 5.15.

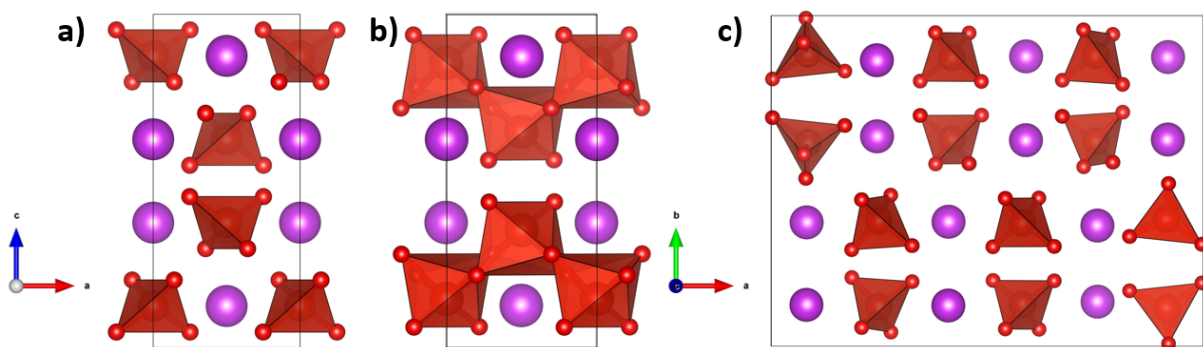


Figure 5.15: Crystallographic models for (a) *t-s*  $I4_1/a$ , based on the high-temperature structure of  $\text{BiVO}_4$ , (b) *m-f*  $I2/b$ , based on the room-temperature structure of  $\text{BiVO}_4$ , and (c) the monoclinic  $P2_1/c$ , based on the room temperature structure of  $\text{TlReO}_4$ .

The NPDF fits of BiVO<sub>4</sub> at 100 K were conducted using each of the structural models across a fitting range of 1.2–30 Å (Figure 5.16). The *t-s*  $I4_1/a$  structure (Figure 5.16a) returns a poor fit at both low and high  $r$ . Upon lowering the symmetry from the tetragonal structure to the monoclinic structure, the fit is greatly improved (Figure 5.16b). It is clear that the local structure of BiVO<sub>4</sub> at 100 K closely resembles the long-range average structure derived from the Bragg diffraction. However, there appears to be peak misfitting at low  $r$ , with the features between 2.0–3.0 Å unable to be fully captured by the  $I2/b$  model. Further symmetry lowering from the  $I2/b$  to the  $P2_1/c$  with rigid tetrahedra resulted in a worse fit than the  $I2/b$  model, which was unexpected considering the  $P2_1/c$  model has the lowest symmetry and the highest number of degrees of freedom (Figure 5.16c). Although the local region from 2.0–3.0 Å is improved compared to the high symmetry  $I4_1/a$  model, a poorer fit results from the constraints placed on the model, particularly at high  $r$ .

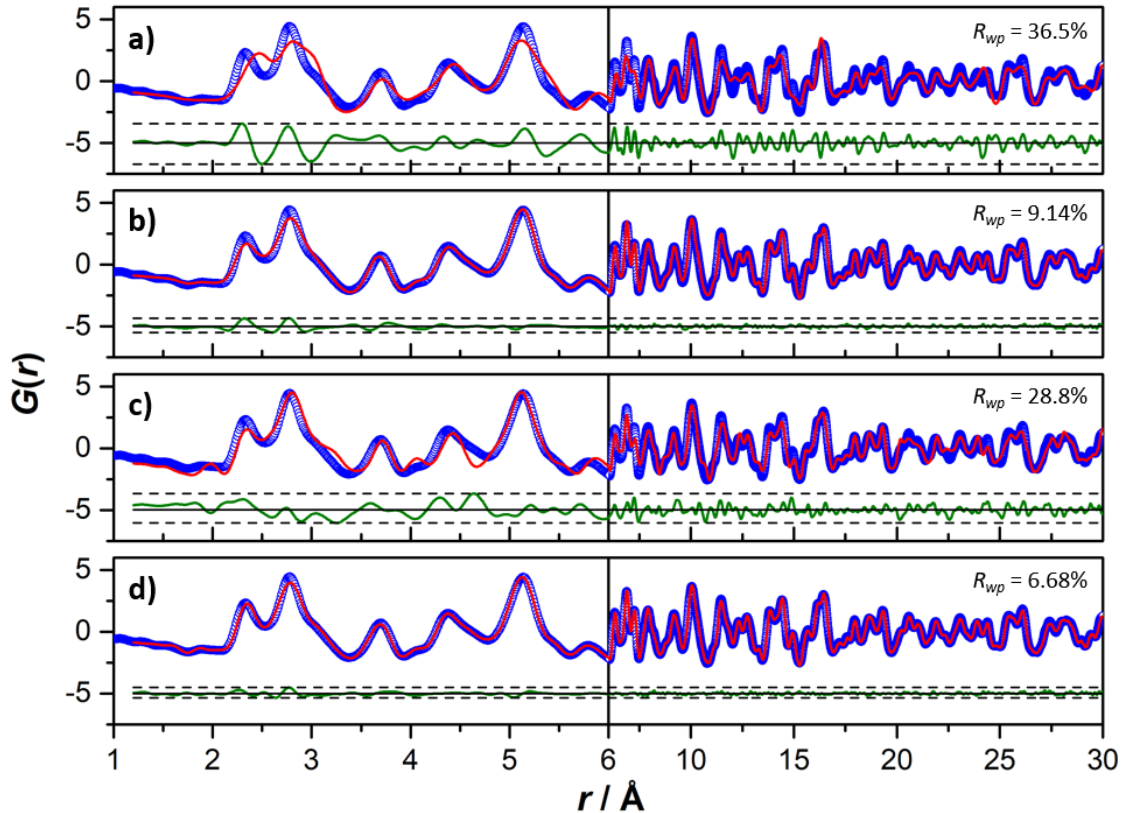


Figure 5.16: Neutron pair distribution function data fits to BiVO<sub>4</sub> at 100 K for (a) *t-s*  $I4_1/a$ , (b) *m-f*  $I2/b$ , and (c) monoclinic  $P2_1/c$  with rigid VO<sub>4</sub> tetrahedra, and (d) monoclinic  $P2_1/c$  with flexible VO<sub>4</sub> tetrahedra. The data is fitted over a range of 1.2–30 Å, with the first half highlighting the fit from 1.2–6.0 Å, and the second half highlighting from 6.0–30 Å. The blue dots represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles.

The misfitting of the local features at 2.0–3.0 Å were further investigated, with the  $P2_1/c$  model (previously used to successfully model the local symmetry of  $\text{TlReO}_4$ ) looked at in more detail.<sup>44</sup> Firstly, in the NPDF of  $\text{TlReO}_4$ , the  $\text{ReO}_4$  tetrahedra were treated as rigid. As explored in more detailed below, this is due to the high oxidation state of  $\text{Re}^{7+}$ , short Re–O bonds ( $\sim 1.73$  Å), and  $5d$  orbital interactions of  $\text{Re}^{7+}$  resulting in a lack of polarisability of the Re–O bonds. However, the  $\text{VO}_4$  tetrahedra modelled by the  $m-f$   $I2/b$  model at 100 K to the Bragg data indicates that the  $\text{VO}_4$  tetrahedra are distorted, with two V–O bond distances ( $\sim 1.69$  and  $1.78$  Å) and different O–V–O bond angles ( $105$ – $118^\circ$ ). Evidently, deformations of the  $\text{VO}_4$  tetrahedra are required to fit the long-range average structure. The fit to the  $P2_1/c$  model was repeated, but with the restriction of the rigid  $\text{VO}_4$  tetrahedra relaxed. Distance restraints of  $1.73 \pm 0.06$  Å for the V–O distances, and  $2.55 \pm 0.3$  Å for the Bi–O distances were imposed. This allowed for deformation of both the  $\text{BiO}_8$  polyhedra, as well as the  $\text{VO}_4$  tetrahedra. The fit with flexible  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra is displayed in Figure 5.16d, and demonstrates an overall improvement in the fit at both low and high  $r$  compared to the  $I2/b$  model. Histograms of the Bi–O and V–O bond distances, and the O–V–O bond angles, for all four models are displayed in Figures 5.17–19 which show how allowing for distortion of the  $\text{VO}_4$  tetrahedra in the monoclinic  $P2_1/c$  model results in Bi–O and V–O bond distance and O–V–O bond angle distributions similar to those observed in the  $m-f$   $I2/b$  model.

To investigate the cause of the deformations in the  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra, the partial NPDFs were plotted to identify the features that the flexible  $P2_1/c$  model fits better compared to the  $I2/b$  model (Figure 5.20). The lack of scatter from the  $\text{V}^{5+}$  cations is noteworthy, where despite their strong partial contribution do not display a peak at  $\sim 1.7$  Å coinciding with the V–O distances within the  $\text{VO}_4$  tetrahedra. Secondly, the features that were inadequately fit in the  $I4_1/a$  and  $I2/b$  structural models between 2.0–3.0 Å require a broad distribution of Bi–O and O–O distances as a result of the deformation of the  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra (Figure 5.18). Therefore, relaxing the symmetry of the long-range average structure from  $m-f$   $I2/b$  to the flexible monoclinic  $P2_1/c$  structure, consistent with the presence of stereochemically active  $6s^2$  lone pair electrons, is required to model the features on the local scale.

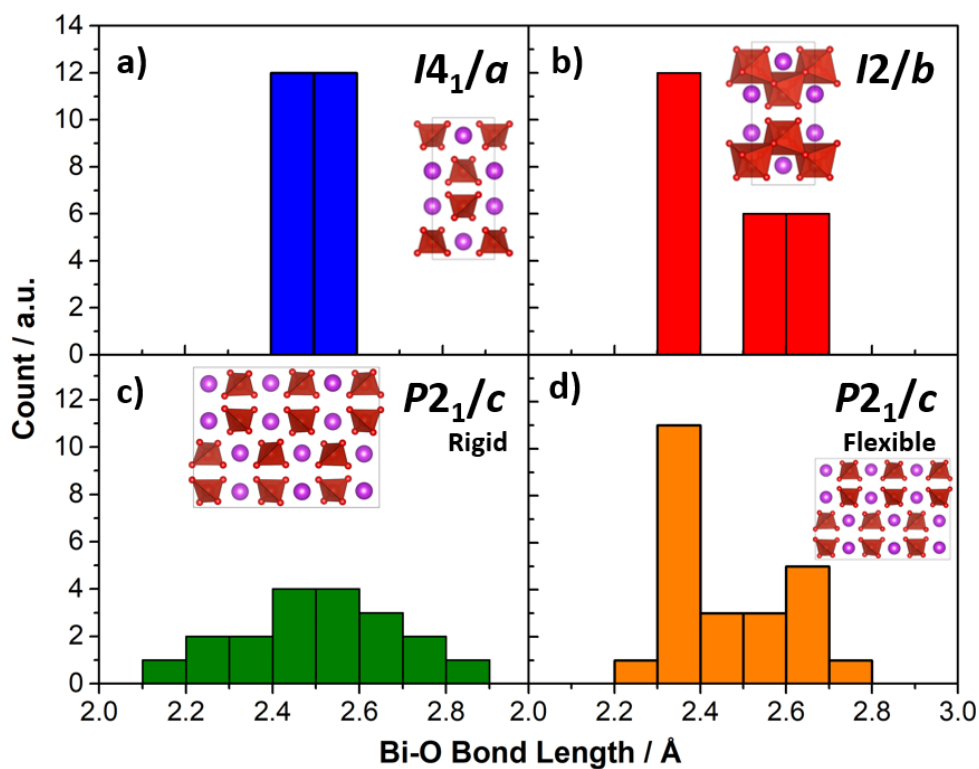


Figure 5.17: Distribution of Bi-O bond distances in the BiO<sub>8</sub> polyhedra of BiVO<sub>4</sub> extracted from the small box fits of the neutron pair distribution function data using the (a)  $t$ - $s$   $I4_1/a$ , (b)  $m$ - $f$   $I2/b$ , (c)  $P2_1/c$  with rigid VO<sub>4</sub> tetrahedra, and (d)  $P2_1/c$  with flexible VO<sub>4</sub> tetrahedra models.

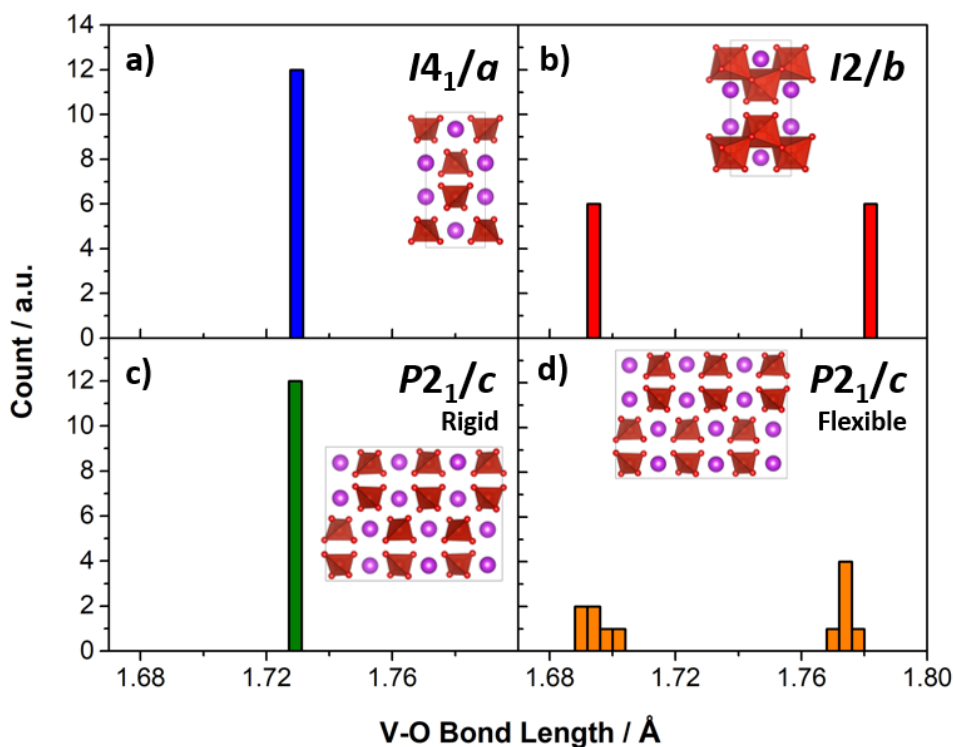


Figure 5.18: Distribution of V-O bond distances in the VO<sub>4</sub> tetrahedra of BiVO<sub>4</sub> extracted from the small box fits of the neutron pair distribution function data using the (a)  $t$ - $s$   $I4_1/a$ , (b)  $m$ - $f$   $I2/b$ , (c)  $P2_1/c$  with rigid VO<sub>4</sub> tetrahedra, and (d)  $P2_1/c$  with flexible VO<sub>4</sub> tetrahedra models.

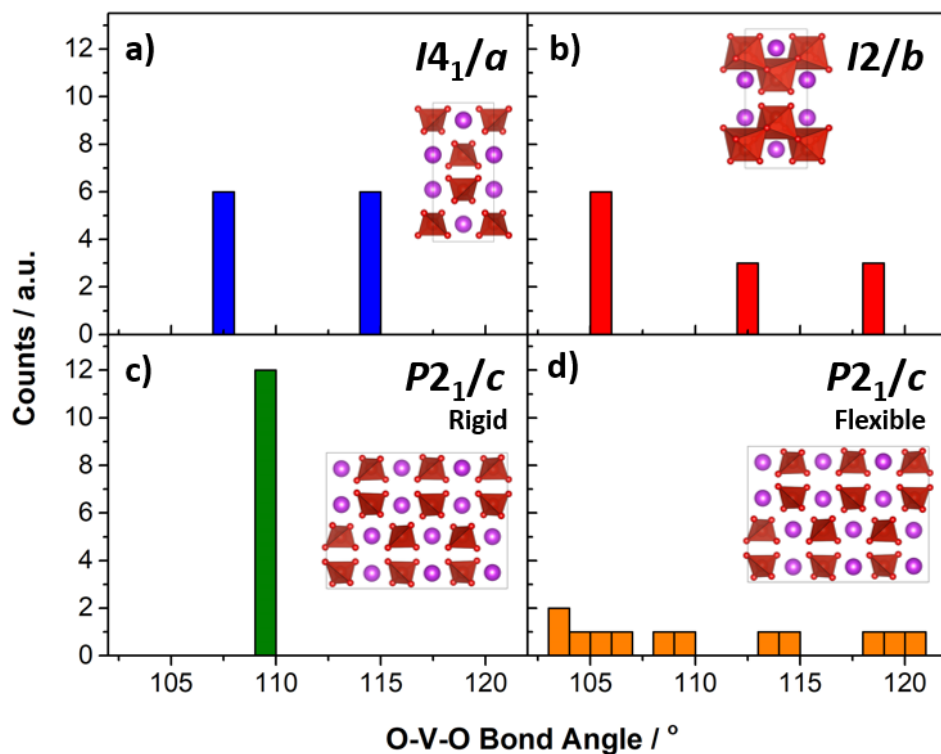


Figure 5.19: Distribution of O-V-O bond angles in the  $\text{VO}_4$  tetrahedra of  $\text{BiVO}_4$  extracted from the small box fits of the neutron pair distribution function data using the (a)  $t$ - $s$   $I4_1/a$ , (b)  $m$ - $f$   $I2/b$ , (c)  $P2_1/c$  with rigid  $\text{VO}_4$  tetrahedra, and (d)  $P2_1/c$  with flexible  $\text{VO}_4$  tetrahedra models.

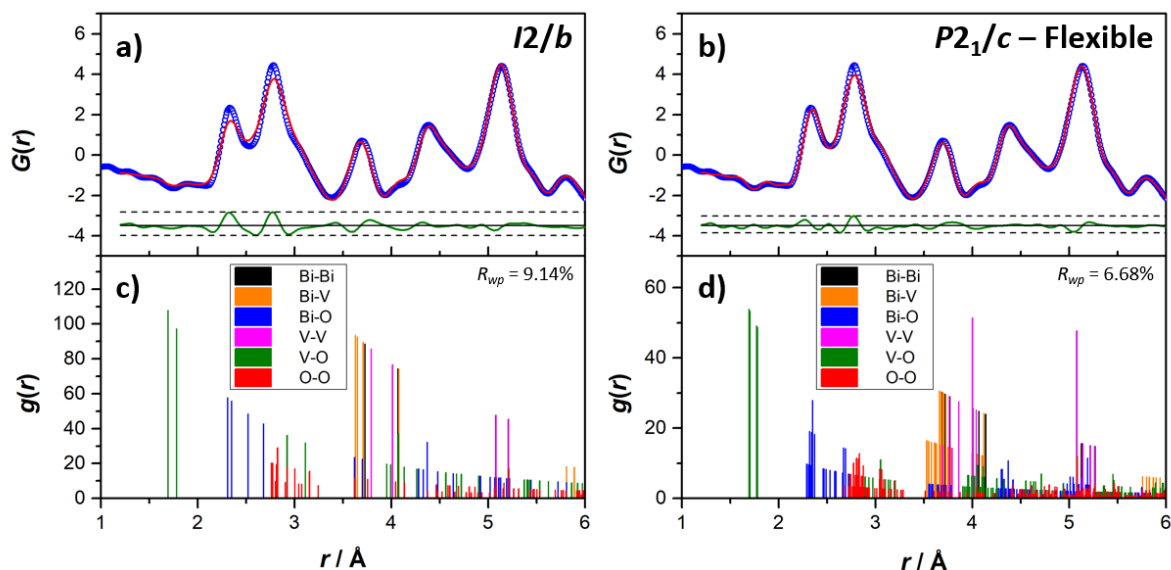


Figure 5.20: Neutron pair distribution function fits to  $\text{BiVO}_4$  at 100 K for (a) the  $m$ - $f$   $I2/b$ , and (b) the monoclinic  $P2_1/c$  model with flexible  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra. (c,d) The calculated partial contributions of each atom-atom pair. The data is fitted over a range of 1.2–30 Å, with a focus on 1.0–6.0 Å. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles.

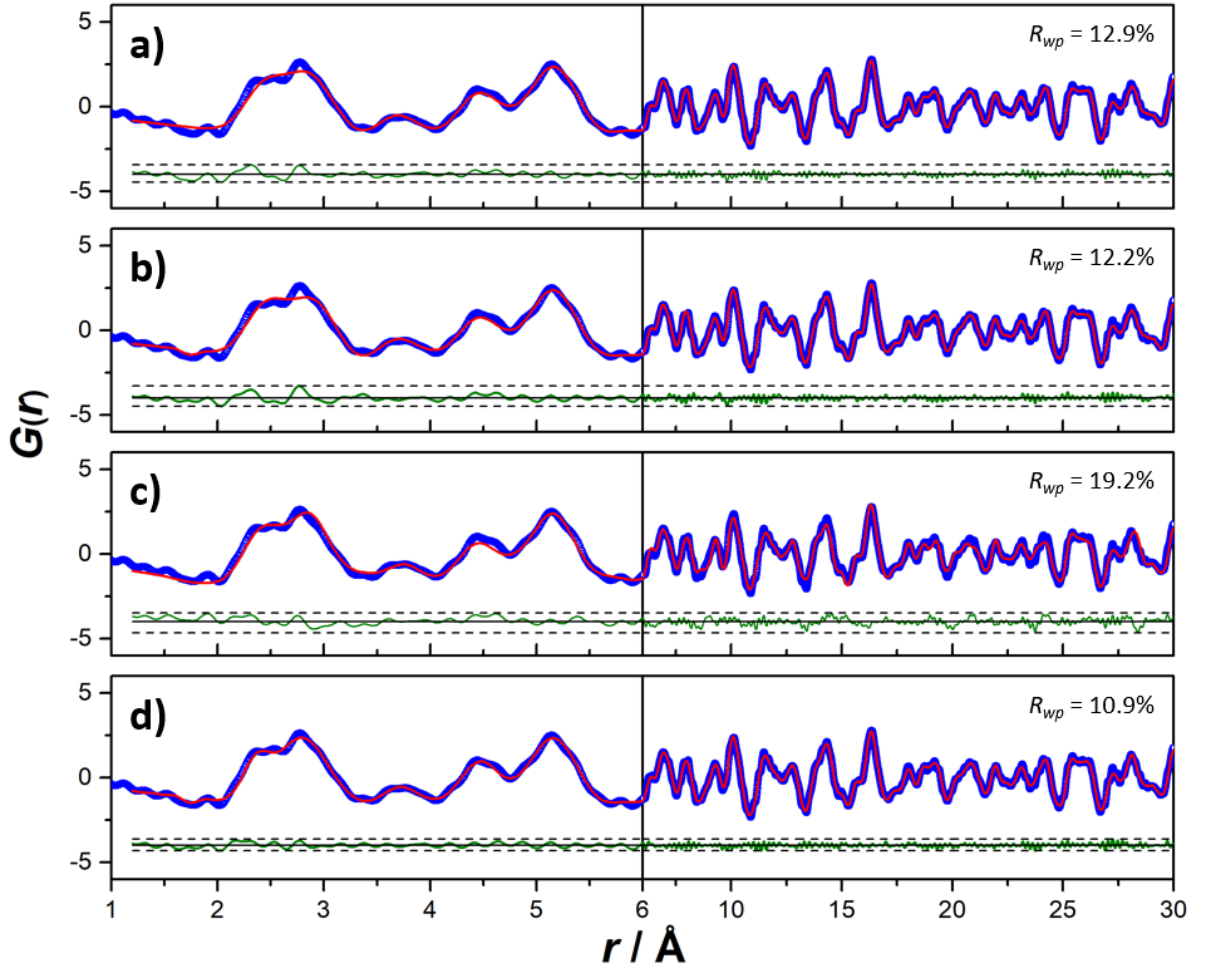


Figure 5.21: Neutron pair distribution function fits to BiVO<sub>4</sub> at 550 K for (a) *t-s*  $I4_1/a$ , (b) *m-f*  $I2/b$ , (c) monoclinic  $P2_1/c$  with rigid VO<sub>4</sub> tetrahedra, and (d) monoclinic  $P2_1/c$  with flexible VO<sub>4</sub> tetrahedra. The data is fitted over a range of 1.2–30 Å, with the first half highlighting the fit from 1.2–6.0 Å, and the second half highlighting from 6.0–30 Å. The blue dots represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles.

The NPDF data measured between 100 and 500 K was well fitted with the monoclinic  $P2_1/c$  flexible model. A similar approach of fitting the four different models to the NPDF of BiVO<sub>4</sub> above the  $I2/b \rightarrow I4_1/a$  phase transition at  $\sim 520$  K was explored. To minimise the contribution of dynamic disorder, the NPDF data collected at 550 K was modelled in detail (just above the  $I2/b \rightarrow I4_1/a$  phase transition). This dataset was confirmed to be long-range *t-s*  $I4_1/a$  from Rietveld refinements performed on the Bragg diffraction data. The fits to the four models are displayed in Figure 5.21. The *t-s*  $I4_1/a$  model fits the data well at high  $r$ , but struggles to account for the local features at low  $r$  (Figure 5.21a). This is similarly seen in the *m-f*  $I2/b$  model, where the local features at  $\sim 3.0$  Å are not well fit (Figure 5.21b). This is despite the  $I2/b$  model returning an almost tetragonal



metric for its unit cell parameters [ $a = 5.153(2)$  Å,  $b = 5.144(2)$  Å,  $c = 11.727(2)$  Å,  $\gamma = 89.94(4)$  °]. Upon lowering the symmetry to the monoclinic  $P2_1/c$  structure with rigid  $\text{VO}_4$  tetrahedra, the local features at low  $r$  are well reproduced (Figure 5.21c). However, this model results in the worst fit out of the four models across the entire 1.2–30 Å fitting region, with a substantial amount of features identified in the difference curve in the long range, high- $r$  region. Finally, the monoclinic  $P2_1/c$  model with flexible  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra produced the best fit to the data, with features well reproduced at both local low  $r$  and long range high  $r$  (Figure 5.21d). Similar results are seen at higher temperatures, with the flexible  $P2_1/c$  model producing the best fits to the NPDF up to 750 K.

The individual  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra environments were analysed upon heating from 100–750 K. In the Bragg diffraction data, the low temperature  $m\text{-}f$   $I2/b$  structure is made up of  $\text{BiO}_8$  polyhedra with four different Bi–O bonds and  $\text{VO}_4$  tetrahedra with two different V–O bonds. In the high temperature  $t\text{-}s$   $I4_1/a$  structure, the  $\text{BiO}_8$  polyhedra consist of two distinct Bi–O bonds, whereas the  $\text{VO}_4$  tetrahedra consist of a single unique V–O bond. A histogram of the Bi–O and V–O bond lengths in their respective polyhedra was extracted from the NPDF fits to the flexible  $P2_1/c$  model, and are shown in Figure 5.22. The average length of the Bi–O and V–O bonds increase with temperature, which is consistent with the thermal expansion of the material. However, the distribution of the bond distances changes with temperature. Firstly, there is a clear change in the distribution of the Bi–O bond distances, with the distribution of bond distances becoming more narrow with increasing temperature. Secondly, there is a larger change in the distribution of V–O bond distances, from distributed around two different bond lengths at lower temperatures, to eventually being distributed around a central value at higher temperatures. Each of these observations are consistent with what occurs in the long-range average structure, with a reduced range of Bi–O and V–O bond distances coinciding with an increase in symmetry. This contrasts with the structural model derived from the variable temperature NPD data, as no discontinuities are evident in the Bi–O and V–O bond distances upon heating (Figure 5.8). Rather, there is a gradual change on the local scale that is eventually reflected in the long-range average Rietveld refinements.



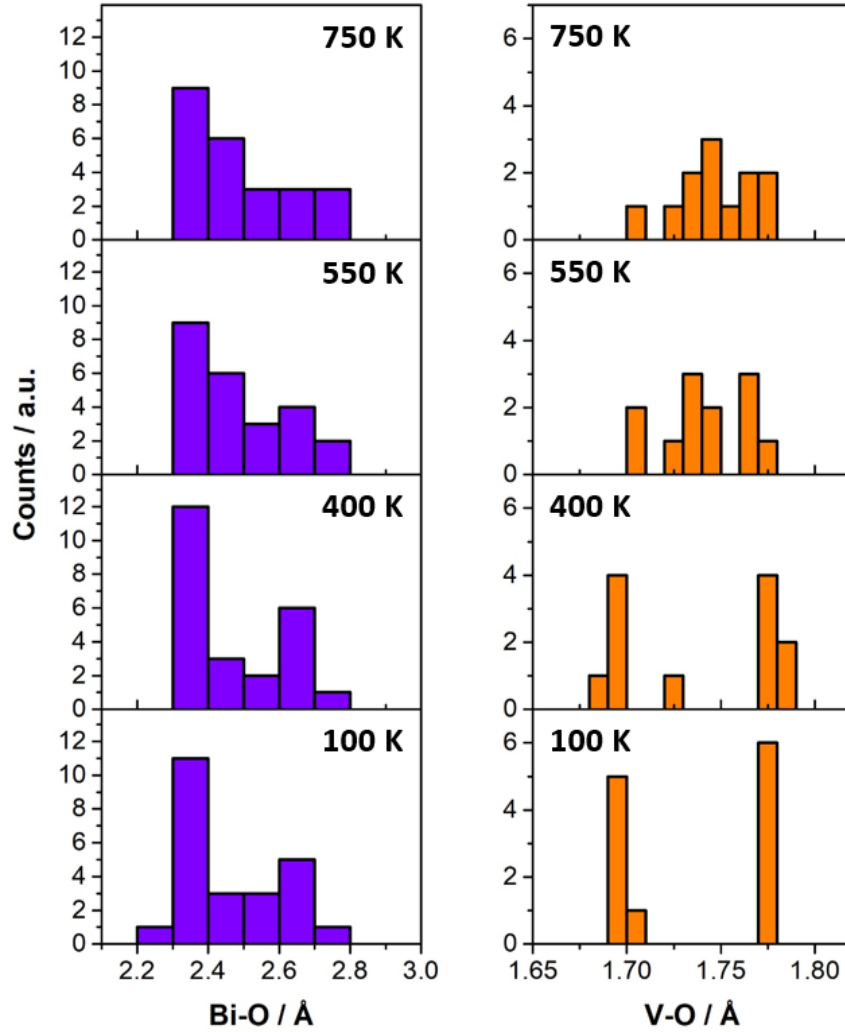


Figure 5.22: The (left, purple) Bi-O and (right, orange) V-O bond distances from the variable temperature neutron pair distribution function data fit to the flexible monoclinic  $P2_1/c$  model.

Using the NPDF data, an attempt was made to understand the unusual behaviour in the monoclinic  $\gamma$  angle observed in the SXRD and NPD variable temperature data. The magnitude of the monoclinic  $\gamma$  angle is expected to saturate at low temperatures. However, the SXRD and NPD variable temperature data showed this decreased below  $\sim 220$  K. With this increased understanding of the local structure of BiVO<sub>4</sub>, this anomalous behaviour was revisited. However, no such trends were able to be elucidated. The monoclinic  $\gamma$  angle showed no correlation with the distortion of the BiO<sub>8</sub> polyhedra or VO<sub>4</sub> tetrahedra, indicating that it may not solely be the result of the Bi<sup>3+</sup> 6s<sup>2</sup> lone pair. Further analysis should look at the possibility of collecting NPDF data at temperatures lower than 100 K using a cryostat to get a better understanding of the local structure with minimal dynamic contribution.

An in-depth SXRD and NPD study has been performed on the photocatalyst  $\text{BiVO}_4$ . This material presents a challenging study using diffraction techniques due to the large X-ray scattering of  $\text{Bi}^{3+}$  and the near-zero neutron scattering of V. Using mode analysis and variable temperature SXRD data, a linear relationship between the atomic displacements of  $\text{Bi}^{3+}$  and  $\text{V}^{5+}$  was established which was used to help determine the atomic coordinates of  $\text{V}^{5+}$  in the NPD studies. The structures of  $\text{BiVO}_4$  at low and high temperature were determined with high precision and accuracy (Table 5.2), with the *m-f*  $I2/b$  structure confirmed to consist of distorted  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra. This contrasts with the related  $\text{LnNbO}_4$  materials studied in Chapter 3 that consists of  $\text{LnO}_8$  polyhedra and  $\text{NbO}_6$  distorted octahedra. However, the high-temperature structure of these two materials appear to be isostructural, indexed to the tetragonal  $I4_1/a$  space group, and consisting of similar  $\text{AO}_8$  polyhedra and  $\text{BO}_4$  tetrahedra. Several anomalies were identified in the  $I2/b \rightarrow I4_1/a$  phase transition, such as the increase in the FWHM of the (200) and (020) reflections (attributed to domain wall broadening) and the increase in the rate of thermal expansion of the  $\text{BiO}_8$  polyhedra (attributed to activity of the  $6s^2$  lone pair electrons). The lack of saturation of the monoclinic  $\gamma$  angle remains unresolved, with lower temperature neutron total scattering data required for further analysis.

The XPDF data of  $\text{BiVO}_4$  showed that the local Bi–O and V–O environments were not accurately modelled from the long-range average structures derived from Rietveld refinements to the Bragg data. By reducing the fitting range to include just the cation–cation distances, a better fit to the data was observed with a high local ADP on the  $\text{Bi}^{3+}$  site that was not seen on the  $\text{V}^{5+}$  site, suggesting potential local-scale distortions associated with the  $\text{Bi}^{3+}$   $6s^2$  lone pair. The NPDF data also revealed the presence of local-scale distortions that were incompatible with either the long-range *t-s*  $I4_1/a$  or *m-f*  $I2/b$  structures. The distortions were most evident in the region of 2.0–3.0 Å, corresponding to the Bi–O and O–O distances across the  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra. This data demonstrates that despite the long-range average structure of  $\text{BiVO}_4$  transforming from heavily distorted  $\text{BiO}_8$  polyhedra in the *m-f*  $I2/b$  structure to less distorted  $\text{BiO}_8$  polyhedra in the *t-s*  $I4_1/a$  structure, the local structure is always best described using the monoclinic  $P2_1/c$  space group with flexible  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra. This demonstrates a change in the correlation length of the  $\text{Bi}^{3+}$  lone pair electrons at the

phase transition; despite the lone pairs being stereochemically active in the average *m-f* *I2/b* structure and inactive in the average *t-s* *I4<sub>1</sub>/a* structure, they remain active on the local scale throughout the entire measured temperature range.

## 5.4 Structural Studies of PbWO<sub>4</sub>

As noted previously, the revised lone pair model identified that for metal oxides, the energy separation between the cation *ns* and O *2p* levels determines the stereochemical activity of the lone pair.<sup>36</sup> This means that the Pb<sup>2+</sup> lone pairs are more likely to exert stereochemical influence than Bi<sup>3+</sup>. However, this is not observed at room temperature in some *ABO*<sub>4</sub> structures, with BiVO<sub>4</sub> adopting a more distorted and lower symmetry structure in the form of the *m-f* *I2/b* structure, compared to PbWO<sub>4</sub> adopting the *t-s* *I4<sub>1</sub>/a* structure.<sup>17,39</sup> Given it was determined from the previous section that BiVO<sub>4</sub> always exhibits *6s*<sup>2</sup> lone pair activity in the short-range local structure, regardless of the long-range average structure observed using diffraction, the presence of similar signatures were investigated in PbWO<sub>4</sub> and PbMoO<sub>4</sub>. This study will also be compared to the isostructural compound CaWO<sub>4</sub>, which adopts the same *I4<sub>1</sub>/a* structure but lack a *6s*<sup>2</sup> cation and any reported photocatalytic activity.<sup>43</sup>

### 5.4.1 *In Situ* Synthesis Studies

PbWO<sub>4</sub> is an important industrial material, finding application as a photocatalyst,<sup>14,15</sup> a scintillator material,<sup>88,89</sup> and a potential ceramic electrolyte for SOFCs.<sup>90,91</sup> Materials that are of interest for these applications are traditionally synthesised through solid state reactions, as the elevated temperatures and prolonged heating times drive the reaction to a stable, thermodynamic product. Recent studies have identified that these reactions occur within a short timeframe, sometimes within seconds of achieving the desired heating temperature.<sup>1,92</sup> There is a growing need to study the kinetics and dynamics of these thermally-driven reactions to identify more energy-efficient architectures for their large-scale industrial synthesis. The RAPTR,<sup>2</sup> developed by the Chapman Research Group at

Stony Brook University, NY, USA, is a new reactor capable of performing time-resolved *in situ* X-ray scattering studies initiated by temperature (Figure A.18). The RAPTR quickly heats and cools samples by translating them in and out of a preheated hot zone, allowing samples to heat to temperatures up to  $\sim 1000$  °C in ten seconds or less.

The *in situ* synthesis of the scheelite-type material  $\text{PbWO}_4$  was evaluated as a model stoichiometric solid state reaction  $(\text{PbO}_{(s)} + \text{WO}_{3(s)} \rightarrow \text{PbWO}_{4(s)})$ .<sup>2</sup> As previously observed in the synthesis of other scheelite-type materials [such as the  $\text{NaA}(\text{BO}_4)_2$  double scheelites in Chapter 4],<sup>65</sup> these materials require heating at high temperatures (700–900 °C) for long time periods (>12 hours). As  $\text{Pb}^{2+}$  and  $\text{W}^{6+}$  are heavy cations, they are expected to be relatively immobile with a slow diffusion reaction anticipated.

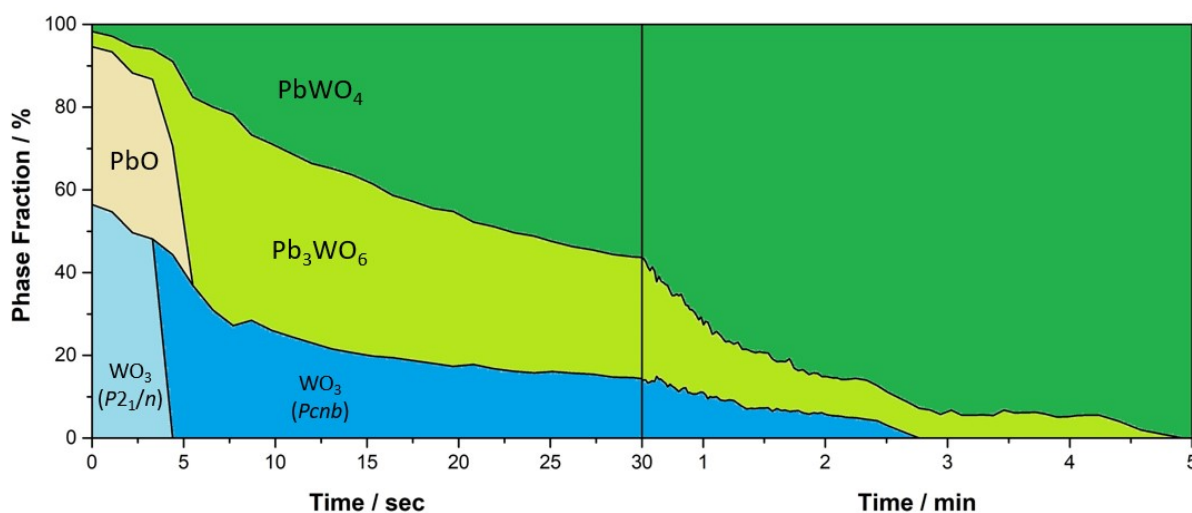
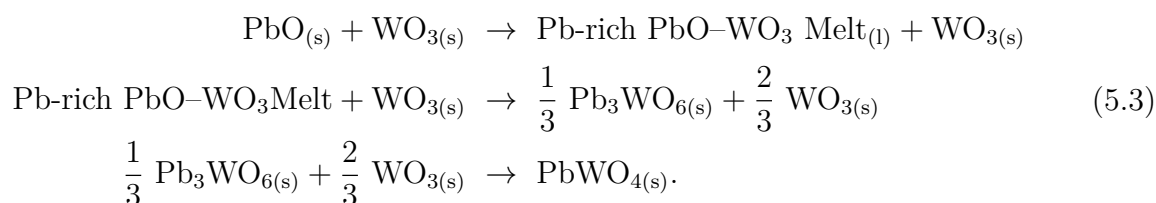


Figure 5.23: The phase evolution during the reaction of  $\text{PbO}$  and  $\text{WO}_3$  at 750 °C within the rapidly-actuating pneumatic thermal reactor furnace, as quantified from Rietveld refinements of the time-resolved X-ray powder diffraction data. The solid vertical line indicates a change in the  $x$ -axis scale from seconds to minutes.

The time-resolved *in situ* diffraction data acquired following rapid heating of the  $\text{PbO} + \text{WO}_3$  mixture showed the solid state synthesis of  $\text{PbWO}_4$  proceeded *via* three steps



During the first ten seconds, as the reaction mixture heats to 750 °C, WO<sub>3</sub> undergoes a  $P2_1/n \rightarrow Pcnb$  phase transition, which is known to occur between 300–350 °C.<sup>93</sup> Crystalline PbO peaks disappear in tandem with the formation of crystalline products and an increase in diffuse scattering (Figure A.19), from either disorder within the crystalline product or from a mixed PbO–WO<sub>3</sub> melt (noting that pure PbO melts at 888 °C). At 750 °C, Rietveld refinements indicate that three phases were present: the WO<sub>3</sub> reagent, the PbWO<sub>4</sub> product, and an additional crystalline intermediate which was indexed as Pb<sub>3</sub>WO<sub>6</sub> in the space group  $P2_1/n$ . The amount of WO<sub>3</sub> and Pb<sub>3</sub>WO<sub>6</sub> decreased as the amount of PbWO<sub>4</sub> product increased, suggesting a reaction between the two. This occurs rapidly in the reaction and gradually slows, with more than half of the PbWO<sub>4</sub> product formed within the first 30 seconds of the reaction (Figure 5.23). After five minutes, only peaks from the PbWO<sub>4</sub> product are observed as a phase-pure reaction product.

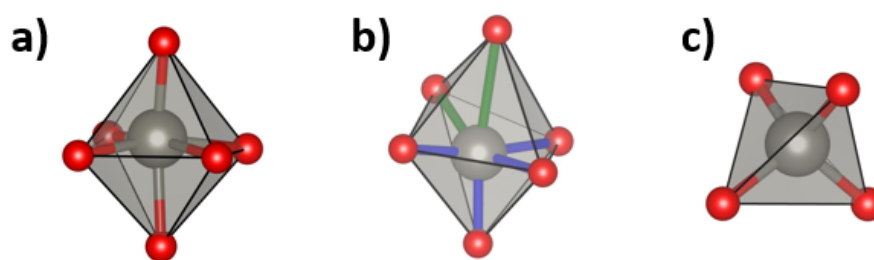


Figure 5.24: The polyhedra environments for W<sup>6+</sup> in each of the three Rietveld refined phases. (a) WO<sub>6</sub> octahedra in WO<sub>3</sub> ( $Pcnb$ ), (b) strained WO<sub>6</sub> octahedra in Pb<sub>3</sub>WO<sub>6</sub> ( $P2_1/n$ ) with the four short W–O bonds drawn in blue and the two long W–O bonds drawn in green, and (c) WO<sub>4</sub> tetrahedra in PbWO<sub>4</sub> ( $I4_1/a$ ).

The Pb<sub>3</sub>WO<sub>6</sub> observed here is a metastable, kinetic product which most likely would have been overlooked in conventional experiments. This is the first time Pb<sub>3</sub>WO<sub>6</sub> has been synthesised using a solid state reaction.<sup>94</sup> This phase has only been reported once, where it was prepared using a hydrothermal synthesis technique. In this phase, the W<sup>6+</sup> cations exist in an extremely-strained six-coordinate octahedra, with four shorter W–O bonds ( $\sim 1.82$ – $2.00$  Å) and two longer W–O contacts ( $\sim 2.11$ – $2.55$  Å). These longer contacts still contribute to the BVS of the strained WO<sub>6</sub> octahedra (0.59 and 0.19, respectively). Therefore, this is seen as an intermediate between the WO<sub>6</sub> octahedra seen in WO<sub>3</sub>, and the WO<sub>4</sub> tetrahedra of PbWO<sub>4</sub> (Figure 5.24).

In Chapter 3, the *in situ* synthesis of  $\text{HoTaO}_4$  was studied using NPD, which was used to identify a  $\text{Ho}_3\text{TaO}_7$  intermediate phase. This required a large sample mass ( $\sim 5$  g) and was ramped from 100–1500 °C over a period of 16 hours. In the case of the RAPTR furnace, the small thermal mass of a single capillary ( $\sim 10$  mg) is important for thermally initiating and quenching reactions. Other fast-heating strategies have been used previously for initiating fast ramping, such as using a hot air blower,<sup>95,96</sup> or a lamp furnace.<sup>97</sup> However, in each of these cases, several minutes are still required to attain thermal equilibrium. As observed from the  $\text{PbO} + \text{WO}_3$  reaction, the delay of a few minutes may result in the formation of short-lived intermediate phases being overlooked. The heating components of the RAPTR furnace are already equilibrated at high temperature, allowing for the identification of a previously unknown solid state  $\text{PbO}\text{--}\text{WO}_3$  intermediate phase.

#### 5.4.2 Room Temperature Synchrotron X-Ray and Neutron Powder Diffraction

A polycrystalline samples of  $\text{PbWO}_4$  was prepared using solid state methods and the structures and phase purity were confirmed using a combined SXRD and NPD Rietveld refinement. SXRD provided accurate unit cell parameters, which are in close agreement with previous studies.<sup>37–39,98</sup> NPD provided accurate Pb–O and W–O bond distances, which were in excellent agreement with the earlier NPD study by Takai *et al.*<sup>99</sup> The BVSs for  $\text{Pb}^{2+}$  and  $\text{W}^{6+}$  were also calculated (Equation 3.1) to be 1.98 and 5.89 for  $\text{Pb}^{2+}$  and  $\text{W}^{6+}$  respectively.<sup>100</sup> The possibility of a longer  $\text{W}\text{--}\text{O}_l$  bond contact was investigated. However, the next-nearest W–O contacts at 3.0958(16) Å are larger than the long Nb– $\text{O}_l$  and Ta– $\text{O}_l$  contacts, and also only contribute a BVS of 0.039.<sup>67,100,101</sup> Therefore, it was determined that at room temperature, the  $\text{PbWO}_4$  structure consisted of a network of  $\text{PbO}_8$  polyhedra and  $\text{WO}_4$  tetrahedra.

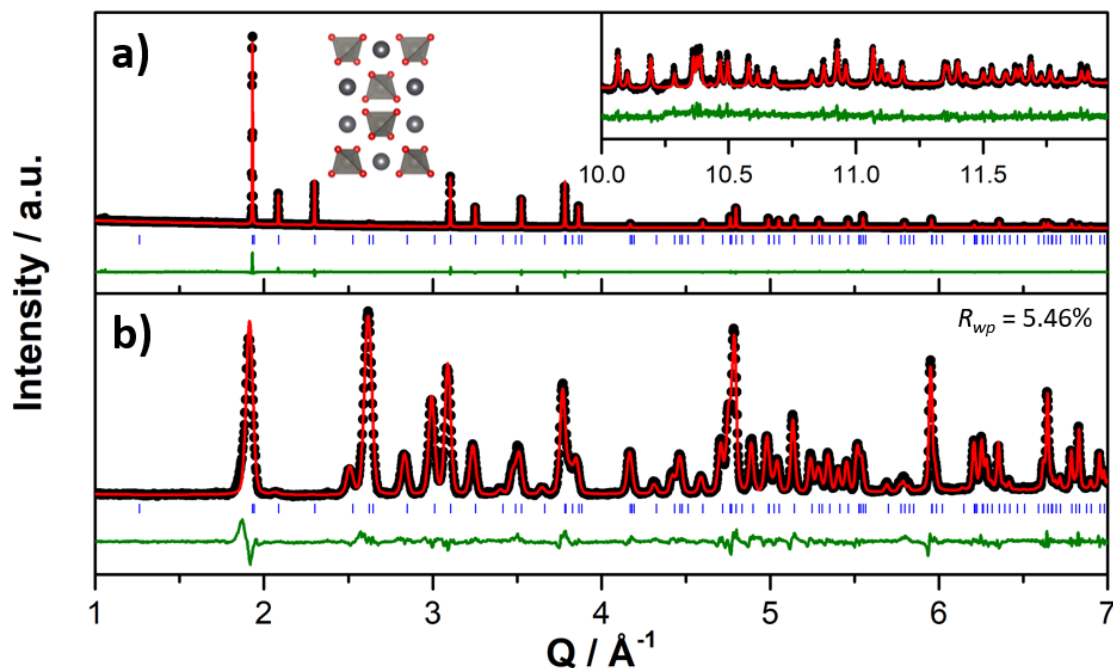


Figure 5.25: Combined Rietveld refinements against the (a) synchrotron X-ray and (b) neutron powder diffraction data of PbWO<sub>4</sub> at room temperature. The structure was refined to the *t-s*  $I4_1/a$  space group, with the inset highlighting the quality of the fit to the synchrotron X-ray diffraction data. The black circles represent the data, the red line represents the calculated profile, the green line is the difference between the data and the calculated profile, and the blue ticks are the space group-allowed reflections.

### 5.4.3 Variable Temperature Neutron Powder Diffraction

Since the stereochemistry of the Pb<sup>2+</sup> cation and the distortion of the PbO<sub>8</sub> polyhedra can be impacted by the 6s<sup>2</sup> electrons, the possibility of symmetry lowering in the structure was explored using NPD. The strategy employed to investigate this was as follows: firstly, the sample was cooled to 3 K to test for long range static disorder whilst minimising thermal disorder. The cell metric was then determined using 2.44 Å neutrons, obtained from the 331 reflection of the vertically focusing Ge monochromator. These data were then combined with a dataset measured at 1.30 Å, obtained using the 337 reflection of the same monochromator. The use of the shorter wavelength extended the measured *d*-range from  $d_{min} = 1.235$  to 0.66 Å. This provides greater sensitivity to small displacements in the atomic positions leading to more precise structural parameters. Additionally, longer wavelength neutrons provide greater sensitivity to any subtle deviation from the *t-s*  $I4_1/a$  symmetry. The wavelength of the 1.30 Å dataset was treated as a variable in the Rietveld refinement, reflecting the greater peak-shape resolution of the 2.44 Å dataset (Figure 5.26).

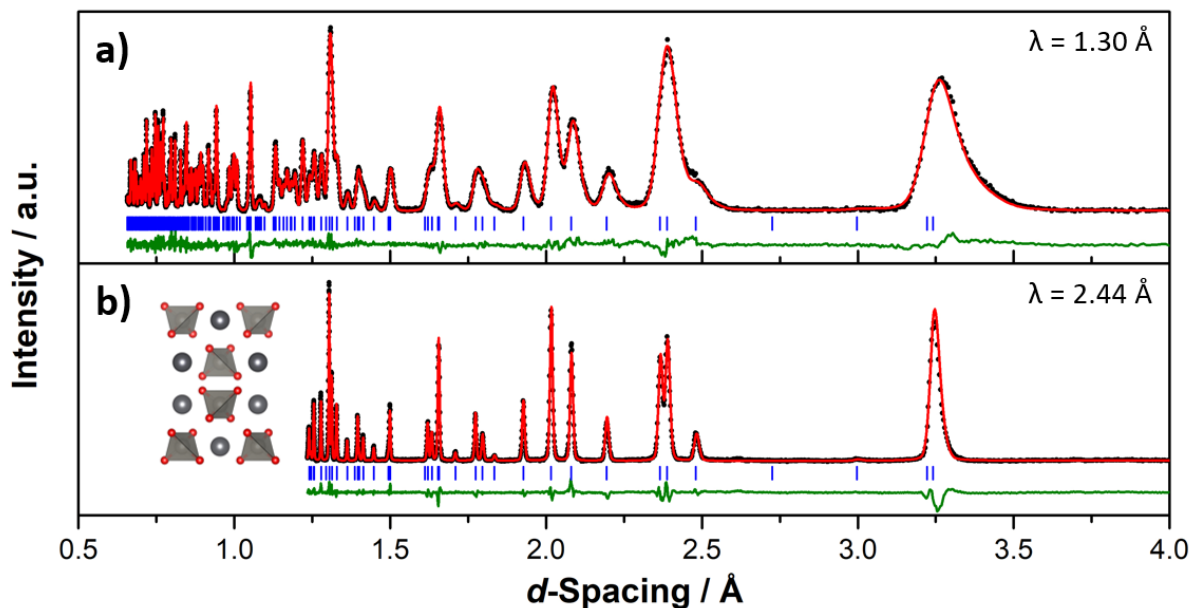


Figure 5.26: Rietveld refinements of  $\text{PbWO}_4$  to the  $t$ - $s$   $I4_1/a$  space group measured at 3 K using neutrons of wavelength (a) 1.30 and (b) 2.44 Å. The black circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles, and the blue markers are the space group-allowed reflections.

In the Rietveld refinements against the dataset measured at 3 K, the magnitude of the isotropic ADPs were determined to be close to zero. The inclusion of the 1.30 Å dataset enabled anisotropic ADPs to be obtained. Anisotropic ADPs have previously been used to model different types of static and dynamic disorder in scheelite-type oxides.<sup>102,103</sup> However, examination of these provided no evidence of any anomalies. Upon cooling, the bond distortion index (Equation 5.2) of the  $\text{PbO}_8$  polyhedra increases slightly from  $D = 0.041$  to 0.053. These values are comparable to those obtained by Chipeaux *et al.* for a NPD study of  $\text{PbWO}_4$  at 1.4 K.<sup>39</sup>

Next, a model was tested using Rietveld refinement where the  $\text{Pb}^{2+}$  cations were disordered onto the  $8e$  Wyckoff position  $(0, 1/4, 5/8+\delta)$ , giving it freedom to move in the  $z$  direction similar to that observed in  $\text{BiVO}_4$  and the local structure of  $\text{NaBi}(\text{WO}_4)_2$ . This resulted in a refined  $\delta$  value of 0.0041(3) and a comparable  $\chi^2$  value to the standard model ( $\chi^2 = 3.74$  vs. 3.75). The refined ADP for the  $\text{Pb}^{2+}$  in this disordered model was also deemed to be nonphysically small ( $B_{eq.}$  returning a zero value within the uncertainties of the refinement). Finally, an attempt was made to refine the structures using the  $m$ - $f$   $I2/b$  model. This yielded an identical  $\chi^2$  with a metrically tetragonal unit cell [ $\gamma = 90.000(7)^\circ$ ] with only a 0.03% difference between the  $a$  and  $b$  lattice parameters. Although the  $\text{Pb}^{2+}$



cation occupies the 4e Wyckoff position  $(0, 1/4, z)$  in the  $m-f$  model, the refined position did not reveal an appreciable displacement from  $z = 5/8$  for the  $t$ -s  $I4_1/a$  structure, with the refined value being 0.6262(3). In short, none of the potential signatures for stereochemical activity of the Pb<sup>2+</sup> 6s<sup>2</sup> lone pair electrons – distortion of the unit cell metric, increased distortion of the PbO<sub>8</sub> polyhedra, or large ADPs – are evident from the low temperature NPD datasets.

#### 5.4.4 X-Ray and Neutron Total Scattering

Two different total scattering experiments were performed to exploit the maximum contrast between the number of electrons and the coherent neutron scattering lengths: PbMoO<sub>4</sub> for X-ray total scattering ( $Z_{\text{Pb}^{2+}} = 80$ ,  $Z_{\text{Mo}^{6+}} = 36$ ,  $Z_{\text{O}^{2-}} = 10$ ), and PbWO<sub>4</sub> for neutron total scattering ( $b_{\text{Pb}} = 9.41$ ,  $b_{\text{W}} = 4.86$ ,  $b_{\text{O}} = 5.80$  fm). Scheelite-type oxides containing either Mo<sup>6+</sup> or W<sup>6+</sup> on the  $B$  site typically display similar structures and properties due to the almost identical IR of Mo<sup>6+</sup> and W<sup>6+</sup> (0.41 *vs.* 0.42 Å).<sup>65,104,105</sup> This was also observed in the study of NaA(BO<sub>4</sub>)<sub>2</sub> ( $B^{6+} = \text{Mo, W}$ ) in Chapter 4.

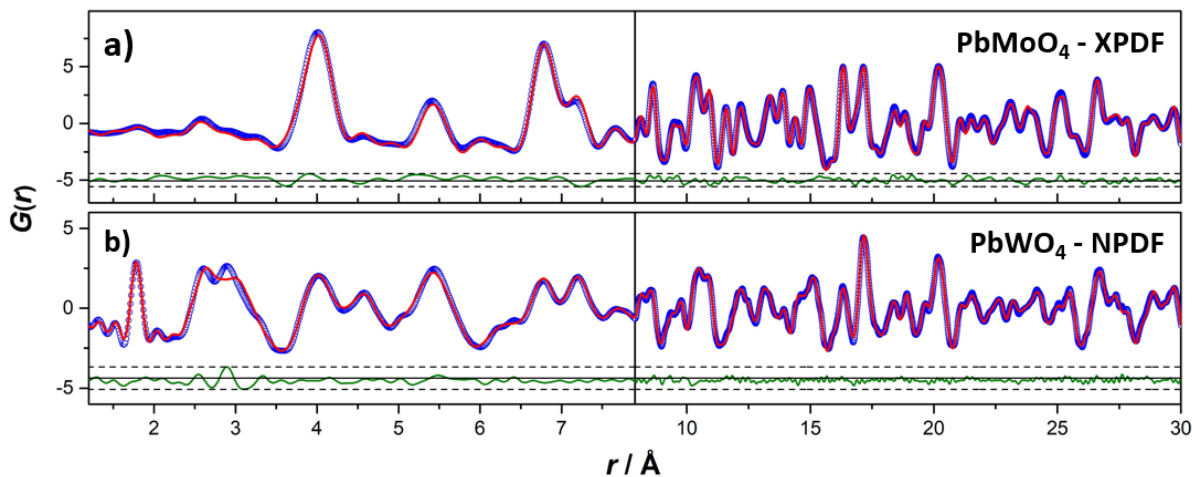


Figure 5.27: (a) X-ray pair distribution function fits of PbMoO<sub>4</sub> at 300 K to the long-range average  $t$ -s  $I4_1/a$  structure. (b) Neutron pair distribution function fits of PbWO<sub>4</sub> at 300 K to the long-range average  $t$ -s  $I4_1/a$  structure. The data were fitted over a range of 1.2–30 Å, with the first half highlighting the fit from 1.2–8.0 Å, and the second half highlighting from 8.0–30 Å. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles.

X-ray total scattering data for  $\text{PbMoO}_4$  were measured at 300 K using I15-1 at the Diamond Light Source, UK. Rietveld refinements were conducted against the experimental X-ray Bragg diffraction data using the  $t$ - $s$   $I4_1/a$  model. The high-quality fits confirm the average structure and the phase purity of the sample. The  $t$ - $s$   $I4_1/a$  fit to the XPDF of  $\text{PbMoO}_4$  is displayed in Figure 5.27a. Unlike the  $m$ - $f$   $I2/b$  structure observed in  $\text{BiVO}_4$ , the increased symmetry of the  $t$ - $s$   $I4_1/a$  structure means there is significant peak overlap in the cation–cation distances. As seen in the XPDF data of  $\text{BiVO}_4$ , the cation–oxygen distances are weakly observed in the  $\text{PbMoO}_4$  XPDF data. The first prominent peak at  $\sim 4.05$  Å corresponds to each of the cation–cation pairs: Pb–Pb, Pb–Mo, and Mo–Mo. This is similar for the peak at  $\sim 5.45$  Å, which is an overlap of Pb–Pb and Mo–Mo distances. The same difficulty in fitting the cation–cation distances in the  $\text{BiVO}_4$  XPDF data was not observed in fitting the  $\text{PbMoO}_4$  XPDF data, suggesting comparatively less  $A$ -site disorder in  $\text{PbMoO}_4$ , in line with the observed long-range average  $t$ - $s$   $I4_1/a$  structure. That the XPDF data is well fitted by the  $I4_1/a$  model suggests that the cations are confined to their symmetry-restrained Wyckoff positions and indicates good agreement between the long- and short-range structural models.

Neutron total scattering data were measured for  $\text{PbWO}_4$ , at both 300 and 115 K, using the NOMAD diffractometer at the SNS, ORNL USA. As stated previously, the NPDF is sensitive to all elements in the structure and is Fourier transformed from a structure function  $S(Q)$  with a larger  $Q$ , providing better short-range resolution for the cation–oxygen and oxygen–oxygen distances that are not visible in the XPDF due to a combination of the weak scattering of X-rays by oxygen and the limited short-range real-space resolution. The 300 K NPDF was fit with an  $r$  range of 1.2–30 Å to compare with the XPDF (Figure 5.27b). Due to the slight differences between  $\text{Mo}^{6+}$  and  $\text{W}^{6+}$  in terms of electron configuration and neutron scattering length, these refinements were performed separately, and not as a combined refinement. Careful examination of the NPDF refinement demonstrates significant misfitting at  $\sim 3.0$  Å, as shown by the prominent features in the residual curve (Figure 5.27b). This misfitting suggests that short-range oxygen arrangements are different from those observed in the long-range average structure. Evidently in  $\text{PbMoO}_4$  and  $\text{PbWO}_4$ , NPDF is necessary to truly understand the local structure.

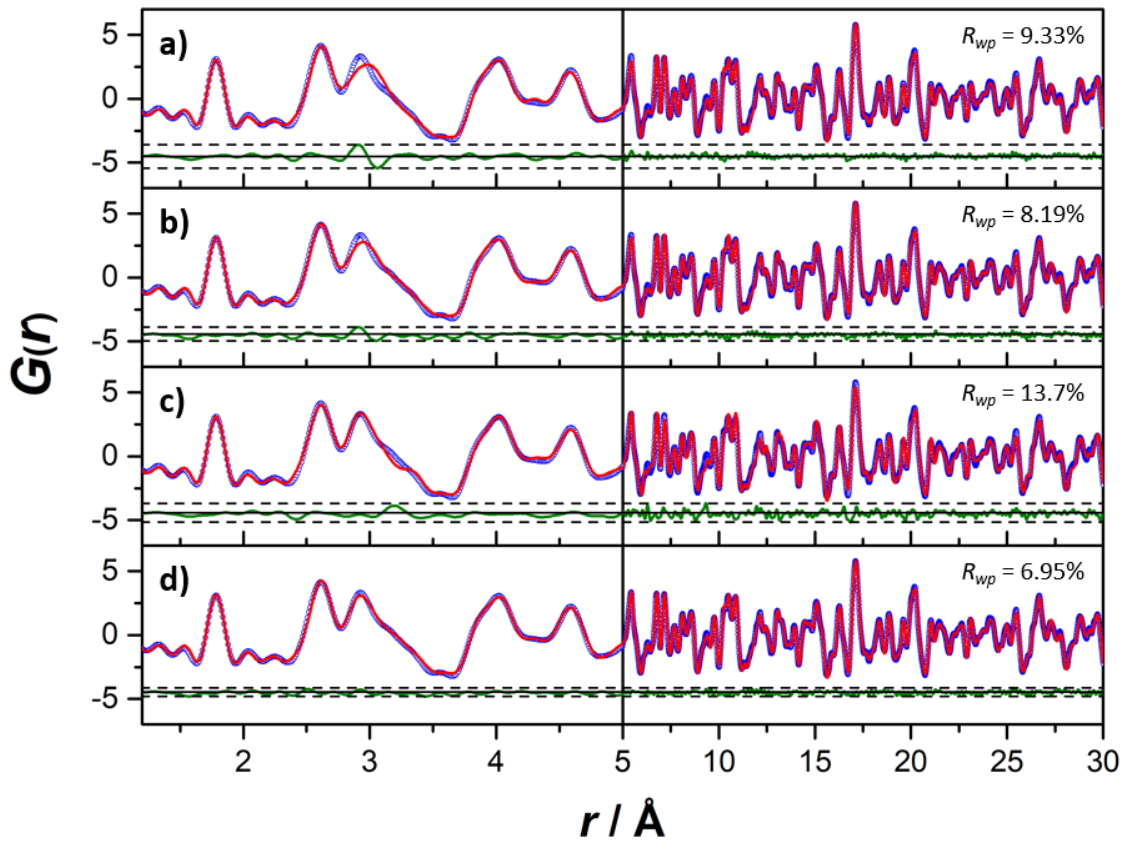


Figure 5.28: Neutron pair distribution function fits to PbWO<sub>4</sub> at 115 K for (a) *t-s*  $I4_1/a$ , (b) *m-f*  $I2/b$ , (c) monoclinic  $P2_1/c$  with rigid WO<sub>4</sub> tetrahedra, and (d) monoclinic  $P2_1/c$  with flexible WO<sub>4</sub> tetrahedra. The data was fitted over a range of 1.2–30 Å, with the first half highlighting the fit from 1.2–5.0 Å, and the second half highlighting from 5.0–30 Å. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles.

Initially, three crystallographic models were tested, similar to the BiVO<sub>4</sub> modelling described earlier in this chapter (Figure 5.15): the *t-s*  $I4_1/a$ , *m-f*  $I2/b$ , and the monoclinic  $P2_1/c$  model with relaxed PbO<sub>8</sub> polyhedra and rigid WO<sub>4</sub> tetrahedra. The NPDF fits of PbWO<sub>4</sub> at 115 K were conducted across a fitting range of 1.2–30 Å (Figure 5.28). The  $I4_1/a$  structure returns a reasonable  $R_{wp}$  and the fit is excellent aside from the 2.7–3.3 Å range. This demonstrates the subtle length scale of the disorder in the system. Lowering the symmetry to the monoclinic  $I2/b$  model improves the fit, but it is still unable to completely capture the information in the observed data at 2.7–3.3 Å. The refined cell metric does not deviate far from the  $I4_1/a$  model [ $a = 5.4534(9)$  Å,  $b = 5.4538(8)$  Å,  $\gamma = 89.931(16)^\circ$ ]. Further symmetry lowering to the rigid  $P2_1/c$  model results in a worse fit than the  $I4_1/a$  model. This is not just the case for the local region of 2.7–3.3 Å, but across the entire 1.2–30 Å fitting range.

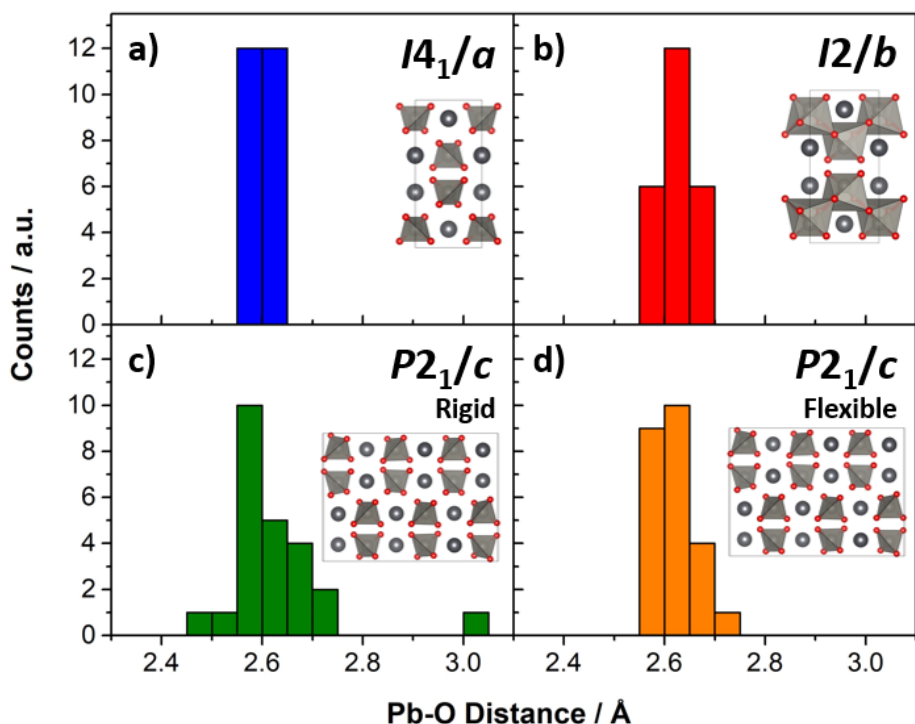


Figure 5.29: Distribution of Pb-O bond distances in the PbO<sub>8</sub> polyhedra of PbWO<sub>4</sub> for the four neutron pair distribution function fits with (a) the *t-s*  $I4_1/a$ , (b) the *m-f*  $I2/b$ , (c) the monoclinic  $P2_1/c$  with rigid WO<sub>4</sub> tetrahedra, and (d) the monoclinic  $P2_1/c$  with flexible WO<sub>4</sub> tetrahedra angles.

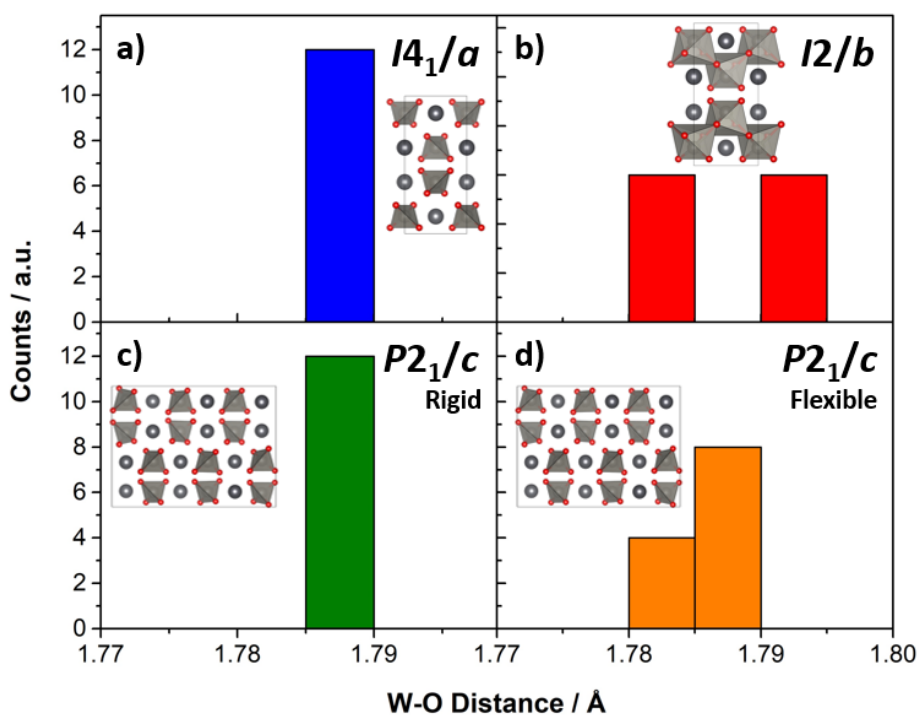


Figure 5.30: Distribution of W-O bond distances in the WO<sub>4</sub> tetrahedra of PbWO<sub>4</sub> for the four neutron pair distribution function fits with (a) the *t-s*  $I4_1/a$ , (b) the *m-f*  $I2/b$ , (c) the monoclinic  $P2_1/c$  with rigid WO<sub>4</sub> tetrahedra, and (d) the monoclinic  $P2_1/c$  with flexible WO<sub>4</sub> tetrahedra angles.

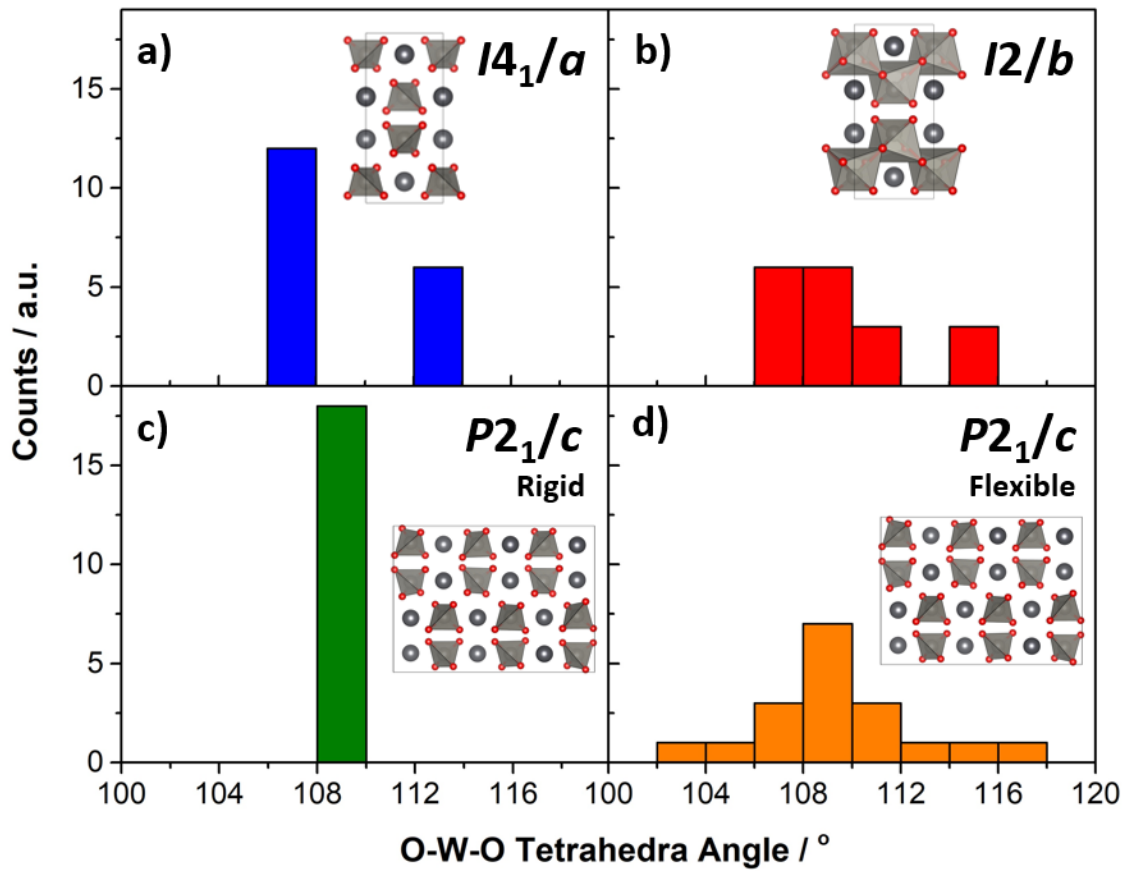


Figure 5.31: Distribution of O–W–O angles in the  $\text{WO}_4$  tetrahedra of  $\text{PbWO}_4$  for the four neutron pair distribution function fits with (a) the  $t$ -s  $I4_1/a$ , (b) the  $m$ -f  $I2/b$ , (c) the monoclinic  $P2_1/c$  with rigid  $\text{WO}_4$  tetrahedra, and (d) the monoclinic  $P2_1/c$  with flexible  $\text{WO}_4$  tetrahedra angles.

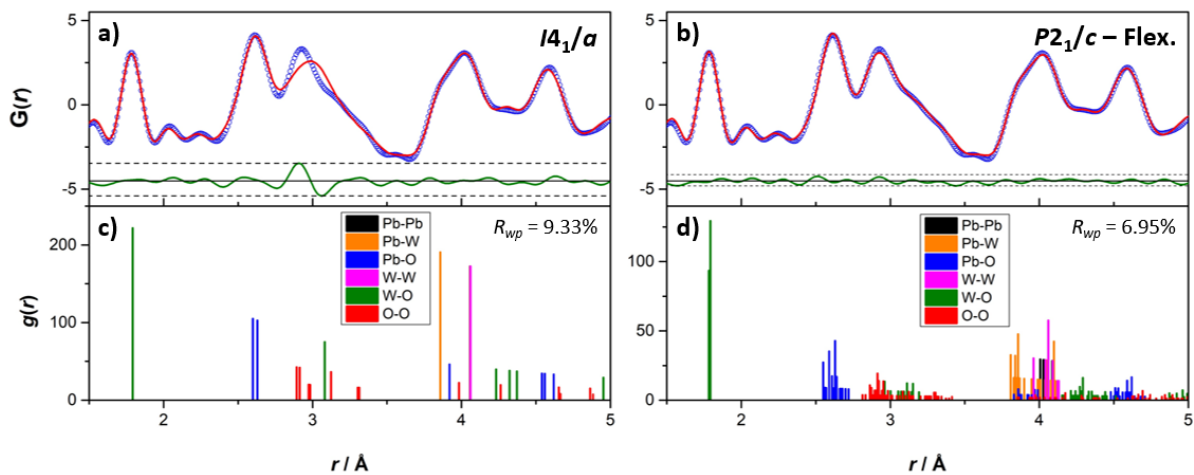


Figure 5.32: Partial neutron pair distribution functions plotted for  $\text{PbWO}_4$  at 115 K using the (a,c) tetragonal  $I4_1/a$  model, and (b,d) monoclinic  $P2_1/c$  model with flexible  $\text{PbO}_8$  polyhedra and  $\text{WO}_4$  tetrahedra. Data was fitted across the 1.2–30 Å range. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles.

The effect of relaxing the restraints of the monoclinic  $P2_1/c$  was explored. In  $\text{PbWO}_4$ , in contrast to  $\text{BiVO}_4$ , the long-range average structure is best fit to the  $t$ - $s$   $I4_1/a$  structure, with NPDF fits to the  $m$ - $f$   $I2/b$  also returning a structural model that does not deviate far from the  $t$ - $s$   $I4_1/a$  model. The  $t$ - $s$   $I4_1/a$  structure differs from the  $m$ - $f$   $I2/b$  structure by having more rigid  $\text{BO}_4$  tetrahedra, with a single unique  $B$ -O bond distance observed in the long-range average structure. Therefore, in the NPDF modelling, the constraint of the rigid tetrahedra was removed for the monoclinic  $P2_1/c$  model, but the W-O bond distances in the  $\text{WO}_4$  tetrahedra were restrained to be as close as possible to one unique value. This means the O-W-O bond angles were relaxed from the expected tetrahedra bond angles of  $109.5^\circ$ , allowing for slight distortions. This monoclinic  $P2_1/c$  model, with the flexible  $\text{WO}_4$  tetrahedra, substantially improved the fit and results in the best fit amongst the four models tested. Additionally, it is able to fit the information in the 2.7–3.3 Å region that was relatively poorly reproduced by both the  $t$ - $s$   $I4_1/a$  and  $m$ - $f$   $I2/b$  models (Figure 5.28d).

To investigate the low- $r$  region more closely, partial PDFs were plotted for each of the four models to identify the features each model struggled to fit (Figure 5.32). The first narrow peak, observed at  $\sim 1.78$  Å, corresponds to the first W-O pair in the  $\text{WO}_4$  tetrahedra. This value matches well with the W-O distances observed in the  $\text{NaA}(\text{WO}_4)_2$  double scheelites in Chapter 4. This peak does not show any splitting, indicating limited variability in the W-O distance in the  $\text{WO}_4$  tetrahedra, as expected in all four models. The next peak at  $\sim 2.6$  Å is due to the first Pb-O pairs in the  $\text{PbO}_8$  polyhedra and, again, is well fitted by all four models. Between 2.7–3.3 Å, there are several features corresponding to the O-O distances across the  $\text{PbO}_8$  polyhedra and  $\text{WO}_4$  tetrahedra, and to the W-O next-nearest-neighbour distances. This next-nearest-neighbour W-O pair corresponds to the distance from a  $\text{W}^{6+}$  cation to the nearest oxygen on a neighbouring  $\text{WO}_4$  tetrahedra. To fit these features, more freedom was required, as seen by the improved fit obtained upon lowering the symmetry from  $t$ - $s$   $I4_1/a$ . This is a result of relaxing the O-W-O tetrahedra angles, as shown in Figure 5.31. The only model that has an ideal  $109.5^\circ$  tetrahedra angle is the rigid  $P2_1/c$  model, which results in the worst fit to the entire NPDF. The  $t$ - $s$   $I4_1/a$  model, although having the highest symmetry, allows for small amounts of tetrahedra distortions, as shown by the small deviation in the tetrahedra angle from  $109.5^\circ$ . That

this results in a better fit than the  $P2_1/c$  model with rigid WO<sub>4</sub> tetrahedra indicates that these distortions are necessary to model the data from  $r > 3.5$  Å.

Increasing the amount the WO<sub>4</sub> tetrahedra can distort improves the fitting of the features between 2.8–3.4 Å, with the flexible  $P2_1/c$  model resulting in the best fit. In all four models, the average tetrahedra angle is 109.5 °, but the standard deviation for each distribution increases as the symmetry is lowered: 2.39 ° for  $I4_1/a$ , 2.94 ° for  $I2/b$ , and 3.20 ° for flexible  $P2_1/c$ . This shows that flexibility in the tetrahedra bond angles is required to accurately describe the local structure. This, in turn, creates the required distribution of next-nearest-neighbour W–O distances and O–O distances. In the case of the rigid  $P2_1/c$  model, the distortions are solely focused on the PbO<sub>8</sub> polyhedra, which misrepresents the structure at all length scales. In the  $t$ - $s$   $I4_1/a$  and  $m$ - $f$   $I2/b$  models, the overall distortions are insufficient to fit the local structure. However, in the flexible  $P2_1/c$  model with flexible WO<sub>4</sub> tetrahedra, the required balance between distortion of both the PbO<sub>8</sub> polyhedra and WO<sub>4</sub> tetrahedra is achieved.

### 5.4.5 Comparison to the Original CaWO<sub>4</sub> Scheelite

To determine whether the distortions observed in both the PbO<sub>8</sub> polyhedra and WO<sub>4</sub> tetrahedra are the result of the stereochemical activity of the Pb<sup>2+</sup> 6s<sup>2</sup> lone pair electrons, a comparative study was performed on the isostructural compound CaWO<sub>4</sub>; the original scheelite material. Recall that although PbWO<sub>4</sub> and CaWO<sub>4</sub> are isostructural, only PbWO<sub>4</sub> has been reported in the literature as a photocatalyst, implying that Pb<sup>2+</sup> 6s<sup>2</sup> lone pair is significant.

Comparing the refined structural parameters for both PbWO<sub>4</sub> and CaWO<sub>4</sub> at room temperature using NPD from the high resolution diffractometer Echidna revealed that the choice of *A*-site cation does not significantly impact the W–O distances (Table 5.3). This appears to be the case for all *B*–O distances across most *ABO*<sub>4</sub> materials, as observed in the  $Ln$ NbO<sub>4</sub> and  $Ln$ TaO<sub>4</sub> structures in Chapter 3, and the Na $Ln$ (WO<sub>4</sub>)<sub>2</sub> double scheelite structures in Chapter 4.<sup>65,67,101,106</sup> The BVSs of Ca<sup>2+</sup> and W<sup>6+</sup> were also consistent with their nominal valences, calculated to be 2.15 and 5.71 respectively. The NPD study at

Table 5.3: Selected Rietveld refinement bond distances and bond angles for  $\text{PbWO}_4$  and  $\text{CaWO}_4$  from variable temperature neutron powder diffraction data.

|                                          | <b>PbWO<sub>4</sub></b> |              | <b>CaWO<sub>4</sub></b> |              |
|------------------------------------------|-------------------------|--------------|-------------------------|--------------|
| <b>Temperature (K)</b>                   | <b>300</b>              | <b>3</b>     | <b>300</b>              | <b>3</b>     |
| <i>a</i> (Å)                             | 5.44973(4)              | 5.436021(5)  | 5.24013(5)              | 5.23336(4)   |
| <i>b</i> (Å)                             | = <i>a</i>              | = <i>a</i>   | = <i>a</i>              | = <i>a</i>   |
| <i>c</i> (Å)                             | 11.98569(12)            | 12.04608(17) | 11.37335(16)            | 11.34578(10) |
| <b>Vol.</b> (Å <sup>3</sup> )            | 355.970(7)              | 353.140(9)   | 312.300(8)              | 310.739(5)   |
| <b>O(1)</b> <i>x</i>                     | 0.23327(11)             | 0.23281(16)  | 0.24246(15)             | 0.24105(12)  |
| <b>O(1)</b> <i>y</i>                     | 0.10780(11)             | 0.10942(13)  | 0.09779(12)             | 0.09769(9)   |
| <b>O(1)</b> <i>z</i>                     | 0.04204(6)              | 0.04304(9)   | 0.03926(7)              | 0.03884(5)   |
| <i>A</i> – <b>O</b> (Å)                  | 2.6275(7)               | 2.6372(9)    | 2.4685(8)               | 2.4704(6)    |
| <i>A</i> – <b>O</b> (Å)                  | 2.5927(7)               | 2.6106(10)   | 2.4388(8)               | 2.4346(6)    |
| <i>AO</i> <sub>8</sub> (Å <sup>3</sup> ) | 31.6148                 | 32.1326      | 26.2149                 | 26.1689      |
| <i>D</i> ( <i>AO</i> <sub>8</sub> )      | 0.0041                  | 0.0053       | 0.0048                  | 0.0059       |
| <b>W</b> – <b>O</b> (Å)                  | 1.7903(7)               | 1.7832(10)   | 1.7892(8)               | 1.7839(6)    |
| <b>O</b> – <b>W</b> – <b>O</b> (°)       | 112.76(7)               | 112.53(4)    | 113.95(6)               | 113.54(4)    |
| <b>O</b> – <b>W</b> – <b>O</b> (°)       | 107.85(3)               | 107.97(2)    | 107.28(3)               | 107.48(2)    |
| <b>WO</b> <sub>4</sub> (Å <sup>3</sup> ) | 2.9388                  | 2.9028       | 2.9260                  | 2.9023       |
| <b>BVS</b> ( <i>AO</i> <sub>8</sub> )    | 2.08                    | 2.01         | 2.15                    | 2.16         |
| <b>BVS</b> ( <b>WO</b> <sub>4</sub> )    | 5.69                    | 5.81         | 5.71                    | 5.79         |

3 K conducted on  $\text{PbWO}_4$  to observe any static disorder was repeated for  $\text{CaWO}_4$ . The magnitude of the isotropic equivalent or anisotropic ADPs for both the  $\text{Pb}^{2+}$  and  $\text{Ca}^{2+}$  cations are comparable at both 300 and 3 K, and revealed no evidence of any anomalies.

Close attention was paid to the individual  $\text{AO}_8$  polyhedra modelled by the Rietveld refinements, as these will be the most sensitive to any anomalies as a result of the introduction of the  $6s^2$  lone pair on the *A*-site cation. Upon cooling in both  $\text{PbWO}_4$  and  $\text{CaWO}_4$ , the shorter *A*–**O** bonds contract whereas the longer *A*–**O** bonds expand leading to an increase in the distortion of the  $\text{AO}_8$  polyhedra. At room temperature, the  $\text{CaO}_8$  polyhedra have a higher distortion index than the  $\text{PbO}_8$  polyhedra ( $D_{\text{CaO}_8} = 0.0048$  *vs.*  $D_{\text{PbO}_8} = 0.0041$ ). After cooling to 3 K, the distortion of the  $\text{CaO}_8$  polyhedra increased by  $\sim 20\%$ , whereas the distortion of the  $\text{PbO}_8$  polyhedra increased by  $\sim 30\%$  ( $D_{\text{CaO}_8} = 0.0059$  *vs.*  $D_{\text{PbO}_8} = 0.0053$ ). These values are comparable to those previously reported in the literature.<sup>39,103</sup> That the  $\text{CaO}_8$  and  $\text{PbO}_8$  polyhedra behave similarly and undergo similar distortions upon cooling suggests that changes in the long-range average structure are not strongly influenced by the presence of the  $6s^2$  lone pair electrons.



As a final comparison, neutron total scattering data for CaWO<sub>4</sub> were taken on the NOMAD diffractometer at 100 and 300 K to conduct NPDF analysis. In particular, attention was paid as to whether there were additional features between 2.0–3.5 Å present in the NPDFs of CaWO<sub>4</sub>, suggesting structural deformation of the CaO<sub>8</sub> polyhedra as seen in PbWO<sub>4</sub> (Figures 5.28 and 5.32). The CaWO<sub>4</sub> structure provides outstanding sensitivity to the AO<sub>8</sub> polyhedra environments due to the structure possessing the smallest amount of static rotational disorder in the WO<sub>4</sub> tetrahedra.<sup>102,103</sup> Firstly, the long-range Bragg diffraction data of CaWO<sub>4</sub> could be well fitted using the *t-s* *I*4<sub>1</sub>/*a* model, confirming the previous CaWO<sub>4</sub> Rietveld refinements to the Echidna data. Secondly, the NPDFs at both 100 and 300 K were fit to the long-range average *t-s* *I*4<sub>1</sub>/*a* structure and showed excellent agreement (Figure 5.33).

The CaWO<sub>4</sub> and PbWO<sub>4</sub> datasets were compared. As previously discussed by Rabuffetti *et al.* and Culver *et al.*,<sup>102,103</sup> anisotropic ADPs are required to fit the NPDF of CaWO<sub>4</sub> due to the potential rotation of the WO<sub>4</sub> tetrahedra within the structure. As TOPAS6 lacks the capability of modelling anisotropic ADPs in NPDF fits, the fits were repeated in PDFgui.<sup>61</sup> The fitting range was reduced to 1.2–10 Å to more accurately capture the local features of the data. Allowing for symmetry constrained anisotropic ADPs (Ca<sup>2+</sup> and W<sup>6+</sup>:  $U_{11} = U_{22} \neq U_{33}$ , O<sup>2-</sup>:  $U_{11} \neq U_{22} \neq U_{33}, U_{12} \neq U_{13} \neq U_{23}$ ), fitting CaWO<sub>4</sub> to the *t-s* *I*4<sub>1</sub>/*a* model resulted in an excellent fit to the data (Figure 5.33a). However, the same fitting strategy did not produce a good fit to PbWO<sub>4</sub>, with the features corresponding to the PbO<sub>8</sub> polyhedra and WO<sub>4</sub> tetrahedra between 2.5–3.5 Å poorly fit (Figure 5.33b). This reinforces the conclusion that the local distortions present within the PbWO<sub>4</sub> structure are the result of the stereochemistry of the 6s<sup>2</sup> lone pair electrons.

As a final note, a comparison between the local structures of ABO<sub>4</sub> materials with 6s<sup>2</sup> lone pairs on the A-site cations can be made. In TlReO<sub>4</sub>, a combination of the longer Tl–O bonds (due to the lower oxidation state of Tl<sup>+</sup>) and the more rigid ReO<sub>4</sub> tetrahedra (due to the higher oxidation state of Re<sup>7+</sup>, shorter Re–O bonds, and smaller IR) mean that it is more favourable for the 6s<sup>2</sup> lone pair to distort the TlO<sub>8</sub> polyhedra than the ReO<sub>4</sub> tetrahedra. This was observed in the NPDF modelling of TlReO<sub>4</sub>, where variations in the Tl–O bond lengths had a bigger impact on the fit.<sup>44</sup> Although the average Tl–O bond

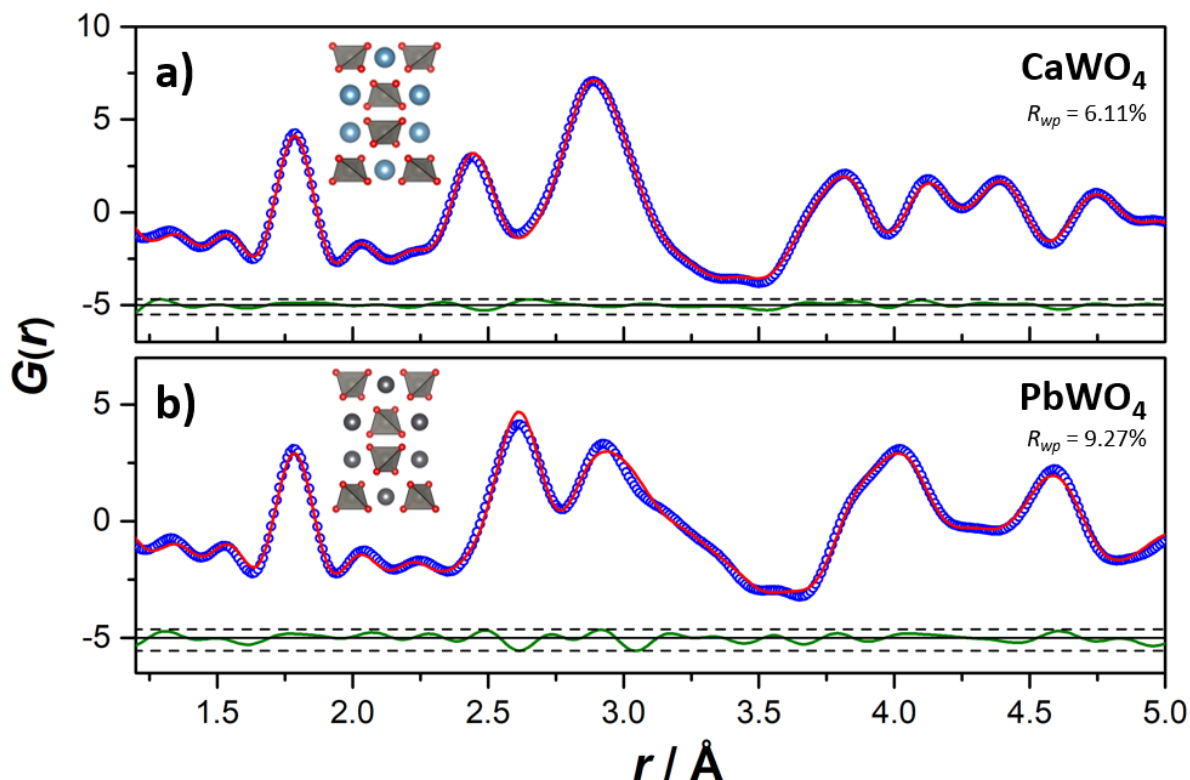


Figure 5.33: Neutron pair distribution function fits to the  $t$ - $s$   $I4_1/a$  structural model with anisotropic atomic displacement parameters. (a)  $\text{CaWO}_4$  at 100 K, and (b)  $\text{PbWO}_4$  at 115 K. The data was fitted over a range of 1.2–10 Å. The blue circles represent the measured data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles.

length in  $\text{TlReO}_4$  is  $\sim 2.95$  Å, modelling the NPDF revealed a broad distribution of Tl–O distances between 2.5–3.4 Å was necessary to accurately reproduce the low- $r$  features. This also leads to changes in the long-range average structure, as the flexibility of the  $\text{TlO}_8$  polyhedra and the rigidity of the  $\text{ReO}_4$  tetrahedra have been used to explain a change in the correlation length of the  $6s^2$  lone pair electrons, leading to a  $I4_1/a \rightarrow P2_1/c \rightarrow I4_1/a$  re-entrant phase transition that occurs upon heating between 150–400 K. This will be returned to in Chapter 6 of this dissertation.

For  $\text{PbWO}_4$ , the average Pb–O bond distance is shorter than the comparable average Tl–O bond distance (2.63 *vs.* 2.95 Å), attributed to the higher oxidation state of  $\text{Pb}^{2+}$  compared to  $\text{Tl}^+$ . Furthermore, the IR of  $\text{W}^{6+}$  is slightly larger than that of  $\text{Re}^{7+}$  (0.66 *vs.* 0.63 Å) and the W–O bonds in the  $\text{WO}_4$  tetrahedra are longer than the corresponding Re–O bonds in the  $\text{ReO}_4$  tetrahedra (1.78 *vs.* 1.73 Å). The ability for polyhedra to distort is expected to be a function of both the average length of the bonds that correlates with the IR of the central cation. As a result of the shorter A–O and longer B–O bonds in

PbWO<sub>4</sub> compared to TlReO<sub>4</sub>, it is more likely that the  $6s^2$  lone pair of Pb<sup>2+</sup> will slightly deform the WO<sub>4</sub> tetrahedra as opposed to the PbO<sub>8</sub> polyhedra. As the PbO<sub>8</sub> polyhedra are less flexible than the TlO<sub>8</sub> polyhedra, this also explains why PbWO<sub>4</sub> does not undergo a similar re-entrant phase transition in the long-range structure upon heating like TlReO<sub>4</sub>.

The most extreme example of this is BiVO<sub>4</sub>. The average Bi–O bond lengths are shorter still due to the higher oxidation state of Bi<sup>3+</sup>, measuring 2.53 Å in the *m-f* *I*2/*b* structure. As seen in the long-range average structure, this leads to the largest deformation in the tetrahedra, with two distinct V–O bonds and multiple different O–V–O bond angles. It should also be noted that V<sup>5+</sup> is a *3d* cation whereas both W<sup>6+</sup> and Re<sup>7+</sup> are *5d* cations, meaning the V–O bonds may be more polarisable and the VO<sub>4</sub> tetrahedra more susceptible to distortions. It is difficult to compare to a *5d* equivalent, as BiTaO<sub>4</sub> forms a unique triclinic structure at room temperature consisting of heavily distorted BiO<sub>4</sub> polyhedra and TaO<sub>6</sub> octahedra.<sup>107</sup> Nevertheless, the NPDF analysis suggests there is a clear relationship between the deformation of the polyhedra and the IR of the cations on both the *A* and *B* sites in these *ABO*<sub>4</sub> oxides. As V<sup>5+</sup>, W<sup>6+</sup>, and Re<sup>7+</sup> are all *d*<sup>0</sup> cations, they are additionally likely to have an electronic contribution, such as susceptibility to second order Jahn-Teller distortions similar to that observed in some perovskites and double perovskites.<sup>108–110</sup> The importance of this is evident in the BiBO<sub>4</sub> (*B*<sup>5+</sup> = V, As) compounds, where the VO<sub>4</sub> (*d*<sup>0</sup>) tetrahedra are more distorted than the related AsO<sub>4</sub> (*d*<sup>10</sup>) tetrahedra, in line with the V<sup>5+</sup> cations having a larger IR than As<sup>5+</sup> (0.355 *vs.* 0.335 Å).<sup>104,111</sup> NPDF studies on these related compounds would be beneficial to fully understand the interaction between the  $6s^2$  lone pair electrons, the AO<sub>8</sub> polyhedra, and the BO<sub>4</sub> tetrahedra in other *ABO*<sub>4</sub> structures.

### 5.4.6 Computational Studies

Although not the focus of this dissertation, it is important to note that computational studies of these *ABO*<sub>4</sub> materials are often nontrivial. Energy differences between the structures associated with their phase transitions are traditionally very small, which poses a serious challenge to computational studies when navigating the energy landscape. It is

important to have accurate and precise structural information for these materials to aid further computational studies, such as those deduced from NPDF studies. This was seen in the study of  $\text{TlReO}_4$ , where the structural parameters determined from NPDF were used in first principle DFT calculations to identify a difference in energy between the low temperature  $I4_1/a$  and room temperature  $P2_1/c$  phases due to the ordering (or lack thereof) of the  $\text{Tl}^+ 6s^2$  lone pairs.<sup>44</sup> This, in turn, was used to identify the mechanism behind the re-entrant  $I4_1/a \rightarrow P2_1/c \rightarrow I4_1/a$  phase transition. In a recent DFT study of  $\text{BiVO}_4$  by Liu *et al.*, it was necessary to use a hybrid functional with a  $\sim 60\%$  HF exchange as a consequence of the subtle interplay between the structural and electronic properties to stabilise the experimentally observed  $m-f$  structure.<sup>112</sup> This was also found for other  $\text{ABO}_4$  materials that can adopt both  $m-f$  and  $t-s$  symmetries, such as  $\text{YTbO}_4$  and  $\text{ScVO}_4$ .

Geometry optimisation calculations were performed for  $\text{PbWO}_4$  by collaborators of the author's research group, where the experimental parameters from the NPDF study were used as input parameters. Although the present calculations invariably resulted in a metrically tetragonal structure, a small distortion of the  $\text{PbO}_8$  polyhedra and  $\text{WO}_4$  tetrahedra that is symmetry forbidden in the tetragonal unit cell was reproduced (Table A.10). The pDoS of  $\text{PbWO}_4$  also showed that the Pb  $6s$  states dominate near the Fermi level, where they hybridise with the O  $2p$  states. Similar hybridisation between the Bi  $6s$  and O  $2p$  states at the top of the valence band has been previously described for  $\text{BiVO}_4$ .<sup>113,114</sup> This hybridisation between the  $ns$  and O  $2p$  orbitals has been noted with respect to the revised lone pair model used to explain the structural distortions observed in post-transition metal oxides.<sup>115</sup> In particular, the relative energy differences between the electronic states involved in the orbital interactions can explain the strength (or absence) of the structural distortions associate with the lone pair electrons.<sup>36</sup> Therefore, given that both  $\text{BiVO}_4$  and  $\text{PbWO}_4$  possess strong hybridisation between their  $ns$  and O  $2p$  states at the Fermi level, and the presumed absence of this interaction in  $\text{CaWO}_4$ , this may be used to explain the presence of photocatalytic properties in these two oxides despite their different structural symmetries.

It is important for the local structures of functional energy materials to be determined with a high degree of precision and accuracy. A uniformly accurate reproduction of the relevant parts of the energy landscape is an important prerequisite for providing detailed insight into the properties of materials at the atomic level using DFT calculations. These insights may then be used to better understand our current materials, and can be used to further ‘tailor make’ them to better perform their functional purposes.

## 5.5 Conclusions and Towards the Future Design of Photocatalysts

The present work details a thorough investigation into the structures of  $\text{BiVO}_4$  and  $\text{PbWO}_4$ , both structures which contain *A*-site cations possessing  $6s^2$  lone pair electrons and have been shown to exhibit photocatalytic activity. The room temperature structure of  $\text{BiVO}_4$  was determined using a combination of SXRD and NPD, giving sensitivity to all cations and anions within the structure. This was refined to the *m-f*  $I2/b$  structure, consisting of  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra. Using a combination of mode analysis and variable temperature SXRD, a linear relationship between  $\text{Bi}(z)$  and  $\text{V}(z)$  was established that was used as a constraint in the variable temperature NPD analysis. This style of analysis could potentially be used on other vanadium-containing functional energy materials, such as vanadium oxide-based redox flow batteries for energy storage,<sup>116</sup> and  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  superconductors for zero-loss power transmission.<sup>117</sup> Ideally, a method like this could be partnered with interaction potentials to further ‘pin down’ the atomic coordinates of vanadium in NPD studies without relying solely on symmetry arguments and mode analysis. This has been successfully used in the hybrid reverse Monte Carlo (HRMC) method, however is currently focused for use on carbon structures.<sup>118,119</sup>

The  $I2/b \rightarrow I4_1/a$  phase transition observed in  $\text{BiVO}_4$  upon heating displayed anisotropic expansion, as well as an increase in the rate of volume expansion in the *t-s*  $I4_1/a$  structure. This transformation displayed differences to the  $I2/a \rightarrow I4_1/a$  phase transitions observed in  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$  in Chapter 3 of this dissertation, with a large

discontinuity observed in the lattice parameters and bond lengths, as well as anomalous peak shapes due to domain wall broadening in the SXRD data, and a lack of saturation of the monoclinic  $\gamma$  angle. XPDF studies reproduced all the main features from the previous SXRD and NPD studies, but also identified changes in the local  $\text{VO}_4$  and  $\text{BiO}_8$  environments. Constraining the fits to a shorter range of 3.3–30 Å also led to an increase in the local ADPs of  $\text{Bi}^{3+}$ , possibly hinting at local static disorder. NPDF studies went on to further confirm that the local symmetry of  $\text{BiVO}_4$  was monoclinic  $P2_1/c$  compared to the long-range average structures of either *t-s*  $I4_1/a$  or *m-f*  $I2/b$ . This was due to the stereochemically active  $6s^2$  lone pair leading to distortions in both the  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra. A broad distribution of Bi–O, V–O, and O–O distances were needed to most accurately reproduce all of the local features observed in the NPDF data from 100–750 K.

NPDF analysis of the similar *t-s*  $I4_1/a$  structure of  $\text{PbWO}_4$  revealed the presence of local-scale distortions that are incompatible with the long-range average structure determined by Rietveld analysis against both SXRD and NPD data. These distortions in the region of 2.8–3.4 Å are correlated with the stereochemical activity of the  $\text{Pb}^{2+}$   $6s^2$  lone pair electrons. There were no signs of this activity using traditional diffraction measurements, with the bond distortion index of  $\text{PbO}_8$  calculated to be similar to that of  $\text{CaO}_8$  at 3 K. However, NPDF studies were able to demonstrate that the *t-s*  $I4_1/a$  long-range average structure of  $\text{CaWO}_4$  was in excellent agreement with the short-range local structure, demonstrating that the local distortions in the  $\text{PbWO}_4$  structure are most likely the result of the stereochemically active  $6s^2$  lone pair of the  $\text{Pb}^{2+}$  cation. The absence of strong coupling between the lone pair-induced deformation of the structure and the high symmetry long-range average structure is believed to be facilitated by deformation of the  $\text{WO}_4$  tetrahedra. The NPDF analysis demonstrated that although there was little variation in the W–O bond lengths, it was necessary to allow for a wide range of O–W–O angles to fit the NPDF.

This new structural information of  $\text{BiVO}_4$  and  $\text{PbWO}_4$  is potentially important for the design of compositionally- and structurally-related systems. Most importantly, the three studied  $\text{ABO}_4$  structures that contain a stereochemically active  $6s^2$  electron lone

pair on their *A* site ( $\text{BiVO}_4$ ,  $\text{PbWO}_4$ , and  $\text{TlReO}_4$ ) all possess different local distortions: such as extended distributions of  $\text{Ti-O}$  bond distances, distorted  $\text{WO}_4$  tetrahedra, and distortions in both the  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra. Each of these deformations is allowed by the monoclinic  $P2_1/c$  structure first observed in  $\text{TlReO}_4$  that has been used to fit the NPDFs of all three of the preceding structures, regardless of the temperature at which the material is measured. The subtle nature of these distortions, with some existing on a scale of less than 0.4 nm, were only determinable from the information present in the neutron total scattering data. That these distorted  $\text{AO}_8$  polyhedra and  $\text{BO}_4$  tetrahedra are present in known photocatalysts (such as  $\text{BiVO}_4$  and  $\text{PbWO}_4$ ), but absent in the nonactive photocatalyst  $\text{CaWO}_4$ , indicates that these distortions are important for the photocatalytic activity of these materials. Furthermore, that these distortions are present in the long-range average structure of  $\text{BiVO}_4$ ,<sup>18</sup> but only present in the short-range local structure of  $\text{PbWO}_4$ , provides a relationship between the correlation length of the disorder and the activity of the photocatalyst, with higher activity being recorded in  $\text{BiVO}_4$  than  $\text{PbWO}_4$ .<sup>120</sup>

This study highlights the importance of utilising multiple techniques such as SXR, NPD, XPDF, and NPDF to determine the true structural features in metal oxides. It can be postulated that local scale symmetry breaking may play a role in separating the photogenerated electron-hole pairs. Such an approach is being utilised in materials that contain defects such as vacancies, interstitials, antisites, and chemical doping. It is important to use the full suite of analytical techniques in order to further understand the role of such defects to develop robust structure-functionality relationships.





# Bibliography

- (1) Hu, D.; Beauvais, M. L.; Kamm, G. E.; Mullens, B. G.; Sanchez Monserrate, B. A.; Vornholt, S. M.; Chupas, P. J.; Chapman, K. W. Resolving fast relative kinetics in inorganic solid-state synthesis. *Journal of the American Chemical Society* **2023**, *145*, 26545–26549.
- (2) Hu, D.; Beauvais, M. L.; Mullens, B. G.; Monserrate, S.; Vornholt, S. M.; Kamm, G. E.; Ferrari, J. J.; Chupas, P. J.; Chapman, K. W. The RAPTR furnace: A rapid heating and cooling sample furnace for *insitu* X-ray scattering studies of temperature-induced reactions. *Journal of Applied Crystallography* **2024**, *57*.
- (3) Djurišić, A. B.; Leung, Y. H.; Ng, A. M. C. Strategies for improving the efficiency of semiconductor metal oxide photocatalysis. *Materials Horizons* **2014**, *1*, 400–410.
- (4) Guang-Lei, T.; Hong-Bo, H.; Jian-Da, S. Effect of microstructure of TiO<sub>2</sub> thin films on optical band gap energy. *Chinese Physics Letters* **2005**, *22*, 1787.
- (5) Fortunato, E.; Barquinha, P.; Pimentel, A.; Goncalves, A.; Marques, A.; Pereira, L.; Martins, R. Recent advances in ZnO transparent thin film transistors. *Thin Solid Films* **2005**, *487*, 205–211.
- (6) Zhu, D.; Zhou, Q. Novel Bi<sub>2</sub>WO<sub>6</sub> modified by N-doped graphitic carbon nitride photocatalyst for efficient photocatalytic degradation of phenol under visible light. *Applied Catalysis B: Environmental* **2020**, *268*, 118426.
- (7) Zhang, N.; Ouyang, S.; Li, P.; Zhang, Y.; Xi, G.; Kako, T.; Ye, J. Ion-exchange synthesis of a micro/mesoporous Zn<sub>2</sub>GeO<sub>4</sub> photocatalyst at room temperature for photoreduction of CO<sub>2</sub>. *Chemical Communications* **2011**, *47*, 2041–2043.

- (8) Ye, J.; Zou, Z.; Oshikiri, M.; Matsushita, A.; Shimoda, M.; Imai, M.; Shishido, T. A novel hydrogen-evolving photocatalyst  $\text{InVO}_4$  active under visible light irradiation. *Chemical Physics Letters* **2002**, *356*, 221–226.
- (9) Patial, S.; Hasija, V.; Raizada, P.; Singh, P.; Singh, A. A. P. K.; Asiri, A. M. Tunable photocatalytic activity of  $\text{SrTiO}_3$  for water splitting: strategies and future scenario. *Journal of Environmental Chemical Engineering* **2020**, *8*, 103791.
- (10) Malathi, A.; Madhavan, J.; Ashokkumar, M.; Arunachalam, P. A review on  $\text{BiVO}_4$  photocatalyst: Activity enhancement methods for solar photocatalytic applications. *Applied Catalysis A: General* **2018**, *555*, 47–74.
- (11) Hu, Y.; Fan, J.; Pu, C.; Li, H.; Liu, E.; Hu, X. Facile synthesis of double cone-shaped  $\text{Ag}_4\text{V}_2\text{O}_7/\text{BiVO}_4$  nanocomposites with enhanced visible light photocatalytic activity for environmental purification. *Journal of Photochemistry and Photobiology A: Chemistry* **2017**, *337*, 172–183.
- (12) Lv, D.; Zhang, D.; Pu, X.; Kong, D.; Lu, Z.; Shao, X.; Ma, H.; Dou, J. One-pot combustion synthesis of  $\text{BiVO}_4/\text{BiOCl}$  composites with enhanced visible-light photocatalytic properties. *Separation and Purification Technology* **2017**, *174*, 97–103.
- (13) Xue, Y.; Wang, X. The effects of Ag-doping on crystalline structure and photocatalytic properties of  $\text{BiVO}_4$ . *International Journal of Hydrogen Energy* **2015**, *40*, 5878–5888.
- (14) Zinatloo-Ajabshir, S.; Baladi, M.; Salavati-Niasari, M. Enhanced visible-light-driven photocatalytic performance for degradation of organic contaminants using  $\text{PbWO}_4$  nanostructure fabricated by a new, simple and green sonochemical approach. *Ultrasonics Sonochemistry* **2021**, *72*, 105420.
- (15) Kadowaki, H.; Saito, N.; Nishiyama, H.; Kobayashi, H.; Shimodaira, Y.; Inoue, Y. Overall splitting of water by  $\text{RuO}_2$ -loaded  $\text{PbWO}_4$  photocatalyst with  $d^{10}s^2 - d^0$  configuration. *The Journal of Physical Chemistry C* **2007**, *111*, 439–444.
- (16) Saito, N.; Kadowaki, H.; Kobayashi, H.; Ikarashi, K.; Nishiyama, H.; Inoue, Y. A new photocatalyst of  $\text{RuO}_2$ -loaded  $\text{PbWO}_4$  for overall splitting of water. *Chemistry Letters* **2004**, *33*, 1452–1453.

## BIBLIOGRAPHY

---

- (17) Sánchez-Martín, J.; Errandonea, D.; Pellicer-Porres, J.; Vázquez-Socorro, D.; Martínez-García, D.; Achary, S. N.; Popescu, C. Phase transitions of  $\text{BiVO}_4$  under high pressure and high temperature. *The Journal of Physical Chemistry C* **2022**, *126*, 7755–7763.
- (18) Sleight, A.; Chen, H.-Y.; Ferretti, A.; Cox, D. Crystal growth and structure of  $\text{BiVO}_4$ . *Materials Research Bulletin* **1979**, *14*, 1571–1581.
- (19) Mariathasan, J.; Hazen, R.; Finger, L. Crystal structure of the high-pressure form of  $\text{BiVO}_4$ . *Phase Transitions: A Multinational Journal* **1986**, *6*, 165–173.
- (20) Bhattacharya, A.; Mallick, K.; Hartridge, A. Phase transition in  $\text{BiVO}_4$ . *Materials Letters* **1997**, *30*, 7–13.
- (21) David, W.; Glazer, A.; Hewat, A. The structure and ferroelastic phase transition of  $\text{BiVO}_4$ . *Phase Transitions: A Multinational Journal* **1979**, *1*, 155–169.
- (22) Li, G.; Bai, Y.; Zhang, W. Difference in valence band top of  $\text{BiVO}_4$  with different crystal structure. *Materials Chemistry and Physics* **2012**, *136*, 930–934.
- (23) Stoltzfus, M. W.; Woodward, P. M.; Seshadri, R.; Klepeis, J.-H.; Bursten, B. Structure and bonding in  $\text{SnWO}_4$ ,  $\text{PbWO}_4$ , and  $\text{BiVO}_4$ : Lone pairs *vs.* inert pairs. *Inorganic Chemistry* **2007**, *46*, 3839–3850.
- (24) Yu, J.; Kudo, A. Effects of structural variation on the photocatalytic performance of hydrothermally synthesized  $\text{BiVO}_4$ . *Advanced Functional Materials* **2006**, *16*, 2163–2169.
- (25) Baur, W. The geometry of polyhedral distortions. Predictive relationships for the phosphate group. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* **1974**, *30*, 1195–1215.
- (26) Gillespie, R.; Nyholm, R. Inorganic stereochemistry. *Quarterly Reviews, Chemical Society* **1957**, *11*, 339–380.
- (27) Gillespie, R. Fifty years of the VSEPR model. *Coordination Chemistry Reviews* **2008**, *252*, 1315–1327.

- (28) Shi, J.; Rubinstein, E. A.; Li, W.; Zhang, J.; Yang, Y.; Lee, T.-L.; Qin, C.; Yan, P.; MacManus-Driscoll, J. L.; Scanlon, D. O. Modulation of the  $\text{Bi}^{3+} 6s^2$  lone pair state in perovskites for high-mobility *p*-type oxide semiconductors. *Advanced Science* **2022**, *9*, 2104141.
- (29) Li, F.; Lin, D.; Chen, Z.; Cheng, Z.; Wang, J.; Li, C.; Xu, Z.; Huang, Q.; Liao, X.; Chen, L.-Q. Ultrahigh piezoelectricity in ferroelectric ceramics by design. *Nature Materials* **2018**, *17*, 349–354.
- (30) Shrout, T. R.; Zhang, S. J. Lead-free piezoelectric ceramics: Alternatives for PZT? *Journal of Electroceramics* **2007**, *19*, 113–126.
- (31) Wang, Y.; Zhang, Z.; Usui, T.; Benedict, M.; Hirose, S.; Lee, J.; Kalb, J.; Schwartz, D. A high-performance solid-state electrocaloric cooling system. *Science* **2020**, *370*, 129–133.
- (32) Agbeworvi, G.; Zaheer, W.; Ponis, J. D.; Handy, J. V.; Ayala, J. R.; Andrews, J. L.; Schofield, P.; Jaye, C.; Weiland, C.; Fischer, D. A. Effect of stereochemically active electron lone pairs on magnetic ordering in trivanadates. *Inorganic Chemistry* **2023**, *62*, 12965–12975.
- (33) Du, B.; Zhang, R.; Chen, K.; Mahajan, A.; Reece, M. J. The impact of lone-pair electrons on the lattice thermal conductivity of the thermoelectric compound  $\text{CuSbS}_2$ . *Journal of Materials Chemistry A* **2017**, *5*, 3249–3259.
- (34) Dou, Y.; Li, J.; Xie, Y.; Wu, X.; Hu, L.; Liu, F.; Ao, W.; Liu, Y.; Zhang, C. Lone-pair engineering: Achieving ultralow lattice thermal conductivity and enhanced thermoelectric performance in Al-doped GeTe-based alloys. *Materials Today Physics* **2021**, *20*, 100497.
- (35) Walsh, A.; Yan, Y.; Huda, M. N.; Al-Jassim, M. M.; Wei, S.-H. Band edge electronic structure of  $\text{BiVO}_4$ : Elucidating the role of the Bi *s* and V *d* orbitals. *Chemistry of Materials* **2009**, *21*, 547–551.
- (36) Walsh, A.; Payne, D. J.; Egdell, R. G.; Watson, G. W. Stereochemistry of post-transition metal oxides: Revision of the classical lone pair model. *Chemical Society Reviews* **2011**, *40*, 4455–4463.

## BIBLIOGRAPHY

---

- (37) Moreau, J.; Galez, P.; Peigneux, J.; Korzhik, M. Structural characterization of  $\text{PbWO}_4$  and related new phase  $\text{Pb}_7\text{W}_8\text{O}_{32-x}$ . *Journal of Alloys and Compounds* **1996**, *238*, 46–48.
- (38) Kaurova, I.; Kuz'micheva, G.; Brykovskiy, A.; Rybakov, V.; Gorobets, Y. N.; Shekhovtsov, A.; Cousson, A. Influence of growth conditions on structural parameters of scheelite  $\text{PbTO}_4$  ( $T = \text{Mo}, \text{W}$ ) crystals. *Materials & Design* **2016**, *97*, 56–63.
- (39) Chipaux, R.; Andre, G.; Cousson, A. Crystal structure of lead tungstate at 1.4 and 300 K. *Journal of Alloys and Compounds* **2001**, *325*, 91–94.
- (40) Saraf, R.; Shivakumara, C.; Behera, S.; Nagabhushana, H.; Dhananjaya, N. Facile synthesis of  $\text{PbWO}_4$ : Applications in photoluminescence and photocatalytic degradation of organic dyes under visible light. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2015**, *136*, 348–355.
- (41) Asha, S.; Hentry, C.; Bindhu, M.; Al-Mohaimed, A. M.; AbdelGawwad, M. R.; Elshikh, M. S. Improved photocatalytic activity for degradation of textile dyeing waste water and thiazine dyes using  $\text{PbWO}_4$  nanoparticles synthesized by co-precipitation method. *Environmental Research* **2021**, *200*, 111721.
- (42) Yu, C.; Cao, F.; Li, X.; Li, G.; Xie, Y.; Jimmy, C. Y.; Shu, Q.; Fan, Q.; Chen, J. Hydrothermal synthesis and characterization of novel  $\text{PbWO}_4$  microspheres with hierarchical nanostructures and enhanced photocatalytic performance in dye degradation. *Chemical Engineering Journal* **2013**, *219*, 86–95.
- (43) Inoue, Y. Photocatalytic water splitting by  $\text{RuO}_2$ -loaded metal oxides and nitrides with  $d^0$ - and  $d^{10}$ -related electronic configurations. *Energy & Environmental Science* **2009**, *2*, 364–386.
- (44) Saura-Múzquiz, M.; Marlton, F. P.; Mullens, B. G.; Manjón-Sanz, A. M.; Neufeind, J. C.; Everett, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Understanding the re-entrant phase transition in a non-magnetic scheelite. *Journal of the American Chemical Society* **2022**, *144*, 15612–15621.

- (45) Saura-Múzquiz, M.; Marlton, F. P.; Mullens, B. G.; Liu, J.; Vogt, T.; Maynard-Casely, H. E.; Avdeev, M.; Blom, D. A.; Kennedy, B. J. Cation and lone pair order–disorder in the polymorphic mixed metal bismuth scheelite  $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$ . *Chemistry of Materials* **2022**, *35*, 123–135.
- (46) Knox, K.; Bozin, E.; Malliakas, C.; Kanatzidis, M.; Billinge, S. Local off-centering symmetry breaking in the high-temperature regime of SnTe. *Physical Review B* **2014**, *89*, 014102.
- (47) Yu, R.; Bozin, E. S.; Abeykoon, M.; Sangiorgio, B.; Spaldin, N. A.; Malliakas, C. D.; Kanatzidis, M. G.; Billinge, S. J. Emphanitic anharmonicity in PbSe at high temperature and anomalous electronic properties in the  $\text{PbQ}$  ( $Q = \text{S}, \text{Se}, \text{Te}$ ) system. *Physical Review B* **2018**, *98*, 144108.
- (48) Hernández-Uresti, D.; Martínez-De La Cruz, A.; Aguilar-Garib, J. Photocatalytic activity of  $\text{PbMoO}_4$  molybdate synthesized by microwave method. *Catalysis Today* **2013**, *212*, 70–74.
- (49) Wallwork, K. S.; Kennedy, B. J.; Wang, D. In *AIP Conference Proceedings*, 2007; Vol. 879, pp 879–882.
- (50) Toby, B. H.; Von Dreele, R. B. GSAS-II: The genesis of a modern open-source all purpose crystallography software package. *Journal of Applied Crystallography* **2013**, *46*, 544–549.
- (51) Liss, K.-D.; Hunter, B.; Hagen, M.; Noakes, T.; Kennedy, S. Echidna — The new high-resolution powder diffractometer being built at OPAL. *Physica B: Condensed Matter* **2006**, *385*, 1010–1012.
- (52) Studer, A. J.; Hagen, M. E.; Noakes, T. J. Wombat: The high-intensity powder diffractometer at the OPAL reactor. *Physica B: Condensed Matter* **2006**, *385*, 1013–1015.
- (53) Coelho, A. A. TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++. *Journal of Applied Crystallography* **2018**, *51*, 210–218.

## BIBLIOGRAPHY

---

- (54) Thompson, P.; Cox, D.; Hastings, J. Rietveld refinement of Debye–Scherrer synchrotron X-ray data from  $\text{Al}_2\text{O}_3$ . *Journal of Applied Crystallography* **1987**, *20*, 79–83.
- (55) Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* **2011**, *44*, 1272–1276.
- (56) Chupas, P. J.; Chapman, K. W.; Kurtz, C.; Hanson, J. C.; Lee, P. L.; Grey, C. P. A versatile sample-environment cell for non-ambient X-ray scattering experiments. *Journal of Applied Crystallography* **2008**, *41*, 822–824.
- (57) Juhás, P.; Davis, T.; Farrow, C. L.; Billinge, S. J. PDFgetX3: A rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions. *Journal of Applied Crystallography* **2013**, *46*, 560–566.
- (58) Yang, X.; Juhas, P.; Farrow, C. L.; Billinge, S. J. xPDFsuite: An end-to-end software solution for high throughput pair distribution function transformation, visualization and analysis. *arXiv preprint arXiv:1402.3163* **2014**.
- (59) Basham, M.; Filik, J.; Wharmby, M. T.; Chang, P. C.; El Kassaby, B.; Gerring, M.; Aishima, J.; Levik, K.; Pulford, B. C.; Sikharulidze, I. Data analysis workbench (DAWN). *Journal of Synchrotron Radiation* **2015**, *22*, 853–858.
- (60) Neuefeind, J.; Feygenson, M.; Carruth, J.; Hoffmann, R.; Chipley, K. K. The nanoscale ordered materials diffractometer NOMAD at the spallation neutron source SNS. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **2012**, *287*, 68–75.
- (61) Farrow, C.; Juhas, P.; Liu, J.; Bryndin, D.; Božin, E.; Bloch, J.; Proffen, T.; Billinge, S. PDFfit2 and PDFgui: Computer programs for studying nanostructure in crystals. *Journal of Physics: Condensed Matter* **2007**, *19*, 335219.
- (62) Kshetri, Y. K.; Chaudhary, B.; Kamiyama, T.; Kim, T.-H.; Rosei, F.; Lee, S. W. Determination of ferroelastic phase transition temperature in  $\text{BiVO}_4$  by Raman spectroscopy. *Materials Letters* **2021**, *291*, 129519.

- (63) Hazen, R.; Mariathasan, J. Bismuth vanadate: A high-pressure, high-temperature crystallographic study of the ferroelastic-paraelastic transition. *Science* **1982**, *216*, 991–993.
- (64) He, X.; Zhang, C.; Tian, D. The structure, vibrational spectra, and thermal expansion study of  $AVO_4$  ( $A = \text{Bi, Fe, Cr}$ ) and  $\text{Co}_2\text{V}_2\text{O}_7$ . *Materials* **2020**, *13*, 1628.
- (65) Mullens, B. G.; Nicholas, M. K.; Marlton, F. P.; Brand, H. E.; Gu, Q.; Maynard-Casely, H. E.; Kennedy, B. J. Long-range  $A$ -site cation disorder in  $\text{NaA}(\text{MO}_4)_2$  ( $M = \text{Mo, W}$ ) double scheelite oxides. *Journal of Solid State Chemistry* **2023**, *321*, 123871.
- (66) Sarin, P.; Hughes, R. W.; Lowry, D. R.; Apostolov, Z. D.; Kriven, W. M. High-temperature properties and ferroelastic phase transitions in rare-earth niobates ( $\text{LnNbO}_4$ ). *Journal of the American Ceramic Society* **2014**, *97*, 3307–3319.
- (67) Arulnesan, S. W.; Kayser, P.; Kimpton, J. A.; Kennedy, B. J. Studies of the fergusonite to scheelite phase transition in  $\text{LnNbO}_4$  orthoniobates. *Journal of Solid State Chemistry* **2019**, *277*, 229–239.
- (68) Saura-Múzquiz, M.; Mullens, B. G.; Maynard-Casely, H. E.; Kennedy, B. J. Neutron diffraction study of the monoclinic–tetragonal phase transition in  $\text{NdNbO}_4$  and  $\text{NdTaO}_4$ . *Dalton Transactions* **2021**, *50*, 11485–11497.
- (69) Stokes, H. T.; Orden, S. v.; Campbell, B. J. ISOSUBGROUP: An internet tool for generating isotropy subgroups of crystallographic space groups. *Journal of Applied Crystallography* **2016**, *49*, 1849–1853.
- (70) Auckett, J. E.; Lopez-Odriozola, L.; Clark, S. J.; Evans, I. R. Exploring the nature of the fergusonite–scheelite phase transition and ionic conductivity enhancement by  $\text{Mo}^{6+}$  doping in  $\text{LaNbO}_4$ . *Journal of Materials Chemistry A* **2021**, *9*, 4091–4102.
- (71) Salje, E. K.; Hayward, S. A.; Lee, W. T. Ferroelastic phase transitions: Structure and microstructure. *Acta Crystallographica Section A: Foundations of Crystallography* **2005**, *61*, 3–18.
- (72) Pinczuk, A.; Burns, G.; Dacol, F. Soft optical phonon in ferroelastic  $\text{BiVO}_4$ . *Solid State Communications* **1977**, *24*, 163–165.



## BIBLIOGRAPHY

---

- (73) Pinczuk, A.; Welber, B.; Dacol, F. Mechanism of the ferroelastic transition of  $\text{BiVO}_4$ . *Solid State Communications* **1979**, *29*, 515–518.
- (74) Gu, B.; Cummins, H.; Qiu, S.; Copic, M. Acoustic soft modes and the ferroelastic phase transition in  $\text{BiVO}_4$  and  $\text{LaNbO}_4$ . *Ferroelectrics* **1983**, *52*, 45–57.
- (75) Guchhait, S.; Ambika, D.; Ding, Q.-P.; Uhlarz, M.; Furukawa, Y.; Tsirlin, A.; Nath, R. Deformed spin-1/2 square lattice in antiferromagnetic  $\text{NaZnVOPO}_4(\text{HPO}_4)$ . *Physical Review B* **2022**, *106*, 024426.
- (76) Carpenter, M. A. Thermodynamics of phase transitions in minerals: A macroscopic approach. *The Stability of Minerals* **1992**, 172–215.
- (77) Carpenter, M. A. Elastic anomalies accompanying phase transitions in  $(\text{Ca},\text{Sr})\text{TiO}_3$  perovskites: Part I. Landau theory and a calibration for  $\text{SrTiO}_3$ . *American Mineralogist* **2007**, *92*, 309–327.
- (78) Salje, E.; Carpenter, M. Linear–quadratic order parameter coupling and multiferroic phase transitions. *Journal of Physics: Condensed Matter* **2011**, *23*, 462202.
- (79) Bierlein, J.; Sleight, A. Ferroelasticity in  $\text{BiVO}_4$ . *Solid State Communications* **1975**, *16*, 69–70.
- (80) David, W.; Wood, I. Ferroelastic phase transition in  $\text{BiVO}_4$ : V. Temperature dependence of  $\text{Bi}^{3+}$  displacement and spontaneous strains. *Journal of Physics C: Solid State Physics* **1983**, *16*, 5127.
- (81) Stubičan, V. High-temperature transitions in rare-earth niobates and tantalates. *Journal of the American Ceramic Society* **1964**, *47*, 55–58.
- (82) Garg, A.; Errandonea, D.; Rodríguez-Hernández, P.; Muñoz, A. High-pressure monoclinic–monoclinic transition in fergusonite-type  $\text{HoNbO}_4$ . *Journal of Physics: Condensed Matter* **2021**, *33*, 195401.
- (83) Zhou, D.; Qu, W.; Randall, C.; Pang, L.; Wang, H.; Wu, X.; Guo, J.; Zhang, G.; Shui, L.; Wang, Q., et al. Ferroelastic phase transition compositional dependence for solid-solution  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  scheelite-structured microwave dielectric ceramics. *Acta Materialia* **2011**, *59*, 1502–1509.

- (84) Lim, A. R.; Choh, S. H.; Jang, M. S. Prominent ferroelastic domain walls in  $\text{BiVO}_4$  crystal. *Journal of Physics: Condensed Matter* **1995**, *7*, 7309.
- (85) Jeong, I.-K.; Heffner, R.; Graf, M.; Billinge, S. Lattice dynamics and correlated atomic motion from the atomic pair distribution function. *Physical Review B* **2003**, *67*, 104301.
- (86) Chay, C.; Avdeev, M.; Brand, H. E.; Injac, S.; Whittle, T. A.; Kennedy, B. J. Crystal structures and phase transition behaviour in the  $5d$  transition metal oxides  $A\text{ReO}_4$  ( $A = \text{Ag}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$  and  $\text{Tl}$ ). *Dalton Transactions* **2019**, *48*, 17524–17532.
- (87) Kennedy, B. J.; Injac, S.; Thorogood, G. J.; Brand, H. E.; Poineau, F. Structures and phase transitions in pertechnetates. *Inorganic Chemistry* **2019**, *58*, 10119–10128.
- (88) Dorenbos, P.; Van Eijk, C. W., *Proceedings of the International Conference on Inorganic Scintillators and their Applications, Delft, The Netherlands, 28 August-September 1, 1995: SCINT 95*; Delft University Press: 1996.
- (89) Adzic, P.; Almeida, N.; Andelin, D.; Anicin, I.; Antunovic, Z.; Arcidiacono, R.; Arenton, M.; Auffray, E.; Argiro, S.; Askew, A. Radiation hardness qualification of  $\text{PbWO}_4$  scintillation crystals for the CMS Electromagnetic Calorimeter. *Journal of Instrumentation* **2010**, *5*, P03010.
- (90) Esaka, T.; Mina-ai, T.; Iwahara, H. Oxide ion conduction in the solid solution based on the scheelite-type oxide  $\text{PbWO}_4$ . *Solid State Ionics* **1992**, *57*, 319–325.
- (91) Takai, S.; Satou, M.; Yoshida, T.; Chikashige, N.; Kita, T.; Esaka, T. Conduction property of  $\text{PbWO}_4$ -and  $\text{PbMoO}_4$ -based oxide ion conductors in lower oxygen partial pressures. *Electrochemistry* **2011**, *79*, 696–700.
- (92) Kamm, G. E.; Huang, G.; Vornholt, S. M.; McAuliffe, R. D.; Veith, G. M.; Thornton, K. S.; Chapman, K. W. Relative kinetics of solid-state reactions: The role of architecture in controlling reactivity. *Journal of the American Chemical Society* **2022**, *144*, 11975–11979.
- (93) Vogt, T.; Woodward, P. M.; Hunter, B. A. The high-temperature phases of  $\text{WO}_3$ . *Journal of Solid State Chemistry* **1999**, *144*, 209–215.

## BIBLIOGRAPHY

---

- (94) Wang, H.; Chen, H.-H.; Borrmann, H.; Zhang, Z.-J.; Zhao, J.-T. Crystal growth and characterization of new-type lead tungstate single crystal. *Journal of Alloys and Compounds* **2012**, *545*, 135–138.
- (95) Lock, N.; Christensen, M.; Jensen, K. M.; Iversen, B. B. Rapid one-step low-temperature synthesis of nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. *Angewandte Chemie* **2011**, *123*, 7183–7185.
- (96) Chen, J.; Bai, J.; Chen, H.; Graetz, J. *In situ* hydrothermal synthesis of LiFePO<sub>4</sub> studied by synchrotron X-ray diffraction. *The Journal of Physical Chemistry Letters* **2011**, *2*, 1874–1878.
- (97) Sarin, P.; Yoon, W.; Jurkschat, K.; Zschack, P.; Kriven, W. Quadrupole lamp furnace for high temperature (up to 2050 K) synchrotron powder X-ray diffraction studies in air in reflection geometry. *Review of Scientific Instruments* **2006**, *77*.
- (98) Keqin, X.; Jiyue, X.; Yang, D.; Guanglie, L. Discovery of stolzite in China and refinement of its crystal structure. *Acta Geologica Sinica - English Edition* **1995**, *8*, 111–117.
- (99) Takai, S.; Touda, S.; Oikawa, K.; Mori, K.; Torii, S.; Kamiyama, T.; Esaka, T. Powder neutron diffraction study of *Ln*-substituted PbWO<sub>4</sub> oxide ion conductors. *Solid State Ionics* **2002**, *148*, 123–133.
- (100) Brese, N.; O’Keeffe, M. Bond-valence parameters for solids. *Acta Crystallographica Section B: Structural Science* **1991**, *47*, 192–197.
- (101) Mullens, B. G.; Saura-Múzquiz, M.; Marlton, F. P.; Avdeev, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Beyond the ionic radii: A multifaceted approach to understand differences between the structures of *Ln*NbO<sub>4</sub> and *Ln*TaO<sub>4</sub> fergusonites. *Journal of Alloys and Compounds* **2023**, *930*, 167399.
- (102) Rabuffetti, F. A.; Culver, S. P.; Suescun, L.; Brutchey, R. L. Structural disorder in AMoO<sub>4</sub> (*A* = Ca, Sr, Ba) scheelite nanocrystals. *Inorganic Chemistry* **2014**, *53*, 1056–1061.
- (103) Culver, S. P.; Brutchey, R. L. Thermally activated rotational disorder in CaMoO<sub>4</sub> nanocrystals. *CrystEngComm* **2016**, *18*, 4485–4488.

- (104) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **1976**, *32*, 751–767.
- (105) Amarasinghe, D. K.; Perera, S. S.; Rabuffetti, F. A. Rotational disorder in scheelite-type  $\text{NaRE}(\text{MO}_4)_2$  ( $\text{RE}$  = Rare-Earth, Y;  $M$  = Mo, W). *Crystal Growth & Design* **2020**, *20*, 3442–3448.
- (106) Mullens, B. G.; Avdeev, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Insights into the structural variations in  $\text{Sm}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  and  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  combined experimental and computational studies. *Dalton Transactions* **2021**, *50*, 9103–9117.
- (107) Zhuk, N.; Krzhizhanovskaya, M.; Belyy, V.; Sekushin, N.; Chichineva, A. The bismuth orthotantalate with high anisotropic thermal expansion. *Scripta Materialia* **2019**, *173*, 6–10.
- (108) Lufaso, M. W.; Woodward, P. M. Jahn-Teller distortions, cation ordering and octahedral tilting in perovskites. *Acta Crystallographica Section B: Structural Science* **2004**, *60*, 10–20.
- (109) Kumar, A.; Jain, A.; Yusuf, S.; Dhaka, R. Observation of anisotropic thermal expansion and the Jahn-Teller effect in double perovskites  $\text{Sr}_{2-x}\text{La}_x\text{CoNbO}_6$  using neutron diffraction. *The Journal of Physical Chemistry Letters* **2022**, *13*, 3023–3031.
- (110) Bersuker, I. B. Pseudo Jahn-Teller origin of perovskite multiferroics, magnetic-ferroelectric crossover, and magnetoelectric effects: The  $d^0 - d^{10}$  problem. *Physical Review Letters* **2012**, *108*, 137202.
- (111) Mooney, R. C. Crystal structure of tetragonal bismuth arsenate,  $\text{BiAsO}_4$ . *Acta Crystallographica* **1948**, *1*, 163–165.
- (112) Liu, T.; Zhang, X.; Guan, J.; Catlow, C. R. A.; Walsh, A.; Sokol, A. A.; Buckeridge, J. Insight into the Fergusonite–Scheelite phase transition of  $\text{ABO}_4$ -type oxides by density functional theory: A case study of the subtleties of the ground state of  $\text{BiVO}_4$ . *Chemistry of Materials* **2022**, *34*, 5334–5343.

- (113) Kudo, A.; Omori, K.; Kato, H. A novel aqueous process for preparation of crystal form-controlled and highly crystalline  $\text{BiVO}_4$  powder from layered vanadates at room temperature and its photocatalytic and photophysical properties. *Journal of the American Chemical Society* **1999**, *121*, 11459–11467.
- (114) Payne, D.; Robinson, M.; Egdell, R.; Walsh, A.; McNulty, J.; Smith, K.; Piper, L. The nature of electron lone pairs in  $\text{BiVO}_4$ . *Applied Physics Letters* **2011**, *98*, 212110.
- (115) Payne, D.; Egdell, R.; Walsh, A.; Watson, G.; Guo, J.; Glans, P.-A.; Learmonth, T.; Smith, K. Electronic origins of structural distortions in post-transition metal oxides: Experimental and theoretical evidence for a revision of the lone pair model. *Physical Review Letters* **2006**, *96*, 157403.
- (116) Liu, F.-J.; Luo, W.-L.; Zhang, Z.; Yu, J.; Cai, J.-X.; Yang, Z.-Y. Cation-doped  $\text{V}_2\text{O}_5$  microsphere as a bidirectional catalyst to activate sulfur redox reactions for lithium-sulfur batteries. *Chemical Engineering Journal* **2023**, *456*, 140948.
- (117) Yamauchi, T.; Ueda, Y.; Môri, N. Pressure-induced superconductivity in  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  beyond charge ordering. *Physical Review Letters* **2002**, *89*, 057002.
- (118) Opletal, G.; Petersen, T.; O'Malley, B.; Snook, I.; McCulloch, D. G.; Marks, N. A.; Yarovsky, I. Hybrid approach for generating realistic amorphous carbon structure using metropolis and reverse Monte Carlo. *Molecular Simulation* **2002**, *28*, 927–938.
- (119) Nicholas, T. C.; Stones, A. E.; Patel, A.; Michel, F. M.; Reeder, R. J.; Aarts, D. G.; Deringer, V. L.; Goodwin, A. L. Geometrically-frustrated interactions drive structural complexity in amorphous calcium carbonate. *arXiv preprint arXiv:2303.06178* **2023**.
- (120) Luévano-Hipólito, E.; Martinez-De la Cruz, A. Photooxidation of  $\text{NO}_x$  using scheelite-type  $\text{ABO}_4$  ( $A = \text{Ca}, \text{Pb}$ ;  $B = \text{W}, \text{Mo}$ ) phases as catalysts. *Advanced Powder Technology* **2017**, *28*, 1511–1518.



---

**Part III:**  
**Additional Studies of Functional**  
**Energy Materials**

---





# Chapter 6

## Safe Storage of Radioactive Waste

*This chapter is adapted from the following manuscripts:*

- Marlton, F.P.; Mullens, B.G.; Chater, P.A.; Kennedy, B.J.; Tetrahedral Displacive Disorder in the Scheelite-Type Oxide RbReO<sub>4</sub>. *Inorganic Chemistry*, **2022**, 61 (38), 15130-15137.<sup>1</sup>
- Saura-Múzquiz, M; Marlton, F.P.; Mullens, B.G.; Manjón-Sanz, A.M.; Neufeind, J.C.; Everett, M.; Brand, H.E.A.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B.J.; Understanding the Re-Entrant Phase Transition in a Non-Magnetic Scheelite. *Journal of the American Chemical Society*, **2022**, 144 (34), 15612-15621.<sup>2</sup>



## 6.1 Introduction: Matrices for Radioactive Waste

The increasing concern of carbon emissions, in the context of climate change, has caused a global shift in the world's reliance on carbon-based fuels. This has led to a renewed interest in nuclear power, which provided almost half of the United States carbon-neutral energy in 2022.<sup>3</sup> The safe storage of the fission products from spent nuclear fuel remains a major challenge and impediment to the continued use of nuclear power. One of the most challenging fission products in this context is technetium, that has a mass yield of  $\sim 6\%$  in fission reactions. Technetium-99m ( $^{99\text{m}}\text{Tc}$ ) is currently used as a medical radioisotope for selective imaging diagnosis due to its relative short half life, accounting for over half of all nuclear medicine procedures. However its decay product,  $^{99}\text{Tc}$  (upon decaying from  $^{99\text{m}}\text{Tc}$  *via* isomeric transition), presents an environmental challenge due to its high mobility, high  $\beta^-$  emission, and half life of around 211 000 years.<sup>4</sup>

In developing technologies for the safe storage of Tc-containing waste, it is necessary to consider the chemistry of the commonly encountered oxidation states; namely  $\text{Tc}^{4+}$  and  $\text{Tc}^{7+}$ . The  $\text{Tc}^{4+}$  oxidation state is only soluble in acidic conditions (below pH  $\sim 3$ ), meaning it often precipitates out as solid  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  under environmental conditions.<sup>5,6</sup> However,  $\text{Tc}^{7+}$  forms a water soluble and highly stable pertechnetate anion  $\text{TcO}_4^-$  that is much more mobile.<sup>7</sup> The presence of Tc can lead to corrosion of the Fe- and Zr-based steel containers commonly used for storing radioactive waste.<sup>8,9</sup> As a consequence, different materials have been investigated to store Tc-containing waste and prevent it from leaching into the environment. These storage mechanisms include metal oxides,<sup>10</sup> glasses,<sup>11,12</sup> and MOFs.<sup>13</sup>

Since Tc has no stable isotopes, it is common for Tc studies to use Re as a nonradioactive surrogate.<sup>14–17</sup> This is due to the predicted similarities in the chemical behaviour of  $\text{Tc}^{7+}$  and  $\text{Re}^{7+}$  attributed to their identical oxidation state and similar IR ( $\text{Tc}^{7+} = 0.37$  *vs.*  $\text{Re}^{7+} = 0.38$  Å in tetrahedra geometry).<sup>18</sup> There is, however, a growing body of literature showing  $\text{Tc}^{7+}$  and  $\text{Re}^{7+}$  do not always act similarly. For example, Lukens *et al.* reported that  $\text{Tc}^{7+}$  is significantly more volatile than  $\text{Re}^{7+}$ , leading to a decreased amount stabilised in waste glasses.<sup>19</sup> Gan *et al.* also described the different behaviour of Tc and Re under various redox conditions,<sup>20</sup> as seen in the lower standard

reduction potential of  $\text{Re}^{7+}$  ( $\text{ReO}_4^-/\text{ReO}_2 = 0.510 \text{ V}$ ) compared to  $\text{Tc}^{7+}$  ( $\text{TcO}_4^-/\text{TcO}_2 = 0.738 \text{ V}$ ).<sup>21</sup> These differences have been reflected in the perovskite-type oxides, where  $\text{CaTcO}_3$  and  $\text{SrTcO}_3$  show interesting magnetic properties, whereas the rhenium analogues remain unknown.<sup>22–24</sup> This suggests the differences in the electronic structures between the two cations are important, and leads to differences in stability, electronic properties, and magnetic properties. Re has more radially-extended  $5d$  valence orbitals than the  $4d$  valence orbitals in Tc, potentially impacting its reactivity and redox stability.<sup>21</sup> Subtle differences between  $4d$  and  $5d$  metal oxides were also described in Chapter 3 of this dissertation, where the more radially-extended  $5d$  orbitals of  $\text{Ta}^{5+}$  led to more covalent character in the  $\text{Ta-O}_l$  bonds compared to  $\text{Nb-O}_l$ .<sup>25–27</sup>

### 6.1.1 Similarities and Differences Between $\text{ATcO}_4$ and $\text{AReO}_4$

Pertechnetate salts of the type  $\text{ATcO}_4$  ( $A^+ = \text{NH}_4, \text{K}, \text{Cs}, \text{Ag}$ ) were among the first Tc oxides isolated and studied. A variety of powder diffraction and single crystal studies have reported the structures and phase transitions in  $\text{ATcO}_4$  and  $\text{AReO}_4$  salts.<sup>28–33</sup> Recent synchrotron X-ray diffraction studies of some  $\text{ATcO}_4$  and  $\text{AReO}_4$  oxides by Chay *et al.* and Kennedy *et al.* showed that most are isostructural at room temperature.<sup>34,35</sup> The structures of the four salts ( $A^+ = \text{Na}, \text{K}, \text{Rb}, \text{Ag}$ ) were refined to the tetragonal  $I4_1/a$  scheelite-type structure. The symmetry of these  $\text{ATcO}_4$  and  $\text{AReO}_4$  structures can be rationalised from the ratios of  $r_A/r_O$  and  $r_B/r_O$ , as previously seen in the Errandonea *et al.* phase diagram (Figure 1.3).<sup>36,37</sup> Changes in these ratios are reflected in changes of the symmetry of the structure, such that  $\text{RbTcO}_4$  and  $\text{RbReO}_4$  ( $r_A/r_O \sim 1.13$ ) exhibit the  $I4_1/a$  tetragonal scheelite structure, whereas  $\text{CsTcO}_4$  and  $\text{CsReO}_4$  ( $r_A/r_O \sim 1.23$ ) exhibit the  $Pnma$  orthorhombic pseudo-scheelite structure at room temperature.<sup>18,34,38</sup>

Previous studies have identified differences between  $\text{ATcO}_4$  and  $\text{AReO}_4$  salts. Reynolds *et al.* highlighted differences in the thermal behaviour between  $\text{NH}_4\text{TcO}_4$  and  $\text{NH}_4\text{ReO}_4$  attributed to subtle differences between the  $\text{Tc-O}$  and  $\text{Re-O}$  bonds within their respective  $\text{TcO}_4$  and  $\text{ReO}_4$  tetrahedra.<sup>21</sup> More dramatic differences are evident between the two thallium salts  $\text{TlTcO}_4$  and  $\text{TlReO}_4$ . The former adopts the orthorhombic

$Pnma$  pseudo-scheelite structure at room temperature, whereas  $\text{TlReO}_4$  exhibits a monoclinic  $P2_1/c$  structure.<sup>34,35,39</sup> The temperature dependence of the two structures are also different.  $\text{TlTcO}_4$  undergoes a  $Pnma \rightarrow I4_1/amd$  phase transition at 500 K,<sup>38</sup> whereas  $\text{TlReO}_4$  displays an unusual re-entrant  $I4_1/a \rightarrow P2_1/c \rightarrow I4_1/a$  phase transition behaviour upon heating.<sup>40,41</sup> A neutron total scattering study by Saura-Múzquiz *et al.* revealed that the local structure of  $\text{TlReO}_4$  was always best fitted to the  $P2_1/c$  space group, with a change in the correlation length of the  $\text{Tl}^+ 6s^2$  lone pairs used to explain its re-entrant phase transition.<sup>2</sup> This behaviour appears to be unique to  $\text{TlReO}_4$ , and has not been reported in the closely-related oxide  $\text{TlTcO}_4$ , despite sharing similar  $r_{A/O}$  and  $r_{B/O}$  ratios, as well as the presence of the  $\text{Tl}^+ 6s^2$  lone pair.<sup>36,42</sup>

There have also been various studies on scheelite-structured compounds suggesting the presence of local-scale disorder.<sup>43–46</sup> In particular, variable temperature X-ray total scattering of  $\text{AMoO}_4$  ( $A^{2+} = \text{Ca}, \text{Sr}, \text{Ba}$ ) indicated the presence of rotational disorder of the  $\text{MoO}_4$  tetrahedra in the  $I4_1/a$  structure.<sup>44,45</sup> This was influenced by both the IR of the  $A$ -site cation and temperature. A different type of local disordering was observed in the X-ray total scattering study of  $\text{RbReO}_4$ , where it was identified from the Bragg diffraction data that the  $I4_1/a \rightarrow I4_1/amd$  phase transition at  $\sim 620$  K proceeded *via* rotation of the  $\text{ReO}_4$  tetrahedra about the  $c$ -axis of the unit cell. However, these Rietveld refinements indicated a significant and nonphysical shortening of the  $\text{Re-O}$  distances upon heating. Analysing the local structure showed that this was not the case, with a consistent  $\text{Re-O}$  bond distance in line with the rigid  $\text{ReO}_4$  tetrahedra. However, the rare  $I4_1/a \rightarrow I4_1/amd$  phase transition was found to proceed by a change from static to dynamic disorder on the local scale.

This chapter takes an in-depth look at two members of the  $\text{ABO}_4$  structure class that both exhibit the orthorhombic  $Pnma$  pseudo-scheelite structure at room temperature:  $\text{CsReO}_4$  and  $\text{TlTcO}_4$ . Firstly, an X-ray total scattering study on  $\text{CsReO}_4$  is performed analogous to  $\text{RbReO}_4$ , which identified dynamic disorder on the local scale preceding the  $I4_1/a \rightarrow I4_1/amd$  phase transition. A combination of Bragg diffraction and XPDF analysis will be used to determine whether a similar phenomenon occurs in the  $Pnma \rightarrow I4_1/a$  phase transition. Secondly, a neutron total scattering study is performed

on  $\text{TlTcO}_4$ , with the nature of the  $Pnma \rightarrow I4_1/amd$  phase transition examined, with a comparison to  $\text{TlReO}_4$ .

## 6.2 Synthesis Procedure and Experimental Methods

### 6.2.1 Sample Synthesis

*Caution! Thallium salts are potentially fatal if swallowed. Appropriate personal protective equipment and safe work procedures were employed during sample preparation and sample manipulation.*

*Caution! Technetium-99 is a  $\beta^-$  emitter ( $E_{max} = 0.29$  MeV). All operations relating to the synthesis of  $\text{TlTcO}_4$  were performed by Associate Professor Frederic Poineau in a licensed radiochemical laboratory at the University of Las Vegas, Nevada, USA. Appropriate shielding was employed during all manipulations and while loading the sample into a vanadium can for analysis.*

The synthesis of  $\text{CsReO}_4$  is outlined in previous work.<sup>2,34</sup> A polycrystalline sample  $\text{CsReO}_4$  was prepared using a coprecipitation method by reacting perrhenic acid with caesium carbonate. A 0.2 M solution of rhenium metal (Aithaca Chemicals, 99.99%) in fresh 30%  $\text{H}_2\text{O}_2$  was prepared and left stirring overnight to form perrhenic acid. An aqueous solution of  $\text{Cs}_2\text{CO}_3$  (Sigma-Aldrich, 99.0%) was prepared by dissolving the compound in deionised water. The carbonate solution was poured into the corresponding amount of  $\text{HReO}_4$  solution, which led to the formation of a white precipitate. The supernatant was discarded, and the precipitate was dried overnight in an oven at 120 °C. The powders were then annealed in a muffle furnace at 550 °C for 72 hours. Each material was then finely ground into a powder for further analysis.

The synthesis of  $\text{TlTcO}_4$  is outlined in previous work.<sup>38</sup> A polycrystalline sample of  $\text{TlTcO}_4$  was used as prepared by Associate Professor Frederic Poineau.

### 6.2.2 X-Ray and Neutron Total Scattering

X-ray total scattering experiments were performed at beamline I15-1 of the Diamond Light Source, UK ( $\lambda = 0.161669$  Å, 76.69 keV). A small amount of the finely ground sample was loaded into a borosilicate capillary (inner diameter of 0.78 mm) to a height of 3.5 cm. Data were collected under ambient conditions for the sample, an empty capillary, and the empty instrument. The temperature was controlled using a cryostream for data measured in the range 100–500 K, and a hot air blower for 400–800 K. Both temperature devices were calibrated using an external standard prior to data collection. Diffraction data was collected using two 2D area detectors at different distances relative to the sample for Rietveld refinement (860 mm from the sample) and PDF analysis (200 mm from the sample). A detector malfunction resulted in Bragg diffraction data not being collected at 580 K. 2D diffraction data was corrected for the polarisation, detector transmission, and flat field, and badly performing pixels were masked prior to integration to 1D using DAWN.<sup>47</sup> The PDFs  $G(r)$  were calculated using PDFgetX3 software from the xPDFsuite with a  $Q_{max}$  of  $25 \text{ Å}^{-1}$ .<sup>48,49</sup>

Neutron scattering data for  $\text{TiTeO}_4$  were collected at 50, 300, 450, and 600 K using the POWGEN diffractometer at the SNS located at ORNL.<sup>50</sup> The sample was loaded into a 6 mm vanadium can. Diffraction data suitable for PDF analysis were collected with a centre wavelength of 0.8 Å. For the NPDF calculation, the neutron scattering data were corrected for instrument background, the incident neutron spectrum, absorption, and multiple scattering events before normalisation. The software PDFgetN3 was used to calculate the NPDF from the POWGEN data with a  $Q_{max}$  of  $30.0 \text{ Å}^{-1}$ .<sup>51</sup> A Savitzky-Golay filter was applied to the  $S(Q)$  for  $Q > 9.0 \text{ Å}^{-1}$  to reduce the noise in the broad regions of the reciprocal space data.

Structural refinements using the Rietveld refinement method were carried out against both the diffraction and PDF data using the software TOPAS6.<sup>52</sup> For the X-ray and neutron diffraction data, the background of each pattern was estimated using a 12<sup>th</sup>- and 6<sup>th</sup>-order Chebyshev polynomial respectively. Additionally, a broad Gaussian peak at  $Q \sim 1.5 \text{ Å}^{-1}$  was included in the Bragg Rietveld refinements to account for the borosilicate

capillary. The scale factor, lattice parameters, atomic coordinates, and ADPs were refined simultaneously with the peak profile parameters. Structural illustrations were drawn using the program VESTA.<sup>53</sup> For the PDF data, the  $R$  parameter referenced in the fits is defined as

$$R = \sqrt{\frac{\sum [G(r)_{obs.} - G(r)_{calc.}]^2}{\sum [G(r)_{obs.}]^2}} \times 100\% \quad (6.1)$$

where  $G(r)_{obs.}$  and  $G(r)_{calc.}$  are the observed and calculated data respectively.

## 6.3 Structural Studies of CsReO<sub>4</sub>

A polycrystalline sample of CsReO<sub>4</sub> was synthesised successfully. X-ray Bragg diffraction data indicate that CsReO<sub>4</sub> undergoes a phase transition from orthorhombic  $Pnma$  to tetragonal  $I4_1/a$  at  $\sim 450$  K (Figure A.20). Despite this change in long-range average structure, little change was observed in the short-range local structure. It is concluded that CsReO<sub>4</sub> also possesses the same dynamic disorder as RbReO<sub>4</sub>, which preceded the melting of the sample.

### 6.3.1 Long-Range Average Structure X-Ray Diffraction Studies

Rietveld refinements were conducted against the synchrotron X-ray Bragg diffraction data of CsReO<sub>4</sub> across the entire temperature range, and showed good agreement with previous studies.<sup>34,39</sup> Representative refinements are depicted in Figure 6.1. The high-quality fits confirm the average structure previously reported, as well as the phase purity of the sample. At 100 K, the CsReO<sub>4</sub> structure was well fitted to the orthorhombic  $Pnma$  pseudo-scheelite structure. The Cs<sup>+</sup> cations are eight-coordinate, with Cs–O bond lengths ranging from 2.992(15)–3.253(5) Å. The Re<sup>7+</sup> cations are bound to four oxygen atoms (three of which are at unique Wyckoff positions), leading to the formation of distorted ReO<sub>4</sub> tetrahedra [Re–O(1) = 1.738(12), Re–O(2) = 1.736(13), Re–O(3) = 1.749(9) Å] and an average Re–O bond length of 1.742(12) Å.



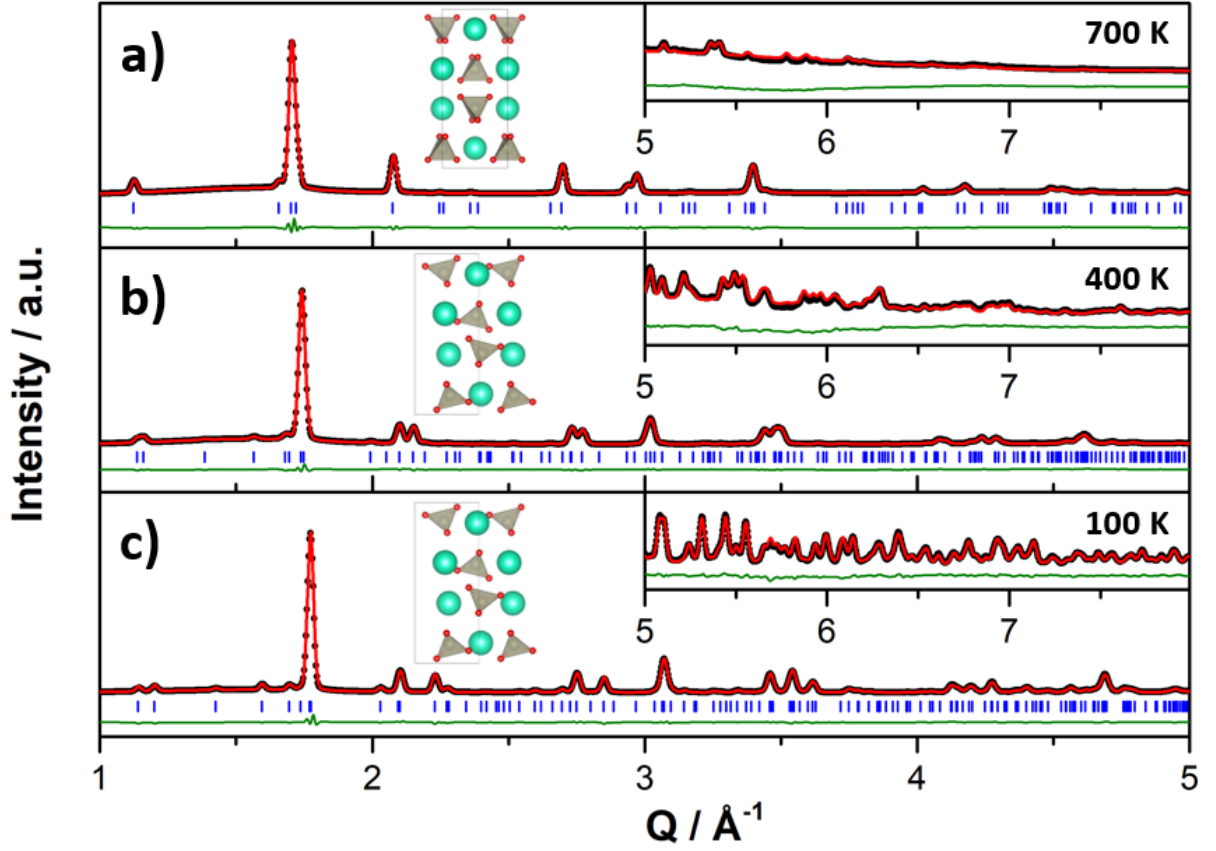


Figure 6.1: Rietveld refinements to the X-ray Bragg data of CsReO<sub>4</sub> at (a) 700 K to the tetragonal  $I4_1/a$  space group, (b) 400 K to the orthorhombic  $Pnma$  space group, and (c) 100 K to the orthorhombic  $Pnma$  space group. The insets show the high quality fit to the data at high  $Q$ . The black circles represent the data, the red line represents the fit to the data, the green line represents the difference between the data and the fit, and the blue dashes represent the space group-allowed reflections.

Heating CsReO<sub>4</sub> from 100 K results in a reduction of the orthorhombic distortion of the unit cell, as evidenced in Figure 6.2. A phase transition is observed at  $\sim 450$  K, where the  $a$  and  $b$  lattice parameters become equal, indicating an increase in symmetry. The unit cell volume increases linearly across the temperature range, with a change in the rate of expansion across the phase transition.

The  $Pnma \rightarrow I4_1/a$  phase transition observed in CsReO<sub>4</sub> has been studied previously.<sup>33,34,54</sup> Early reports by Kanellakopoulos *et al.* identified a reversible phase transition occurring between 400–460 K to a proposed  $I4_1/a$  structure. Range *et al.* concluded, based on the observation of transition enthalpy using differential scanning calorimetry (DSC), that the phase transition must be first order.<sup>54</sup> However, they identified the high-temperature structure to be the true scheelite aristotype  $I4_1/amd$  using infrared spectroscopy. This was based on the absence of a vibrational band at

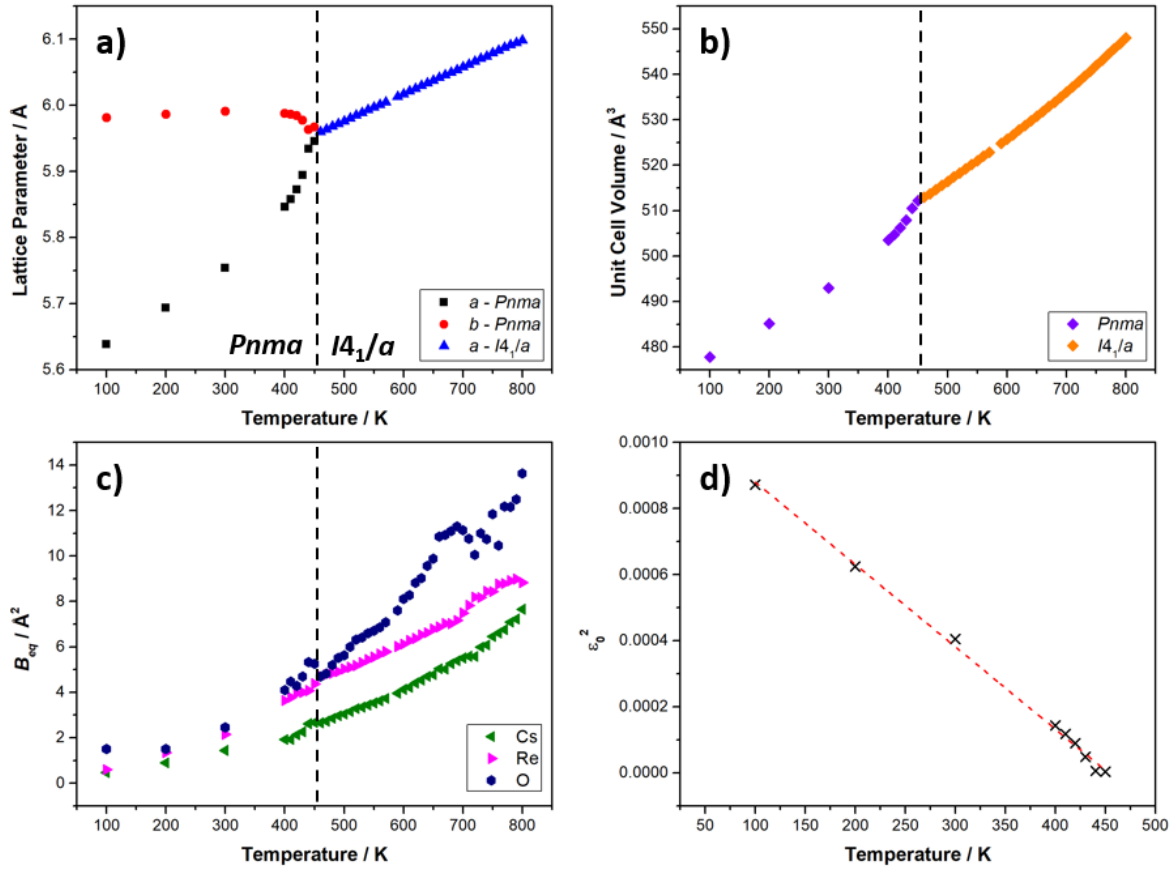


Figure 6.2: Rietveld refinements for the variable temperature data of CsReO<sub>4</sub>, with (a) the *a* and *b* lattice parameters, (b) the unit cell volume, (c) the atomic displacement parameters measured as *B*<sub>eq</sub>, and (d) the relationship between the square of the strain in the orthorhombic *Pnma* phase and the temperature. the black dashed line represents the temperature of the *Pnma* → *I*4<sub>1</sub>/*a* phase transition, and the red dashed line represents a linear fit.

$\nu \sim 300 \text{ cm}^{-1}$  which is forbidden in *I*4<sub>1</sub>/*amd* but allowed in *I*4<sub>1</sub>/*a*.<sup>54</sup> A more recent study by Chay *et al.*, using high resolution SXRD, identified a two-phase region between 425–500 K, which was determined to be a mix of orthorhombic *Pnma* and tetragonal *I*4<sub>1</sub>/*a*. The identification of the *I*4<sub>1</sub>/*a* structure was based on the small amount of intensity at the (114) reflection position, which is forbidden in *I*4<sub>1</sub>/*amd* by the  $2h+l = 4n$  reflection condition, but allowed in *I*4<sub>1</sub>/*a*.<sup>34</sup>

The tetragonal *I*4<sub>1</sub>/*amd* structure is considered the true scheelite aristotype structure, and has been observed upon heating in related materials, such as RbTcO<sub>4</sub>,<sup>38</sup> RbReO<sub>4</sub>,<sup>1,34</sup> RbOsO<sub>4</sub>,<sup>55</sup> and TiTcO<sub>4</sub>.<sup>38</sup> The orthorhombic *Pnma* and tetragonal *I*4<sub>1</sub>/*a* structures may be derived from the scheelite aristotype *I*4<sub>1</sub>/*amd* structure by well-defined rotations of the BO<sub>4</sub> tetrahedra. In the case of CsReO<sub>4</sub>, the orthorhombic *Pnma* structure differs from

Table 6.1: Selected Rietveld refinement structural parameters and bond distances for CsReO<sub>4</sub> using synchrotron X-ray diffraction data.

| Temperature (K)                                | 100         | 400         | 700                     |
|------------------------------------------------|-------------|-------------|-------------------------|
| Space Group                                    | <i>Pnma</i> | <i>Pnma</i> | <i>I4<sub>1</sub>/a</i> |
| <i>a</i> (Å)                                   | 5.63825(12) | 5.8469(2)   | 6.06256(15)             |
| <i>b</i> (Å)                                   | 5.98153(11) | 5.9888(3)   | = <i>a</i>              |
| <i>c</i> (Å)                                   | 14.1696(3)  | 14.3866(5)  | 14.6177(6)              |
| Vol. (Å <sup>3</sup> )                         | 477.873(16) | 503.77(3)   | 537.27(3)               |
| Cs <i>x</i>                                    | 0.0294(2)   | 0.0194(6)   | = 0                     |
| Cs <i>z</i>                                    | 0.12667(15) | 0.1269(4)   | = 5/8                   |
| Re <i>x</i>                                    | 0.0477(2)   | 0.0305(5)   | = 0                     |
| Re <i>z</i>                                    | 0.38113(9)  | 0.3788(3)   | = 1/8                   |
| O(1) <i>x</i>                                  | 0.8443(19)  | 0.799(4)    | 0.031(4)                |
| O(1) <i>y</i>                                  | = 1/4       | = 1/4       | 0.4718(14)              |
| O(1) <i>z</i>                                  | 0.0817(8)   | 0.0722(17)  | 0.1951(9)               |
| O(2) <i>x</i>                                  | 0.8533(16)  | 0.805(4)    | –                       |
| O(2) <i>y</i>                                  | = 1/4       | = 1/4       | –                       |
| O(2) <i>z</i>                                  | 0.4777(8)   | 0.4591(15)  | –                       |
| O(3) <i>x</i>                                  | 0.0066(13)  | -0.007(3)   | –                       |
| O(3) <i>y</i>                                  | 0.5082(11)  | 0.513(2)    | –                       |
| O(3) <i>z</i>                                  | 0.6859(6)   | 0.6907(10)  | –                       |
| <i>B</i> <sub>eq.</sub> (Cs) (Å <sup>2</sup> ) | 0.32(4)     | 1.89(11)    | 6.12(12)                |
| <i>B</i> <sub>eq.</sub> (Re) (Å <sup>2</sup> ) | 0.70(3)     | 3.57(10)    | 7.14(9)                 |
| <i>B</i> <sub>eq.</sub> (O) (Å <sup>2</sup> )  | 0.71(15)    | 4.1(4)      | 12.4(6)                 |
| Re–O(1) (Å)                                    | 1.753(11)   | 1.72(3)     | 1.701(11)               |
| Re–O(2) (Å)                                    | 1.753(11)   | 1.75(3)     | –                       |
| Re–O(3) (Å)                                    | 1.757(8)    | 1.742(14)   | –                       |
| <i>R</i> <sub>wp</sub> (%)                     | 2.52        | 2.23        | 2.53                    |

the tetragonal *I4<sub>1</sub>/amd* structure by rotations of the ReO<sub>4</sub> tetrahedra around the *b*-axis, as described by the *irrep* M<sub>4</sub><sup>+</sup>. The *I4<sub>1</sub>/a* structure differs from the *I4<sub>1</sub>/amd* structure by rotation of the ReO<sub>4</sub> tetrahedra around the *c*-axis, as described by the *irrep* Γ<sub>3</sub><sup>+</sup>.<sup>34</sup> However, it is not possible for the *Pnma* → *I4<sub>1</sub>/a* phase transition to be continuous as the *Pnma* space group operators cannot be mapped onto the operators of the parent *I4<sub>1</sub>/a* space group.<sup>56</sup> As the ReO<sub>4</sub> tetrahedra rotations are governed by different *irreps*, *Pnma* → *I4<sub>1</sub>/a* must be therefore be a first order phase transition. This representational analysis, as well as the DSC result reported by Range *et al.*,<sup>54</sup> indicate that the high temperature phase of CsReO<sub>4</sub> is most likely to be *I4<sub>1</sub>/a*.

An analysis similar to that described by Chay *et al.* was attempted with the current X-ray Bragg diffraction data. Firstly, the possibility of a two-phase region was investigated by analysing the data in the region of 400–550 K to single phase models for both the orthorhombic  $Pnma$  and tetragonal  $I4_1/a$  structures separately. The resulting  $R_{wp}$  was plotted, and is displayed in Figure 6.3a. Between 400–420 K, the patterns are well fitted to the orthorhombic  $Pnma$  structure. However, between 430–450 K a significant increase in the  $R_{wp}$  values for the  $Pnma$  structure is observed, along with a sudden decrease in the  $R_{wp}$  associated with the  $I4_1/a$  structure. This is similarly seen in the Rietveld refinements, with an increase in the ADPs observed in this temperature region (Figure 6.2c). A two-phase model comprising of both the orthorhombic  $Pnma$  and tetragonal  $I4_1/a$  structures was tested across the potential two-phase region. However, this did not substantially improve the fit, with the secondary phase contributing <4% of the phase fraction. The combination of high energy X-rays and lower peak-shape resolution at the I15-1 beamline at Diamond Light Source made it difficult to distinguish this two-phase region due to the closely-spaced reflections.

The exact structure of the high-temperature tetragonal phase was also investigated. Previously, Chay *et al.* identified the (114) reflection at 500 K using SXRD, which is allowed in  $I4_1/a$  but forbidden in  $I4_1/amd$ .<sup>34</sup> However, it was highlighted that this reflection was only about 0.08% the intensity of the strongest (112) reflection, being close to the sensitivity limit of the measurements. The weakness of this reflection is a result of the relative lack of scattering from the oxygen atoms in the presence of highly X-ray attenuating elements such as  $\text{Cs}^+$  and  $\text{Re}^{7+}$  ( $Z_{\text{Cs}^+} = 54$ ,  $Z_{\text{Re}^{7+}} = 68$ ,  $Z_{\text{O}^{2-}} = 10$ ). Attempts were made to observe this in the current dataset, given the higher intensity of the I15-1 beamline and the use of a 2D area detector. However, the low peak-shape resolution caused the (114) reflection to overlap with the stronger (220) reflection. This is unlike determining the  $I4_1/a \rightarrow I4_1/amd$  phase transition in  $\text{RbTcO}_4$  and  $\text{RbReO}_4$ , where the (114) reflection was adequately resolved and was able to be tracked across the entire temperature range.<sup>1,34,38</sup>

Inspection of the unit cell volume and ADPs across the 100–800 K temperature range (Figure 6.2b,c) indicated some anomalies in the data. Namely, a slight change in the rate

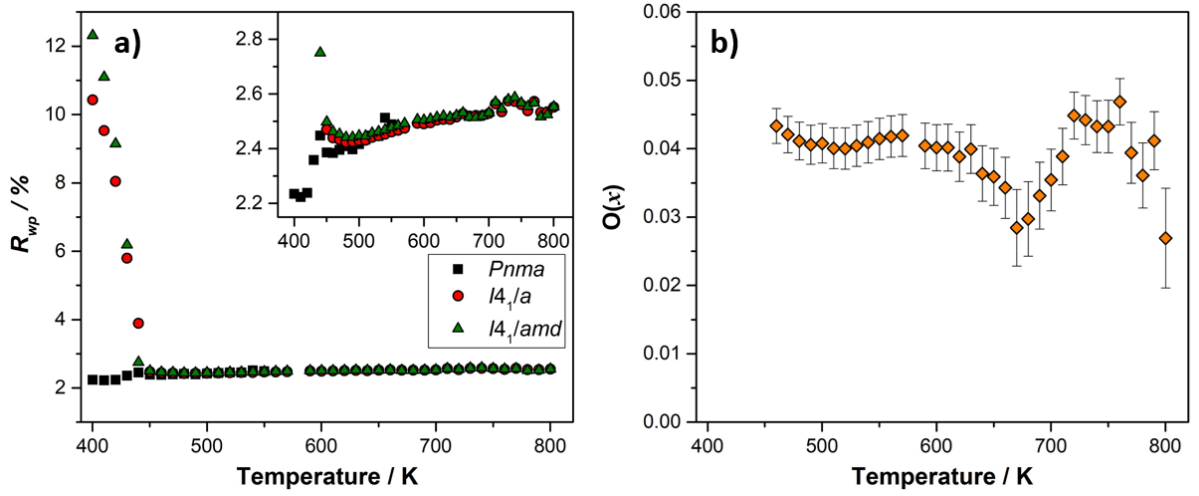


Figure 6.3: (a) The  $R_{wp}$  values from the Rietveld refinements of (black squares) orthorhombic  $Pnma$ , (red circles) tetragonal  $I4_1/a$ , and (green triangles) tetragonal  $I4_1/amd$ . (b) The refined oxygen  $x$  atomic coordinate from the Rietveld refinements to the tetragonal  $I4_1/a$  model.

of expansion in the unit cell above 700 K, coupled with a sporadic relationship with the  $O^{2-}$  ADP. As a result, the dataset at 700 K was refined to both the tetragonal  $I4_1/a$  and  $I4_1/amd$  models to determine whether this was a result of the change in symmetry of the structure. Recall that the difference between the tetragonal  $I4_1/a$  and  $I4_1/amd$  structures is due to the rotation of the  $BO_4$  tetrahedra about the  $c$ -axis, and the two structures can be differentiated by the atomic coordinates of the oxygen atoms [being at  $16f$  ( $x, y, z$ ) and  $16h$  ( $0, y, z$ ) in the  $I4_1/a$  and  $I4_1/amd$  structures, respectively]. Each model gave an identical quality of fit ( $R_{wp} = 2.53\%$  for both  $I4_1/a$  and  $I4_1/amd$ ). The  $I4_1/a$  structural model gave  $O(x) = 0.035(4)$  and  $B_{eq.}(O^{2-}) = 11.1(8) \text{ \AA}^2$ , whereas the  $I4_1/amd$  structural model had  $O(x) = 0$  and  $B_{eq.}(O^{2-}) = 13.5(7) \text{ \AA}^2$ . Although  $O(x)$  is statistically nonzero within the precision of the refinements, the identical quality of the fits demonstrates the lack of sensitivity of the data to this. This is further seen with the  $R_{wp}$  values plotted for both the tetragonal  $I4_1/a$  and  $I4_1/amd$  structures across the 400–800 K (Figure 6.3a), demonstrating the inability to distinguish between the two structures despite the  $O(x)$  parameter is refined to be statistically nonzero (Figure 6.3b). It is also possible that this anomalous behaviour  $>700$  K is related to the melting of the sample. Although CsReO<sub>4</sub> has a reported melting point of  $\sim 890$  K,<sup>57,58</sup> the sample was found to melt near 600 K in a NPD study conducted under vacuum.<sup>34</sup> This potential onset of melting is observed in the reduction of intensity of the Bragg reflections at high  $Q$  with increasing temperature (Figure 6.1), indicating a possible loss of crystallinity.

Whilst the  $Pnma \rightarrow I4_1/a$  phase transition is first order, as evidenced by Range *et al.* and Chay *et al.*,<sup>34,54</sup> the evolution of the lattice parameters in the orthorhombic phase is reminiscent of a continuous phase transition. This can be seen by considering the spontaneous strains associated with the distortion of the orthorhombic  $Pnma$  structure from the tetragonal  $I4_1/a$  structure. The linear strain components,  $\epsilon_1, \epsilon_2$ , and  $\epsilon_3$ , are given by

$$\begin{aligned}\epsilon_1 &= \frac{a - a_0}{a_0} \\ \epsilon_2 &= \frac{b - a_0}{a_0} \\ \epsilon_3 &= \frac{c - c_0}{c_0} \\ \Rightarrow \epsilon_0 &= \frac{1}{2}(\epsilon_2 - \epsilon_1)\end{aligned}\tag{6.2}$$

where  $a$ ,  $b$ , and  $c$  are the lattice parameters for the orthorhombic  $Pnma$  structure, and the reference parameters  $a_0$  and  $c_0$  are extrapolated from the values of the (strain-free) tetragonal  $I4_1/a$  structure to lower temperatures.<sup>34,59</sup> In this case, the subscript ‘o’ for ‘orthorhombic’ is omitted as not to be confused with the subscript ‘0’ for the strain-free structure. A plot of  $\epsilon_0^2$  varies linearly with temperature, as seen in Figure 6.2d, indicating that this transition possesses second order characteristics.

### 6.3.2 Short-Range Local Structure X-Ray PDF Studies

The XPDFs at 100, 300, 500, and 700 K for  $\text{CsReO}_4$  are displayed in Figure 6.4, with an extended dataset presented in Figure A.21. In the 100 K dataset, the first peak at  $r \sim 1.74 \text{ \AA}$  corresponds to the Re–O distances that occur within the  $\text{ReO}_4$  tetrahedra. The subsequent O–O peaks are not observed due to the relatively weak scattering of oxygen with X-rays. The Cs–O peaks between 2.9–3.3  $\text{\AA}$  are weakly observed at 100 K, but are indistinguishable from the Fourier termination ripples at higher temperatures. The subsequent peaks in the XPDF correspond to various cation–cation pairs in the structure, as indicated by the vertical ticks. In the orthorhombic  $Pnma$  structure, the  $\text{Cs}^+$  and  $\text{Re}^{7+}$  cations are located at the  $4c$  Wyckoff position, with variable  $x$  and  $z$  atomic coordinates

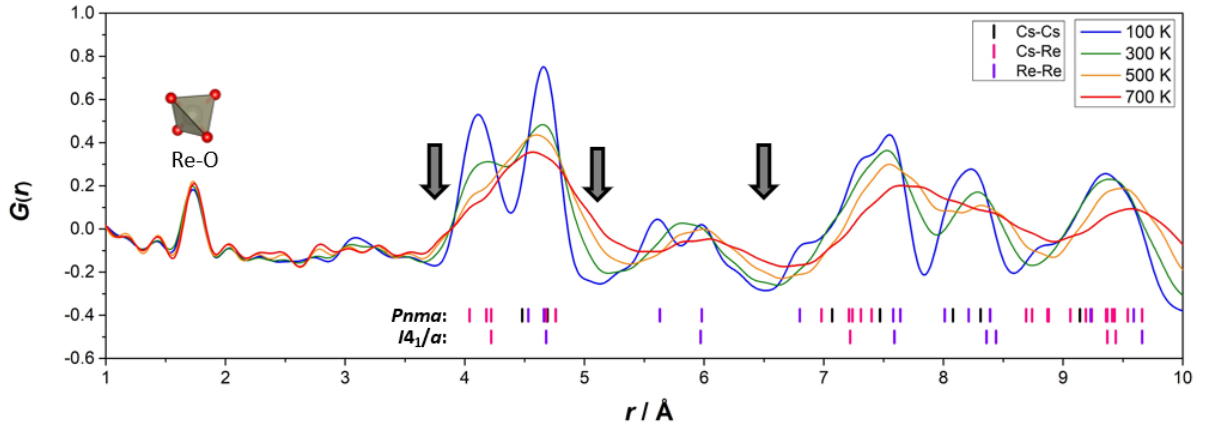


Figure 6.4: Variable temperature X-ray pair distribution function data of CsReO<sub>4</sub> at 100 (blue), 300 (green), 500 (orange), and 700 K (red). The vertical markers correspond to some of the nearest atom-atom pairs in both the orthorhombic *Pnma* at 100 K (above) and the tetragonal *I*<sub>41</sub>/*a* structure at 700 K (below). Black arrows indicate extra features in the pair distribution function that are not described by the model.

that are temperature dependent. This leads to several unique cation-cation distances. In the tetragonal *I*<sub>41</sub>/*a* structure (and similar to the *I*<sub>41</sub>/*amd* structure), Cs<sup>+</sup> and Re<sup>7+</sup> are at the special symmetry-constrained 4*b* and 4*c* sites respectively, with no variable atomic coordinates. This means that there is significant overlap between the Cs-Cs, Cs-Re, and Re-Re distances in the tetragonal *I*<sub>41</sub>/*a* structure coinciding with an increase in symmetry.

Observing the temperature dependence of the XPDFs in Figure 6.4 shows that the first Re-O peak at  $r \sim 1.74$  Å remains consistent across the measured temperature range. However, the remaining peaks ( $r > 3.5$  Å), corresponding to the various cation-cation pairs, show very different behaviour with increasing temperature. The peaks at  $\sim 4.22$  Å (corresponding to Cs-Re distances) and at  $\sim 4.68$  Å (corresponding to Cs-Cs and Re-Re distances) increase significantly in peak width with increasing temperature. In XPDF, an increase of peak width occurs due to an increase in disorder at the atomic site, and can be modelled with two different contributions: a dynamic contribution from an increase in disorder or thermal motion of the cations, and as a static contribution from splitting of the atomic site into multiple different cation-cation distances. These extra features have been labelled with black arrows (Figure 6.4). Initial small box fits to the data indicate that this increase in peak width is more indicative of splitting into multiple cation environments, as thermal broadening struggled to account for the peak shape. However, for peak splitting

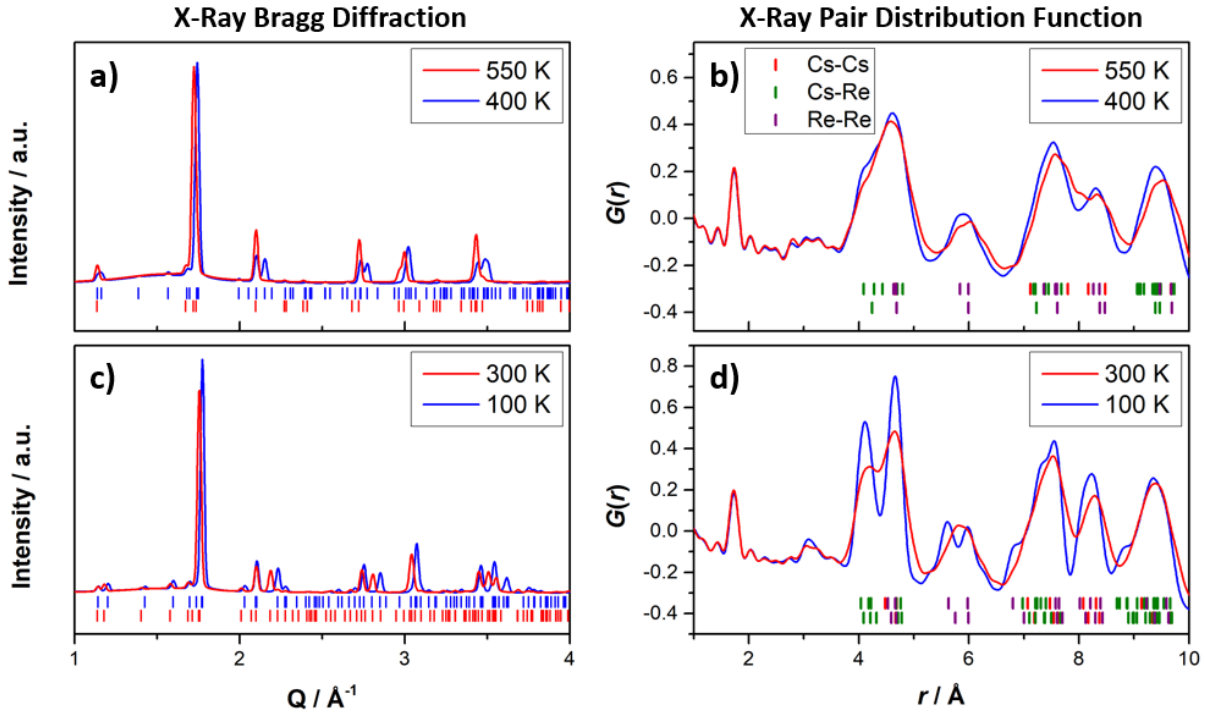


Figure 6.5: A comparison of the (a,c) synchrotron X-ray Bragg diffraction and (b,d) X-ray pair distribution function data at two pairs of temperatures: (a,b) 400 and 550 K, and (c,d) 100 and 300 K. In each panel, the red line represents the higher temperature data and the blue line represents the lower temperature data. In the synchrotron X-ray diffraction plots, the space group-allowed reflections are indicated, whereas in the X-ray pair distribution function data, the cation-cation distances are indicated.

to occur, there must be multiple cation-cation distances that are not allowed by the symmetry-constrained positions of the cations in the long-range average symmetry of the  $I4_1/a$  (or the  $I4_1/amd$ ) structure. This indicates that there is symmetry lowering occurring on the local scale of  $\text{CsReO}_4$  upon heating.

To investigate this potential symmetry-lowering phenomena, a comparison between the X-ray Bragg and XPDF data were made at two pairs of temperatures: 100 and 300 K, as well as 400 and 550 K. These comparisons are displayed in Figure 6.5. The 100 and 300 K temperatures were compared to demonstrate the effect of thermal broadening in the XPDFs without changing the long-range structure of the material. In the X-ray Bragg data, there is no observed change in the long-range average structure, with Bragg reflections moving to lower  $Q$  due to thermal expansion. In the XPDF, the features remain the same with a similar observation of some cation-cation distances shifting to higher  $r$ , indicating an expansion of the unit cell. The 400 and 550 K temperatures were compared to demonstrate what effect a change in the long-range average structure



has on the short-range local structure of the material. These two temperatures were chosen to avoid the possibility of a two-phase orthorhombic  $Pnma$  and tetragonal  $I4_1/a$  mixture observed by Chay *et al.* between 425–500 K.<sup>34</sup> Despite the change in long-range average structure evident in the X-ray Bragg data resulting in a reduction in the number of observed reflections at 550 K (and by the Rietveld refinements in Figure 6.2), very little change is observed in the XPDF data. In particular, the features between 4.0–5.0 Å (corresponding to a combination of Cs–Cs, Cs–Re, and Re–Re distances in the tetragonal  $I4_1/a$  model) only display slight broadening, despite being reduced from nine unique cation–cation distances in the orthorhombic  $Pnma$  model to two unique distances in the tetragonal  $I4_1/a$  model.

Small box fits (also referred to as real space Rietveld refinements) were undertaken on the XPDF data. The XPDF data at 100 K was first fit using the long-range orthorhombic  $Pnma$  model derived from the X-ray Bragg diffraction Rietveld refinements. When fitting the XPDF data, a spherical correlation function was used to model the change in  $B_{iso}$  with respect to  $r$ . This accounts for the differences in correlation length for the atom–atom pairs with shorter and longer interatomic distances. Additionally, a constant  $B_{iso}$  for the Re<sup>7+</sup> and O<sup>2−</sup> sites was used for  $1.2 < r < 2.7$  Å to capture the rigid ReO<sub>4</sub> tetrahedra, which is referred to as  $B_l$  for ‘local’. A single  $B_l$  parameter was refined against the 100 K XPDF data to give  $B_l = 0.224(12)$ . Additionally, the three Re–O bond distances were restrained to be approximately the same value, and the O–Re–O tetrahedra angles were restrained to be close to the ideal angle of 109.5°. This was in line with previous total scattering studies that have identified rigid ReO<sub>4</sub> tetrahedra units,<sup>1,2</sup> as well as a lack of splitting in the first Re–O distance at  $\sim 1.74$  Å. The  $B_l$  parameter and the ReO<sub>4</sub> restrictions were kept fixed for all temperatures, and example fits (Figure 6.6) showed that this approach did not prevent high quality fits to the XPDF data.

Fits to the XPDF data were conducted using the long-range average orthorhombic  $Pnma$  (100–800 K), tetragonal  $I4_1/a$  (400–800 K), and tetragonal  $I4_1/amd$  (400–800 K) models. The resulting structural parameters are displayed in Figure 6.7 as a comparison between the X-ray Bragg diffraction and XPDF fits for all measured temperatures. To assess the suitability of the data, the  $R$  values for the XPDF fits were calculated using

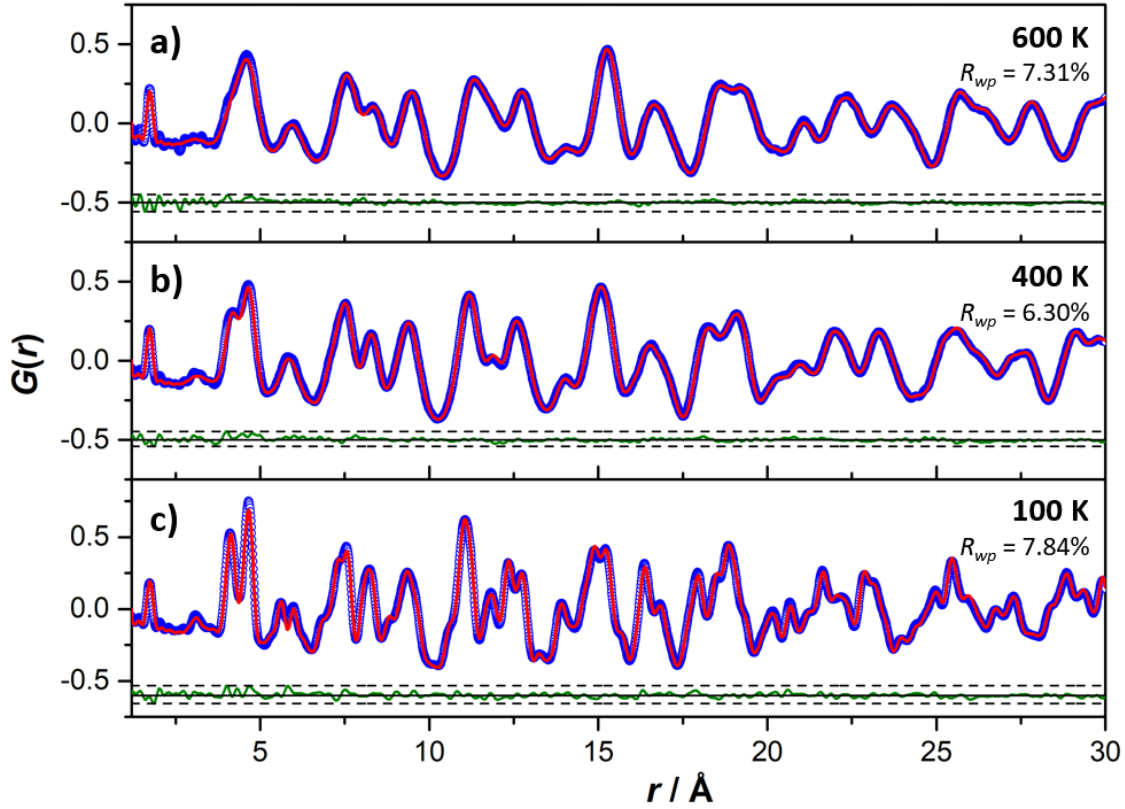


Figure 6.6: Variable temperature X-ray pair distribution function data of  $\text{CsReO}_4$  at (a) 600 K fitted to the tetragonal  $I4_1/a$  model, (b) 400 K fitted to the orthorhombic  $Pnma$  model, and (c) 100 K fitted to the orthorhombic  $Pnma$  model. The blue circles represent the data, the red line represents the small box fit to the data, and the green line represents the difference between the two.

Equation 6.1. In this approach, the fit is performed over the entire  $1.2 \leq r \leq 30 \text{ \AA}$  to capture the effect of the local correlations, however the  $R$  values for the XPDF fits were calculated over a reduced range ( $3.5 \leq r \leq 30$ ) to capture the features in the XPDF data that significantly change with temperature whilst avoiding the Fourier ripples that were prominent at lower temperature.<sup>1</sup>

Considering the X-ray Bragg fits, from 100–450 K the data is best fitted using the orthorhombic  $Pnma$  model. The tetragonal  $I4_1/a$  and  $I4_1/amd$  models struggle to fit the data from 400–450 K, but eventually display an  $R_{wp}$  value consistent with the  $Pnma$  orthorhombic model. For  $>600 \text{ K}$ , the  $Pnma$  refinements were unstable and returned large  $R_{wp}$  values, and hence were excluded from Figure 6.7a. As stated previously, there is little to distinguish the tetragonal  $I4_1/a$  and  $I4_1/amd$  structures using X-ray diffraction, and therefore the Rietveld refinements return fits of near-identical quality. However, there appears to be a slight difference between the quality of the XPDF fits depending on the

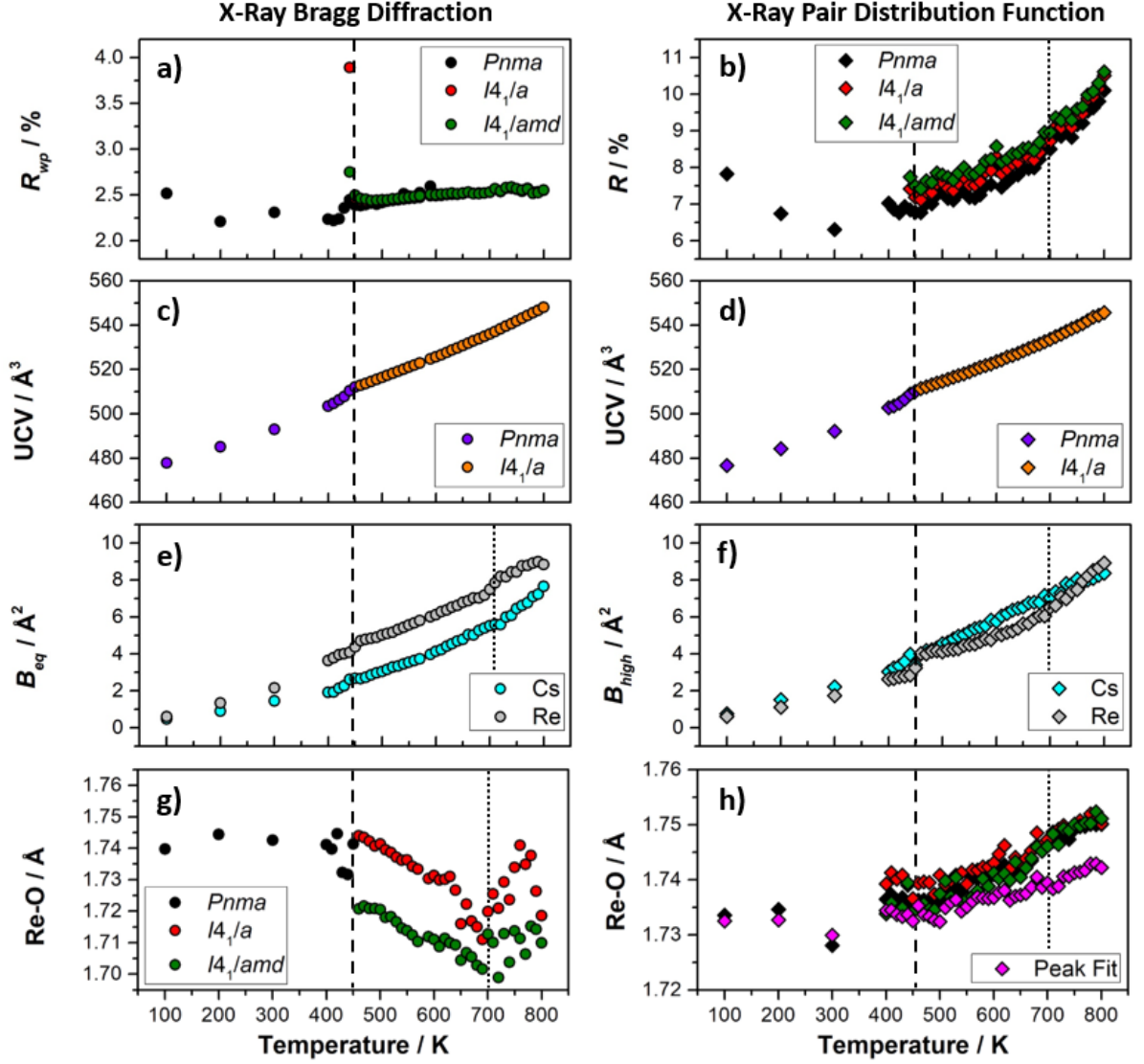


Figure 6.7: Results from the fits of the (a,c,e,g) X-ray Bragg diffraction and (b,d,f,h) X-ray pair distribution function of the CsReO<sub>4</sub> data from 100–800 K using the orthorhombic *Pnma* (black), tetragonal *I4<sub>1</sub>/a* (red), and *I4<sub>1</sub>/amd* (green) models. (a,b) The  $R_{wp}$  from the Bragg fits, and the  $R$  parameter from the X-ray pair distribution function fits, with the parameter described in text. (c,d) The unit cell volume (UCV) across the entire temperature range. (e,f) The atomic displacement parameters extracted for Cs<sup>+</sup> and Re<sup>7+</sup> from the X-ray Bragg ( $B_{eq}$ ) and the X-ray pair distribution function ( $B_{high}$ ) fits. (g,h) The Re–O bond distances, with an additional peak-fitting technique performed for the X-ray pair distribution function data described in text. For clarity, the error bars have been omitted. The dashed line at 450 K represents the *Pnma* → *I4<sub>1</sub>/a* phase transition observed in the X-Ray Bragg fits, whereas the dotted line at 700 K represents the onset of local disorder in the X-ray pair distribution function.

model used (Figure 6.7b). This possibly indicates that there are local features that are captured by the greater number of degrees of freedom allowed in the orthorhombic  $Pnma$  structure (22 parameters) compared to the tetragonal  $I4_1/a$  (13 parameters) and  $I4_1/amd$  (12 parameters) structures.

The unit cell volumes derived from the X-ray Bragg and XPDF fits are also shown (Figure 6.7c,d). The features identified in the long-range average Bragg refinements, such as a change in the rate of expansion after the  $Pnma \rightarrow I4_1/a$  phase transition and the linear nature of each, are reproduced in the XPDF fits. In both the X-ray Bragg and XPDF modelling, equivalent lattice parameters were obtained when fitting the  $I4_1/a$  and  $I4_1/amd$  models to data  $>450$  K, and therefore only the  $I4_1/a$  unit cell volume is plotted. While the lower  $R$  value for the orthorhombic  $Pnma$  structure indicates that there are local features within the XPDF data, the consistency of the unit cell volumes in both the X-ray Bragg and XPDF fits indicate this local disorder is not apparent in the ‘average’ unit cell of the structure.

The  $B_{eq.}$  and  $B_{high}$  values from the X-ray Bragg and XPDF fits that capture the ADPs are shown in Figure 6.7e,f. Observing the ADPs is important in structural refinements, as an incorrect structural model used to fit the data can result in larger values.<sup>60</sup> In the X-ray Bragg fits, these describe the average atomic displacements which increase almost linearly with temperature. In the XPDF fits,  $B_{high}$  corresponds to the cation–cation correlations at high  $r$ , with  $B_l$  fixed to the 100 K dataset to capture the nearest neighbour correlations (such as the rigid  $\text{ReO}_4$  tetrahedra). The trend in the XPDF fits differ to that of the X-ray Bragg fits. In the X-ray Bragg fits, the  $\text{Re}^{7+}$  ADPs are larger than that of the  $\text{Cs}^+$  cations. However, this is reversed in the XPDF fits, with the  $\text{Cs}^+$  ADPs larger than those of the  $\text{Re}^{7+}$  cations. Furthermore, the thermal behaviour of  $\text{Re}^{7+}$  is nonlinear, with a point of inflection observed at  $\sim 700$  K.

Finally, the behaviour of the  $\text{ReO}_4$  tetrahedra were investigated based on both the X-ray Bragg and XPDF fits (Figure 6.7g,h). As seen previously in a study from the author’s research group on the  $I4_1/a \rightarrow I4_1/amd$  phase transition observed in  $\text{RbReO}_4$ ,<sup>1</sup> and in other scheelite-type oxides,<sup>44,45</sup> hints of local disorder can often be observed in the anomalous behaviour of the  $B$ –O bond lengths upon heating. This was also seen in the

Rietveld refinements of CsReO<sub>4</sub>, with the average Re–O bond length at 100 K refined as 1.74(2) Å, but decreasing down to a minimum of 1.711(14) at 690 K in the  $I4_1/a$  model. This decrease of  $\sim 2\%$  is not of the same magnitude as observed in the variable temperature work of RbReO<sub>4</sub> ( $\Delta\text{Re–O} = \sim 11\%$ ),<sup>1</sup> but is still statistically significant as it is larger than the calculated uncertainties. In the XPDF, the Re–O distances show very different behaviour, with only a subtle change due to thermal expansion. As the Re–O distance is influenced by the Re–O peak at  $\sim 1.74$  Å (Figure 6.4), an additional fitting was performed where this peak was fitted with a single Gaussian peak. This yielded a similar trend with a smaller uncertainty. However, there is a deviation between the fitted XPDF values and the Gaussian peak values from  $\sim 700$  K, similar to the onset of additional Re<sup>7+</sup> thermal motion observed in Figure 6.7f.

Different physical phenomena were considered to explain the differences between the X-ray Bragg and XPDF fits. Firstly, the large ADPs for Re<sup>7+</sup> and a change in the Re–O bond distance observed in the X-ray Bragg fits indicate that there is possible off centring of the Re<sup>7+</sup> cations. That is, a displacement of Re<sup>7+</sup> from the symmetry-constrained 4c (0, 1/4, 1/8) Wyckoff position. This would explain the lower  $R$  value obtained when fitting the XPDF to the orthorhombic  $Pnma$  structure, as the model has more degrees of freedom than the tetragonal  $I4_1/a$  and  $I4_1/amd$  models associated with the general  $x$  and  $z$  atomic coordinates of Re<sup>7+</sup>. However, off centring of Re<sup>7+</sup> would lift the degeneracy of the Re–O bond distances, which is not reflected in the unchanged and unsplit Re–O distance at  $\sim 1.74$  Å in the XPDF data.

Next, the possibility of incoherent rotations of the ReO<sub>4</sub> tetrahedra was considered. Such rotations have been used to explain the apparent B–O bond length shortening in the average structure of other ABO<sub>4</sub> materials.<sup>44,45,61</sup> These rotations are analogous to ABO<sub>3</sub> perovskites, where rotation of the BO<sub>6</sub> octahedra leads to a reduction in symmetry of the overall structure.<sup>62</sup> However, coherent rotations of the tetrahedra should not change the quality of the fits to the XPDF data over different length scales. XPDF refinements were conducted from 460–800 K using the tetragonal  $I4_1/a$  model but with  $r_{max}$  varied to allow different length scales to be investigated.<sup>1,63</sup> Two fitting ranges were conducted: one from  $1.2 \leq r \leq 30$  Å to capture the longer-range structure, and one

from  $1.2 \leq r \leq 10 \text{ \AA}$  to capture the shorter-range features. These fits were then used to determine  $\Delta l = l_2 - l_1$ , where  $l_1$  and  $l_2$  correspond to the lattice parameters obtained from the fits to  $r_{max} = 10$  and  $30 \text{ \AA}$  respectively. The results of these fits are shown in Figure 6.8. That there are substantial differences between the two fits across the 460–800 K temperature range indicates that this local-scale disorder is not from uncorrelated  $\text{ReO}_4$  rotations.

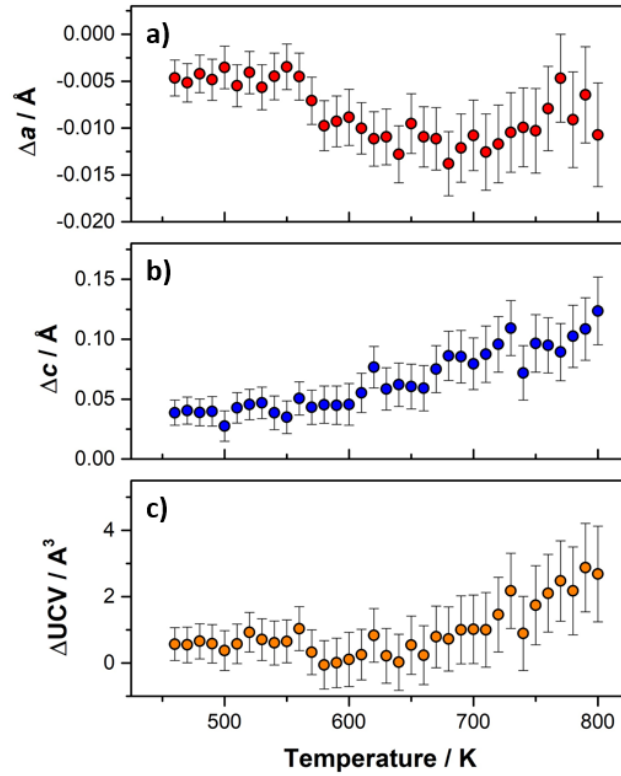


Figure 6.8: Results from the variable  $r$  range X-ray pair distribution function fits with the  $I4_1/a$  model. The value of  $\Delta l$  is described in text, with two different  $r_{max}$  of 10 and  $30 \text{ \AA}$  used. The values of  $\Delta a$ ,  $\Delta c$ , and  $\Delta \text{UCV}$  correspond to the differences between the lattice parameters between the two fits.

As neither off centring of the  $\text{Re}^{7+}$  cations, nor incoherent  $\text{ReO}_4$  tetrahedra rotations can explain the local scale symmetry lowering, the possibility of incoherent  $\text{ReO}_4$  tetrahedra translations upon heating was investigated. Whereas  $\text{ABO}_3$  perovskites consist of a network of corner-sharing  $\text{BO}_6$  octahedra that facilitates coherent tilting, the  $\text{BO}_4$  tetrahedra in the  $\text{ABO}_4$  structures share no such connection. Rather, the tetrahedra are joined through the  $A$ -site cation that allows for additional freedom in the relative position and orientation of the individual  $\text{BO}_4$  tetrahedra. Such changes would effectively displace the  $\text{Re}^{7+}$  cation from the space group Wyckoff special position, whilst maintaining constant Re–O bond lengths across the temperature range. This phenomena would

explain the differences between  $B_{eq.}$  and  $B_{high}$  in the X-ray Bragg and XPDF fits (by allowing for multiple Re<sup>7+</sup> cation sites), as well as the apparent differences between the Re–O bond distances (modelled as decreased bond lengths in the Bragg fits, but maintaining a consistent Re–O bond distance in the XPDF). This would also be consistent with the  $r_{max}$ -dependent trends observed in Figure 6.8, where there is a difference between the short-range local and long-range average structures in the XPDF. These incoherent tetrahedra translations appear to be thermally activated, with a greater disparity between the two length scales at higher temperatures. It should be noted that these thermal displacements may have a preferred direction at lower temperatures, with a significant drop in  $\Delta a$  observed around  $\sim 550$  K, before a similar jump is observed in  $\Delta c$  at around  $\sim 700$  K. Therefore, it is possible that these incoherent tetrahedra translations may first occur within the  $ab$  plane at  $\sim 550$  K, before being observed in the  $c$  direction from  $\sim 700$  K.

Recall that the X-ray Bragg diffraction showed a change in the slope of the unit cell volume at  $\sim 700$  K, as well as a decrease in crystallinity that was tentatively ascribed to the onset of melting of the sample. However, the same change in the slope of the unit cell volume is also observed in the XPDF, meaning that it is also occurring on the local scale. The observed change in the  $B_{high}$  of Re<sup>7+</sup> in the XPDF at  $\sim 700$  K, coupled with the increase in the difference between the lattice parameters at different length scales indicates that this is related to the possible thermally-activated ReO<sub>4</sub> incoherent tetrahedra displacements, and that they may proceed the melting of the sample.

An X-ray total scattering study of CsReO<sub>4</sub> identified a  $Pnma \rightarrow I4_1/a$  phase transition occurs at  $\sim 450$  K, accompanied by a linear increase in the lattice parameters and unit cell volume. However, the XPDF data showed little change upon heating, with broadening observed that was indicative of atomic displacements. Additional differences between the X-ray Bragg and XPDF fits were observed, such as the differences in ADPs, as well as the difference in the behaviour of the Re–O distances. In determining a model that would be consistent with both the X-ray Bragg and XPDF data, it is predicted that the ReO<sub>4</sub> tetrahedra undergo incoherent translations within the structure, giving rise to local dynamic disorder.

## 6.4 Structural Studies of $\text{TlTcO}_4$

Neutron Bragg diffraction data of  $\text{TlTcO}_4$  indicate a  $Pnma \rightarrow I4_1/amd$  phase transition occurs upon heating, as indicated by the lack of observation of the (114) reflection indicative of the  $I4_1/a$  structure. NPDF fits identify the rigid nature of the  $\text{TcO}_4$  tetrahedra, as was similarly seen in a comparative study to  $\text{TlReO}_4$ .

### 6.4.1 Long-Range Average Structure Neutron Powder Diffraction Studies

NPD data were collected for  $\text{TlTcO}_4$  on POWGEN at the SNS at 50, 300, 450, and 600 K. These temperatures were selected based on the orthorhombic-to-tetragonal phase transition observed at  $\sim 500$  K in a previous SXRD study conducted by the author's research group.<sup>38</sup> Rietveld refinements to these data show good agreement with the previous SXRD study.<sup>38</sup> Similar to  $\text{CsReO}_4$ ,  $\text{TlTcO}_4$  adopts an orthorhombic  $Pnma$  structure at low temperatures. At 50 K, the structure consists of a network of  $\text{TlO}_8$  polyhedra and  $\text{TcO}_4$  tetrahedra. The  $\text{TlO}_8$  polyhedra contain  $\text{Tl-O}$  bonds between 2.689(14)–3.052(6) Å, whereas the  $\text{TcO}_4$  tetrahedra are distorted with  $\text{Tc-O}$  bonds between 1.724(10)–1.767(16) Å and an average  $\text{Tc-O}$  bond length of 1.745(14) Å, and  $\text{O-Tc-O}$  bond angles ranging from 105.6(8)–111.9(5) °.

Previous analysis of the  $\text{TlTcO}_4$  high-temperature phase was inconclusive, with both  $I4_1/a$  and  $I4_1/amd$  structural models returning equivalent fits using SXRD data. The two structures differ by a rotation of the  $\text{TcO}_4$  tetrahedra around the  $c$ -axis governed by the  $\Gamma_3^+$  mode, and can be differentiated by the presence (or absence) of the (114) reflection.<sup>34,35</sup> A similar analysis was conducted where both the  $I4_1/a$  and  $I4_1/amd$  structures were fitted to the 600 K dataset, and these resulted in almost identical quality of fits (for  $I4_1/a$ :  $R_{wp} = 2.00\%$  with 37 parameters *vs.* for  $I4_1/amd$ :  $R_{wp} = 2.02\%$  with 36 parameters). Despite the improved sensitivity to the oxygen atomic coordinates and ADPs using neutron diffraction, the Rietveld refinements were still insensitive to the atomic coordinates of the oxygen atoms. The tetragonal  $I4_1/a$  structure returned a nonzero



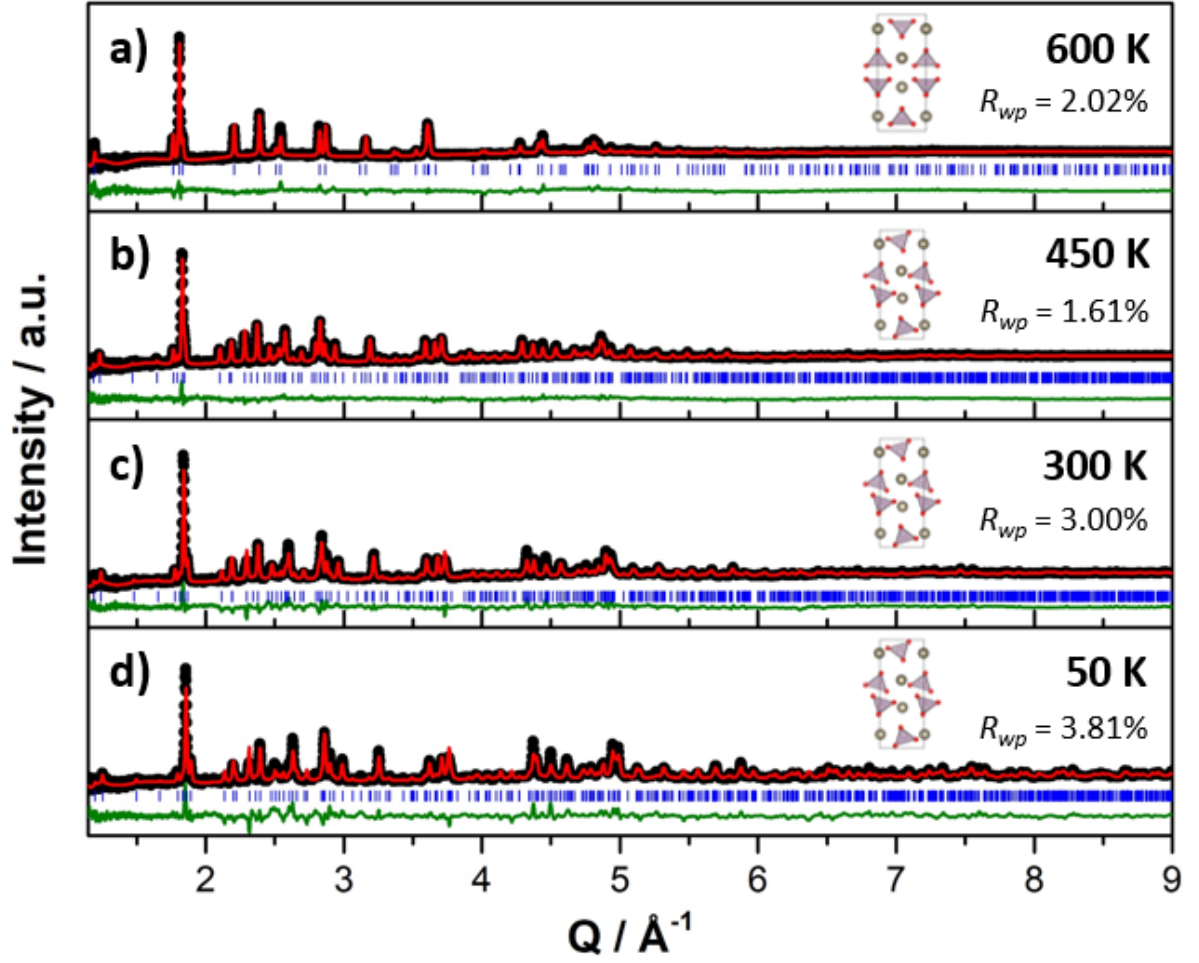


Figure 6.9: Rietveld refinements to the neutron Bragg data of  $\text{TiTeO}_4$  at (a) 600 K to the tetragonal  $I4_1/amd$  space group, (b) 450 K to the orthorhombic  $Pnma$  space group, (c) 300 K to the orthorhombic  $Pnma$  space group, and (d) 50 K to the orthorhombic  $Pnma$  space group. The black circles represent the data, the red line represents the fit to the data, the green line represents the difference between the data and the fit, and the blue dashes represent the space group-allowed reflections.

oxygen position and a large oxygen ADP [ $O(x) = 0.0584(5)$  and  $B_{eq.}(O) = 8.6(4) \text{ \AA}^2$ ], which was smaller than observed for the tetragonal  $I4_1/amd$  structure [ $O(x) = 0$  and  $B_{eq.}(O) = 9.9(4) \text{ \AA}^2$ ], demonstrating insensitivity to the data.

The Rietveld refinements to the 600 K dataset were examined in more detail, and are presented in Figure 6.10. The intensity associated with the (114) reflection (which is allowed in  $I4_1/a$  but forbidden in  $I4_1/amd$ ) at  $Q \sim 2.4 \text{ \AA}^{-1}$  is noteworthy. In the refinements to the  $I4_1/a$  space group, additional intensity is placed at the position of this reflection, as indicated by the negative feature in the difference curve. In fitting the  $I4_1/amd$  structure, the diffraction pattern in this region is adequately fit. Furthermore, the (211) reflection at  $\sim 2.5 \text{ \AA}^{-1}$  is better fit using the tetragonal  $I4_1/amd$

Table 6.2: Selected Rietveld refinement structural parameters and bond distances for  $\text{TlTcO}_4$  using neutron powder diffraction data.

| Temperature (K)                  | 50          | 300         | 600        |
|----------------------------------|-------------|-------------|------------|
| Space Group                      | $Pnma$      | $Pnma$      | $I4_1/amd$ |
| $a$ (Å)                          | 5.4381(7)   | 5.4867(8)   | 5.7112(9)  |
| $b$ (Å)                          | 5.7252(6)   | 5.7576(8)   | $= a$      |
| $c$ (Å)                          | 13.3167(16) | 13.4977(19) | 13.746(2)  |
| Vol. (Å <sup>3</sup> )           | 414.60(8)   | 426.40(10)  | 448.37(16) |
| Tl $x$                           | 0.0057(11)  | 0.0136(13)  | $= 0$      |
| Tl $z$                           | 0.1264(5)   | 0.1261(5)   | $= 1/8$    |
| Tc $x$                           | 0.0347(15)  | 0.0312(17)  | $= 0$      |
| Tc $z$                           | 0.3769(8)   | 0.3795(8)   | $= 3/8$    |
| O(1) $x$                         | 0.840(3)    | 0.820(3)    | $= 0$      |
| O(1) $y$                         | $= 1/4$     | $= 1/4$     | 0.5137(16) |
| O(1) $z$                         | 0.0849(10)  | 0.0809(9)   | 0.6909(5)  |
| O(2) $x$                         | 0.858(2)    | 0.840(3)    | –          |
| O(2) $y$                         | $= 1/4$     | $= 1/4$     | –          |
| O(2) $z$                         | 0.4896(10)  | 0.4772(12)  | –          |
| O(3) $x$                         | 0.0387(15)  | 0.0348(14)  | –          |
| O(3) $y$                         | 0.5041(13)  | 0.5035(12)  | –          |
| O(3) $z$                         | 0.6883(6)   | 0.6893(5)   | –          |
| $B_{eq.}$ (Tl) (Å <sup>2</sup> ) | 0.00(11)    | 1.41(17)    | 4.1(4)     |
| $B_{eq.}$ (Tc) (Å <sup>2</sup> ) | 0.73(17)    | 2.3(2)      | 4.6(4)     |
| $B_{eq.}$ (O) (Å <sup>2</sup> )  | 2.1(2)      | 4.8(3)      | 10.1(4)    |
| Tc–O(1) (Å)                      | 1.736(19)   | 1.672(19)   | 1.625(9)   |
| Tc–O(2) (Å)                      | 1.782(17)   | 1.69(2)     | –          |
| Tc–O(3) (Å)                      | 1.702(10)   | 1.734(10)   | –          |
| $R_{wp}$ (%)                     | 3.81        | 3.00        | 2.02       |

as opposed to the  $I4_1/a$  structure that overestimates the intensity. Therefore, it is tentatively concluded that  $\text{TlTcO}_4$  adopts the  $I4_1/amd$  scheelite-type aristotype structure at elevated temperatures. However, it is worth noting that high resolution diffraction data experiments should be conducted to confirm the presence (or absence) of the (114) reflection at elevated temperatures.

The 50, 300, and 450 K datasets were fit using the orthorhombic  $Pnma$  model, whereas the 600 K dataset was fit with the tetragonal  $I4_1/amd$  model. Parallels were immediately noted with the  $Pnma \rightarrow I4_1/a$  phase transition observed in  $\text{CsReO}_4$ , such as the anisotropic expansion of the  $a$  and  $b$  lattice parameters coupled with the unit cell volume showing a change at the transition (Figure 6.11a,b). The unit cell volume of the tetragonal  $I4_1/amd$  phase at 600 K appears to be larger than the extrapolated

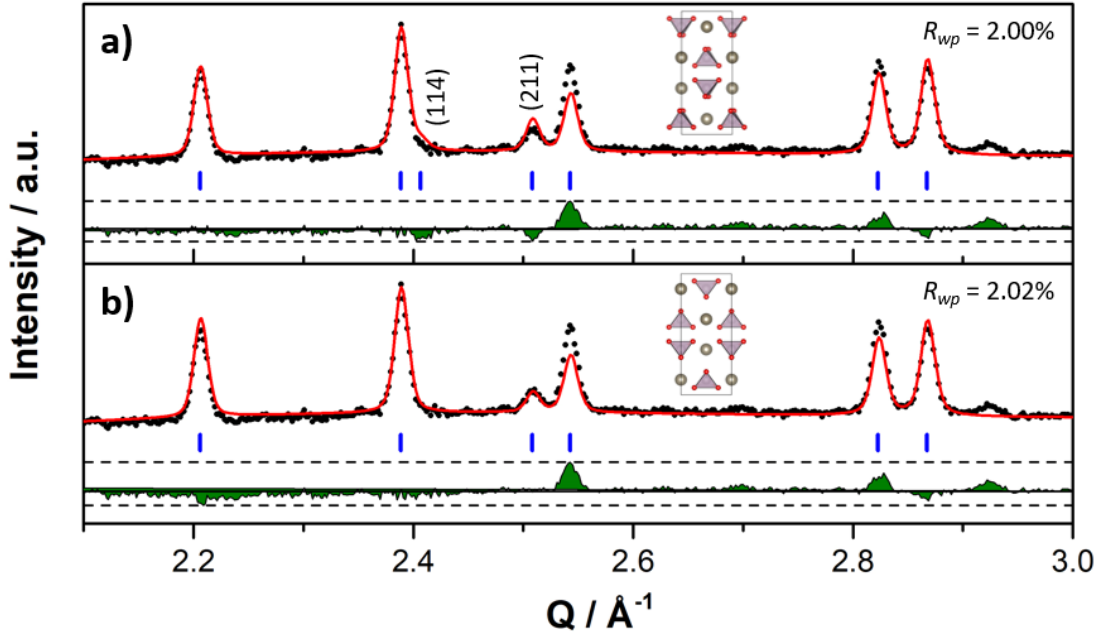


Figure 6.10: Rietveld refinements to the neutron Bragg data of  $\text{TiTeO}_4$  at 600 K to the (a) tetragonal  $I4_1/a$  space group, and the (b) tetragonal  $I4_1/amd$  structure. The black circles represent the data, the red line represents the fit to the data, the green line and shaded area represent the difference between the data and the fit, and the blue dashes represent the space group allowed reflections.

unit cell volume of the orthorhombic  $Pnma$  structure. This point will be returned to below. The ADPs for the oxygen sites at 50 K are invariably larger than that of the cations, possibly hinting at static disorder in the structure. This is presumably due to the stereochemical activity of the  $\text{Ti}^+$   $6s^2$  lone pair electrons causing incoherent static displacements and short-range correlations. The ADPs show anomalous temperature-dependent behaviour, where an increase is observed between 50 and 300 K for both  $\text{Te}^{7+}$  and  $\text{O}^{2-}$ , before dropping at 450 K. This was hypothesised to be a result of the rare isosymmetric ( $Pnma \rightarrow Pnma$ ) phase transition that was previously described for  $\text{TiTeO}_4$ .<sup>38</sup> This phase transition was identified to be a first order due to the coexistence of the two orthorhombic  $Pnma$  structures between 300–400 K. It is possible that the increase in ADPs at 300 K may be a result of this two-phase region that is inadequately resolved in the POWGEN dataset. A further interesting result of the Rietveld refinements is the increase in ADPs of the oxygen site at 600 K, coupled with an apparent reduction in the Te–O bond lengths in the  $\text{TeO}_4$  tetrahedra upon heating. As seen previously in the study of  $\text{CsReO}_4$  and other  $\text{ABO}_4$  metal oxides, Rietveld refinements often result in anomalous behaviour of the oxygen anions when either static (such as cation off centring) or dynamic (such as tetrahedra translations) disordering is occurring.

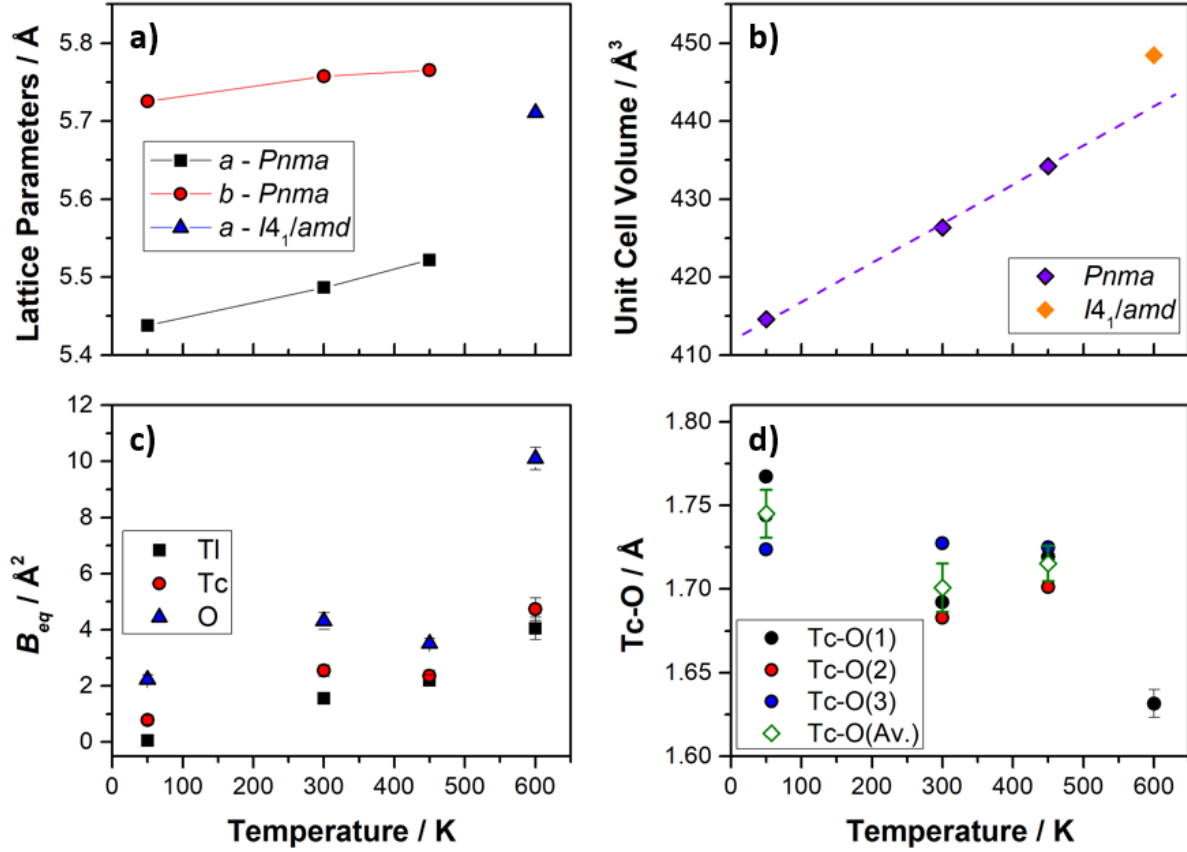


Figure 6.11: Rietveld refinements for the variable temperature data of  $\text{TiTcO}_4$  with (a) the  $a$  and  $b$  lattice parameters, (b) the unit cell volume, (c) the atomic displacement parameters measured as  $B_{eq}$ , and (d) the Tc-O bond distances, where only the uncertainties of the average value has been displayed for clarity.

The trend in the unit cell volume is noteworthy. Although there is only one temperature point taken above the phase transition in the current neutron total scattering study, the synchrotron XRD study conducted by the author's research group shows the same trend.<sup>38</sup> There appears to be a relationship between the presence of  $6s^2$  lone pair electrons on the  $A$ -site cation, and the magnitude of change in the unit cell volume of the high-temperature structure, relative to the low-temperature structure. This is summarised in Figure 6.12. By extrapolating the unit cell volume of the lower-temperature phases, the high-temperature phases of  $\text{TiTcO}_4$ , and  $\text{BiVO}_4$  from Chapter 5, are significantly higher in volume. In contrast, the unit cell volume of  $\text{NdNbO}_4$  taken from Saura-Múzquiz *et al.* and the unit cell volume of  $\text{HoNbO}_4$  from Chapter 3 of this dissertation appear to undergo little change in unit cell volume through the phase transition.<sup>25</sup> This effect of the  $6s^2$  lone pair electrons could potentially relate to the compressibility of the  $\text{AO}_8$  polyhedra, where high-pressure studies have noted that  $\text{BiVO}_4$  undergoes a  $I2/b \rightarrow I4_1/a$  phase transition

at 1.5 GPa,<sup>64</sup> whereas  $\text{HoNbO}_4$  undergoes a  $I2/a \rightarrow P2_1/c$  phase transition at 19.0 GPa.<sup>65</sup> It is unclear whether this is an effect of the  $6s^2$  lone pair electrons as noted similarly in Figure 5.9, and is a result worth further investigating.

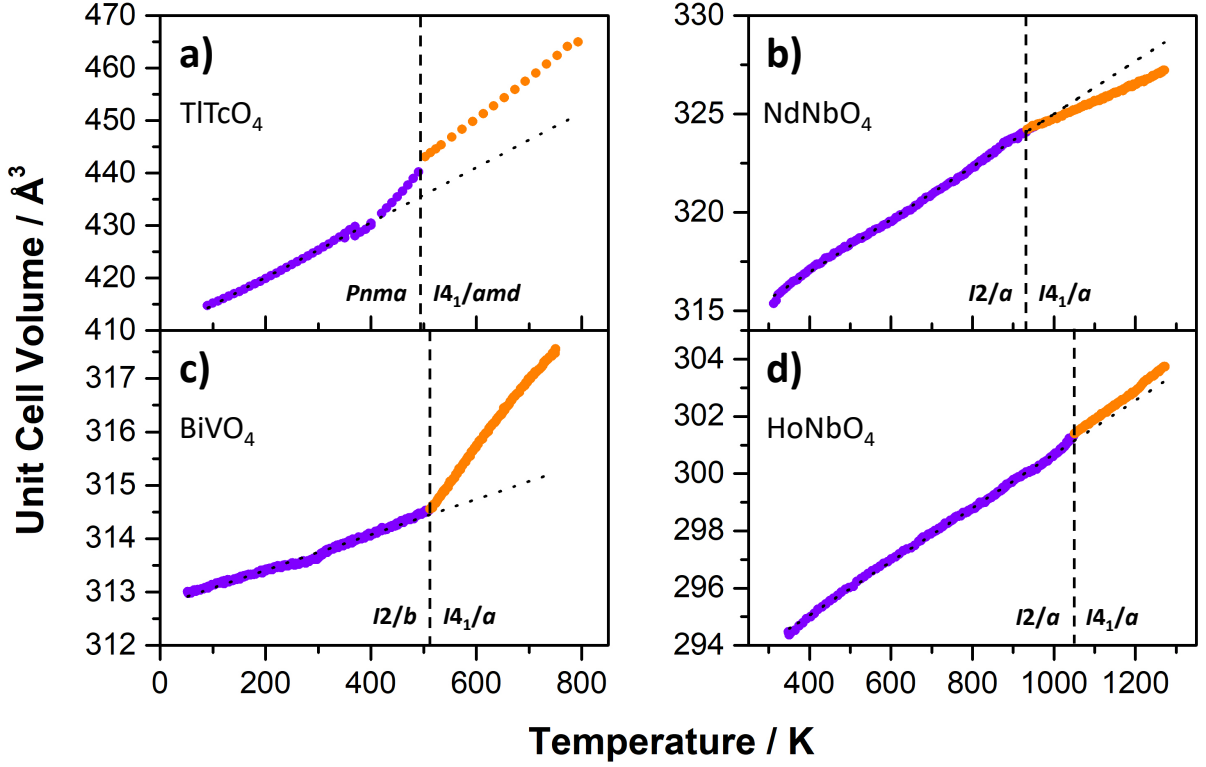


Figure 6.12: Unit cell volumes of the various  $\text{ABO}_4$  phase transitions, (a)  $Pnma \rightarrow I4_1/amd$  in  $\text{TiTeO}_4$  taken from synchrotron X-ray diffraction by Kennedy *et al.*,<sup>38</sup> (b)  $I2/a \rightarrow I4_1/a$  in  $\text{NdNbO}_4$  taken from neutron powder diffraction by Saura-Múzquiz *et al.*,<sup>25</sup> (c)  $I2/b \rightarrow I4_1/a$  in  $\text{BiVO}_4$  taken from neutron powder diffraction data, and (d)  $I2/a \rightarrow I4_1/a$  in  $\text{HoNbO}_4$  taken from neutron powder diffraction data. The purple circles represent the low-temperature data, the orange circles represent the high-temperature data, the dashed line indicates the phase transition temperature, and the dotted line is extrapolated from the low-temperature data and is used to guide the eyes.

### 6.4.2 Short-Range Local Structure Neutron PDF Studies

The NPDF data of  $\text{TiTeO}_4$  at 50, 300, 450, and 600 K are plotted in Figure 6.13. At all temperatures, the peak at  $\sim 1.72$  Å corresponds to the first Tc–O pair within the  $\text{TeO}_4$  tetrahedra. This shows neither splitting nor broadening at any of the measured temperatures. The first O–O distances, corresponding to the edge of the  $\text{TeO}_4$  tetrahedra, results in a consistent peak at  $\sim 2.80$  Å. That neither the first Tc–O, nor O–O distances change over the measured temperature range implies the presence of rigid  $\text{TeO}_4$  tetrahedra. These tetrahedra were then modelled by placing restraints on the Tc–O bonds such that they were equal and fixing the O–Tc–O bond angles within the  $\text{TeO}_4$  tetrahedra at  $109.5^\circ$ .

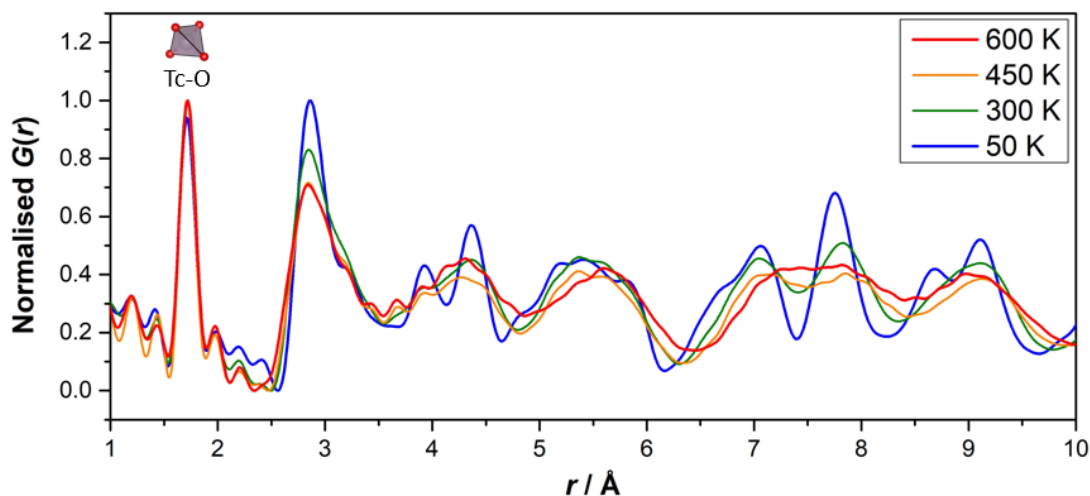


Figure 6.13: Variable temperature neutron pair distribution function data of  $\text{TlTcO}_4$  at 50 (blue), 300 (green), 450 (orange), and 600 K (red).

As seen in previous total scattering studies, such as the  $\text{NaBi(WO}_4)_2$  double scheelites in Chapter 4, and  $\text{BiVO}_4$  and  $\text{PbWO}_4$  in Chapter 5, stereochemically active lone pair electrons cause cations to disorder through well-defined displacements from their centrosymmetric position (giving a static contribution to the ADPs) as well as increased thermal motion (giving a dynamic contribution).<sup>2,60,66,67</sup> The 50 K data was first modelled to minimise the dynamic component. Fits were conducted using three models: the high temperature tetragonal  $I4_1/amd$  structure derived from the Bragg fits, the long-range average orthorhombic  $Pnma$  structure derived from the Bragg fits, and the monoclinic  $P2_1/c$  structural model observed in  $\text{TlReO}_4$  (and previously used to model the local structure of  $\text{BiVO}_4$  and  $\text{PbWO}_4$  in Chapter 5). These fits are shown in Figure 6.14 over a range of 1.2–30 Å. Not surprisingly, the tetragonal  $I4_1/amd$  model fits the data poorly at both low and high  $r$ . The fits to the orthorhombic  $Pnma$  structure provided an adequate fit at high  $r$  consistent with the long-range Bragg fitting, but failed to provide a satisfactory fit at low  $r$ . The monoclinic  $P2_1/c$  model provides the best fit to both the low and high  $r$ , implying that similar local features that were present in  $\text{TlReO}_4$  – the displacement of cations from their centrosymmetric positions and deformation of the  $\text{TlO}_8$  polyhedra – are also present in  $\text{TlTcO}_4$ .

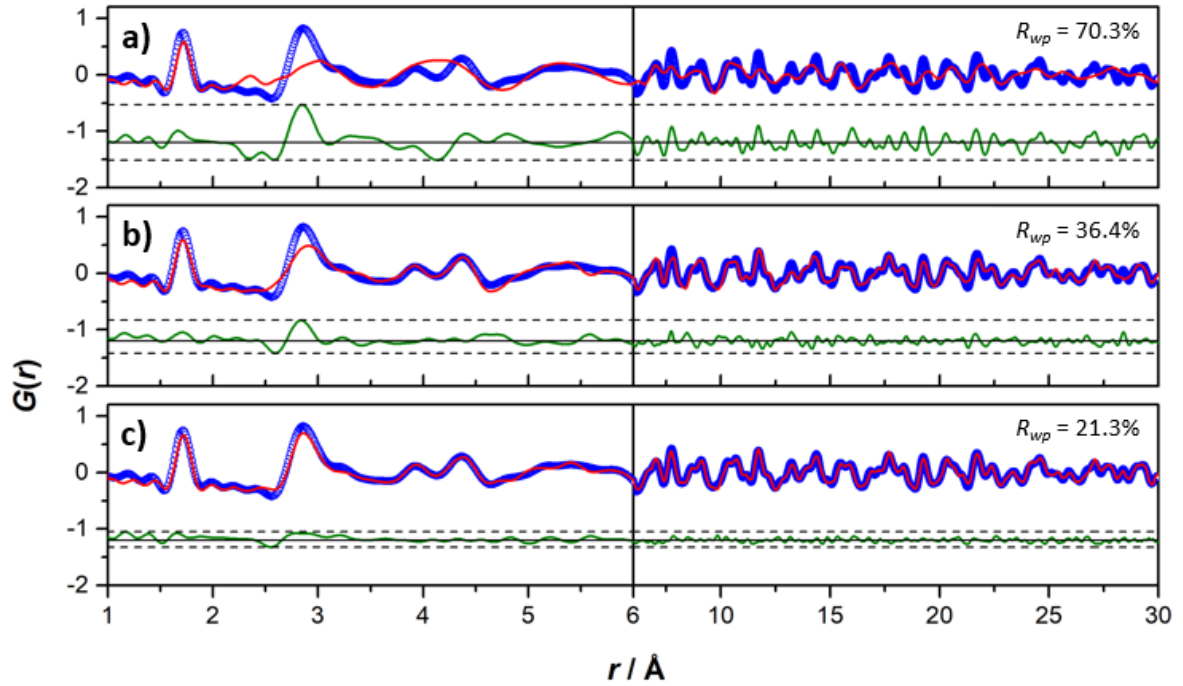


Figure 6.14: Neutron pair distribution function data of  $\text{TiTeO}_4$  measured at 50 K fitted to the (a) tetragonal  $I4_1/amd$ , (b) orthorhombic  $Pnma$ , and (c) monoclinic  $P2_1/c$  structure. The blue circles represent the data, the red line represents the small box fit to the data, and the green line represents the difference between the two. The  $\text{TcO}_4$  tetrahedra in the  $P2_1/c$  model were constrained to be rigid.

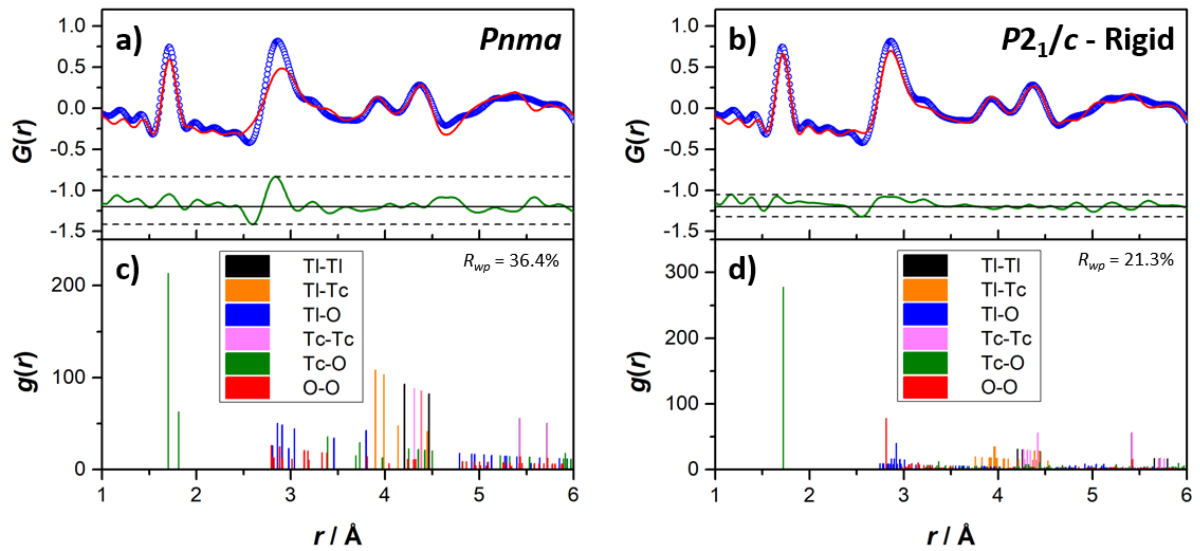


Figure 6.15: Variable temperature neutron pair distribution function data of  $\text{TiTeO}_4$  at 50 K fitted to the (a) tetragonal  $I4_1/amd$ , (b) orthorhombic  $Pnma$ , and (c) monoclinic  $P2_1/c$  structure with rigid  $\text{TeO}_4$  tetrahedra. The blue circles represent the data, the red line represents the small box fit to the data, and the green line represents the difference between the two.



To better understand the deformation of the  $\text{TlO}_8$  polyhedra and its contributions to the NPDF, partial PDFs of the orthorhombic  $Pnma$  and monoclinic  $P2_1/c$  models were plotted (Figure 6.15). Each model shows the peak at  $\sim 1.72$  Å being well fitted to the Tc–O distance in the  $\text{TcO}_4$  tetrahedra. The region from 2.5–3.5 Å is comprised of O–O distances across the  $\text{TcO}_4$  tetrahedra and  $\text{TlO}_8$  polyhedra, as well as the Tl–O distances within the  $\text{TlO}_8$  polyhedra. Most importantly, the strong peak at  $\sim 2.84$  Å is best fit with a single O–O distance consistent with the rigid  $\text{TcO}_4$  tetrahedra in the monoclinic  $P2_1/c$  model. As observed in the NPDF fits to the 50 K dataset, allowing for multiple different O–O distances as a result of the deformed  $\text{TcO}_4$  tetrahedra results in poor fitting of these features using either the tetragonal  $I4_1/amd$  and orthorhombic  $Pnma$  models. For both these models, this region of the fit is significantly broadened, accompanied by large ADPs to minimise the residual curve in the least squares fitting process. Therefore, the monoclinic  $P2_1/c$  model allows for the fitting of the rigid  $\text{TcO}_4$  tetrahedra, whilst the flexibility of the  $\text{TlO}_8$  polyhedra allows for optimal fitting of the additional features.

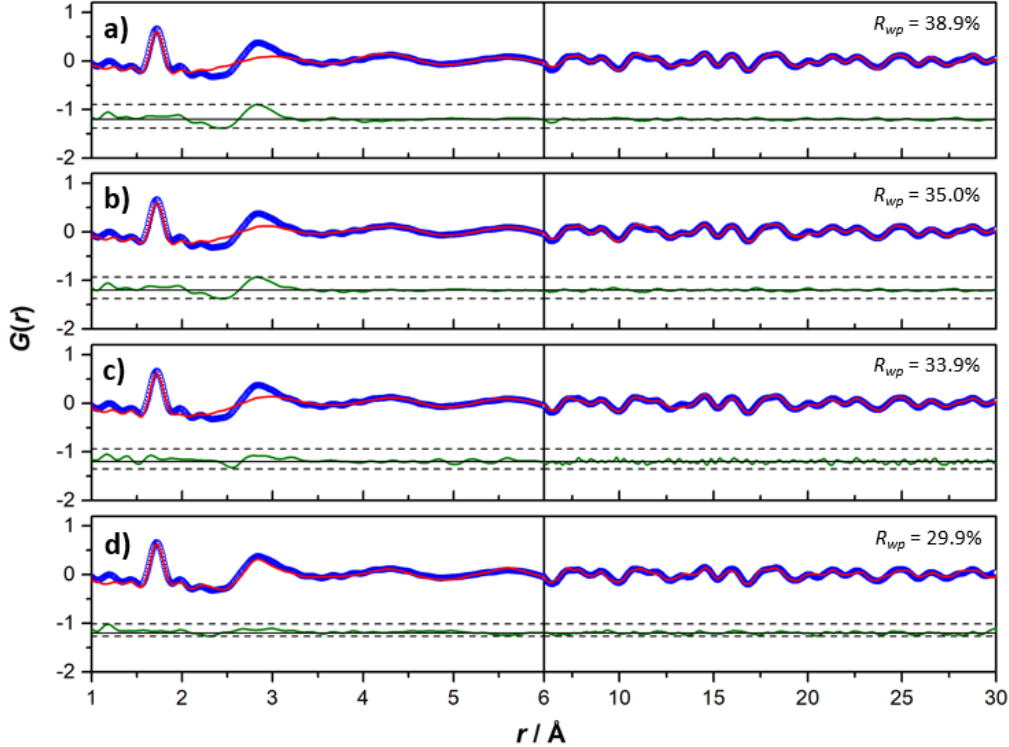


Figure 6.16: Neutron pair distribution function data of  $\text{TlTcO}_4$  at 600 K fitted to the (a) tetragonal  $I4_1/amd$ , (b) tetragonal  $I4_1/a$ , (c) orthorhombic  $Pnma$ , and (d) monoclinic  $P2_1/c$  structure. The blue circles represent the data, the red line represents the small box fit to the data, and the green line represents the difference between the two. The  $\text{TcO}_4$  tetrahedra in the monoclinic  $P2_1/c$  model were constrained to be rigid.



The fitting process was repeated for the 600 K dataset to determine whether any differences between the tetragonal  $I4_1/a$  or  $I4_1/amd$  models were apparent. Local probes are often necessary to fully understand the structure of materials, as seen with other related metal oxide structures.<sup>68</sup> Similar to the 50 K dataset, different models were fitted to the data to determine an appropriate short-range structural model. As noted previously, the Tc–O peak at  $\sim 1.72$  Å remains relatively unchanged between the 50 and 600 K datasets, while the prominent peak at  $\sim 2.84$  Å shows significantly less thermal broadening compared to the other peaks within the NPDF datasets, reflecting the rigid  $\text{TcO}_4$  tetrahedra in the structure. As seen in Figure 6.16, both the tetragonal  $I4_1/amd$  and  $I4_1/a$  models produce poor fits to the NPDF data at 600 K over a fitting range of 1.2–30 Å. Both models struggle to account for the feature at  $\sim 2.84$  Å, presumably due to a combination of the lack of constant O–O distances across their distorted  $\text{TcO}_4$  tetrahedra, as well as the near equality of the Tl–O bond distances that result in relatively consistent  $\text{TlO}_8$  polyhedra. A small improvement in the fit was obtained with the lower symmetry orthorhombic  $Pnma$  model, although this model gave a poor fit to the 2.5–3.5 Å region. The monoclinic  $P2_1/c$  model fits the NPDF features at both low and high  $r$  the best.

To place  $\text{TlTcO}_4$  in the context of the other metal oxides studied in this dissertation, it has flexible  $\text{AO}_8$  polyhedra and rigid  $\text{BO}_4$  tetrahedra. In  $\text{PbWO}_4$  and  $\text{BiVO}_4$  in Chapter 5, there was a subtle interplay between the flexibility of these two environments to accommodate the steric demand of the  $6s^2$  lone pair electrons. Due to the moderate length of the Pb–O bonds, it was more favourable for the  $\text{Pb}^{2+}$  lone pair to slightly deform the  $\text{WO}_4$  tetrahedra, as evident in the relaxation of the O–W–O bond angles from  $109.5^\circ$ . Conversely, the polarisability of the V–O bonds in the  $\text{VO}_4$  tetrahedra caused deformations across both the  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra that are preserved in the long-range average structure. The  $A$  and  $B$  site bonding environments between  $\text{TlTcO}_4$ ,  $\text{PbWO}_4$ , and  $\text{BiVO}_4$  are compared in Figure 6.17. In the case of  $\text{TlTcO}_4$ , the  $\text{TlO}_8$  polyhedra are larger than that of the  $\text{PbO}_8$  and  $\text{BiO}_8$  polyhedra [at room temperature,  $V(\text{TlO}_8) = 41.1$  Å<sup>3</sup>,  $V(\text{PbO}_8) = 31.7$  Å<sup>3</sup>,  $V(\text{BiO}_8) = 25.6$  Å<sup>3</sup>], and the Tc–O bonds are less polarisable than the V–O bonds due to their additional  $4d$  orbital contribution. Therefore, the deformation occurs within the  $\text{TlO}_8$  polyhedra, with a range of Tl–O bond lengths observed.

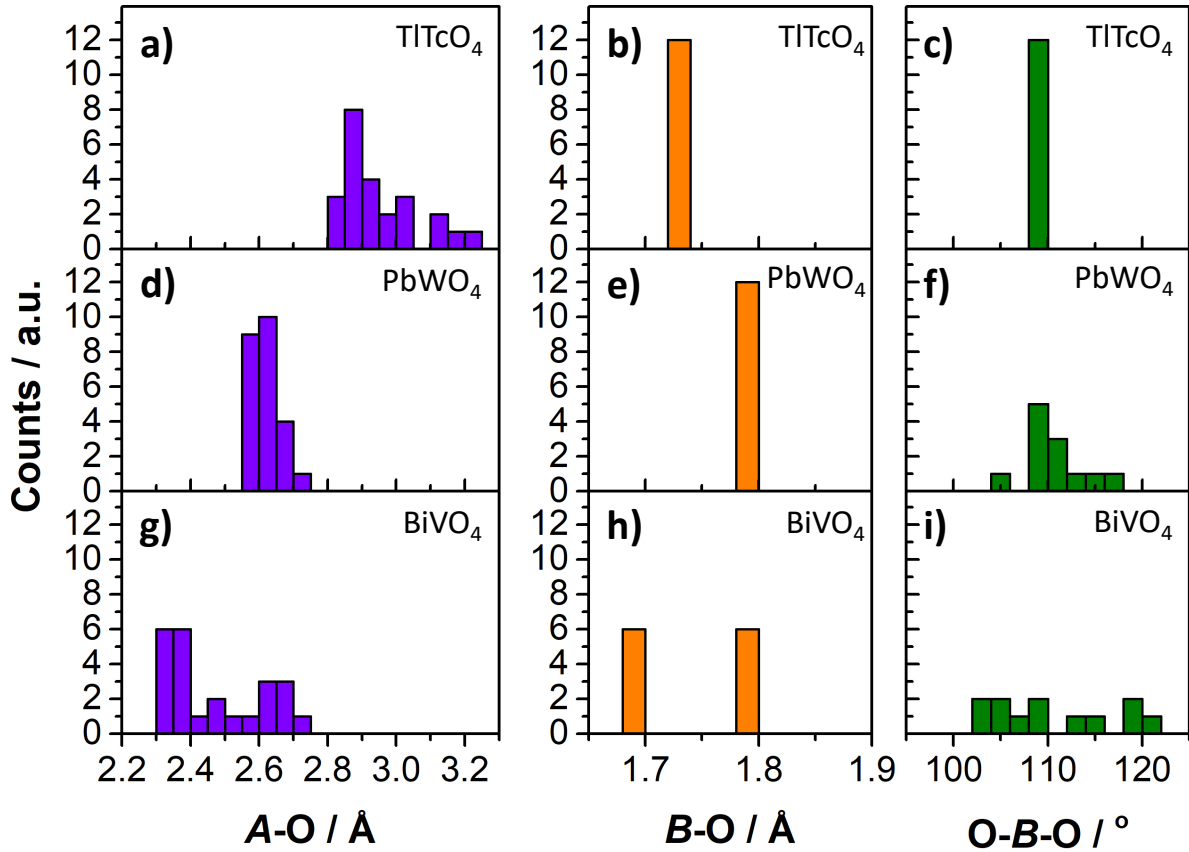


Figure 6.17: The  $A-O$ ,  $B-O$  bond lengths, and  $O-B-O$  bond angles from (a–c)  $TiTcO_4$ , (d–f)  $PbWO_4$ , and (g–i)  $BiVO_4$ , taken from the neutron pair distribution function fits at 300 K to the monoclinic  $P2_1/c$  model.

As a final aside, a brief comparison between  $TiTcO_4$  to  $TlReO_4$  will be made. Previous studies by Chay *et al.* and Kennedy *et al.* identified the  $ATcO_4$  and  $AREO_4$  salts ( $A^+ = Na, K, Rb, Cs$ ) to be isostructural except for  $A^+ = Tl$ .<sup>34,38</sup> Whereas  $TiTcO_4$  exhibits the orthorhombic  $Pnma$  long-range average structure at room temperature,  $TlReO_4$  exhibits the monoclinic  $P2_1/c$  structure at room temperature. Based on the IR alone, as proposed by the Errandonea *et al.* phase diagram (Figure 1.3),<sup>37</sup>  $TlReO_4$  should adopt a tetragonal  $I4_1/a$  structure similar to  $RbReO_4$  due to the similar size of the two  $A$ -site cations ( $Tl^+ = 1.59$  vs.  $Rb^+ = 1.61$  Å).<sup>18</sup> In fact, at temperatures  $\leq 150$  K and  $\geq 400$  K,  $TlReO_4$  displays tetragonal  $I4_1/a$  symmetry, with the room temperature monoclinic  $P2_1/c$  structure a result of long-range ordering of the  $Tl^+$   $6s^2$  lone pairs.<sup>2</sup> A change in symmetry from tetragonal  $I4_1/a$  to orthorhombic  $Pnma$ , according to the Errandonea *et al.* phase diagram (Figure 1.3),<sup>37</sup> is expected if there is either an increase in the size of the  $A$ -site cation (such as  $RbReO_4$  being tetragonal  $I4_1/a$  and  $CsReO_4$

being orthorhombic  $Pnma$ ),<sup>34</sup> or a decrease in the size of the  $B$ -site cation (such as  $\text{RbReO}_4$  being tetragonal  $I4_1/a$  and  $\text{RbClO}_4$  being orthorhombic  $Pnma$ ).<sup>69</sup> Based on the IR,  $\text{Tc}^{7+}$  is slightly smaller than  $\text{Re}^{7+}$  (0.37 *vs.* 0.38 Å).<sup>18</sup> This is reflected in the NPDF refinements that show the first peak, corresponding to the Tc–O and Re–O bonds, are at slightly different positions (Tc–O = 1.72 *vs.* Re–O = 1.74 Å). It is possible that this small change in the  $B$ -site cation IR is enough to favour the formation of the orthorhombic  $Pnma$ , rather than the tetragonal  $I4_1/a$  structure, in the long-range average structure.

It is unusual that although  $\text{TlTcO}_4$  and  $\text{TlReO}_4$  adopt different long-range average structures, their local structure is both best fit to the monoclinic  $P2_1/c$  model with rigid  $\text{BO}_4$  tetrahedra. Previously, the long-range average structure of  $\text{TlReO}_4$  has been described in terms of the rotations of the  $\text{ReO}_4$  tetrahedra, possessing rotations associated with the *irreps*  $\Gamma_3^+$  and  $\text{M}_4^+$ . In the monoclinic  $P2_1/c$  structure,  $\text{TlReO}_4$  has two distinct  $\text{ReO}_4$  tetrahedra sites rotated about the  $b$ -axis (associated with the *irrep*  $\Gamma_3^+$ , analogous to the  $I4_1/a \rightarrow I4_1/amd$  phase transition), and one distinct  $\text{ReO}_4$  tetrahedra site rotated about the  $a$ -axis (associated with the *irrep*  $\text{M}_4^+$ , analogous to the  $Pnma \rightarrow I4_1/amd$  phase transition). The same *irreps* are identified in  $\text{TlTcO}_4$ . However, the opposite trend is observed, with two distinct  $\text{TcO}_4$  tetrahedra sites rotated about the  $a$ -axis, and one distinct  $\text{TcO}_4$  tetrahedra site rotated about the  $b$ -axis. This explains why despite  $\text{TlTcO}_4$  and  $\text{TlReO}_4$  exhibiting the same monoclinic  $P2_1/c$  local structure, an ‘averaging out’ of the rotations of the  $\text{BO}_4$  tetrahedra leads to the observation of different long-range average structures.

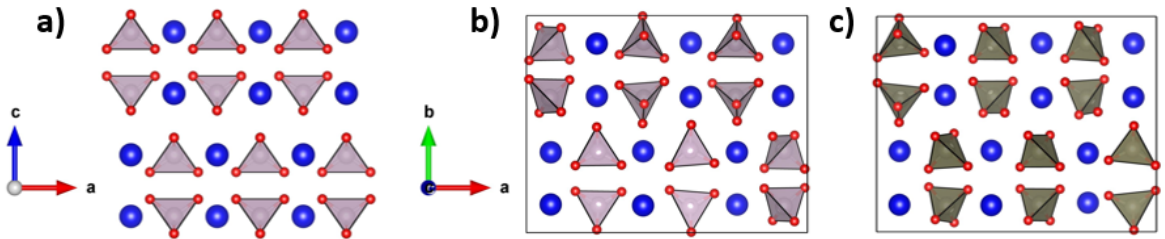


Figure 6.18: (a) The scheelite-type aristotype in the tetragonal  $I4_1/amd$  structure. (b) The monoclinic  $P2_1/c$  structure of  $\text{TlTcO}_4$  derived from the neutron pair distribution function refinements. Looking along the top row, one  $\text{TcO}_4$  tetrahedra is rotated about the  $b$ -axis, whereas two are rotated about the  $a$ -axis. (c) The monoclinic  $P2_1/c$  structure of  $\text{TlReO}_4$  derived from the Saura Múzquiz *et al.* neutron pair distribution function refinements.<sup>2</sup> Looking along the top row, one  $\text{ReO}_4$  tetrahedra is rotated about the  $a$ -axis, whereas two are rotated about the  $b$ -axis.

A further difference between the  $\text{TlTcO}_4$  and  $\text{TlReO}_4$  materials is their phase transition behaviour upon heating. Whereas  $\text{TlTcO}_4$  undergoes a  $Pnma \rightarrow I4_1/amd$  phase transition,  $\text{TlReO}_4$  undergoes a first order re-entrant phase transition from  $I4_1/a \rightarrow P2_1/c \rightarrow I4_1/a$ . This was reasoned due to a change in the correlation length of the  $\text{Tl}^+$   $6s^2$  lone pairs.<sup>2</sup> At low temperatures, the unit cell is significantly contracted such that the lone pairs are only correlated on the short-range scale, leading to the observed ‘average’ tetragonal  $I4_1/a$  structure. Upon heating, the lattice expands enough such that there is enough space to allow the lone pairs to align macroscopically, resulting in a lowering of symmetry and an adoption of the short-range local  $P2_1/c$  structure on the long-range average scale. This lone pair ordering is then lost upon further heating, as the increased thermal motion of the  $\text{ReO}_4$  tetrahedra cause the ordering of the lone pairs to be lost. This is commonly referred to as ‘melting’ of the lone pairs by analogy with the melting of ice, and is dependent on thermal motion.<sup>70</sup>

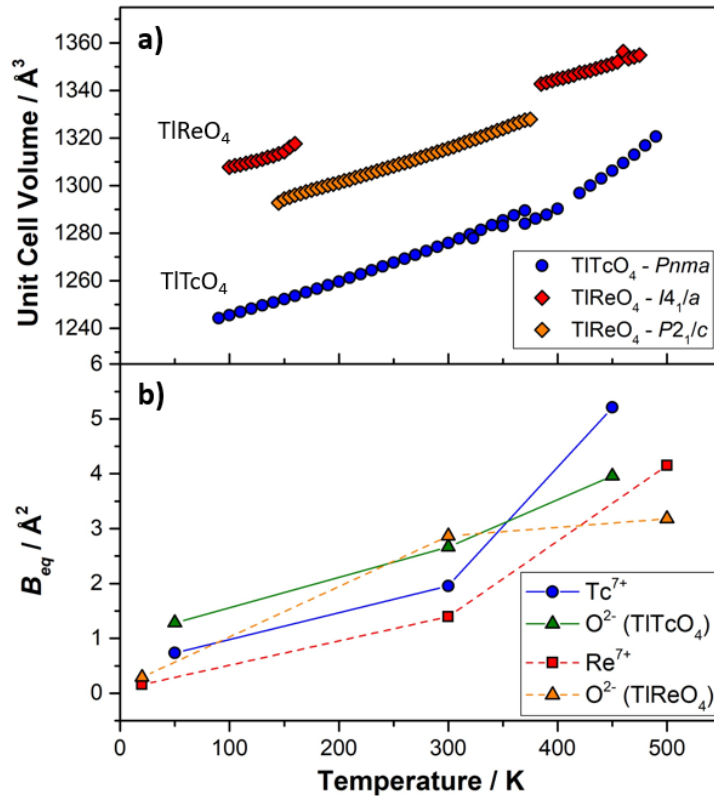


Figure 6.19: (a) The unit cell volumes of  $\text{TlTcO}_4$  and  $\text{TlReO}_4$  taken from the studies by Kennedy *et al.* and Chay *et al.*, respectively.<sup>34,38</sup> Data were taken from the Rietveld refinements of synchrotron X-ray diffraction data, with the unit cell volume tripled to allow for a comparison between the orthorhombic  $Pnma$ , tetragonal  $I4_1/a$ , and monoclinic  $P2_1/c$  structures. (b) The atomic displacement parameters of  $\text{Tc}^{7+}$  and  $\text{O}^{2-}$  in  $\text{TlTcO}_4$  compared with that of  $\text{Re}^{7+}$  and  $\text{O}^{2-}$  in  $\text{TlReO}_4$ . Data were derived from the neutron pair distribution function fits to the monoclinic  $P2_1/c$  structure, and from Saura-Múzquiz *et al.*<sup>2</sup>

To investigate this further, the thermal expansion of the unit cell volumes of TlTcO<sub>4</sub> and TlReO<sub>4</sub> were compared. This comparison was performed using SXRD data presented in previous work by the author's research group,<sup>2,34,38</sup> as the high peak-shape resolution allowed for accurate quantification of the lattice parameters and unit cell volumes. These are plotted in Figure 6.19a, with the orthorhombic *Pnma* and tetragonal *I4<sub>1</sub>/a* unit cell volumes multiplied by three to account for the tripling of the *a*-axis in the monoclinic *P2<sub>1</sub>/c* structure. It is noted that the unit cell volume of TlTcO<sub>4</sub> is ~5% smaller than TlReO<sub>4</sub>, reflecting the difference in IR of the Tl<sup>7+</sup> and Re<sup>7+</sup> cations. Therefore, it is possible that the larger unit cell of TlReO<sub>4</sub> allows for the macroscopic alignment of the Tl<sup>+</sup> 6s<sup>2</sup> lone pairs, whereas the more contracted structure of TlTcO<sub>4</sub> does not.

Despite the more contracted unit cell volume of TlTcO<sub>4</sub>, it is still possible for the Tl<sup>+</sup> 6s<sup>2</sup> lone pairs to align once the structure has undergone thermal expansion. However, as seen in TlReO<sub>4</sub>, increased thermal motion of the rigid ReO<sub>4</sub> tetrahedra units can cause this ordering to be lost. To compare the thermal motion of the TcO<sub>4</sub> and ReO<sub>4</sub> tetrahedra in their respective structures, the  $B_{high}$  values for both TlTcO<sub>4</sub> and TlReO<sub>4</sub> at different temperatures were compared in the NPDF fits of the monoclinic *P2<sub>1</sub>/c* structure (Figure 6.19b). This revealed consistently more thermal motion in the TcO<sub>4</sub> tetrahedra of TlTcO<sub>4</sub> than in the ReO<sub>4</sub> tetrahedra of TlReO<sub>4</sub>. This is presumably due to the Tc–O bonds being less polarisable than the Re–O bonds, which has been implied in similar Tc<sup>7+</sup> and Re<sup>7+</sup> studies.<sup>21</sup> Furthermore, Tc<sup>7+</sup> has almost half of the atomic mass of Re<sup>7+</sup> (98 *vs.* 186 amu), potentially leading to greater sensitivity to temperature and larger thermal displacements. Although thermal expansion of the structure may facilitate long-range ordering of the Tl<sup>+</sup> 6s<sup>2</sup> lone pairs, the increased thermal motion of the TcO<sub>4</sub> tetrahedra appears to inhibit the lone pairs ordering at elevated temperatures. Therefore, a combination of the smaller unit cell volume and the more thermal motion of the TcO<sub>4</sub> tetrahedra may potentially explain why TlTcO<sub>4</sub> does not exhibit a re-entrant phase transition.

## 6.5 Conclusions and Future Work

The present work provides an accurate description of both the long-range average and short-range local structures of two  $ABO_4$  materials that exhibit the orthorhombic  $Pnma$  pseudo-scheelite structure type at room temperature:  $CsReO_4$  and  $TlTcO_4$ . Both materials displayed unusual features in their long-range average Rietveld refinements that required the use of either X-ray or neutron pair distribution function analysis to fully describe.

An X-ray total scattering study of  $CsReO_4$  identified a  $Pnma \rightarrow I4_1/a$  phase transition that occurs at  $\sim 450$  K. An increase in the ADPs between 400–450 K upon approaching the phase transition suggest the possibility of a two-phase region. However, due to the lack of peak-shape resolution afforded by the I15-1 beamline at the Diamond Light Source, this was unable to be explored further. A linear relationship was also identified between the spontaneous strains of the orthorhombic  $Pnma$  structure and the temperature, suggesting that although the  $Pnma \rightarrow I4_1/a$  phase transition is required to be first order (due to the different rotations of the  $ReO_4$  tetrahedra), it displays characteristics that resemble that of a second order phase transition.

XPDF studies of  $CsReO_4$  revealed symmetry lowering in the local structure, with features in the low- $r$  region not accounted for by fitting to the long-range average structural models. In observing the XPDF data between 400 and 550 K, little change was observed despite a change in long-range average symmetry. Several features were also modelled differently by the XRD and XPDF fits, such as the  $Re^{7+}$  ADPs and the Re–O bond distances. The mismatch between the two length scales was presumed to be the result of incoherent  $ReO_4$  translations that allowed for the introduction of multiple Re–Re distances, while keeping the Re–O bonds constant in the XPDF. This model could also explain the increase in the  $Re^{7+}$   $B_{eq}$  modelled in the Rietveld refinements. Further work using NPD and NPDF would be required to confirm the mechanism of such local phenomena due to its sensitivity to the oxygen anionic sublattice. It is also possible that these incoherent tetrahedra translations initially occur with a preferred orientation, with a difference in the  $a$  lattice parameter evident in the XPDF at  $\sim 550$  K, before a similar

change is observed in the  $c$  lattice parameter at  $\sim 700$  K. The nature of these displacements could be probed by using other local structure characterisation techniques, such as solid state NMR spectroscopy, as well as identifying their directional nature using 3D- $\Delta$ PDF.<sup>71</sup>

A neutron total scattering study of  $\text{TlTcO}_4$  identified an orthorhombic-to-tetragonal phase transition, which was tentatively ascribed as  $Pnma \rightarrow I4_1/amd$  due to the apparent extinction of the (114) reflection at 600 K in the NPD. The NPD data showed anomalous behaviour in the oxygen ADPs and Tc–O bond lengths, indicating that local disorder is present. A follow-up XPDF study on  $\text{TlTcO}_4$  could be beneficial due to the fast acquisition of data. This could be used to understand whether this local disordering is similar to that observed in  $\text{CsReO}_4$  and  $\text{RbReO}_4$ ,<sup>1</sup> or whether the  $\text{Tl}^+$   $6s^2$  lone pair causes additional local features and disordering to occur. It is noted the isosymmetric  $Pnma \rightarrow Pnma$  phase transition reported previously may attribute additional difficulties to these measurements.<sup>38</sup>

NPDF studies of  $\text{TlTcO}_4$  identified the  $\text{TcO}_4$  tetrahedra to be rigid across the entire temperature range. This resulted in the identification of the local symmetry to be monoclinic  $P2_1/c$ , in line with other lone pair-bearing  $A$ -site cations such as  $\text{TlReO}_4$ ,<sup>2</sup> as well as  $\text{PbWO}_4$  and  $\text{BiVO}_4$  described in Chapter 5. Although each of these materials contain lone pair-bearing cations, their local structures distort in very different ways depending on the size of the  $\text{AO}_8$  polyhedra and the polarisability of the  $B$ –O bonds. Similar observations are also used to explain the apparent differences between  $\text{TlTcO}_4$  and  $\text{TlReO}_4$  despite their similar IR. Each material possesses the same monoclinic  $P2_1/c$  structure, however the bonding requirements of the  $B$ -site cation cause the  $\text{BO}_4$  tetrahedra to rotate in different ways, leading to the observation of different long-range average structures. The smaller unit cell volume and increased thermal motion in  $\text{TlTcO}_4$  compared to  $\text{TlReO}_4$  was used to explain why  $\text{TlTcO}_4$  does not undergo a re-entrant phase transition like its  $\text{TlReO}_4$  counterpart.

Observations of the differences between  $\text{TlTcO}_4$  and  $\text{TlReO}_4$  demonstrate the importance of understanding the assumptions made when performing work with chemical surrogates. As stated previously, the chemical behaviour of  $\text{Tc}^{7+}$  and  $\text{Re}^{7+}$  are expected to be similar due to their same oxidation state and similar IR. However, the consideration of other factors, such as the contribution of their  $4d$  and  $5d$  orbitals and susceptibility to thermal motion, can effect their behaviour and lead to different chemical phenomena. It is important to fully understand the differences between  $\text{Tc}^{7+}$  and  $\text{Re}^{7+}$  and their behaviour in materials capable of safely sequestering radioactive waste.



# Bibliography

- (1) Marlton, F. P.; Mullens, B. G.; Chater, P. A.; Kennedy, B. J. Tetrahedral displacive disorder in the scheelite-type oxide  $\text{RbReO}_4$ . *Inorganic Chemistry* **2022**, *61*, 15130–15137.
- (2) Saura-Múzquiz, M.; Marlton, F. P.; Mullens, B. G.; Manjón-Sanz, A. M.; Neufeind, J. C.; Everett, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Understanding the re-entrant phase transition in a non-magnetic scheelite. *Journal of the American Chemical Society* **2022**, *144*, 15612–15621.
- (3) US Office of Nuclear Energy. Five Fast Facts About Nuclear Energy, <https://www.energy.gov/ne/articles/5-fast-facts-about-nuclear-energy> Last accessed on 2023-09-30.
- (4) Xie, W.; Koyama, M. Theoretical design of a technetium-like alloy and its catalytic properties. *Chemical Science* **2019**, *10*, 5461–5469.
- (5) Skomurski, F. N.; Rosso, K. M.; Krupka, K. M.; McGrail, B. P. Technetium incorporation into hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ). *Environmental Science & Technology* **2010**, *44*, 5855–5861.
- (6) Meyer, R.; Arnold, W.; Case, F.; O’Kelley, G. Solubilities of Tc (IV) oxides. *Radiochimica Acta* **1991**, *55*, 11–18.
- (7) Lieser, K.; Bauscher, C. Technetium in the hydrosphere and in the geosphere. Pt. 1. Chemistry of technetium and iron in natural waters and influence of the redox potential on the sorption of technetium. *Radiochimica Acta* **1987**, *42*.
- (8) Taylor, C. D. Surface segregation and adsorption effects of iron–technetium alloys from first-principles. *Journal of Nuclear Materials* **2011**, *408*, 183–187.

- (9) Keiser Jr, D.; Abraham, D.; Richardson Jr, J. Influence of technetium on the microstructure of a stainless steel–zirconium alloy. *Journal of Nuclear Materials* **2000**, *277*, 333–338.
- (10) Burton-Pye, B. P.; Radivojevic, I.; McGregor, D.; Mbomekalle, I. M.; Lukens Jr, W. W.; Francesconi, L. C. Photoreduction of  $^{99}\text{Tc}$  pertechnetate by nanometer-sized metal oxides: New strategies for formation and sequestration of low-valent technetium. *Journal of the American Chemical Society* **2011**, *133*, 18802–18815.
- (11) Pegg, I. L. Behavior of technetium in nuclear waste vitrification processes. *Journal of Radioanalytical and Nuclear Chemistry* **2015**, *305*, 287–292.
- (12) Jin, T.; Kim, D.; Tucker, A. E.; Schweiger, M. J.; Kruger, A. A. Reactions during melting of low-activity waste glasses and their effects on the retention of rhenium as a surrogate for technetium-99. *Journal of Non-Crystalline Solids* **2015**, *425*, 28–45.
- (13) Kang, K.; Shen, N.; Wang, Y.; Li, L.; Zhang, M.; Zhang, X.; Lei, L.; Miao, X.; Wang, S.; Xiao, C. Efficient sequestration of radioactive  $^{99}\text{TcO}_4^-$  by a rare 3-fold interlocking cationic metal-organic framework: A combined batch experiments, pair distribution function, and crystallographic investigation. *Chemical Engineering Journal* **2022**, *427*, 130942.
- (14) Dickson, J. O.; Harsh, J. B.; Lukens, W. W.; Pierce, E. M. Perrhenate incorporation into binary mixed sodalites: The role of anion size and implications for technetium-99 sequestration. *Chemical Geology* **2015**, *395*, 138–143.
- (15) Favre-Réguillon, A.; Draye, M.; Cote, G.; Czerwinsky, K. R. Insights in uranium extraction from spent nuclear fuels using dicyclohexano-18-crown-6 – Fate of rhenium as technetium homolog. *Separation and Purification Technology* **2019**, *209*, 338–342.
- (16) Fei, H.; Bresler, M. R.; Oliver, S. R. A new paradigm for anion trapping in high capacity and selectivity: Crystal-to-crystal transformation of cationic materials. *Journal of the American Chemical Society* **2011**, *133*, 11110–11113.

## BIBLIOGRAPHY

---

- (17) McCloy, J. S.; Riley, B. J.; Goel, A.; Liezers, M.; Schweiger, M. J.; Rodriguez, C. P.; Hrma, P.; Kim, D.-S.; Lukens, W. W.; Kruger, A. A. Rhenium solubility in borosilicate nuclear waste glass: Implications for the processing and immobilization of technetium-99. *Environmental Science & Technology* **2012**, *46*, 12616–12622.
- (18) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **1976**, *32*, 751–767.
- (19) Lukens, W. W.; McKeown, D. A.; Buechele, A. C.; Muller, I. S.; Shuh, D. K.; Pegg, I. L. Dissimilar behavior of technetium and rhenium in borosilicate waste glass as determined by X-ray absorption spectroscopy. *Chemistry of Materials* **2007**, *19*, 559–566.
- (20) Gan, H.; McKeown, D. A.; Xie, X.; Pegg, I. L. Assessment of rhenium as a surrogate for technetium in Hanford low activity waste borosilicate glasses: Speciation, solubility, and redox effects. *International Journal of Applied Glass Science* **2023**, *14*, 97–112.
- (21) Reynolds, E. M.; Yu, M.; Thorogood, G. J.; Brand, H. E.; Poineau, F.; Kennedy, B. J. Thermal expansion of ammonium pertechnetate and ammonium perrhenate. *Journal of Solid State Chemistry* **2019**, *274*, 64–68.
- (22) Avdeev, M.; Thorogood, G. J.; Carter, M. L.; Kennedy, B. J.; Ting, J.; Singh, D. J.; Wallwork, K. S. Antiferromagnetism in a technetium oxide. Structure of  $\text{CaTcO}_3$ . *Journal of the American Chemical Society* **2011**, *133*, 1654–1657.
- (23) Rodriguez, E. E.; Poineau, F.; Llobet, A.; Kennedy, B. J.; Avdeev, M.; Thorogood, G. J.; Carter, M. L.; Seshadri, R.; Singh, D. J.; Cheetham, A. K. High temperature magnetic ordering in the 4d perovskite  $\text{SrTcO}_3$ . *Physical Review Letters* **2011**, *106*, 067201.
- (24) Thorogood, G. J.; Avdeev, M.; Carter, M. L.; Kennedy, B. J.; Ting, J.; Wallwork, K. S. Structural phase transitions and magnetic order in  $\text{SrTcO}_3$ . *Dalton Transactions* **2011**, *40*, 7228–7233.

- (25) Saura-Múzquiz, M.; Mullens, B. G.; Maynard-Casely, H. E.; Kennedy, B. J. Neutron diffraction study of the monoclinic–tetragonal phase transition in  $\text{NdNbO}_4$  and  $\text{NdTaO}_4$ . *Dalton Transactions* **2021**, 50, 11485–11497.
- (26) Mullens, B. G.; Avdeev, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Insights into the structural variations in  $\text{Sm}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  and  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  combined experimental and computational studies. *Dalton Transactions* **2021**, 50, 9103–9117.
- (27) Mullens, B. G.; Saura-Múzquiz, M.; Marlton, F. P.; Avdeev, M.; Brand, H. E.; Mondal, S.; Vaitheeswaran, G.; Kennedy, B. J. Beyond the ionic radii: A multifaceted approach to understand differences between the structures of  $\text{LnNbO}_4$  and  $\text{LnTaO}_4$  fergusonites. *Journal of Alloys and Compounds* **2023**, 930, 167399.
- (28) Boyd, G. Technetium and promethium. *Journal of Chemical Education* **1959**, 36, 1–14.
- (29) Faggiani, R.; Gillespie, R.; Lock, C.; Pocé, J. The structure of ammonium pertechnetate at 295, 208 and 141 K. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* **1980**, 36, 231–233.
- (30) Krebs, B.; Hasse, K.-D. Refinements of the crystal structures of  $\text{KTcO}_4$ ,  $\text{KReO}_4$  and  $\text{OsO}_4$ . The bond lengths in tetrahedral oxoanions and oxides of  $d^0$  transition metals. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* **1976**, 32, 1334–1337.
- (31) Weaver, J.; Soderquist, C. Z.; Washton, N. M.; Lipton, A. S.; Gassman, P. L.; Lukens, W. W.; Kruger, A. A.; Wall, N. A.; McCloy, J. S. Chemical trends in solid alkali pertechnetates. *Inorganic Chemistry* **2017**, 56, 2533–2544.
- (32) McDonald, B.; Tyson, G. The crystal structure of caesium, ammonium and potassium pertechnetates. *Acta Crystallographica* **1962**, 15, 87–87.
- (33) Kanellakopulos, B. Zur kenntnis der hochtemperaturmodifikation einiger verbindungen des typs  $\text{Me}^I\text{XO}_4$  ( $\text{Me} = \text{Cs, Tl}$ ;  $\text{X} = \text{Re, Tc, Cl}$ ). *Journal of Inorganic and Nuclear Chemistry* **1966**, 28, 813–816.

## BIBLIOGRAPHY

---

- (34) Chay, C.; Avdeev, M.; Brand, H. E.; Injac, S.; Whittle, T. A.; Kennedy, B. J. Crystal structures and phase transition behaviour in the 5d transition metal oxides  $A\text{ReO}_4$  ( $A = \text{Ag, Na, K, Rb, Cs}$  and  $\text{Tl}$ ). *Dalton Transactions* **2019**, 48, 17524–17532.
- (35) Kennedy, B. J. Structure of  $\text{ABi}_2\text{Nb}_2\text{O}_9$  ( $A = \text{Sr, Ba}$ ): Refinement of powder neutron diffraction data. *Journal of Solid State Chemistry* **1996**, 126, 135–141.
- (36) Bastide, J. Systématique simplifiée des composés  $\text{ABX}_4$  ( $X = \text{O}^{2-}, \text{F}^-$ ) et evolution possible de leurs structures cristallines sous pression. *Journal of Solid State Chemistry* **1987**, 71, 115–120.
- (37) Errandonea, D.; Manjon, F. J. Pressure effects on the structural and electronic properties of  $\text{ABX}_4$  scintillating crystals. *Progress in Materials Science* **2008**, 53, 711–773.
- (38) Kennedy, B. J.; Injac, S.; Thorogood, G. J.; Brand, H. E.; Poineau, F. Structures and phase transitions in pertechnates. *Inorganic Chemistry* **2019**, 58, 10119–10128.
- (39) Rögner, P.; Range, K.-J. The crystal structure of  $\beta$ -thallium perhenate. *Zeitschrift für Anorganische und Allgemeine Chemie* **1993**, 619, 1017–1022.
- (40) Jayaraman, A.; Kourouklis, G.; Fleming, R.; Van Uitert, L. Temperature-induced phase transitions in  $\text{TlReO}_4$ : A Raman spectroscopic and X-ray diffraction study. *Physical Review B* **1988**, 37, 664.
- (41) De Waal, D.; Kiefer, W. Raman investigation of the low temperature phase transitions in monoclinic  $\text{TlReO}_4$ . *Zeitschrift für Anorganische und Allgemeine Chemie* **2004**, 630, 127–130.
- (42) Errandonea, D.; Kumar, R. S.; Ma, X.; Tu, C. High-pressure X-ray diffraction study of  $\text{SrMoO}_4$  and pressure-induced structural changes. *Journal of Solid State Chemistry* **2008**, 181, 355–364.
- (43) Maczka, M.; Kokanyan, E.; Hanuza, J. Vibrational study and lattice dynamics of disordered  $\text{NaBi}(\text{WO}_4)_2$ . *Journal of Raman Spectroscopy* **2005**, 36, 33–38.

- (44) Rabuffetti, F. A.; Culver, S. P.; Suescun, L.; Brutchey, R. L. Structural disorder in  $\text{AMoO}_4$  ( $A = \text{Ca}, \text{Sr}, \text{Ba}$ ) scheelite nanocrystals. *Inorganic Chemistry* **2014**, *53*, 1056–1061.
- (45) Culver, S. P.; Brutchey, R. L. Thermally activated rotational disorder in  $\text{CaMoO}_4$  nanocrystals. *CrystEngComm* **2016**, *18*, 4485–4488.
- (46) Lacorre, P.; Pautonnier, A.; Coste, S.; Barré, M.; Béchade, E.; Suard, E. Cationic order–disorder in double scheelite type oxides: The case study of fergusonite  $\text{La}_2\text{SiMoO}_8$ . *Inorganic Chemistry* **2021**, *60*, 2623–2633.
- (47) Basham, M.; Filik, J.; Wharmby, M. T.; Chang, P. C.; El Kassaby, B.; Gerring, M.; Aishima, J.; Levik, K.; Pulford, B. C.; Sikharulidze, I. Data analysis workbench (DAWN). *Journal of Synchrotron Radiation* **2015**, *22*, 853–858.
- (48) Juhás, P.; Davis, T.; Farrow, C. L.; Billinge, S. J. PDFgetX3: A rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions. *Journal of Applied Crystallography* **2013**, *46*, 560–566.
- (49) Yang, X.; Juhas, P.; Farrow, C. L.; Billinge, S. J. xPDFsuite: An end-to-end software solution for high throughput pair distribution function transformation, visualization and analysis. *arXiv preprint arXiv:1402.3163* **2014**.
- (50) Huq, A.; Kirkham, M.; Peterson, P. F.; Hodges, J. P.; Whitfield, P. S.; Page, K.; Hügle, T.; Iverson, E. B.; Parizzi, A.; Rennich, G. POWGEN: Rebuild of a third-generation powder diffractometer at the Spallation Neutron Source. *Journal of Applied Crystallography* **2019**, *52*, 1189–1201.
- (51) Juhás, P.; Louwen, J. N.; Eijck, L. v.; Vogt, E. T.; Billinge, S. J. PDFgetN3: Atomic pair distribution functions from neutron powder diffraction data using ad hoc corrections. *Journal of Applied Crystallography* **2018**, *51*, 1492–1497.
- (52) Coelho, A. A. TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++. *Journal of Applied Crystallography* **2018**, *51*, 210–218.
- (53) Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* **2011**, *44*, 1272–1276.

## BIBLIOGRAPHY

---

- (54) Range, K.-J.; Rögner, P. An X-Ray, Raman and IR study of  $\alpha$ -CsReO<sub>4</sub>, the high-temperature modification of cesium perrhenate. *Zeitschrift für Naturforschung B* **1992**, *47*, 1513–1520.
- (55) Injac, S.; Yuen, A. K.; Avdeev, M.; Wang, C.-H.; Turner, P.; Brand, H. E.; Kennedy, B. J. Structural and magnetic studies of  $ABO_4$ -type ruthenium and osmium oxides. *Inorganic Chemistry* **2020**, *59*, 2791–2802.
- (56) Stokes, H. T.; Orden, S. v.; Campbell, B. J. ISOSUBGROUP: An internet tool for generating isotropy subgroups of crystallographic space groups. *Journal of Applied Crystallography* **2016**, *49*, 1849–1853.
- (57) Lukas, W.; Gaune-Escard, M. Temperatures and enthalpies of melting of alkali-metal perrhenates. *The Journal of Chemical Thermodynamics* **1982**, *14*, 593–597.
- (58) Smith Jr, W. T.; Long, S. H. The salts of perrhenic acid. I. The alkali metals and ammonium. *Journal of the American Chemical Society* **1948**, *70*, 354–356.
- (59) Carpenter, M. A.; Salje, E. K.; Graeme-Barber, A. Spontaneous strain as a determinant of thermodynamic properties for phase transitions in minerals. *European Journal of Mineralogy* **1998**, 621–691.
- (60) Knox, K.; Bozin, E.; Malliakas, C.; Kanatzidis, M.; Billinge, S. Local off-centering symmetry breaking in the high-temperature regime of SnTe. *Physical Review B* **2014**, *89*, 014102.
- (61) Amarasinghe, D. K.; Perera, S. S.; Rabuffetti, F. A. Rotational disorder in scheelite-type  $NaRE(MO_4)_2$  ( $RE$  = Rare-Earth, Y;  $M$  = Mo, W). *Crystal Growth & Design* **2020**, *20*, 3442–3448.
- (62) Howard, C. J.; Stokes, H. T. Group-theoretical analysis of octahedral tilting in perovskites. *Acta Crystallographica Section B: Structural Science* **1998**, *54*, 782–789.
- (63) Culbertson, C. M.; Flak, A. T.; Yatskin, M.; Cheong, P. H.-Y.; Cann, D. P.; Dolgos, M. R. Neutron total scattering studies of group I titanates ( $ATiO_3$ ,  $A^{2+}$  = Mg, Ca, Sr, Ba). *Scientific Reports* **2020**, *10*, 3729.

- (64) Sánchez-Martín, J.; Errandonea, D.; Pellicer-Porres, J.; Vázquez-Socorro, D.; Martínez-García, D.; Achary, S. N.; Popescu, C. Phase transitions of  $\text{BiVO}_4$  under high pressure and high temperature. *The Journal of Physical Chemistry C* **2022**, *126*, 7755–7763.
- (65) Garg, A.; Errandonea, D.; Rodríguez-Hernández, P.; Muñoz, A. High-pressure monoclinic–monoclinic transition in fergusonite-type  $\text{HoNbO}_4$ . *Journal of Physics: Condensed Matter* **2021**, *33*, 195401.
- (66) Dutta, M.; Pal, K.; Etter, M.; Waghmare, U. V.; Biswas, K. Emphasisis in cubic  $(\text{SnSe})_{0.5}(\text{AgSbSe}_2)_{0.5}$ : Dynamical off-centering of anion leads to low thermal conductivity and high thermoelectric performance. *Journal of the American Chemical Society* **2021**, *143*, 16839–16848.
- (67) Xie, H.; Bozin, E. S.; Li, Z.; Abeykoon, M.; Banerjee, S.; Male, J. P.; Snyder, G. J.; Wolverton, C.; Billinge, S. J.; Kanatzidis, M. G. Hidden local symmetry breaking in silver diamondoid compounds is root cause of ultralow thermal conductivity. *Advanced Materials* **2022**, *34*, 2202255.
- (68) Gussev, I. M.; O’Quinn, E. C.; Baldinozzi, G.; Neuefeind, J.; Ewing, R. C.; Zhang, F.; Lang, M. Local order of orthorhombic weberite-type  $\text{Y}_3\text{TaO}_7$  as determined by neutron total scattering and density functional theory calculations. *Acta Materialia* **2020**, *196*, 704–709.
- (69) Granzin, J. Refinement of the crystal structures of  $\text{RbClO}_4$  and  $\text{CsClO}_4$ . *Zeitschrift für Kristallographie-Crystalline Materials* **1988**, *184*, 157–160.
- (70) Shoemaker, D. P.; Seshadri, R.; Hector, A. L.; Llobet, A.; Proffen, T.; Fennie, C. J. Atomic displacements in the charge ice pyrochlore  $\text{Bi}_2\text{Ti}_2\text{O}_6\text{O}'$  studied by neutron total scattering. *Physical Review B* **2010**, *81*, 144113.
- (71) Roth, N.; Iversen, B. B. Solving the disordered structure of  $\beta\text{-Cu}_{2-x}\text{Se}$  using the three-dimensional difference pair distribution function. *Acta Crystallographica Section A: Foundations and Advances* **2019**, *75*, 465–473.



## Chapter 7

# Adventures Outside of Metal Oxides – Magnetism in $\text{CsMnF}_4$

*This chapter is adapted from the following manuscript:*

- Mullens, B.G.; Saura-Múzquiz, M.; Yuen, A.K.L.; Bennett, C.J.; Avdeev, M.; Brand, H.E.A.; Kennedy, B.J.; Structural and Magnetic Studies of the 2D Planar Ferromagnet  $\text{CsMnF}_4$ .

*Manuscript in Preparation.*



## 7.1 Introduction: CsMnF<sub>4</sub> as a Spintronic Material

The study of spintronics (a portmanteau of *spin transport electronics*) is based on understanding the role of the intrinsic spin of electrons and their associated magnetic moment on the structure of solid state materials.<sup>1</sup> By incorporating both the charge and spin of electrons, an extra degree of freedom may be realised, leading to greater efficiency in data storage and transfer.<sup>2–4</sup> The study of spintronic devices has led to the discovery of many different phenomena, such as giant magnetoresistance used to read data in hard disk drives (the subject of the Nobel Prize in Physics in 2007),<sup>5–7</sup> as well as the quantum Hall effect used to benchmark electrical resistance with extreme precision.<sup>8</sup> The study of such phenomena is fertile ground for novel science in solid state and condensed matter chemistry and physics.

A feature of solid state chemistry is that the desired topology of particular magnetic phenomena can be synthesised by utilising common structural motifs. This ranges from the corner-sharing tetrahedra in Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlores used to study spin-ice phenomena,<sup>9,10</sup> to 1D ferromagnetic chains found in Li<sub>3</sub>Cu<sub>2</sub>SbO<sub>6</sub> Kagomé lattices.<sup>11</sup> Layered perovskites have also been used to study novel 2D magnetism, as the dominant magnetic interactions only occur in a particular crystallographic plane.<sup>12–14</sup> Materials such as CsMnF<sub>4</sub> have been identified as potentially possessing nodal rings (a band crossing at the Fermi level of the material),<sup>15</sup> a feature of interest in developing topological materials and further advanced spintronic devices due to their ultra-high electron velocities.<sup>16–18</sup>

The layered perovskite family of AMnF<sub>4</sub> materials have been well studied due to their interesting magnetic properties. These structures consist of layers of corner-sharing MnF<sub>6</sub> octahedra separated by layers of large, ionically-bound A<sup>+</sup> cations (Figure 7.1).<sup>15</sup> Early studies identified that the size of the A<sup>+</sup> ion plays a role in the structure of the AMnF<sub>4</sub> materials. AMnF<sub>4</sub> materials with smaller A<sup>+</sup> cations (A<sup>+</sup> = K, Rb) crystallise in the monoclinic *P*2<sub>1</sub>/*a* space group, whereas larger A<sup>+</sup> cations (A<sup>+</sup> = Cs) crystallise in the higher-symmetry tetragonal *P*4/*nmm* space group.<sup>19,20</sup> It is predicted that the larger A<sup>+</sup> cation leads to a larger spacing between the MnF<sub>6</sub> layers, reducing their interaction through electrostatic forces that can rotate the MnF<sub>6</sub> octahedra and lead to a lowering

of symmetry.<sup>21</sup> This was illustrated by Morón *et al.*, who demonstrated that the MnF<sub>6</sub> octahedra found in the materials with smaller  $A^+$  cations had three sets of Mn–F bond lengths, whereas  $A^+ = \text{Cs}$  only had two sets. It was proposed that the size of the  $A^+$  cation may play a role in moderating the Jahn-Teller effects present in the MnF<sub>6</sub> octahedra.

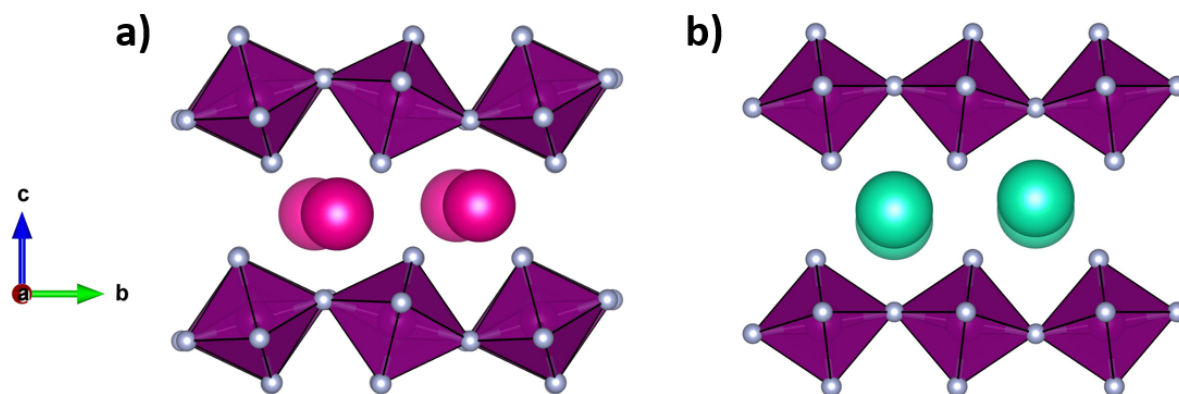


Figure 7.1: Crystal structures of (a) RbMnF<sub>4</sub> in the space group  $P2_1/a$ , and (b) CsMnF<sub>4</sub> in the space group  $P4/nmm$ . The pink spheres represent Rb<sup>+</sup>, the cyan spheres represent Cs<sup>+</sup>, and the purple octahedra represent the MnF<sub>6</sub> octahedra. Note the difference in Mn–F–Mn bond angle between the two structures.

Differences have been noted in the magnetic behaviour of the  $AMnF_4$  structures. Both KMnF<sub>4</sub> and RbMnF<sub>4</sub> order antiferromagnetically, with a Néel temperature ( $T_N$ ) of 5.2 and 3.7 K respectively.<sup>19,22</sup> Similar studies of CsMnF<sub>4</sub> concluded that the material is ferromagnetic below  $T_C = 18.9$  K.<sup>23</sup> This is unusual, as most 2D magnetic materials are reported to be antiferromagnetic.<sup>24,25</sup> Furthermore, the isotypic material CsFeF<sub>4</sub> orders antiferromagnetically with  $T_N = 235(15)$  K.<sup>23,26</sup> This has led some researchers to attempt to understand the difference between these materials and determine what structural features of CsMnF<sub>4</sub> allow it to order ferromagnetically.<sup>15,23</sup>

Magnetism in materials with transition metals is governed by the Goodenough-Kanamori-Anderson (GKA) rules.<sup>27–29</sup> These rules were proposed independently by John B. Goodenough, Junjiro Kanamori, and Philip W. Anderson in the mid-20th century and are frequently used to predict magnetic interactions in various materials.<sup>30</sup> The GKA rules describe the magnetic ordering that arises from superexchange interactions between neighbouring magnetic ions by considering their geometric arrangement and electronic configuration. The former governs the degree of orbital overlap between the  $d$  (or  $f$ ) orbitals of the magnetic ions and the corresponding anions or ligands influencing the

strength of the superexchange interaction, whereas the latter determines how effective magnetic moments can order based on the filling of the  $d$  (or  $f$ ) orbitals of the magnetic ion and its number of unpaired electrons. These rules have been used to explain the complex magnetism found in various materials.<sup>31,32</sup>

Due to the strong Jahn–Teller effect of the octahedrally-coordinated  $\text{Mn}^{3+}$  cation and the weak field  $\text{F}^-$  ligand, the  $\text{Mn}^{3+}$  fivefold degenerate  $3d$  orbitals are split into doubly degenerate  $e_g$  and triply degenerate  $t_{2g}$  levels with an energy splitting of  $\Delta_o = 1.36$  eV.<sup>15</sup> However, due to the compression of the  $\text{MnF}_6$  octahedra layers along the  $c$ -axis by the large  $\text{Cs}^+$  cations, the  $e_g$  and  $t_{2g}$  environments are further split, with the orbitals along the  $c$ -axis being higher in energy. This results in a 0.08 eV energy difference between the  $d_{xy}$  and the degenerate  $d_{xz}$  and  $d_{yz}$  orbitals, as well as a 0.18 eV splitting between the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals.<sup>15</sup> This is schematically shown in Figure 7.2. The weak field  $\text{F}^-$  ligand means  $\text{Mn}^{3+}$  exists in a high-spin ( $S = 2$ ) state with each of the  $d^4$  electrons unpaired. Based on the GKA rules, it is predicted that the difference in magnetic ordering between  $\text{CsMnF}_4$  and  $\text{CsFeF}_4$  is due to the unique Mn–F–Mn bond angles (as seen in Figure 1.10), which leads to a higher degree of overlap between the  $\text{Mn}^{3+}$   $3d$  and  $\text{F}^-$   $2p$  orbitals. The difference in Mn–F–Mn bond angles between  $\text{RbMnF}_4$  ( $147.6^\circ$ ) and  $\text{CsMnF}_4$  ( $162.5^\circ$ ) is evident in Figure 7.1.<sup>19,23</sup>

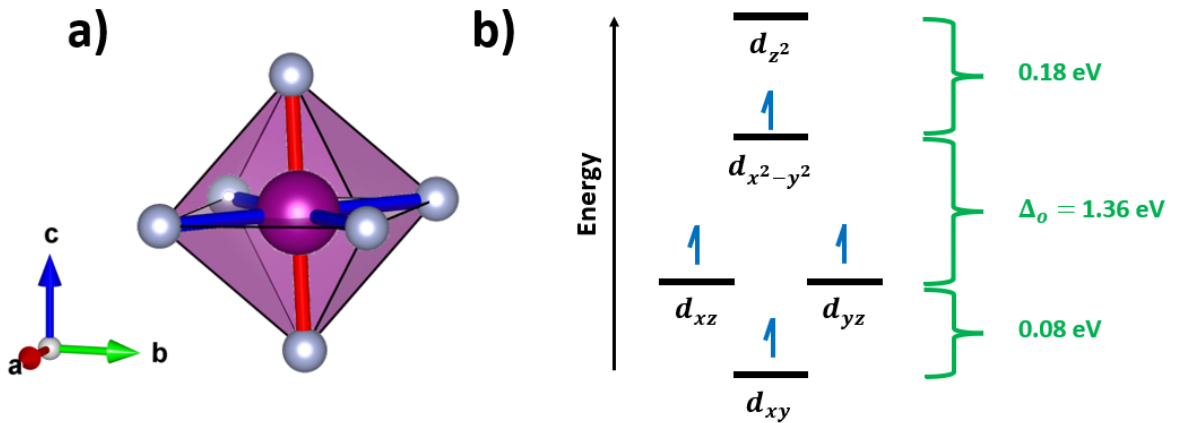


Figure 7.2: (a) The  $\text{MnF}_6$  octahedra in the  $\text{CsMnF}_4$  material. The red axial Mn–F bonds ( $\sim 1.8$  Å) are shorter than the blue equatorial Mn–F bonds ( $\sim 2.0$  Å). (b) The  $3d$  orbital energy diagram of  $\text{Mn}^{3+}$ . The energy levels are shown in black, with the high-spin electrons shown as blue half arrows. The energy splittings are shown in green, and are taken from Behatha *et al.*<sup>15</sup>

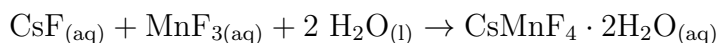
This chapter is separated into three short sections. Firstly, the synthesis of CsMnF<sub>4</sub> is outlined using a coprecipitation method, with the room temperature structure confirmed using a combination of laboratory XRD and NPD. Next, the magnetic properties of CsMnF<sub>4</sub> were investigated using a PPMS, where CsMnF<sub>4</sub> was found to exhibit ferromagnetic ordering below 20 K. Finally, variable temperature NPD was used to determine the intensities of the magnetic Bragg peaks below 20 K, which were used to identify the Shubnikov space group of its magnetic structure.

## 7.2 Synthesis Procedure and Experimental Methods

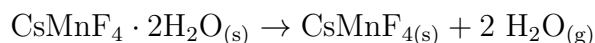
### 7.2.1 Sample Synthesis

*Caution! Hydrofluoric acid is extremely corrosive, as well as fatal if swallowed, in contact with skin, or if inhaled. All reactions must be carried out using plastic or Teflon equipment. No glass was used for the entirety of the synthesis.*

CsMnF<sub>4</sub> was synthesised by first coprecipitating a CsMnF<sub>4</sub>·2H<sub>2</sub>O precursor.<sup>33</sup> An appropriate amount of CsF (21.2674 g, Sigma-Aldrich, 99.9%) was dissolved in 70 mL of HF (20% w/w) to create a CsF solution (2 M). Separately, Mn<sub>2</sub>O<sub>3</sub> (2.2103 g, Sigma-Aldrich, 99%) was dissolved in 14 mL of HF (20% w/w) to create a MnF<sub>3</sub> solution (2 M). The two solutions were added together in a Cs<sup>+</sup>:Mn<sup>3+</sup> ratio of 5:1 and left to stand for one week.



The supernatant was decanted off and the resulting brown-violet crystals were washed three times with methanol. To dehydrate CsMnF<sub>4</sub>·2H<sub>2</sub>O, the crystals were transferred to a Teflon beaker and heated to 120 °C using a muffle furnace in a fumehood for 12 hours. The CsMnF<sub>4</sub> sample was stored in a sample vial sealed under argon to prevent rehydration.



### 7.2.2 X-Ray and Neutron Powder Diffraction

Samples were first characterised using laboratory XRD. The sample was loaded into a 0.2 mm diameter borosilicate glass capillary and mounted on a spinning capillary stage. Data were collected using a STOE STADI P X-ray diffractometer using Mo K $_{\alpha}$  radiation in Debye-Scherrer geometry over a range of  $5 \leq 2\theta \leq 55^{\circ}$  for 30 minutes.

NPD measurements were performed on the high resolution powder diffractometer Echidna at the OPAL reactor, operated by ANSTO.<sup>34</sup> A powdered sample was loaded into a 6 mm vanadium can under an argon atmosphere, before being loaded into a cryostat. An initial pattern was collected at room temperature using 1.62 Å wavelength neutrons. The sample was then cooled from room temperature to 3 K, with data collected over a range of  $5 \leq 2\theta \leq 160^{\circ}$  with an incident neutron wavelength of 1.62 and 2.44 Å. Data were then collected upon heating from 5–40 K with an incident neutron wavelength of 2.44 Å.

Structure refinements were carried out using the Rietveld method as implemented in the program TOPAS6.<sup>35</sup> The peak shapes were modelled using a pseudo-Voigt function, with the Thompson-Cox-Hastings model used to account for the asymmetry in the peaks.<sup>36</sup> The background of each pattern was estimated using a Chebyshev polynomial. The scale factor, lattice parameters, atomic coordinates, and ADPs were refined simultaneously with the peak profile parameters. In the final refinement cycle, all refined parameters were fully relaxed. The crystal structures were drawn in VESTA.<sup>37</sup> As TOPAS6 lacks the advanced modelling techniques required for the analysis of magnetic structures, the magnetic analysis was performed using the Fullprof Suite software package.<sup>38</sup> The refinements were repeated, with the addition of anisotropic magnetic peak broadening modelled using spherical harmonics.

### 7.2.3 Physical Property Measurements

Temperature-dependent bulk magnetic susceptibility measurements were undertaken using a 0.1 T field under both FC and ZFC conditions using a Quantum Design PPMS. Approximately 20 mg of CsMnF<sub>4</sub> was finely ground and placed in a tubular brass sample holder, held in place between two tightly fit plastic rods. The sample holder was then loaded into the PPMS and cooled to 1.8 K. Data on the magnetic susceptibility were taken using the VSM technique, with two magnetic field sweeps of  $\pm 5$  T measured at 1.8 and 20 K.

## 7.3 Room Temperature Nuclear Structure of CsMnF<sub>4</sub>

Room temperature structural studies of CsMnF<sub>4</sub> proved challenging. As well as the hazardous synthesis procedure, samples readily rehydrated to give a combination of both CsMnF<sub>4</sub> and the hydrated CsMnF<sub>4</sub>·2H<sub>2</sub>O phases. Initial NPD data measured using Echidna also revealed the presence of other undesirable phases, such as Cs<sub>2</sub>MnF<sub>6</sub>, that were not evident in the XRD pattern of the material immediately after synthesis (Figure A.22). Consequently, a fresh batch of CsMnF<sub>4</sub> was prepared and stored under argon gas before each measurement to minimise its exposure to the environment.

The Rietveld refinement for CsMnF<sub>4</sub> against laboratory XRD data is shown in Figure 7.3. A model first described by Massa *et al.* was used, and this resulted in excellent agreement.<sup>23</sup> The XRD taken immediately after dehydration showed the sample to be single phase, with no reflections from the CsF or Mn<sub>2</sub>O<sub>3</sub> reagents, or from the hydrated CsMnF<sub>4</sub>·2H<sub>2</sub>O phase. NPD data were collected at room temperature on the same sample using Echidna with 1.62 Å wavelength neutrons. The Rietveld refinement is shown in Figure 7.4. A satisfactory fit was obtained with the same structural model previously described for the analysis of the XRD data.<sup>23</sup> The structure is composed of Cs<sup>+</sup> cations separating layers of MnF<sub>6</sub> octahedra. The MnF<sub>6</sub> octahedra appear to exhibit Jahn–Teller



distortions, with two short axial bonds of 1.8234(19) Å, and four longer equatorial bonds of 2.0070(3) Å. The in-plane Mn–F–Mn bond angle was calculated to be 163.00(11) °.

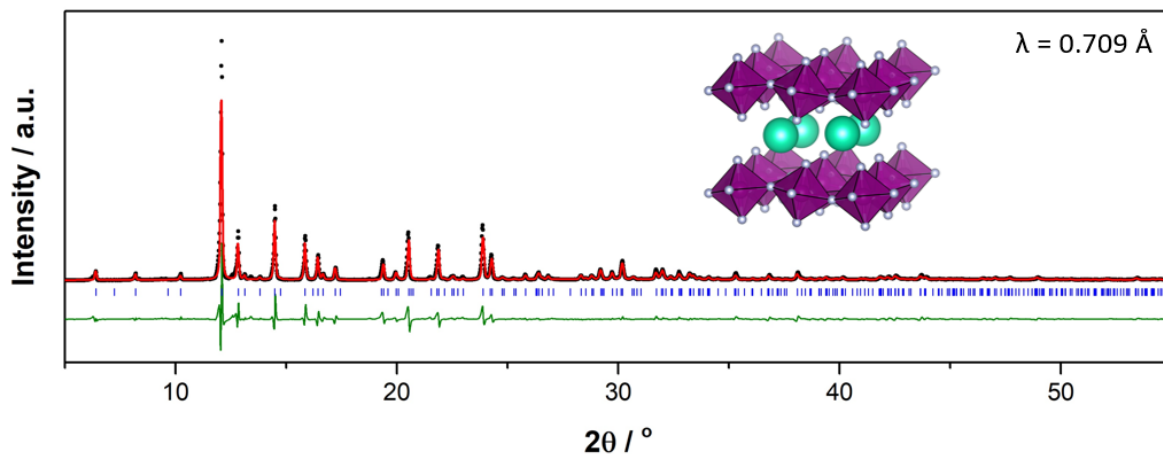


Figure 7.3: The Rietveld refinement of CsMnF<sub>4</sub> immediately after synthesis using monochromatic Mo source laboratory X-ray diffraction to the tetragonal  $P4/nmm$  space group. The black circles represent the data, the red line represents the calculated profile, and the green line represents the difference between the two. The blue ticks indicate the space group-allowed reflections.

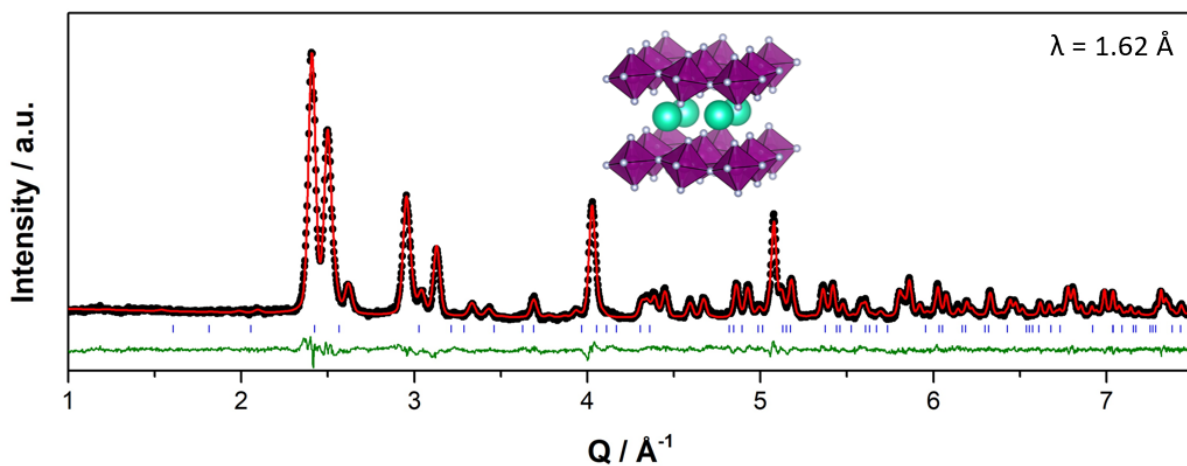


Figure 7.4: The Rietveld refinement of CsMnF<sub>4</sub> immediately after synthesis against neutron powder diffraction to the tetragonal  $P4/nmm$  space group at room temperature. The black circles represent the data, the red line represents the calculated profile, and the green line represents the difference between the two. The blue ticks indicate the space group-allowed reflections.

Table 7.1: Selected Rietveld refinement structural parameters and bond distances for CsMnF<sub>4</sub> using neutron powder diffraction data collected at room temperature.

| Space Group            | $P4/nmm$     |
|------------------------|--------------|
| $a$ (Å)                | 7.93984(16)  |
| $c$ (Å)                | 6.3355(3)    |
| Vol. (Å <sup>3</sup> ) | 399.40(2)    |
| Cs(2) $z$              | 0.4471(7)    |
| F(1) $y$               | -0.0014(4)   |
| F(1) $z$               | 0.0468(3)    |
| F(2) $x$               | -0.02766(18) |
| F(2) $y$               | = F(2) $x$   |
| F(2) $z$               | 0.2836(3)    |
| Cs(1)–F(1) (Å)         | 3.484(3)     |
| Cs(1)–F(2) (Å)         | 3.1395(16)   |
| Cs(2)–F(1) (Å)         | 3.227(5)     |
| Cs(2)–F(2) (Å)         | 3.285(3)     |
| Mn–F(1) (Å)            | 2.0070(3)    |
| Mn–F(2) (Å)            | 1.8234(19)   |
| Mn–F–Mn (°)            | 163.00(11)   |
| $R_{wp}$ (%)           | 3.88         |

## 7.4 Magnetic Susceptibility Studies of CsMnF<sub>4</sub>

The temperature dependent magnetic susceptibility of CsMnF<sub>4</sub> was investigated. The magnetic susceptibilities were measured under both FC and ZFC conditions from 300 to 1.8 K using an applied magnetic field of 0.1 T. The paramagnetic magnetic susceptibility ( $\chi_P$ ) was determined by correcting the measured magnetic susceptibility ( $\chi_{meas.}$ ) of the diamagnetic contribution of the sample. This process is outlined by Bain *et al.*,<sup>39</sup> and was calculated as

$$\chi_P = \chi_{meas.} - \chi_D \quad (7.1)$$

where  $\chi_P$  is the paramagnetic susceptibility and  $\chi_D$  is the diamagnetic susceptibility.

Next, the values were normalised by the mass of the sample to calculate the magnetic susceptibility per mole ( $\chi$ ). The FC and ZFC magnetic susceptibilities are shown in Figure 7.5. These curves show a point of inflection near 20 K, suggesting the onset of long-range magnetic ordering. The magnetism of CsMnF<sub>4</sub> can be modelled using the Curie-Weiss law (Equation 2.31), which describes how the magnetic susceptibility changes with temperature.<sup>40</sup>

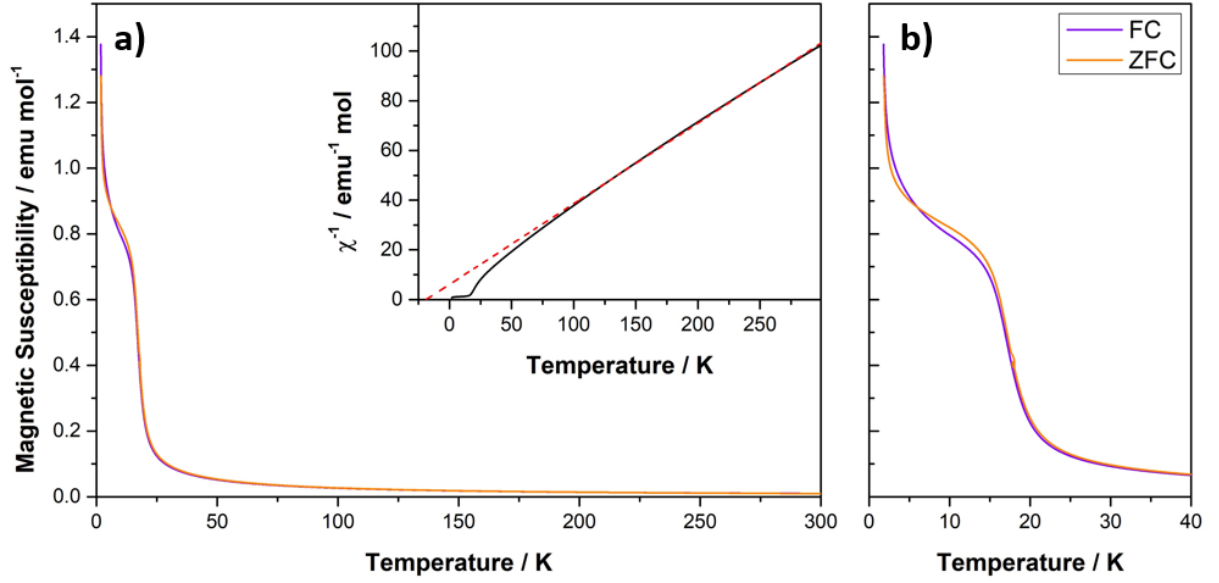


Figure 7.5: Magnetic susceptibility of CsMnF<sub>4</sub> collected under field cooled and zero field cooled conditions using a physical property measurement system. (a) The susceptibility collected between 1.8–300 K, with a focus from 1.8–40 K shown in (b). The inset shows the inverse magnetic susceptibility fit from 80–300 K, with the Curie-Weiss fit shown as a red dashed line.

In order to extrapolate the Curie constant and Curie temperature of CsMnF<sub>4</sub>, Equation 2.31 may be linearised as

$$\chi_P^{-1} = \frac{1}{C}T - \frac{T_C}{C}. \quad (7.2)$$

A linear fit to the Curie-Weiss law is shown in the inset of Figure 7.5. The fitting was performed over the paramagnetic region of 80–300 K to exclude any potential magnetic contributions. The fit returns a Curie constant of 3.0807(1) mol emu<sup>-1</sup> K<sup>-1</sup>, which calculates  $\mu_s = 4.96(2) \mu_B$  in close agreement with the expected spin only magnetic moment of 4.90  $\mu_B$ .<sup>19</sup> Furthermore, by extrapolating the linear Curie-Weiss fit, the Curie temperature is calculated as  $T_C = 18.8(4)$  K, which is in agreement with the value of  $T_C = 18.9$  K previously reported by Morón *et al.* and Massa *et al.*<sup>21,23</sup> The value of  $T_C$  is greater than zero, confirming that CsMnF<sub>4</sub> orders ferromagnetically below 18.9 K. Magnetic isotherms were performed at both 1.8 and 20 K; temperatures above and below  $T_C$ . An opening of the hysteresis loop is observed at 1.8 K which is subsequently lost at 20 K. The lack of saturation in the magnetic moment at high magnetic field also indicates that this ordering is ferromagnetic.

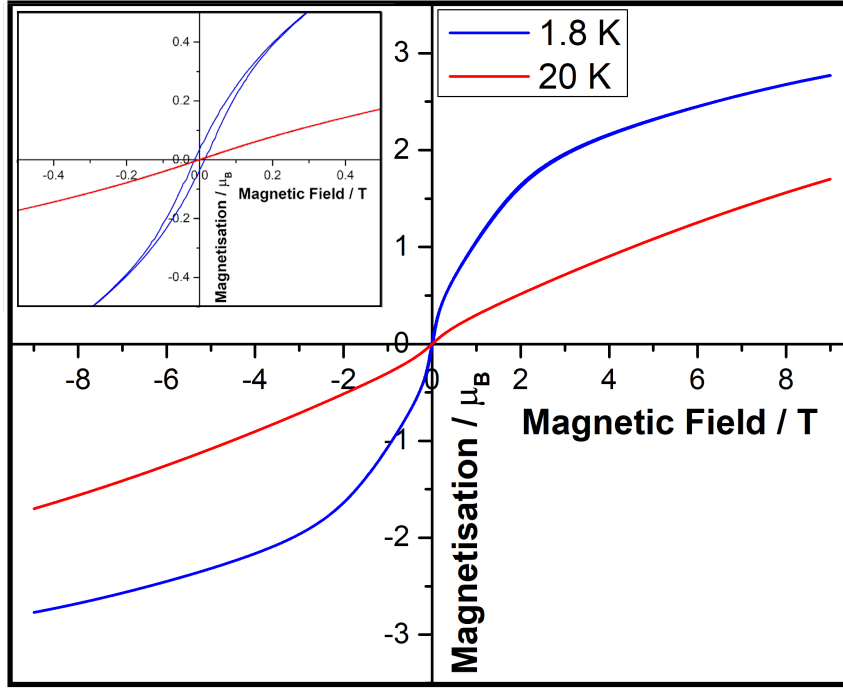


Figure 7.6: Magnetisation of  $\text{CsMnF}_4$  collected with a variable magnetic field using a physical property measurement system. The data collected at 1.8 K is shown as the blue line, and the data collected at 20 K is shown as the red line. The inset highlights the opening of the hysteresis loop at 1.8 K (and lack of opening at 20 K) at low magnetic field strength.

## 7.5 Magnetic Structure of $\text{CsMnF}_4$

Using the Echidna neutron powder diffractometer, variable temperature NPD data were collected using 2.44 Å neutrons after cooling to 3 K, then heating from 5–50 K. Additional Bragg reflections emerge at 3 K and persist until 20 K, consistent with the onset of ferromagnetic ordering observed in the PPMS data. Changes in selected structural parameters are plotted in Figure 7.7. Despite little change in the nuclear structure occurring between 3–50 K, an abrupt increase in the Mn–F–Mn angle is observed near 20 K, potentially due to magnetostriction (Figure 7.7d). A similar change is evident in the unit cell volume (Figure 7.7b).

Comparison of the NPD patterns collected at 3 and 30 K is shown in Figure 7.8, along with the difference between the two. It is clear that five additional Bragg reflections emerge in the 3 K dataset below  $55^\circ 2\theta$ , indicative of the onset of long-range magnetic ordering. The following outlines the procedure undertaken to fit the magnetic structure of  $\text{CsMnF}_4$ .

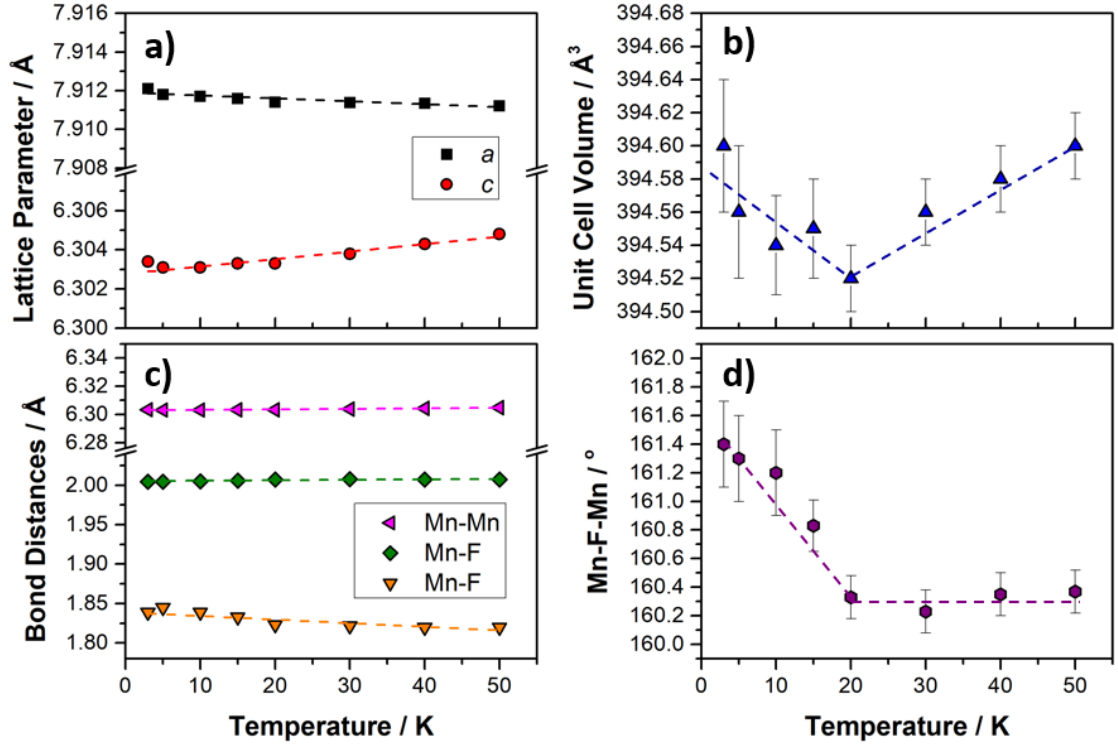


Figure 7.7: The dependence of the structural parameters of CsMnF<sub>4</sub> with respect to temperature based on Rietveld refinements of neutron powder diffraction data. (a) The  $a$  and  $c$  lattice parameters, (b) unit cell volume, (c) Mn-F and Mn-Mn distances, and (d) the Mn-F-Mn bond angle. Dashed lines have been drawn to guide the eyes.

Firstly, a propagation vector ( $\vec{k}$ ) was identified. Data acquired using the PPMS indicates that CsMnF<sub>4</sub> is ferromagnetic,<sup>19</sup> and the NPD data displays additional magnetic Bragg peaks at the  $hkl$ -allowed positions of the nuclear  $P4/nmm$  structure. The five peaks are obvious in the difference plot, and were indexed at (001), (200), (201), (002), and (220) using the same size cell as the nuclear structure. Hence, a propagation vector of  $\vec{k} = [0, 0, 0]$  is appropriate. Next, representational analysis performed using BasIReps in the Fullprof Suite determined an active *irrep*  $\Gamma_5^+$ , which is equivalent to the monoclinic magnetic space group  $P2'/c'$  (or, Shubnikov space group #13.69). This space group splits the 4d Wyckoff position of Mn<sup>3+</sup> (0, 0, 0) into two separate Wyckoff positions: 2a (0, 0, 0) and 2d (1/2, 0, 0).

In undertaking a magnetic structure refinement, the magnetic sites have independent magnetic contributions with freedom of direction. These are traditionally notated as ( $M_x$ ,  $M_y$ ,  $M_z$ ), with the  $x, y, z$  magnetic moment along the  $a, b, c$  directions of the unit cell respectively. According to previous studies,<sup>21,23</sup> as well as DFT studies conducted by our

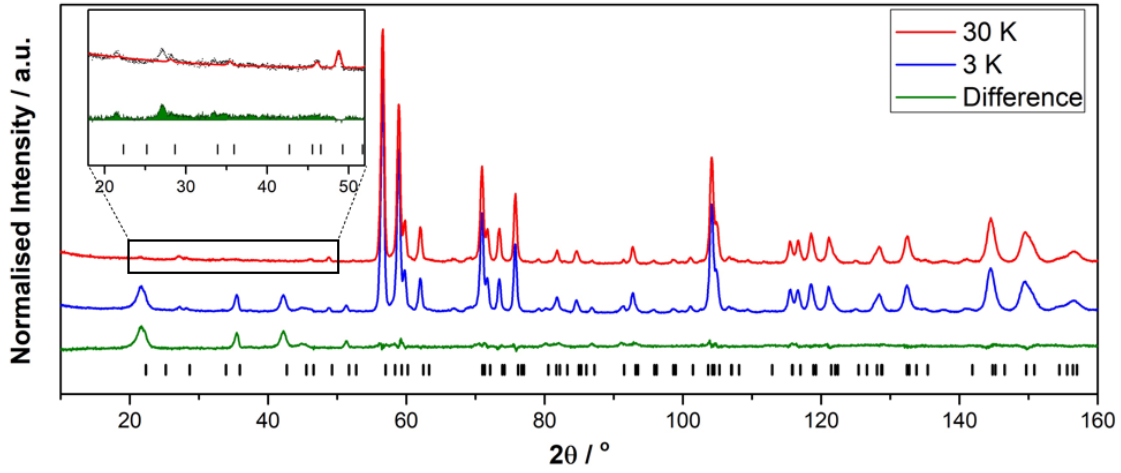


Figure 7.8: Neutron powder diffraction data collected on  $\text{CsMnF}_4$  using  $2.44 \text{ \AA}$ . The red line corresponds to the pattern at 30 K, the blue line at 3 K, and the green line is the difference between them. The black lines are the space group allowed reflections from the nuclear  $P4/nmm$  structure. The five prominent magnetic reflections are seen below  $55^\circ 2\theta$ . The inset highlights the presence of diffuse magnetic features above  $T_C = 18.9 \text{ K}$ , with the 30 K data displayed as black circles, the red line is the calculated profile, and the green shaded area as the difference between the two.

collaborators,<sup>15</sup>  $\text{CsMnF}_4$  is ferromagnetic with only one type of magnetic cation. In the magnetic refinements, the magnetic moments across the two  $\text{Mn}^{3+}$  Wyckoff positions were fixed to be equal and parallel. A preliminary refinement provided no evidence for either  $M_y$  or  $M_z$ , and these were consequently set to zero. Attempts were made to determine the direction of the magnetic moment. As the (001) reflection was detected, this means the magnetic moment cannot be pointed along the  $c$ -axis, as moments can only contribute if they are perpendicular to the scattering vector. In powder diffraction measurements, the (020) and (200) reflections are indistinguishable due to the tetragonal symmetry of the structure. Therefore, the magnetic moment is confined to the  $ab$  plane, and its orientation cannot be uniquely identified. Further measurements using single crystals of  $\text{CsMnF}_4$  would be required to confirm whether there is a preference for a specific direction within the  $ab$  plane.

The magnetic refinement shows clear anisotropic broadening of the  $(00l)$  magnetic reflections. In order to properly fit these peaks, the anisotropic contribution was modelled as size broadening using spherical harmonics. For the harmonics allowed by the  $4/mmm$  Laue class, only  $Y_{00}$ ,  $Y_{20}$ , and  $Y_{40}$  converged to significantly nonzero values and the rest were fixed to zero. This gives highly anisotropic magnetic domains with a larger contribution along the  $a$ -axis compared to the  $c$ -axis ( $488 \text{ \AA}$  and  $127 \text{ \AA}$ , respectively).

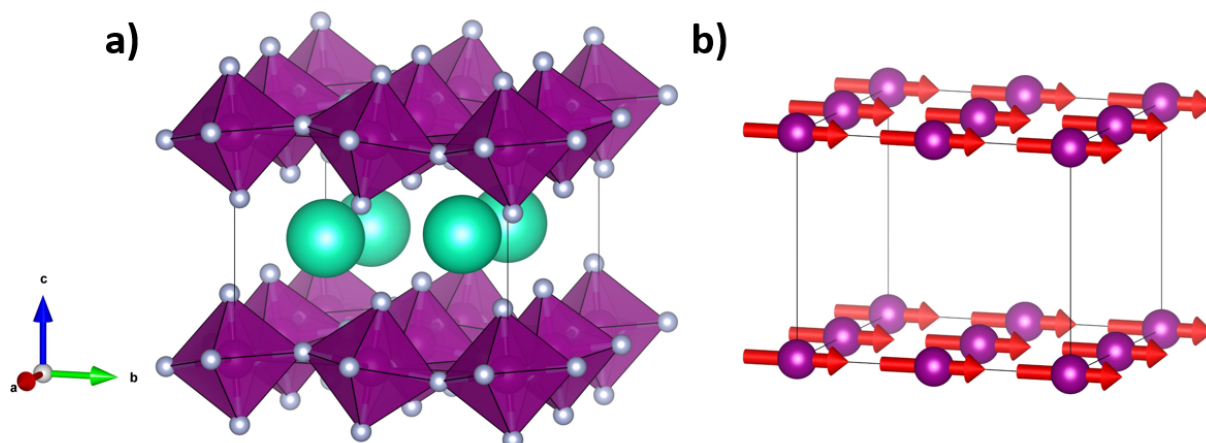


Figure 7.9: The structure of CsMnF<sub>4</sub> derived from neutron powder diffraction data at 3 K. (a) The nuclear structure of CsMnF<sub>4</sub> in the space group  $P4/nmm$  with (b) the magnetic structure as a result of the Mn<sup>3+</sup> cations.

The full nuclear and magnetic refinement of CsMnF<sub>4</sub> at 3 K is shown in Figure 7.10.

The magnitude of the ordered magnetic moment ( $\mu$ ) was determined from the magnetic refinement. As Mn<sup>3+</sup> has four unpaired electrons in a high-spin state (Figure 7.2), it has a theoretical ordered moment of  $2S = 4 \mu_B$ . Based on the magnetic Rietveld refinement, the magnetic moment was determined to be  $3.76(4) \mu_B$ , which is in close agreement with other studies and the theoretical value.<sup>19,23</sup>

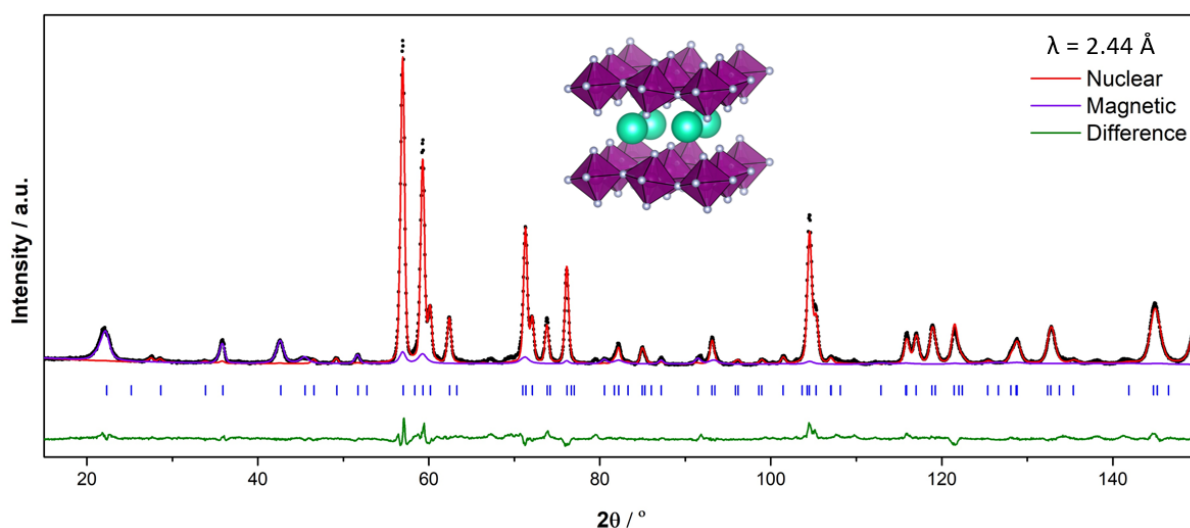


Figure 7.10: Neutron diffraction data collected on CsMnF<sub>4</sub> using  $2.44 \text{ \AA}$  at 3 K. The red line is the fit to the nuclear structure, the purple line is the fit to the magnetic structure, and the green line is the difference between the calculated fit and the data. The blue ticks indicate the space group-allowed reflections.

There appear to be a number of diffuse magnetic features detected by NPD, as evident in the inset in Figure 7.8. This suggests that although long-range magnetic ordering is lost above 18.9 K, it is possible that short-range magnetic correlations are still present at this temperature. Recently, magnetic pair distribution function (mPDF) analysis has been used to disentangle differences in magnetic moments across different length scales within materials.<sup>41</sup> Work on MnTe by Baral *et al.* identified robust short-range magnetic correlations that persisted without the detection of long-range magnetic ordering, and used this to explain the high figure of merit ( $zT$ ) value in these thermoelectric devices.<sup>42,43</sup> This work could be worth pursuing.

## 7.6 Conclusions and Future Work

A sample of CsMnF<sub>4</sub> was successfully synthesised using a coprecipitation reaction in hydrofluoric acid. The structure was characterised at room temperature using X-ray and neutron powder diffraction. The material crystallised in the  $P4/nmm$  space group, consisting of layers of MnF<sub>6</sub> octahedra separated by ionically-bound Cs<sup>+</sup> cations.

The paramagnetic susceptibility was successfully modelled using PPMS data. The spin only effective magnetic moment of  $\mu_s = 4.96(2) \mu_B$  showed close agreement to the expected spin only contribution of  $4.90 \mu_B$ . An extrapolation of the linearised Curie-Weiss law calculated  $T_C = 18.8(4)$  K, which confirms the ferromagnetic ordering observed in previous studies. An opening of the hysteresis loop about the origin was also observed at 1.8 K which was lost at 20 K, further confirming its ferromagnetic nature and the Curie temperature of CsMnF<sub>4</sub>. However, a lack of saturation in the magnetisation data at high magnetic field strength implies that other more complex structures, such as canted antiferromagnets or ferrimagnets, may be possible. Given this is the highest resolution neutron powder diffraction data collect on this material to date, this is worth modelling further.

After cooling CsMnF<sub>4</sub> to 3 K, NPD was used to identify the  $P2'/c'$  magnetic structure (Shubnikov space group #13.69). This showed that each Mn<sup>3+</sup> cation aligned ferromagnetically within the  $ab$  plane. From the magnetic Rietveld refinement, an ordered



## 7.6 Conclusions and Future Work

---

magnetic moment of  $\mu = 3.76(4) \mu_B$  was determined, which is in close agreement with other studies and the theoretical value of  $4 \mu_B$  for a  $S = 2$  ferromagnet. The difference between the experimental and theoretical magnetic moment is presumably due to a combination of spin-orbit coupling and the covalency of the Mn–F bonds. Further mPDF studies could be paired with single crystal studies to determine whether there is any short-range magnetic ordering persistent above  $T_C$ , and whether there is a preferred direction of the magnetic moment within the  $ab$  plane.

Further studies are required to determine the extent of the effect of the Mn–F–Mn bond angles on the magnetism of  $\text{CsMnF}_4$ . Based on the variable temperature Rietveld refinements of  $\text{CsMnF}_4$  between 3–50 K, there is a statistically significant increase in the Mn–F–Mn bond angle, potentially due to magnetostriction. This change in the Mn–F–Mn bond angle could be investigated further using SXRD, where the superior peak-shape resolution could be used to identify any changes in the unit cell above 20 K. Additional studies can also be carried out looking at the effect of changing the bond angle within the magnetic region of  $<20$  K, such as pressurising the sample. Studies by Morón *et al.* have noted that the magnetic nature of  $\text{CsMnF}_4$  switches from ferromagnetic to antiferromagnetic above 1.5 GPa.<sup>21,44</sup> However, the current PPMS set-up at the University of Sydney is limited to a maximum pressure of 1.3 GPa, meaning this could not be observed experimentally. Furthermore, acquiring a magnetic structure below 20 K and at  $>1.5$  GPa remains an engineering challenge, with the Sample Environment team at ANSTO currently not able to run a pressurised cell on Echidna for NPD.

These measurements are also not possible at other high pressure neutron diffraction beamlines around the world, with PEARL (ISIS, UK) currently limited to 50 K using a dual closed cycle refrigeration system, and PLANET (J-PARC, Japan) limited to 1.3 GPa at 7 K using a piston-cylinder cell. The Spallation Neutrons And Pressure (SNAP) beamline (ORNL, USA) is currently the only possibility, with a clamp cell capable of running with a maximum pressure of 2 GPa at 10 K. The SNAP beamline is currently developing a diamond anvil cell capable of achieving a maximum pressure of 40 GPa at temperatures as low as 10 K. Measurements of the pressure-induced magnetic transition at 1.5 GPa should be kept in mind with future sample environment innovations.



# Bibliography

- (1) Bader, S. D.; Parkin, S. Spintronics. *Annual Review of Condensed Matter Physics* **2010**, *1*, 71–88.
- (2) Yakout, S. M. Spintronics: Future technology for new data storage and communication devices. *Journal of Superconductivity and Novel Magnetism* **2020**, *33*, 2557–2580.
- (3) Wolf, S.; Treger, D.; Chtchelkanova, A. Spintronics: The future of data storage? *Mrs Bulletin* **2006**, *31*, 400–403.
- (4) Puebla, J.; Kim, J.; Kondou, K.; Otani, Y. Spintronic devices for energy-efficient data storage and energy harvesting. *Communications Materials* **2020**, *1*, 24.
- (5) Binasch, G.; Grünberg, P.; Saurenbach, F.; Zinn, W. Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange. *Physical Review B* **1989**, *39*, 4828.
- (6) Barnaś, J.; Fuss, A.; Camley, R.; Grünberg, P.; Zinn, W. Novel magnetoresistance effect in layered magnetic structures: Theory and experiment. *Physical Review B* **1990**, *42*, 8110.
- (7) Reig, C.; Cubells-Beltrán, M.-D.; Muñoz, D. R. Magnetic field sensors based on giant magnetoresistance (GMR) technology: Applications in electrical current sensing. *Sensors* **2009**, *9*, 7919–7942.
- (8) He, M.; Sun, H.; He, Q. L. Topological insulator: Spintronics and quantum computations. *Frontiers of Physics* **2019**, *14*, 1–16.

- (9) Fennell, T.; Deen, P.; Wildes, A.; Schmalzl, K.; Prabhakaran, D.; Boothroyd, A.; Aldus, R.; McMorrow, D.; Bramwell, S. Magnetic Coulomb phase in the spin ice  $\text{Ho}_2\text{Ti}_2\text{O}_7$ . *Science* **2009**, *326*, 415–417.
- (10) Liu, D.; Lin, L.; Liu, M.; Yan, Z.; Dong, S.; Liu, J.-M. Multiferroicity in spin ice  $\text{Ho}_2\text{Ti}_2\text{O}_7$ : An investigation on single crystals. *Journal of Applied Physics* **2013**, *113*.
- (11) Bhattacharyya, A.; Bhowmik, T.; Adroja, D.; Rahaman, B.; Kar, S.; Das, S.; Saha-Dasgupta, T.; Biswas, P.; Sinha, T.; Ewings, R. Dynamic spin fluctuations in the frustrated spin chain compound  $\text{Li}_3\text{Cu}_2\text{SbO}_6$ . *Physical Review B* **2021**, *103*, 174423.
- (12) Acharyya, P.; Kundu, K.; Biswas, K. 2D layered all-inorganic halide perovskites: Recent trends in their structure, synthesis and properties. *Nanoscale* **2020**, *12*, 21094–21117.
- (13) Xue, J.; Wang, Z.; Comstock, A.; Wang, Z.; Sung, H. H.; Williams, I. D.; Sun, D.; Liu, J.; Lu, H. Chemical control of magnetic ordering in hybrid Fe–Cl layered double perovskites. *Chemistry of Materials* **2022**, *34*, 2813–2823.
- (14) De Irujo-Labalde, X. M.; Amador, U.; Ritter, C.; Goto, M.; Patino, M. A.; Shimakawa, Y.; García-Martín, S. 3D to 2D magnetic ordering of  $\text{Fe}^{3+}$  oxides induced by their layered perovskite structure. *Inorganic Chemistry* **2021**, *60*, 8027–8034.
- (15) Behatha, A.; Roy, A. J.; Anusree, C.; Ponvijayakanthan, L.; Sharma, V. K.; Kanchana, V. Correlation driven topological nodal ring ferromagnetic spin gapless semimetal:  $\text{CsMnF}_4$ . *Journal of Physics: Condensed Matter* **2021**, *33*, 165803.
- (16) Li, L.; Kong, X.; Peeters, F. M. New nanoporous graphyne monolayer as nodal line semimetal: Double Dirac points with an ultrahigh Fermi velocity. *Carbon* **2019**, *141*, 712–718.
- (17) Zhang, R.-W.; Zhang, Z.; Liu, C.-C.; Yao, Y. Nodal line spin-gapless semimetals and high-quality candidate materials. *Physical Review Letters* **2020**, *124*, 016402.

## BIBLIOGRAPHY

---

- (18) Chen, J.-Y.; Li, X.-X.; Zhou, W.-Z.; Yang, J.-L.; Ouyang, F.-P.; Xiong, X. Large-spin-gap nodal-line half-metal and high-temperature ferromagnetic semiconductor in  $\text{Cr}_2\text{X}_3$  ( $X = \text{O}, \text{S}, \text{Se}$ ) monolayers. *Advanced Electronic Materials* **2020**, *6*, 1900490.
- (19) Morón, M. C.; Palacio, F.; Rodríguez-Carvajal, J. Crystal and magnetic structures of  $\text{RbMnF}_4$  and  $\text{KMnF}_4$  investigated by neutron powder diffraction: The relationship between structure and magnetic properties in the  $\text{Mn}^{3+}$  layered perovskites  $\text{AMnF}_4$  ( $A = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ). *Journal of Physics: Condensed Matter* **1993**, *5*, 4909.
- (20) Molinier, M.; Frommen, C.; Massa, W.; Pebler, J.; Roisnel, T. Magnetism of alkali-tetrafluoromanganates (III)  $\text{AMnF}_4$  ( $A = \text{K}, \text{Rb}, \text{Cs}$ ): Neutron diffraction, Mössbauer and magnetization investigations. *Zeitschrift für Naturforschung A* **1993**, *48*, 1054–1072.
- (21) Morón, M. C.; Palacio, F.; Clark, S.; Paduan-Filho, A. Structural and magnetic behavior of the  $S = 2$  layered ferromagnet  $\text{CsMnF}_4$  under hydrostatic pressure. *Physical Review B* **1995**, *51*, 8660.
- (22) Morón, M. C.; Palacio, F.; Rodríguez-Carvajal, J. Neutron powder diffraction experiments on  $\text{AMnF}_4$  ( $A = \text{K}, \text{Rb}$ ): Nuclear and magnetic structures. *Physica B: Condensed Matter* **1992**, *180*, 125–127.
- (23) Massa, W.; Steiner, M. Crystal and magnetic structure of the planar ferromagnet  $\text{CsMnF}_4$ . *Journal of Solid State Chemistry* **1980**, *32*, 137–143.
- (24) Gibertini, M.; Koperski, M.; Morpurgo, A. F.; Novoselov, K. S. Magnetic 2D materials and heterostructures. *Nature Nanotechnology* **2019**, *14*, 408–419.
- (25) Kim, K.; Lim, S. Y.; Kim, J.; Lee, J.-U.; Lee, S.; Kim, P.; Park, K.; Son, S.; Park, C.-H.; Park, J.-G. Antiferromagnetic ordering in van der Waals 2D magnetic material  $\text{MnPS}_3$  probed by Raman spectroscopy. *2D Materials* **2019**, *6*, 041001.
- (26) Eibschütz, M.; Guggenheim, H.; Holmes, L.; Bernstein, J.  $\text{CsFeF}_4$ : A new planar antiferromagnet. *Solid State Communications* **1972**, *11*, 457–460.
- (27) Goodenough, J. B. Magnetism and the chemical bond. **1963**.

- (28) Kanamori, J. Superexchange interaction and symmetry properties of electron orbitals. *Journal of Physics and Chemistry of Solids* **1959**, *10*, 87–98.
- (29) Anderson, P. Exchange in insulators: Superexchange, direct exchange, and double exchange. *Magnetism* **1963**, 25–83.
- (30) Khomskii, D. In *Spin Electronics*; Springer: 2001, pp 89–116.
- (31) Jana, S.; Aich, P.; Kumar, P. A.; Forslund, O. K.; Nocerino, E.; Pomjakushin, V.; Månsson, M.; Sassa, Y.; Svedlindh, P.; Karis, O. Revisiting Goodenough–Kanamori rules in a new series of double perovskites  $\text{LaSr}_{1-x}\text{Ca}_x\text{NiReO}_6$ . *Scientific Reports* **2019**, *9*, 18296.
- (32) Harris, V. G.; Andalib, P. Goodenough–Kanamori–Anderson Rules of superexchange applied to ferrite systems. *Modern Ferrites: Emerging Technologies and Applications* **2022**, *2*, 31–67.
- (33) Palacio, F.; Andres, M.; Esteban-Calderon, C.; Martinez-Ripoll, M.; Garcia-Blanco, S. Crystal structure and magnetic properties of linear chain potassium aquotetrafluoromanganate (III). *Journal of Solid State Chemistry* **1988**, *76*, 33–39.
- (34) Liss, K.-D.; Hunter, B.; Hagen, M.; Noakes, T.; Kennedy, S. Echidna — The new high-resolution powder diffractometer being built at OPAL. *Physica B: Condensed Matter* **2006**, *385*, 1010–1012.
- (35) Coelho, A. A. TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++. *Journal of Applied Crystallography* **2018**, *51*, 210–218.
- (36) Thompson, P.; Cox, D.; Hastings, J. Rietveld refinement of Debye–Scherrer synchrotron X-ray data from  $\text{Al}_2\text{O}_3$ . *Journal of Applied Crystallography* **1987**, *20*, 79–83.
- (37) Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* **2011**, *44*, 1272–1276.
- (38) Rodríguez-Carvajal, J. Recent advances in magnetic structure determination by neutron powder diffraction. *Physica B: Condensed Matter* **1993**, *192*, 55–69.

- 
- (39) Bain, G. A.; Berry, J. F. Diamagnetic corrections and Pascal's constants. *Journal of Chemical Education* **2008**, *85*, 532.
- (40) Mugiraneza, S.; Hallas, A. M. Tutorial: A beginner's guide to interpreting magnetic susceptibility data with the Curie-Weiss law. *Communications Physics* **2022**, *5*, 95.
- (41) Frandsen, B. A.; Hamilton, P. K.; Christensen, J. A.; Stubben, E.; Billinge, S. J. diffpy. mpdf: Open-source software for magnetic pair distribution function analysis. *Journal of Applied Crystallography* **2022**, *55*.
- (42) Baral, R.; Christensen, J. A.; Hamilton, P. K.; Ye, F.; Chesnel, K.; Sparks, T. D.; Ward, R.; Yan, J.; McGuire, M. A.; Manley, M. E. Real-space visualization of short-range antiferromagnetic correlations in a magnetically enhanced thermoelectric. *Matter* **2022**, *5*, 1853–1864.
- (43) Baral, R.; Abeykoon, A. M.; Campbell, B. J.; Frandsen, B. A. Giant spontaneous magnetostriction in MnTe driven by a novel magnetostructural coupling mechanism. *Advanced Functional Materials* **2023**, 2305247.
- (44) Morón, M. C.; Palacio, F.; Clark, S. Pressure-induced structural phase transitions in the  $AMnF_4$  series ( $A = Cs, Rb, K$ ) studied by synchrotron X-ray powder diffraction: Correlation between hydrostatic and chemical pressure. *Physical Review B* **1996**, *54*, 7052.





---

## Part IV: Conclusions and Future Work

---



## Chapter 8

# Conclusion, Perspectives, and Future Work

The basis of materials science involves studying the delicate interplay between the atomic structure of a material, its influence on its properties and functionalities, and how this affects its application. By understanding what influences this relationship, materials may be further engineered to perform these tasks more efficiently, effectively, and safely. However, understanding these particular relationships is often very complex, requiring knowledge of where atoms are positioned on the nanometre scale, to how this influences the properties of the material on the millimetre scale. These relationships are complex, even for simple binary materials such as the photocatalyst  $\text{TiO}_2$  or the fast ion conductor  $\delta\text{-Bi}_2\text{O}_3$ . This dissertation focused on exploring the ‘chaotic simplicity’ of  $\text{ABO}_4$  metal oxide structures, a seemingly straightforward family of ternary materials that possess a rich phase space due to the wide variety of chemical substitutions that can be made within the structure. Closer inspection of these materials uncovered complex structural features that had previously been overlooked, leading to new descriptions of their atomic structures, behaviours when heated, and functionality.

Chapter 3 of this dissertation focused on the development of ceramic electrolytes for SOFCs. In particular,  $\text{LaNbO}_4$  has shown great promise as a ceramic electrolyte due to its high ionic conductivity and stability in harsh, acidic gaseous environments. However, a first order phase transition at  $\sim 500^\circ\text{C}$  makes this material unsuitable as a ceramic electrolyte, as structural transformations can lead to performance issues associated with

hysteresis, abrupt volume changes, and induced strain leading to degradation. This chapter established accurate and precise structures for all the  $LnNbO_4$  ( $Ln^{3+} = \text{La-Lu}$ ) materials, which were isostructural in the monoclinic-fergusonite  $I2/a$  space group. A relationship was identified between the IR of the  $Ln^{3+}$  cation and the length of the Nb–O<sub>l</sub> bond, providing a structural explanation for the differences in temperature for the observed  $I2/b \rightarrow I4_1/a$  phase transition. Expanding the structure-functionality relationship to include  $LnTaO_4$  proved more complex, with several different structures synthesised depending on the IR of the  $Ln^{3+}$  cation. This was used to understand the differences between the orthoniobates and orthotantalates, and how the more radially extended 5d orbitals leads to stronger, more covalent Ta–O bonds that influence the structure upon heating. For the first time, this study answered the question of how particular  $LnTaO_4$  materials are synthesised in different space groups, by using an *in situ* NPD experiment to quantify the heating temperature in which each phase preferentially formed. The accurate and precise structures derived from a combination of SXRD and NPD was used to explain the ionic conductivity behaviour observed in  $HoNbO_4$  and  $HoTaO_4$ , with the differences between the Nb 4d and Ta 5d orbitals allowing for a quantification of the ‘free space’ within the structure. This allowed for the visualisation of potential ion conduction pathways within the material, and identified specific structural modification that could be made to  $LaNbO_4$ -based ceramic electrolytes to enhance their ionic conductivity, such as incorporating larger A-site cations, increasing the separation between B-site cations, introducing oxygen vacancies within the structure, and suggesting specific chemical substitutions that will affect the  $I2/a \rightarrow I4_1/a$  phase transition. Work is currently being performed to synthesise these suggested materials, as well as understanding their structural and ionic conductivity responses when heated.

Chapter 4 looked at the development of solid state lasers, and how an incomplete structural model is currently used to estimate the local environment of rare-earth ions in double scheelite-type materials. The  $NaA(BO_4)_2$  materials are easily grown as single crystals, and exhibit excellent thermal and hydrolytic stability for their use in lasing materials. Different analytical techniques have previously drawn contradictory conclusions as to the degree of ordering between the A-site cations. Using SXRD, each of the  $NaA(BO_4)_2$  ( $A^{3+} = Ln^{3+}, Bi$ ;  $B^{6+} = Mo, W$ ) materials were refined to the disordered

$I4_1/a$  space group, with no superlattice reflections associated with the partially ordered  $I\bar{4}$  structure observed. NPDF studies demonstrated the subtlety of the length scale of this cationic disorder, with the long-range average structure unable to adequately model the observed local distortions (between 1.2–3.5 Å). A lowering of symmetry, from disordered  $I4_1/a$  to the fully ordered  $I\bar{4}$  structural model was required, indicating that each of the *A*-site cations have a unique  $AO_8$  polyhedra environment. This leads to potential avenues for enhancing the properties of these double scheelite-type structures, including partially substituting larger *A*-site cations to ‘open up’ the structure and potentially increase its  $Na^+$  ionic conductivity, as well as substituting smaller *A*-site cations to introduce more subtle distortions to the rare-earth ion local environment that affects the  $5d$  and  $4f$  energy levels important for lasing. Furthermore, the introduction of  $Bi^{3+}$  with a  $6s^2$  lone pair caused additional structural distortions that were not observed in the similar  $NaLn(WO_4)_2$  ( $Ln^{3+} = La, Lu$ ) materials. These lone pair electrons appear to be important in predicting the structure and functionality of these materials, and the well-modelled local structure derived from this study should be further analysed using DFT and MD techniques to elucidate the role of this lone pair. As seen in other similar functional materials, such as  $BiVO_4$  photocatalysts and  $PbZrO_3$  ferroelectrics, this could lead to important breakthroughs in understanding their performance.

The idea of local distortions as a result of stereochemically active lone pairs was the foundation of Chapter 5. This explored subtle differences between the short-range local and long-range average structures in  $ABO_4$  materials that contain lone pair-bearing cations on the *A* site. Both  $BiVO_4$  and  $PbWO_4$  have found application in PWS due to their favourable band gap. However, a full understanding has not yet been established for these materials.  $BiVO_4$  and  $PbWO_4$  exhibit different long-range average structures, yet both have reported photocatalytic activity. Despite  $CaWO_4$  being isostructural to  $PbWO_4$ , it possesses no such photocatalytic activity. A study was performed on  $BiVO_4$ , where a combination of SXRD, NPD, and mode analysis was used to develop a robust structural model despite the lack of X-ray scattering of oxygen, and the near-zero neutron scattering of vanadium. Although this allowed for the development of a robust structural model, it was insufficient to model the short-range local structure observed in both XPDF and NPDF. Dropping the symmetry from the  $m-f$   $I2/b$  structure to the monoclinic  $P2_1/c$

structure derived from the average structure of  $\text{TlReO}_4$  (also containing lone pair-bearing  $\text{Tl}^+$ ) showed an excellent fit to the data, with local distortions observed in both the  $\text{BiO}_8$  polyhedra and  $\text{VO}_4$  tetrahedra. This study was repeated for  $\text{PbWO}_4$ , a photocatalyst like  $\text{BiVO}_4$  that lacks any long-range average symmetry lowering as a result of the  $\text{Pb}^{2+}$   $6s^2$  lone pair. The NPDF data quantified distortions in the  $\text{PbO}_8$  and  $\text{WO}_4$  tetrahedra that could not be adequately modelled using the long-range average  $t$ - $s$   $I4_1/a$  model, suggesting that the  $\text{Pb}^{2+}$  lone pair was stereochemically active at the local scale, but its correlation length does not extend to that of the long-range average structure. This was compared to the original  $\text{CaWO}_4$  scheelite material, which showed no such distortions in its local structure. This information was used to explain why  $\text{BiVO}_4$  and  $\text{PbWO}_4$  are both identified as photocatalysts with different levels of activity; the  $6s^2$  lone pair electrons appear to be an important chemical feature, and a difference in correlation length determines the extent of their activity.

As an aside, Chapter 6 looked at other possible local distortions within  $\text{ABO}_4$  materials within the context of materials capable of safely storing radioactive waste. Recently, discrepancies have been noted between  $\text{ATcO}_4$  and  $\text{AReO}_4$  materials, despite  $\text{Tc}^{7+}$  and  $\text{Re}^{7+}$  exhibiting the same oxidation state and almost identical IR. As a result, studies often use  $\text{Re}^{7+}$  as a nonradioactive surrogate for  $\text{Tc}^{7+}$ . An X-ray total scattering study was performed on  $\text{CsReO}_4$ , where unusual features such as the anomalous ADPs and shortening of the  $\text{Re-O}$  bond distances upon heating were noted in the XRD Bragg fits. However, local features in the XPDF data were identified that could not be well fitted with the long-range average structure derived from the Bragg fits. This was identified as being different from the local-scale disordering observed in other scheelite-type oxides, such as polyhedra distortions due to stereochemically active lone pairs (as previously observed in  $\text{BiVO}_4$  and  $\text{PbWO}_4$ ), or rotational disorder of the tetrahedra (as observed in  $\text{CaWO}_4$ ). This local-scale disordering was identified as local incoherent  $\text{ReO}_4$  tetrahedra translations, and is currently identified as unique to the  $\text{AReO}_4$  materials. These may be present in other materials that consist of isolated tetrahedra, such as zircons, and are worth investigating further. A neutron total scattering study performed on  $\text{TlTcO}_4$  identified the presence of rigid  $\text{TcO}_4$  tetrahedra, with the identification of its local symmetry as monoclinic  $P2_1/c$  in line with other lone pair-bearing  $A$ -site cations

such as  $\text{TlReO}_4$ ,  $\text{PbWO}_4$ , and  $\text{BiVO}_4$ . This study demonstrates the importance of fine-tuning these interactions on the local scale, with each material distorting differently as a result of the presence of the lone pair electrons. Whilst  $\text{PbWO}_4$  was identified to disorder through subtle deformation of the  $\text{WO}_4$  tetrahedra, the higher flexibility of the  $\text{TlO}_8$  polyhedra in  $\text{TlTcO}_4$  cause these to distort more heavily instead of the rigid  $\text{TcO}_4$  tetrahedra. This contrasts to  $\text{BiVO}_4$ , where the extreme polarisability of the V–O bonds in the  $\text{VO}_4$  tetrahedra cause these distortions to persist at a longer length scale. There appears to be a relationship between the types of distortions identified within these materials, and the polarisability of the B–O bonds in the  $\text{BO}_4$  tetrahedra, which is linked to whether a  $3d$  (like vanadium),  $4d$  (like technetium), or  $5d$  metal (like rhenium) is used. This is worth further investigating, with neutron total scattering studies worth pursuing on other  $\text{ABO}_4$  combinations, such as  $\text{Mo}^{6+}$  and  $\text{Ru}^{6+}$  (as  $4d$  metals) and  $\text{Os}^{6+}$  and  $\text{Ir}^{6+}$  (as  $5d$  metals). Substitutions could also be made on the  $A$  site with other lone pair-bearing cations, such as exploring the  $5s^2$  metals like  $\text{In}^+$ ,  $\text{Sn}^{2+}$ , and  $\text{Sb}^{3+}$ . This could be used to develop a more robust structure-functionality relationship and inform further DFT and MD studies on these materials.

Finally, Chapter 7 explored the world outside of metal oxides and looked at potential spintronic applications using the layered 2D perovskite  $\text{CsMnF}_4$ . This material has received attention due to its potential nodal rings, allowing for ultra-high electron velocities and a wide range of applications in data storage and transfer. This material was successfully synthesised, being classified as a ferromagnet below 18.9 K in the Shubnikov space group #13.69. Despite its spin only magnetic moment being well reproduced, as well as its paramagnetic susceptibility showing good agreement with the literature, a small amount of magnetic diffuse scattering was identified above the Curie temperature at 30 K using NPD. This points to potential short-range magnetic correlations that may persist at temperatures above the Curie temperature. This is worth investigating further, using a local magnetic probe such as mPDF to understand the effect of this on magnetostriction within the structure. A variable temperature SXRD study could also be beneficial to track the Mn–F–Mn bond angles to better model its structure for the application of the GKA rules. This structure should also be kept in mind for a combined magnetism and pressure study, as it is predicted that pressurising the materials  $>1.5$  GPa will cause a

change in its magnetic structure from ferromagnetic to antiferromagnetic that remains unconfirmed.

This dissertation has demonstrated the chaotic chemical and structural complexity of a very small subset of the apparently simple  $ABX_4$  materials. Despite these materials finding applications as ceramic electrolytes, solid state lasers, photocatalysts, radioactive waste matrices, and spintronic devices, there remains an incomplete understanding of their in-depth structure-functionality relationships. Central to the presented dissertation is the employment of systematic approaches to synthesis and experimental design, coupled with the ability to model and understand both the long-range average structure, short-range local structure, as well as the interplay between the two. These new experimental techniques in total scattering analysis have emerged as a result of key large-scale infrastructure designs and upgrades, allowing for the classification of materials on different length scales with an unprecedented level of detail. This capability is only just emerging, and still requires the delicate interplay between experimental and computational modelling to illustrate a more robust understanding. The electronic contribution to chemical structure, from orbital contributions to bonding arrangements and the hybridisation of lone pairs, presents an extremely promising new direction in functional material design. Consequently, the continual advancement of characterisation techniques central to understanding this type of structural disorder is paramount to rich discoveries pertinent to materials science, allowing us to truly design and tailor-make materials capable of specific applications.



# Appendix A

## Supporting Information

### A.1 Chapter 2: Theory and Experimental Techniques

#### A Quick Guide to Fourier Transforms

The Fourier transform of a function  $x(t)$  can be defined as

$$x(\omega) = \int_{-\infty}^{\infty} x(t)e^{-i\omega t} dt \quad (\text{A.1})$$

Taking  $x(t) = \sin(\omega_0 t)$ , the Fourier transform of a sine function is

$$\mathfrak{F}[\sin(\omega_0 t)] = -i\pi [\delta(\omega - \omega_0) - \delta(\omega + \omega_0)] \quad (\text{A.2})$$

where  $\delta$  is the Dirac delta function.

Therefore, taking  $\omega_0 = 1$  we can plot this as

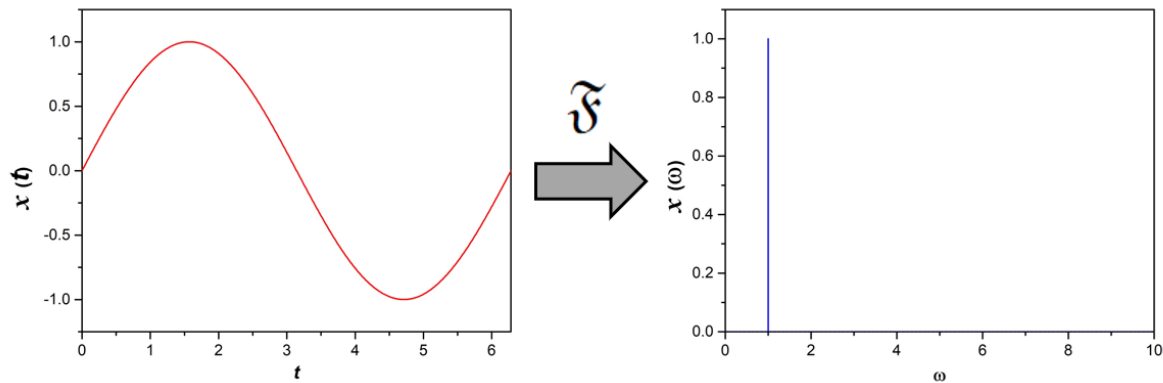


Figure A.1: The Fourier transform,  $x(\omega)$ , of the function,  $x(t)$ . In this case,  $x(t) = \sin(t)$  and  $x(\omega) = \delta(\omega+1)$ .

This can be seen with more complex functions, such as  $x(t) = \sin(t) + \sin(3t) + \sin(7t)$ , such as

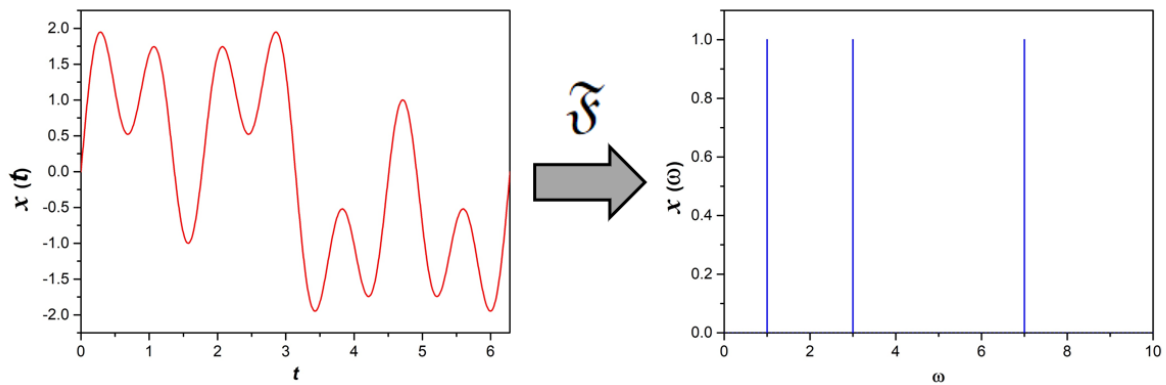


Figure A.2: The Fourier transform,  $x(\omega)$ , of the function,  $x(t)$ . In this case,  $x(t) = \sin(t) + \sin(3t) + \sin(7t)$  and  $x(\omega) = \delta(\omega+1) + \delta(\omega+3) + \delta(\omega+7)$ .

This can be applied to either the X-ray or neutron scattering. For example, X-rays interact with the electron cloud of atoms, where the electron density drops off as a Gaussian function. This shows how the Fourier transform of a Gaussian curve is another Gaussian.

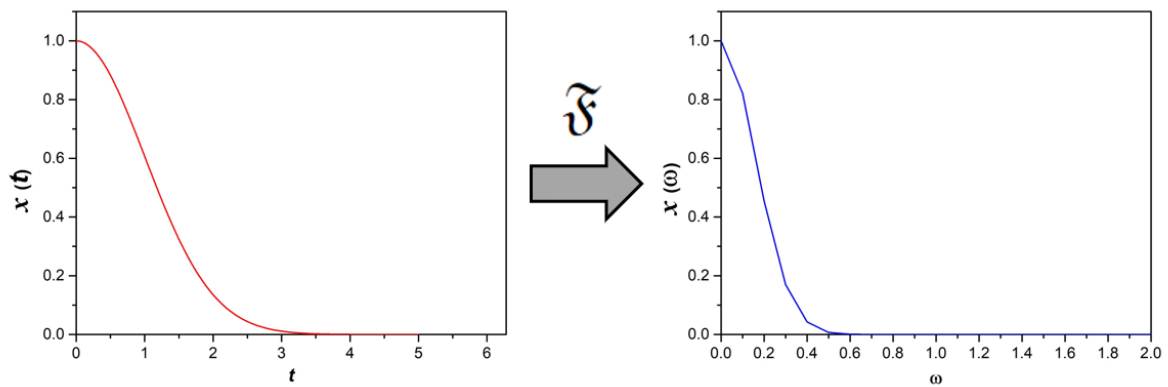


Figure A.3: The Fourier transform,  $x(\omega)$ , of the function,  $x(t)$ . In this case,  $x(t)$  is a Gaussian curve, and  $x(\omega)$  is another Gaussian curve.

Finally, the same can be done with neutron diffraction which interact with point-like particles. This gives a constant scattering factor.

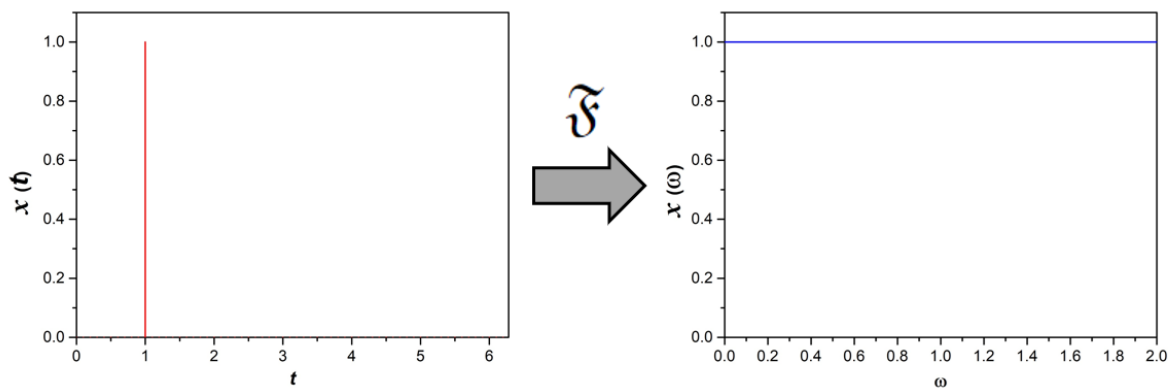


Figure A.4: The Fourier transform,  $x(\omega)$ , of the function,  $x(t)$ . In this case,  $x(t) = \delta(t+1)$  and  $x(\omega) = 1$ .

### Rietveld Analysis Fitting Parameters

The following  $R$ -factors are used to give insight into the quality of a powder diffraction Rietveld refinement.

The profile factor ( $R_p$ ) is used to determine how well each of the calculated intensities align with the observed intensities, and is calculated as

$$R_p = \frac{\sum_i^n |(y_i^{obs.} - y_i^{calc.})|}{\sum_i^n y_i^{obs.}} \quad (\text{A.3})$$

where  $y_i^{obs.}$  and  $y_i^{calc.}$  are the  $i$ th point for the observed and calculated intensities respectively, summed over the total number of observed points  $n$ .

The weighted profile ( $R_{wp}$ ) takes into account an additional weighting factor, which accounts for statistical variance. This is given as

$$W_i = \frac{N}{\sigma_i^2 I_i} \quad (\text{A.4})$$

where  $N$  is the number of detectors contributing to the intensity average,  $\sigma_i$  is the variance at the  $i$ th point, and  $I_i$  is its associated intensity. This allows for the weighted profile to be defined as

$$R_{wp} = \left[ \frac{\sum_i^n W_i (y_i^{obs.} - y_i^{calc.})^2}{\sum_i^n W_i (y_i^{obs.})^2} \right]^{\frac{1}{2}} \quad (\text{A.5})$$

Further to this, a goodness of fit ( $\chi^2$ ) can be thought of as the average between the observed values, and the values when the model is ideal and the standard uncertainty is correct. This is given as

$$\chi^2 = \frac{1}{N} \frac{\sum_i^n (y_i^{obs.} - y_i^{calc.})^2}{\sigma_i^2 I_i} \quad (\text{A.6})$$

Thompson-Cox-Hastings Peak Shape Parameters

The Thompson-Cox-Hastings (TCH) peak shape uses a pseudo-Voigt function. The Gaussian and Lorentzian components are weighted by a mixing parameter,  $\eta$ , as

$$\text{TCH} = \eta L + (1 - \eta) G \quad (\text{A.7})$$

where

$$\begin{aligned} \eta &= 1.36603q - 0.47719q^2 + 0.1116q^3 \\ q &= \Gamma_L / \Gamma \\ \Gamma &= \left( \Gamma_G^5 + A \Gamma_G^4 \Gamma_L + B \Gamma_G^3 \Gamma_L^2 + C \Gamma_G^2 \Gamma_L^3 + D \Gamma_G \Gamma_L^4 + \Gamma_L^5 \right)^{0.5} \end{aligned} \quad (\text{A.8})$$

with  $A = 2.69269$ ,  $B = 2.42843$ ,  $C = 4.47163$ ,  $D = 0.07842$ , and  $\Gamma$  is the full width at half maximum of the Bragg reflection.

The Gaussian and Lorentzian components are calculated as

$$\begin{aligned} \Gamma_G &= \left( U \tan^2 \theta + V \tan \theta + W + Z / \cos^2 \theta \right)^{0.5} \\ \Gamma_L &= X \tan \theta + Y / \cos \theta \end{aligned} \quad (\text{A.9})$$

where  $U$ ,  $V$ ,  $W$ , and  $Z$  are refined as instrument parameters, and  $X$  and  $Y$  are refined as sample parameters.

## A.2 Chapter 3: Ceramic Electrolytes for Solid Oxide Fuel Cells

Supporting information includes a comparison between the laboratory XRD and SXRD of the  $P2/c + I2/a$  mixed phase  $\text{ErTaO}_4$ , refined parameters for the  $\text{LnNbO}_4$ ,  $\text{LnTaO}_4$ , and  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  solid solution series, unit cell volumes and gradients for the  $\text{Ln}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  solid solution series, unit cell volumes for the  $\text{Ln}_2(\text{Zr}_{2-x}\text{Sn}_x)\text{O}_7$  series, refined parameters for the variable temperature data of  $\text{HoNbO}_4$  and  $\text{HoTaO}_4$  using the Wombat neutron powder diffractometer, relationship between activation energy and average O–O distance from electrochemical impedance spectroscopy, and the Arrhenius plots for a follow-up study on  $\text{La}(\text{Nb}_{0.65}\text{V}_{0.30}\text{Mo}_{0.05})\text{O}_{4+\delta}$ .

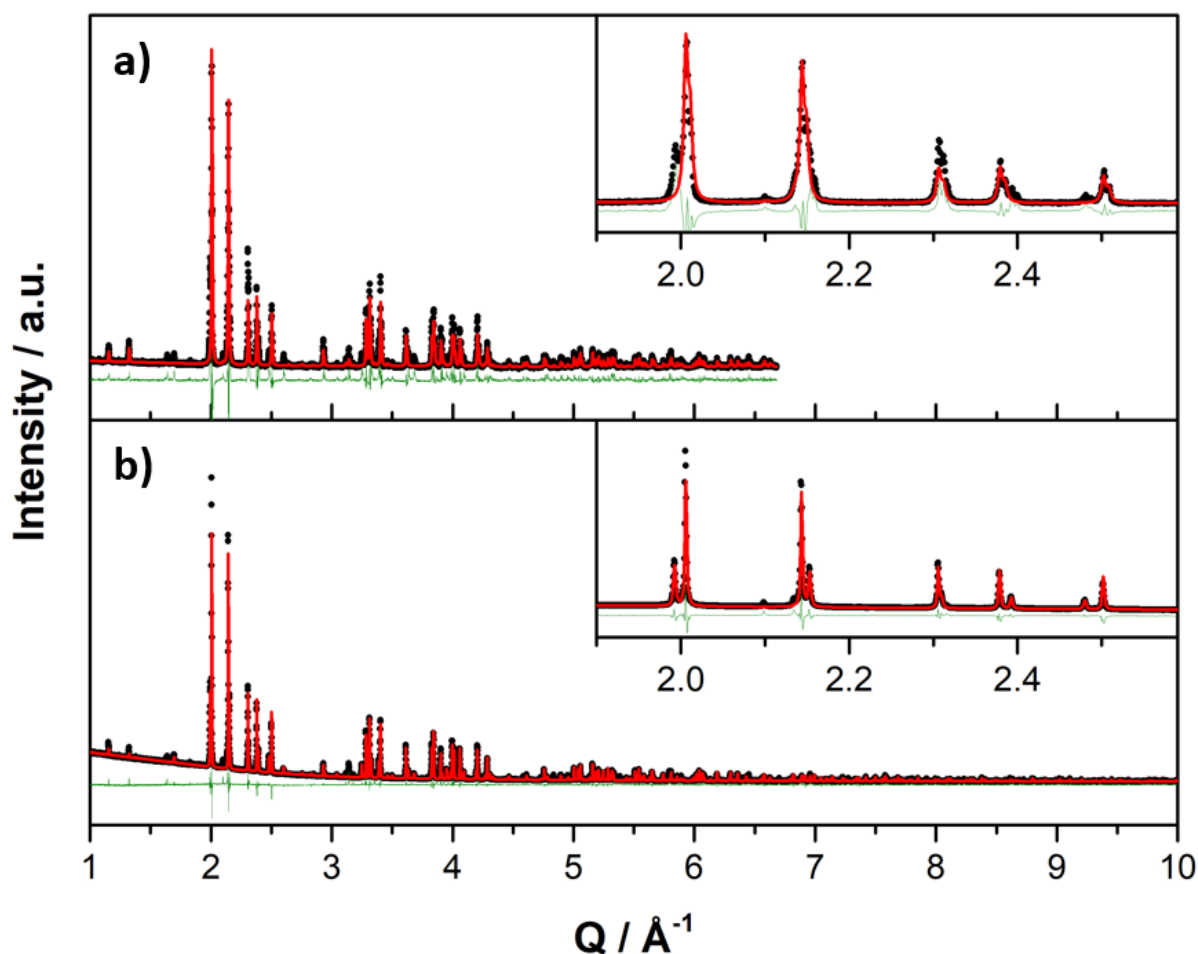


Figure A.5: Room temperature X-ray diffraction studies of  $\text{ErTaO}_4$  heated to 1550 °C. (a) Laboratory X-ray diffraction using copper source, and (b) synchrotron X-ray diffraction. The inset highlights the split reflections between 1.9–2.2 Å<sup>−1</sup>.

Table A.1: Rietveld refinement parameters of  $LnNbO_4$  taken from synchrotron X-ray diffraction data. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection.

| <i>Ln</i>                            | <b>La</b>            | <b>Pr</b>            | <b>Nd</b>            | <b>Sm</b>            | <b>Eu</b>            | <b>Gd</b>            | <b>Tb</b>            | <b>Dy</b>            | <b>Ho</b>            | <b>Er</b>            | <b>Tm</b>            | <b>Yb</b>            | <b>Lu</b>            |
|--------------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| <b>Radii (Å)</b>                     | 1.16                 | 1.126                | 1.109                | 1.079                | 1.066                | 1.053                | 1.04                 | 1.027                | 1.015                | 1.004                | 0.994                | 0.985                | 0.977                |
| <b>Space Group</b>                   | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> |
| <b>a (Å)</b>                         | 5.63469(5)           | 5.56699(2)           | 5.53672(2)           | 5.48729(4)           | 5.46049(3)           | 5.43837(2)           | 5.41620(2)           | 5.38930(2)           | 5.36692(3)           | 5.34623(2)           | 5.33037(4)           | 5.30764(4)           | 5.29225(3)           |
| <b>b (Å)</b>                         | 11.66597(9)          | 11.48030(3)          | 11.42014(4)          | 11.31303(9)          | 11.26669(5)          | 11.23067(4)          | 11.17573(4)          | 11.13006(5)          | 11.08959(5)          | 11.05049(5)          | 11.01473(8)          | 10.97639(8)          | 10.95583(5)          |
| <b>c (Å)</b>                         | 5.26748(4)           | 5.22215(2)           | 5.21051(2)           | 5.18287(4)           | 5.17601(2)           | 5.16944(2)           | 5.15095(2)           | 5.14451(2)           | 5.13632(3)           | 5.12691(2)           | 5.11305(4)           | 5.10795(4)           | 5.10235(3)           |
| <b>β (°)</b>                         | 94.082(1)            | 94.549(1)            | 94.676(1)            | 94.676(1)            | 94.638(1)            | 94.569(1)            | 94.698(1)            | 94.623(1)            | 94.561(1)            | 94.536(1)            | 94.597(1)            | 94.489(1)            | 94.421(1)            |
| <b>Vol. (Å<sup>3</sup>)</b>          | 345.375(8)           | 332.700(1)           | 328.432(2)           | 320.671(7)           | 317.394(4)           | 314.728(4)           | 310.740(4)           | 307.580(4)           | 304.730(4)           | 301.941(4)           | 299.235(6)           | 296.670(6)           | 294.959(4)           |
| <b><i>Ln y</i></b>                   | 0.12033(6)           | 0.12036(10)          | 0.12059(4)           | 0.12069(6)           | 0.12105(4)           | 0.12112(4)           | 0.12125(4)           | 0.12110(5)           | 0.12127(7)           | 0.12123(7)           | 0.12131(7)           | 0.12140(8)           | 0.12136(8)           |
| <b>Nb <i>y</i></b>                   | 0.64604(5)           | 0.64664(9)           | 0.64638(4)           | 0.64587(5)           | 0.64572(4)           | 0.64522(4)           | 0.64538(4)           | 0.64461(5)           | 0.64397(7)           | 0.64360(7)           | 0.64335(8)           | 0.64285(9)           | 0.64232(9)           |
| <b>O(1) <i>x</i></b>                 | 0.0111(6)            | 0.0091(10)           | 0.0090(4)            | 0.0102(6)            | 0.0080(5)            | 0.0052(5)            | 0.0070(4)            | 0.0042(5)            | 0.0013(8)            | 0.0013(8)            | 0.0022(7)            | -0.0005(8)           | -0.0049(8)           |
| <b>O(1) <i>y</i></b>                 | 0.7158(2)            | 0.7173(4)            | 0.7166(2)            | 0.7160(2)            | 0.7139(2)            | 0.7153(2)            | 0.7135(2)            | 0.7163(2)            | 0.7120(3)            | 0.7133(3)            | 0.7145(3)            | 0.7151(3)            | 0.7150(3)            |
| <b>O(1) <i>z</i></b>                 | 0.1915(6)            | 0.1990(10)           | 0.2003(4)            | 0.2038(6)            | 0.2060(5)            | 0.2042(5)            | 0.2078(5)            | 0.2064(5)            | 0.2062(8)            | 0.2083(8)            | 0.5075(8)            | 0.2068(9)            | 0.2028(8)            |
| <b>O(2) <i>x</i></b>                 | 0.8930(5)            | 0.9004(9)            | 0.8995(4)            | 0.8998(5)            | 0.9010(5)            | 0.9058(5)            | 0.9052(4)            | 0.9066(5)            | 0.9059(7)            | 0.9154(7)            | 0.9107(7)            | 0.9119(8)            | 0.9057(8)            |
| <b>O(2) <i>y</i></b>                 | 0.4479(2)            | 0.4538(4)            | 0.45421(17)          | 0.4537(2)            | 0.4573(2)            | 0.4536(2)            | 0.4586(2)            | 0.4555(2)            | 0.4530(3)            | 0.4534(4)            | 0.4593(3)            | 0.4572(3)            | 0.4576(4)            |
| <b>O(2) <i>z</i></b>                 | 0.2378(5)            | 0.2356(8)            | 0.2432(4)            | 0.2425(5)            | 0.2454(4)            | 0.2485(4)            | 0.2467(4)            | 0.2522(5)            | 0.2541(7)            | 0.2550(7)            | 0.2502(7)            | 0.2504(8)            | 0.2644(8)            |
| <b><i>Ln</i>-O(2) (Å)</b>            | 2.599(3)             | 2.539(4)             | 2.523(2)             | 2.5143(3)            | 2.518(2)             | 2.487(2)             | 2.500(2)             | 2.459(3)             | 2.476(4)             | 2.462(4)             | 2.445(4)             | 2.423(4)             | 2.400(4)             |
| <b><i>Ln</i>-O(1) (Å)</b>            | 2.574(3)             | 2.529(5)             | 2.502(2)             | 2.4907(3)            | 2.449(2)             | 2.474(2)             | 2.427(2)             | 2.431(3)             | 2.439(4)             | 2.444(4)             | 2.393(4)             | 2.405(4)             | 2.344(4)             |
| <b><i>Ln</i>-O(2) (Å)</b>            | 2.527(3)             | 2.480(5)             | 2.460(2)             | 2.4323(3)            | 2.3960(2)            | 2.392(2)             | 2.369(2)             | 2.369(3)             | 2.331(4)             | 2.322(4)             | 2.328(4)             | 2.316(4)             | 2.311(4)             |
| <b><i>Ln</i>-O(1) (Å)</b>            | 2.488(3)             | 2.448(5)             | 2.424(2)             | 2.4006(3)            | 2.3959(2)            | 2.348(2)             | 2.364(2)             | 2.323(3)             | 2.305(4)             | 2.259(4)             | 2.306(4)             | 2.287(4)             | 2.275(4)             |
| <b><i>Ln</i>-O<sub>av.</sub> (Å)</b> | 2.547                | 2.499                | 2.477                | 2.459                | 2.440                | 2.425                | 2.415                | 2.400                | 2.388                | 2.372                | 2.368                | 2.358                | 2.333                |
| <b>Nb-O(2) (Å)</b>                   | 2.596(3)             | 2.525(5)             | 2.518(2)             | 2.490(3)             | 2.498(3)             | 2.499(3)             | 2.482(2)             | 2.472(3)             | 2.508(4)             | 2.489(4)             | 2.473(4)             | 2.476(4)             | 2.499(4)             |
| <b>Nb-O(2) (Å)</b>                   | 1.920(3)             | 1.938(5)             | 1.932(2)             | 1.924(3)             | 1.924(2)             | 1.931(3)             | 1.921(2)             | 1.936(3)             | 1.923(4)             | 1.930(4)             | 1.926(4)             | 1.932(4)             | 1.934(4)             |
| <b>Nb-O(1) (Å)</b>                   | 1.810(3)             | 1.839(5)             | 1.856(2)             | 1.832(3)             | 1.863(2)             | 1.851(2)             | 1.870(2)             | 1.860(3)             | 1.840(4)             | 1.860(4)             | 1.863(4)             | 1.846(4)             | 1.878(4)             |
| <b>Nb-O<sub>av.</sub> (Å)</b>        | 2.109                | 2.101                | 2.102                | 2.082                | 2.095                | 2.094                | 2.091                | 2.089                | 2.090                | 2.093                | 2.087                | 2.085                | 2.104                |
| <b>BVS (NbO<sub>4</sub>)</b>         | 4.58                 | 4.29                 | 4.21                 | 4.40                 | 4.14                 | 4.25                 | 4.18                 | 4.17                 | 4.36                 | 4.20                 | 4.20                 | 4.27                 | 4.27                 |
| <b>BVS (NbO<sub>6</sub>)</b>         | 4.89                 | 4.67                 | 4.60                 | 4.82                 | 4.55                 | 4.65                 | 4.61                 | 4.60                 | 4.76                 | 4.61                 | 4.64                 | 4.71                 | 4.67                 |
| <b><i>R<sub>wp</sub></i></b>         | 3.35                 | 3.04                 | 3.65                 | 3.33                 | 4.00                 | 3.55                 | 3.65                 | 3.50                 | 4.69                 | 3.99                 | 4.35                 | 3.83                 | 3.49                 |

Table A.2: Rietveld refinement parameters of  $\text{LnTaO}_4$  taken from synchrotron X-ray diffraction data. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection.

| <i>Ln</i>                                | <b>Nd</b>            | <b>Sm</b>            | <b>Eu</b>            | <b>Gd</b>            | <b>Tb</b>            |                      | <b>Dy</b>            |                      | <b>Ho</b>            |                      | <b>Er</b>            | <b>Tm</b>            | <b>Yb</b>            | <b>Lu</b>            |
|------------------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Radii (Å)                                | 1.109                | 1.079                | 1.066                | 1.053                | 1.04                 |                      | 1.027                |                      | 1.015                |                      | 1.004                | 0.994                | 0.985                | 0.977                |
| Space Group                              | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>I</i> 2/ <i>a</i> | <i>P</i> 2/ <i>c</i> | <i>I</i> 2/ <i>a</i> | <i>P</i> 2/ <i>c</i> | <i>I</i> 2/ <i>a</i> | <i>P</i> 2/ <i>c</i> | <i>P</i> 2/ <i>c</i> | <i>P</i> 2/ <i>c</i> | <i>P</i> 2/ <i>c</i> | <i>P</i> 2/ <i>c</i> |
| <b>a</b> (Å)                             | 5.51510(1)           | 5.45920(1)           | 5.42997(1)           | 5.40654(1)           | 5.38360(1)           | 5.14307(1)           | 5.35385(1)           | 5.13080(1)           | 5.33123(1)           | 5.11631(1)           | 5.10082(1)           | 5.08103(1)           | 5.07127(1)           | 5.06089(1)           |
| <b>b</b> (Å)                             | 11.2388(1)           | 11.1425(1)           | 11.1010(1)           | 11.0666(1)           | 11.0189(1)           | 5.49250(1)           | 10.9765(1)           | 5.47233(1)           | 10.9387(1)           | 5.45420(1)           | 5.44167(1)           | 5.43502(1)           | 5.42469(1)           | 5.42596(1)           |
| <b>c</b> (Å)                             | 5.11584(1)           | 5.09369(1)           | 5.08887(1)           | 5.08388(1)           | 5.06777(1)           | 5.33826(1)           | 5.06265(1)           | 5.31877(1)           | 5.05652(1)           | 5.30355(1)           | 5.28658(1)           | 5.27321(1)           | 5.25493(1)           | 5.23995(1)           |
| <b>β</b> (°)                             | 95.724(1)            | 95.758(1)            | 95.697(1)            | 95.618(1)            | 95.703(1)            | 96.646(1)            | 95.615(1)            | 96.582(2)            | 95.544(1)            | 96.500(1)            | 96.425(1)            | 96.357(1)            | 96.208(1)            | 96.091(1)            |
| <b>Vol.</b> (Å <sup>3</sup> )            | 315.514(1)           | 308.281(1)           | 305.233(1)           | 302.719(1)           | 299.139(1)           | 149.784(1)           | 296.087(1)           | 148.353(1)           | 293.500(1)           | 147.046(1)           | 145.818(1)           | 144.727(1)           | 143.716(1)           | 143.078(1)           |
| <b>Ln y</b>                              | 0.09887(1)           | 0.11808(1)           | 0.11794(1)           | 0.61810(1)           | 0.61787(1)           | 0.23444(1)           | 0.61818(1)           | 0.23463(1)           | 0.63179(1)           | 0.23482(1)           | 0.23399(1)           | 0.23268(1)           | 0.23144(1)           | 0.23032(1)           |
| <b>Ta y</b>                              | 0.63232(1)           | 0.65061(1)           | 0.64981(1)           | 0.14942(1)           | 0.14967(1)           | 0.30712(1)           | 0.14873(1)           | 0.30653(1)           | 0.10149(1)           | 0.30491(1)           | 0.30437(1)           | 0.30483(1)           | 0.30303(1)           | 0.30300(1)           |
| <b>O(1) x</b>                            | 0.23156(1)           | 0.02462(1)           | 0.01498(1)           | 0.09306(1)           | 0.09067(1)           | 0.75496(1)           | 0.08803(1)           | 0.74973(1)           | 0.23880(1)           | 0.75320(1)           | 0.75089(1)           | 0.74947(1)           | 0.75626(1)           | 0.75582(1)           |
| <b>O(1) y</b>                            | 0.03289(1)           | 0.71541(1)           | 0.71898(1)           | 0.45317(1)           | 0.45407(1)           | 0.90616(1)           | 0.45632(1)           | 0.90912(1)           | 0.03752(1)           | 0.90837(1)           | 0.90657(1)           | 0.90830(1)           | 0.90218(1)           | 0.90988(1)           |
| <b>O(1) z</b>                            | 0.03516(1)           | 0.21413(1)           | 0.21598(1)           | 0.25114(1)           | 0.24198(1)           | 0.37934(1)           | 0.24807(1)           | 0.39289(1)           | 0.02710              | 0.38232(1)           | 0.39093(1)           | 0.39205(1)           | 0.39494(1)           | 0.39778(1)           |
| <b>O(2) x</b>                            | 0.14888(1)           | 0.89792(1)           | 0.90100(1)           | -0.0115(1)           | -0.0140(1)           | 0.26849(1)           | -0.0105(1)           | 0.27159(1)           | 0.15727(1)           | 0.27476(1)           | 0.26915(1)           | 0.26975(1)           | 0.26790(1)           | 0.26869(1)           |
| <b>O(2) y</b>                            | 0.20343(1)           | 0.45257(1)           | 0.45599(1)           | 0.71590(1)           | 0.71270(1)           | 0.55629(1)           | 0.71420(1)           | 0.56295(1)           | 0.20645(1)           | 0.55934(1)           | 0.56037(1)           | 0.57330(1)           | 0.57583(1)           | 0.57193(1)           |
| <b>O(2) z</b>                            | 0.50124(1)           | 0.24627(1)           | 0.24008(1)           | 0.28151(1)           | 0.27158(1)           | 0.48406(1)           | 0.28011(1)           | 0.49099(1)           | 0.50704(1)           | 0.48567(1)           | 0.48915(1)           | 0.49722(1)           | 0.49988(1)           | 0.49962(1)           |
| <b>Ln-O(2)</b> (Å)                       | 2.559(6)             | 2.564(5)             | 2.503(7)             | 2.511(6)             | 2.574(8)             | 2.489(8)             | 2.505(6)             | 2.520(8)             | 2.522(6)             | 2.507(8)             | 2.499(6)             | 2.571(9)             | 2.589(9)             | 2.572(9)             |
| <b>Ln-O(1)</b> (Å)                       | 2.450(7)             | 2.445(6)             | 2.409(7)             | 2.428(6)             | 2.392(8)             | 2.387(10)            | 2.387(5)             | 2.373(8)             | 2.350(6)             | 2.376(9)             | 2.355(6)             | 2.346(9)             | 2.343(9)             | 2.314(8)             |
| <b>Ln-O(2)</b> (Å)                       | 2.434(6)             | 2.437(5)             | 2.403(8)             | 2.369(6)             | 2.332(9)             | 2.350(9)             | 2.336(6)             | 2.365(10)            | 2.311(7)             | 2.336(7)             | 2.339(8)             | 2.291(8)             | 2.247(11)            | 2.261(10)            |
| <b>Ln-O(1)</b> (Å)                       | 2.350(6)             | 2.346(5)             | 2.317(7)             | 2.287(5)             | 2.291(8)             | 2.348(8)             | 2.255(5)             | 2.318(8)             | 2.256(6)             | 2.332(7)             | 2.296(6)             | 2.276(11)            | 2.242(9)             | 2.243(8)             |
| <b>Ln-O<sub>av.</sub></b> (Å)            | 2.448(13)            | 2.448(11)            | 2.407(15)            | 2.399(12)            | 2.386(14)            | 2.394(17)            | 2.371(11)            | 2.394(15)            | 2.360(13)            | 2.388(14)            | 2.372(13)            | 2.371(19)            | 2.355(19)            | 2.347(18)            |
| <b>LnO<sub>8</sub></b> (Å <sup>3</sup> ) | 25.22(13)            | 25.25(11)            | 24.05                | 23.77(12)            | 23.18(14)            | 23.51(17)            | 22.94(11)            | 23.58(15)            | 22.60(12)            | 23.38(14)            | 22.88(13)            | 22.85(18)            | 22.33(18)            | 22.09(17)            |
| <b>Ta-O(2)</b> (Å)                       | 2.364(6)             | 2.349(5)             | 2.361(7)             | 2.362(6)             | 2.324(8)             | 2.217(9)             | 2.358(6)             | 2.216(9)             | 2.357(6)             | 2.204(8)             | 2.206(7)             | 2.220(9)             | 2.224(9)             | 2.214(9)             |
| <b>Ta-O(2)</b> (Å)                       | 1.910(7)             | 1.865(6)             | 1.921(8)             | 1.927(7)             | 1.915(9)             | 1.971(10)            | 1.916(7)             | 1.949(10)            | 1.909(7)             | 1.939(9)             | 1.963(8)             | 1.959(11)            | 1.969(11)            | 1.963(11)            |
| <b>Ta-O(1)</b> (Å)                       | 1.865(6)             | 1.825(5)             | 1.853(7)             | 1.843(5)             | 1.874(8)             | 1.833(8)             | 1.868(5)             | 1.823(8)             | 1.873(6)             | 1.825(7)             | 1.816(6)             | 1.814(8)             | 1.820(9)             | 1.842(8)             |
| <b>Ta-O<sub>av.</sub></b> (Å)            | 2.047(11)            | 2.013(9)             | 2.046(13)            | 2.044(1)             | 2.038(14)            | 2.007(16)            | 2.047(1)             | 1.996(15)            | 2.046(11)            | 1.989(14)            | 1.995(12)            | 1.998(16)            | 2.004(17)            | 2.007(16)            |
| <b>TaO<sub>6</sub></b> (Å <sup>3</sup> ) | 10.2(5)              | 9.73(4)              | 10.19(6)             | 10.20(5)             | 10.19(7)             | 9.49(8)              | 10.30(5)             | 9.47(7)              | 10.31(6)             | 9.29(7)              | 9.43(6)              | 9.71(8)              | 9.79(8)              | 9.81(8)              |
| <b>BVS (TaO<sub>4</sub>)</b>             | 4.32                 | 4.84                 | 4.53                 | 4.41                 | 4.18                 | 4.27                 | 4.31                 | 4.24                 | 4.33                 | 4.50                 | 4.42                 | 4.44                 | 4.41                 | 4.23                 |
| <b>BVS (TaO<sub>6</sub>)</b>             | 4.92                 | 5.47                 | 5.18                 | 5.02                 | 4.82                 | 5.17                 | 4.92                 | 5.16                 | 4.94                 | 5.43                 | 5.35                 | 5.33                 | 5.28                 | 5.13                 |
| <b>R<sub>wp</sub></b>                    | 6.16                 | 4.25                 | 4.30                 | 3.15                 | 4.75                 | 3.21                 | 3.40                 | 4.33                 | 3.28                 | 4.26                 | 3.93                 | 4.29                 | 4.31                 | 3.89                 |



Table A.3: Unit cell volumes and associated gradients across the  $Ln(Nb_{1-x}Ta_x)O_4$  solid solution series determined from synchrotron X-ray diffraction.

| $x$       | Ionic Radius (Å) | 0.0        | 0.1        | 0.2        | 0.3        | 0.4        | 0.5        | 0.6        | 0.7        | 0.8        | 0.9        | 1.0        | Gradient  |
|-----------|------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-----------|
| <b>Nd</b> | 1.109            | 316.697(1) |            | 316.278(1) |            | 316.026(1) |            | 315.792(1) |            | 315.581(1) |            | 315.469(1) | -1.21(12) |
| <b>Sm</b> | 1.079            | 309.093(1) | 308.976(1) | 308.795(1) | 308.705(1) | 308.612(1) | 308.477(1) | 308.409(1) | 308.346(1) | 308.281(1) | 308.218(1) | 308.160(1) | -0.92(5)  |
| <b>Gd</b> | 1.053            | 303.507(1) |            | 303.288(1) |            | 303.047(1) |            | 302.916(1) |            | 302.741(1) |            | 302.699(1) | -0.83(8)  |
| <b>Tb</b> | 1.04             | 299.699(1) |            | 299.492(1) |            | 299.326(1) |            | 299.165(1) |            | 298.981(1) |            | 299.125(1) | -0.65(13) |
| <b>Dy</b> | 1.027            | 296.628(1) |            | 296.460(1) |            | 296.286(1) |            | 296.118(1) |            | 296.094(1) |            | 296.067    | -0.58(9)  |
| <b>Ho</b> | 1.015            | 293.904(1) | 293.712(1) | 293.760(1) | 293.700(1) | 293.629(1) | 293.556(1) | 293.577(1) | 293.527(1) | 293.365(1) | 293.447(1) | 293.485(1) | -0.43(6)  |

Table A.4: Rietveld refinement parameters of the  $\text{Ho}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_4$  taken from combined synchrotron X-ray and neutron powder diffraction data. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection.

| Sample                           | $\text{HoNbO}_4$ | $\text{Ho}(\text{Nb}_{0.9}\text{Ta}_{0.1})\text{O}_4$ | $\text{Ho}(\text{Nb}_{0.8}\text{Ta}_{0.2})\text{O}_4$ | $\text{Ho}(\text{Nb}_{0.7}\text{Ta}_{0.3})\text{O}_4$ | $\text{Ho}(\text{Nb}_{0.6}\text{Ta}_{0.4})\text{O}_4$ | $\text{Ho}(\text{Nb}_{0.5}\text{Ta}_{0.5})\text{O}_4$ | $\text{Ho}(\text{Nb}_{0.4}\text{Ta}_{0.6})\text{O}_4$ | $\text{Ho}(\text{Nb}_{0.3}\text{Ta}_{0.7})\text{O}_4$ | $\text{Ho}(\text{Nb}_{0.2}\text{Ta}_{0.8})\text{O}_4$ | $\text{Ho}(\text{Nb}_{0.1}\text{Ta}_{0.9})\text{O}_4$ | $\text{HoTaO}_4$ |
|----------------------------------|------------------|-------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|------------------|
| $x$ Value                        | 0.0              | 0.1                                                   | 0.2                                                   | 0.3                                                   | 0.4                                                   | 0.5                                                   | 0.6                                                   | 0.7                                                   | 0.8                                                   | 0.9                                                   | 1.0              |
| $a$ (Å)                          | 5.302500(9)      | 5.305895(10)                                          | 5.30881(2)                                            | 5.31192(2)                                            | 5.31468(2)                                            | 5.31775(4)                                            | 5.32093(2)                                            | 5.32362(2)                                            | 5.32628(2)                                            | 5.32863(2)                                            | 5.33109(1)       |
| $b$ (Å)                          | 10.95635(2)      | 10.95439(2)                                           | 10.95207(3)                                           | 10.94997(4)                                           | 10.94772(5)                                           | 10.9461(1)                                            | 10.94421(3)                                           | 10.94229(4)                                           | 10.94060(4)                                           | 10.93888(3)                                           | 10.93838(2)      |
| $c$ (Å)                          | 5.074735(9)      | 5.07242(1)                                            | 5.07004(2)                                            | 5.06791(2)                                            | 5.06583(2)                                            | 5.06348(4)                                            | 5.06222(2)                                            | 5.06046(2)                                            | 5.05892(2)                                            | 5.05738(2)                                            | 5.05638(1)       |
| $\beta$ (°)                      | 94.56375(14)     | 94.68914(15)                                          | 94.8046(2)                                            | 94.9180(2)                                            | 95.0227(3)                                            | 95.1256(5)                                            | 95.2277(2)                                            | 95.3179(2)                                            | 95.4038(2)                                            | 95.4769(2)                                            | 95.5435(2)       |
| Vol. (Å <sup>3</sup> )           | 293.887(1)       | 293.837(1)                                            | 293.749(2)                                            | 293.691(2)                                            | 293.617(2)                                            | 293.559(4)                                            | 293.564(2)                                            | 293.516(2)                                            | 293.487(2)                                            | 293.445(1)                                            | 293.476(1)       |
| $\ln y$                          | 0.6205(3)        | 0.6200(3)                                             | 0.6200(3)                                             | 0.62042(10)                                           | 0.62004(11)                                           | 0.61964(15)                                           | 0.6193(3)                                             | 0.61881(10)                                           | 0.61894(10)                                           | 0.6192(4)                                             | 0.6187(3)        |
| $B y$                            | 0.1431(4)        | 0.14422(8)                                            | 0.14530(8)                                            | 0.14594(8)                                            | 0.14639(8)                                            | 0.1468(11)                                            | 0.14708(7)                                            | 0.14744(6)                                            | 0.14785(6)                                            | 0.14811(5)                                            | 0.14845(4)       |
| $\text{O}(1) x$                  | 0.0916(7)        | 0.0909(6)                                             | 0.0937(7)                                             | 0.0936(7)                                             | 0.0923(7)                                             | 0.0929(9)                                             | 0.0920(6)                                             | 0.0917(7)                                             | 0.0968(12)                                            | 0.0925(12)                                            | 0.0923(6)        |
| $\text{O}(1) y$                  | 0.4599(3)        | 0.4595(3)                                             | 0.4599(4)                                             | 0.4602(4)                                             | 0.4605(4)                                             | 0.4607(5)                                             | 0.4591(3)                                             | 0.4602(4)                                             | 0.4575(5)                                             | 0.4553(5)                                             | 0.4605(3)        |
| $\text{O}(1) z$                  | 0.2535(7)        | 0.2549(6)                                             | 0.2549(7)                                             | 0.2544(7)                                             | 0.2548(7)                                             | 0.2556(10)                                            | 0.2559(7)                                             | 0.2545(7)                                             | 0.2407(14)                                            | 0.2401(13)                                            | 0.2547(6)        |
| $\text{O}(2) x$                  | -0.0042(7)       | -0.0044(7)                                            | -0.0028(8)                                            | -0.0036(8)                                            | -0.0036(8)                                            | -0.0032(12)                                           | -0.0057(8)                                            | -0.0055(8)                                            | -0.0103(15)                                           | -0.0127(13)                                           | -0.0051(7)       |
| $\text{O}(2) y$                  | 0.7182(3)        | 0.7184(3)                                             | 0.7185(3)                                             | 0.7183(3)                                             | 0.7181(3)                                             | 0.7181(4)                                             | 0.7180(3)                                             | 0.7181(3)                                             | 0.7188(5)                                             | 0.7194(5)                                             | 0.7185(3)        |
| $\text{O}(2) z$                  | 0.2906(7)        | 0.2883(6)                                             | 0.2892(7)                                             | 0.2885(7)                                             | 0.2867(7)                                             | 0.2854(11)                                            | 0.2835(7)                                             | 0.2828(7)                                             | 0.2837(15)                                            | 0.2824(14)                                            | 0.2805(6)        |
| $\text{Ho-O}(2)$ (Å)             | 2.417(5)         | 2.422(5)                                              | 2.414(5)                                              | 2.421(5)                                              | 2.424(5)                                              | 2.427(7)                                              | 2.440(5)                                              | 2.435(5)                                              | 2.434(6)                                              | 2.433(5)                                              | 2.441(5)         |
| $\text{Ho-O}(1)$ (Å)             | 2.372(5)         | 2.379(5)                                              | 2.370(5)                                              | 2.364(5)                                              | 2.367(5)                                              | 2.365(7)                                              | 2.374(5)                                              | 2.370(5)                                              | 2.359(7)                                              | 2.356(5)                                              | 2.360(5)         |
| $\text{Ho-O}(2)$ (Å)             | 2.335(4)         | 2.333(4)                                              | 2.333(5)                                              | 2.335(5)                                              | 2.329(5)                                              | 2.326(7)                                              | 2.331(5)                                              | 2.328(5)                                              | 2.326(6)                                              | 2.326(5)                                              | 2.329(4)         |
| $\text{Ho-O}(1)$ (Å)             | 2.311(4)         | 2.307(4)                                              | 2.318(4)                                              | 2.315(4)                                              | 2.311(4)                                              | 2.313(6)                                              | 2.304(4)                                              | 2.302(4)                                              | 2.302(5)                                              | 2.307(5)                                              | 2.299(4)         |
| $\text{Ho-O}_{av.}$ (Å)          | 2.359(5)         | 2.360(5)                                              | 2.359(5)                                              | 2.359(5)                                              | 2.358(5)                                              | 2.358(7)                                              | 2.362(5)                                              | 2.359(5)                                              | 2.355(6)                                              | 2.356(5)                                              | 2.357(5)         |
| $\text{HoO}_8$ (Å <sup>3</sup> ) | 22.76(4)         | 22.76(4)                                              | 22.75(5)                                              | 22.73(5)                                              | 22.68(5)                                              | 22.67(6)                                              | 22.76(5)                                              | 22.65(5)                                              | 22.56(6)                                              | 22.58(5)                                              | 22.58(4)         |
| $B\text{-O}(2)$ (Å)              | 2.424(5)         | 2.406(4)                                              | 2.403(4)                                              | 2.394(4)                                              | 2.386(4)                                              | 2.379(6)                                              | 2.364(4)                                              | 2.358(4)                                              | 2.359(5)                                              | 2.359(4)                                              | 2.340(4)         |
| $B\text{-O}(2)$ (Å)              | 1.930(5)         | 1.934(4)                                              | 1.934(5)                                              | 1.931(5)                                              | 1.936(5)                                              | 1.941(6)                                              | 1.937(5)                                              | 1.940(5)                                              | 1.945(5)                                              | 1.947(5)                                              | 1.950(4)         |
| $B\text{-O}(1)$ (Å)              | 1.838(5)         | 1.838(4)                                              | 1.840(4)                                              | 1.847(4)                                              | 1.853(4)                                              | 1.852(6)                                              | 1.847(4)                                              | 1.857(4)                                              | 1.865(5)                                              | 1.861(5)                                              | 1.861(4)         |
| $B\text{-O}_{av.}$ (Å)           | 2.064(5)         | 2.060(4)                                              | 2.059(4)                                              | 2.058(4)                                              | 2.058(4)                                              | 2.057(6)                                              | 2.049(4)                                              | 2.052(4)                                              | 2.056(5)                                              | 2.055(5)                                              | 2.051(4)         |
| $\text{BO}_6$ (Å <sup>3</sup> )  | 10.26(2)         | 10.23(2)                                              | 10.26(2)                                              | 10.27(2)                                              | 10.31(2)                                              | 10.32(3)                                              | 10.22(2)                                              | 10.26(2)                                              | 10.35(3)                                              | 10.35(2)                                              | 10.28(2)         |
| $R_{wp}$                         | 7.01             | 5.53                                                  | 6.15                                                  | 5.85                                                  | 5.69                                                  | 5.89                                                  | 4.29                                                  | 4.49                                                  | 4.87                                                  | 5.91                                                  | 3.25             |

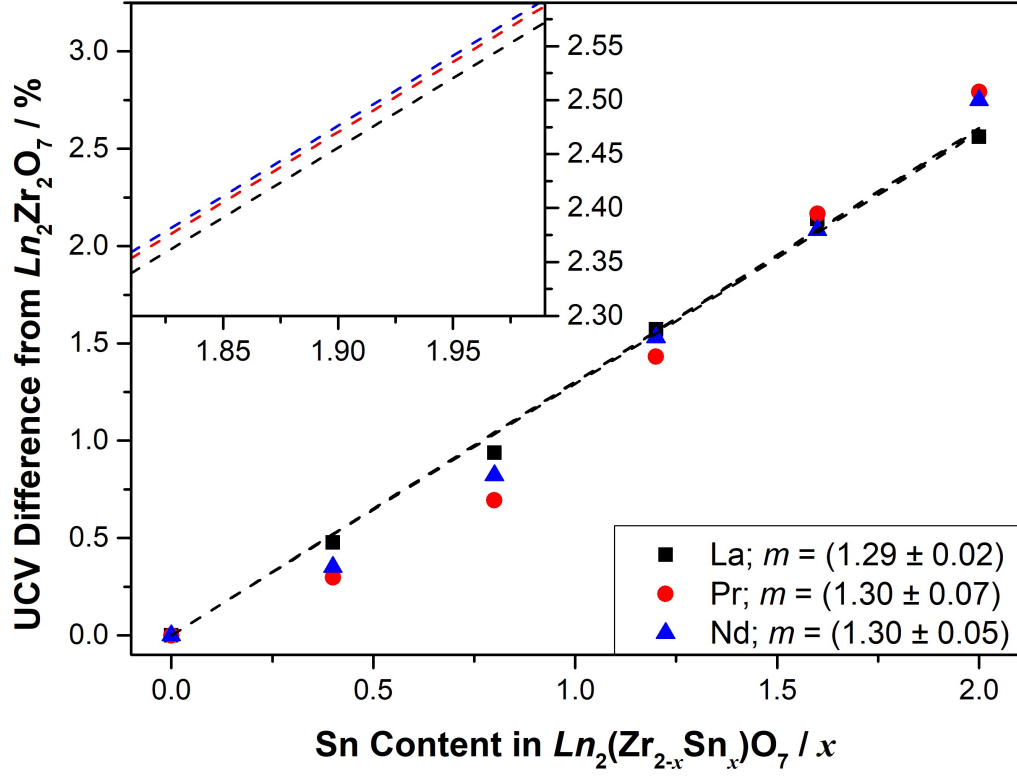


Figure A.6: Unit cell volumes of  $Ln_2(Zr_{2-x}Sn_x)O_7$  ( $Ln^{3+} = La, Nd, Sm$ ) pyrochlores plotted as a difference from the original  $Ln_2Zr_2O_7$  structure. The linear lines have been added as lines of best fit, with the gradients included in the legend. The inset demonstrates the lack of significant variation between the lines of best fit.

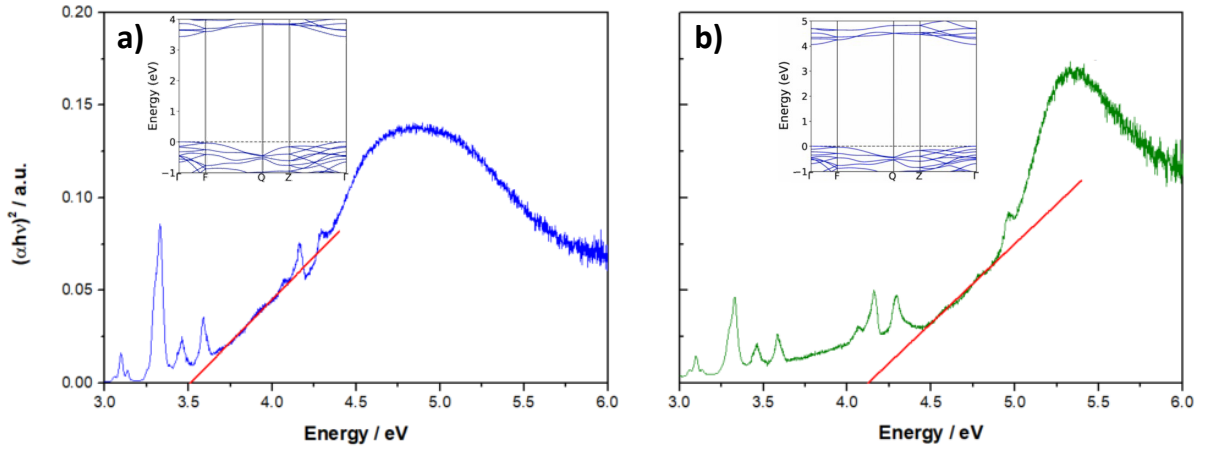


Figure A.7: The Tauc plots for (a)  $HoNbO_4$  and (b)  $HoTaO_4$  obtained from UV-Vis diffuse reflection spectroscopy. Data is presented as the Kubunka-Munk transform of a direct-allowed transition. The insets show the electronic band structure along the high-symmetry path  $\Gamma$ -F-Q-Z- $\Gamma$ .

Table A.5: Refined parameters for  $\text{HoTaO}_4$  at low and high temperatures using neutron powder diffraction.

|                                             | $\text{HoTaO}_4$ (50 °C) | $\text{HoTaO}_4$ (1500 °C) | $\text{HoTaO}_4$ (50 °C) |
|---------------------------------------------|--------------------------|----------------------------|--------------------------|
| <b>Space Group</b>                          | $P2/c$                   | $I4_1/a$                   | $I2/a$                   |
| <b>a (Å)</b>                                | 5.1444(4)                | 5.2803(3)                  | 5.3660(5)                |
| <b>b (Å)</b>                                | 5.4926(5)                | = b                        | 11.0257(12)              |
| <b>c (Å)</b>                                | 5.3343(4)                | 11.2061(10)                | 5.0948(5)                |
| <b><math>\beta</math> (°)</b>               | 96.407(6)                | = 90                       | 95.320(9)                |
| <b>Volume (Å<sup>3</sup>)</b>               | 149.79(2)                | 312.45(4)                  | 300.13(5)                |
| <b>Ho y</b>                                 | 0.2333(7)                | = 1/8                      | 0.6198(5)                |
| <b>Nb y</b>                                 | 0.3043(7)                | = 1/8                      | 0.1472(5)                |
| <b>Ho-O (Å)</b>                             | 2.304(5)                 | 2.366(3)                   | 2.336(6)                 |
| <b>Ho-O (Å)</b>                             | 2.311(5)                 | --                         | 2.340(7)                 |
| <b>Ho-O (Å)</b>                             | 2.357(5)                 | 2.412(3)                   | 2.404(7)                 |
| <b>Ho-O (Å)</b>                             | 2.554(5)                 | --                         | 2.472(7)                 |
| <b>HoO<sub>8</sub> Vol. (Å<sup>3</sup>)</b> | 23.05                    | 23.86                      | 23.48                    |
| <b>Ta-O(1) (Å)</b>                          | 1.882(5)                 | 1.918(4)                   | 1.845(7)                 |
| <b>Ta-O(2) (Å)</b>                          | 2.015(5)                 | --                         | 1.955(7)                 |
| <b>Ta-O(2) (Å)</b>                          | 2.222(5)                 | 2.809(3)                   | 2.362(7)                 |
| <b>BVS TaO<sub>4</sub></b>                  | 3.80                     | 4.72                       | 4.27                     |
| <b>BVS TaO<sub>6</sub></b>                  | 4.72                     | --                         | 4.88                     |

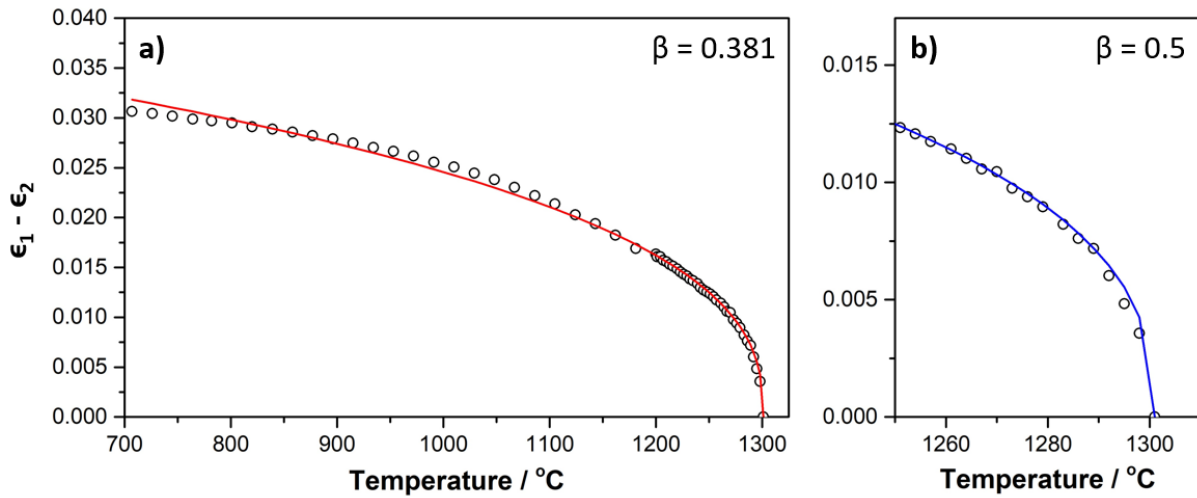


Figure A.8: Strain analysis based on the lattice parameters from the variable temperature Rietveld refinements of  $\text{HoTaO}_4$  upon cooling. (a) The  $(\epsilon_1 - \epsilon_2)$  strain component, as calculated using the expression from Equation 3.5, fitted over the whole measured temperature range, and (b) the fit performed in a range 50 °C below  $T_c$  with  $\beta = 0.5$ . Although the data was fit down to 100 °C, the plots show from 700–1300 °C for clarity.

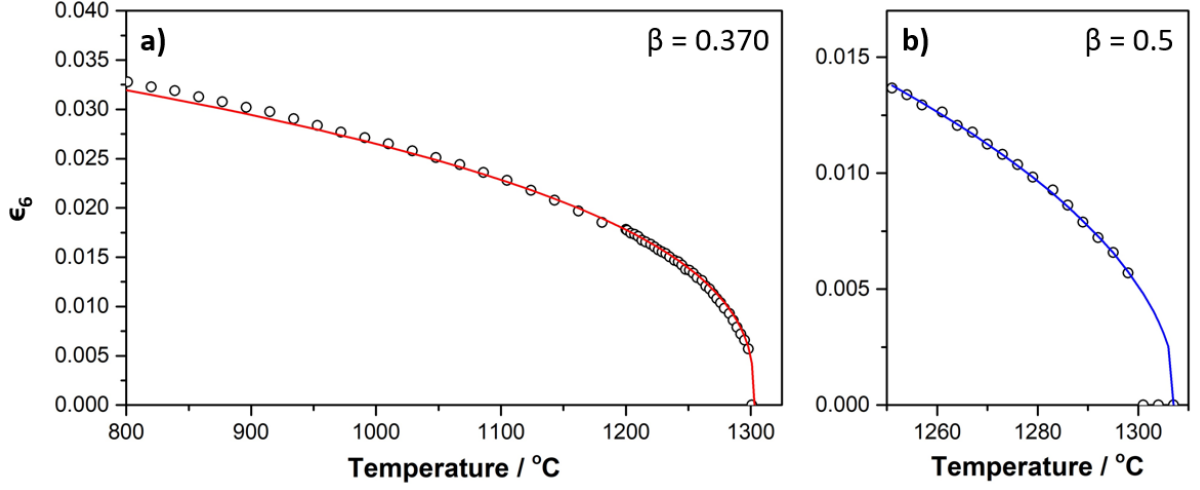


Figure A.9: Strain analysis based on the lattice parameters from the variable temperature Rietveld refinements of  $\text{HoTaO}_4$  upon cooling. (a) The  $\epsilon_6$  strain component, as calculated using the expression from Equation 3.5, fitted over the 800–1300 °C temperature range, and (b) the fit performed in a range 50 °C below  $T_c$  with  $\beta = 0.5$ . Data was fit over a reduced region due to the saturation of the strain component.

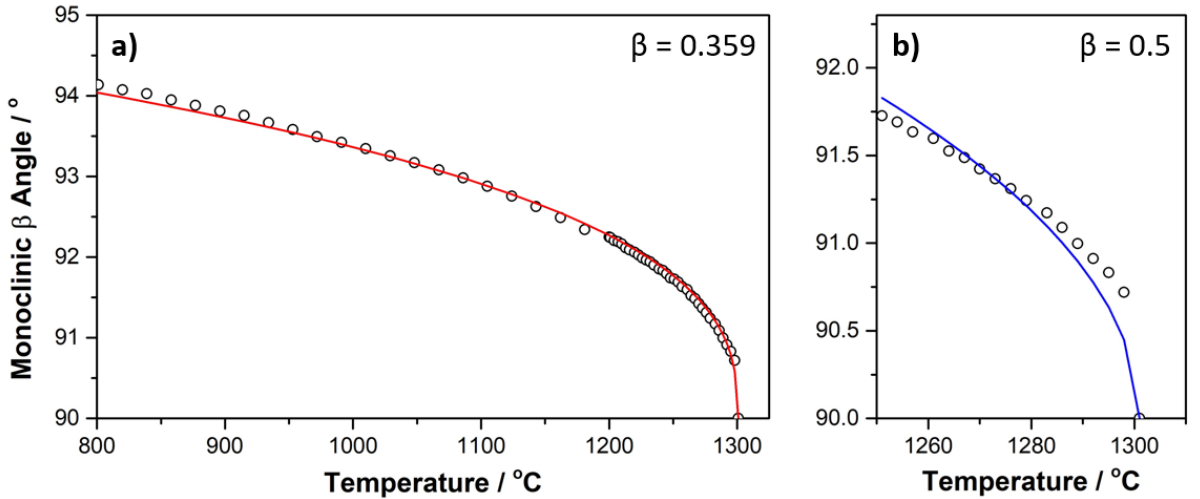


Figure A.10: The monoclinic  $\beta$  angle from the variable temperature Rietveld refinements of  $\text{HoTaO}_4$  upon cooling. (a) The monoclinic  $\beta$  angle fitted over the whole measured temperature range, and (b) the fit performed in a range 50 °C below  $T_c$  with  $\beta = 0.5$ . Although the data was fit down to 100 °C, the plots show from 700–1300 °C for clarity.

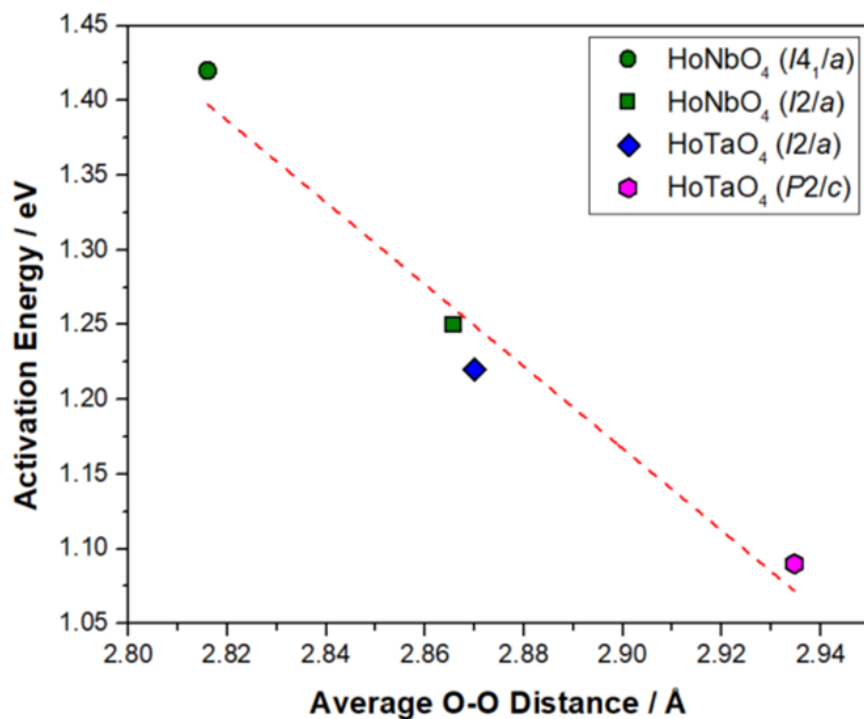


Figure A.11: Relationship between the activation energy calculated from the electrochemical impedance spectroscopy measured in air, and the average O–O distances taken from the Rietveld refinements of the neutron powder diffraction datasets.

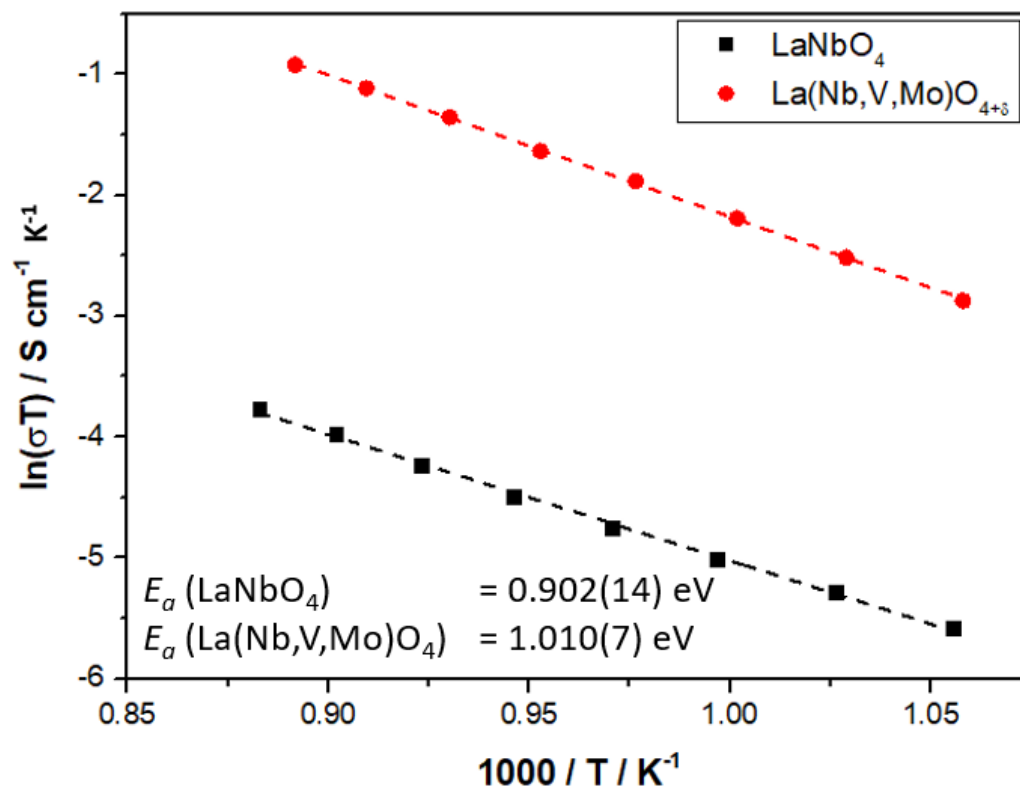


Figure A.12: Arrhenius plots of (black squares) LaNbO<sub>4</sub> and (red circles) La(Nb<sub>0.65</sub>V<sub>0.30</sub>Mo<sub>0.05</sub>)O<sub>4+δ</sub> from the electrochemical impedance spectroscopy measured in air. The activation energies are listed as an inset.

## A.3 Chapter 4: Rare-Earth Ion Matrices for Solid State Lasers

Supporting information includes refined parameters for the  $\text{NaA}(\text{WO}_4)_2$  ( $A^{3+} = \text{La, Pr, Nd, Lu, Bi}$ ) samples, refined parameters for the  $\text{NaA}(\text{MoO}_4)_2$  ( $A^{3+} = \text{La, Eu, Lu, Bi}$ ) samples, synchrotron X-ray and neutron powder diffraction patterns for  $\text{NaA}(\text{MoO}_4)_2$ , unit cell parameters and bond lengths of the  $\text{NaA}(\text{MoO}_4)_2$ .

Table A.6: Refinement parameters of  $\text{NaA}(\text{WO}_4)_2$  ( $A^{3+} = \text{La, Pr, Nd, Lu, Bi}$ ) derived from combined synchrotron X-ray and neutron powder diffraction data to the tetragonal  $I4_1/a$  space group. Refinement parameters for  $\text{NaSm}(\text{WO}_4)_2$  are derived only from synchrotron X-ray diffraction data. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection.

|                                                                  | $\text{NaLa}(\text{WO}_4)_2$ | $\text{NaPr}(\text{WO}_4)_2$ | $\text{NaNd}(\text{WO}_4)_2$ | $\text{NaSm}(\text{WO}_4)_2$ | $\text{NaLu}(\text{WO}_4)_2$ | $\text{NaBi}(\text{WO}_4)_2$ |
|------------------------------------------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| <b><math>A^{3+}</math> Radius (<math>\text{\AA}</math>)</b>      | 1.16                         | 1.126                        | 1.109                        | 1.079                        | 0.977                        | 1.17                         |
| <b>a (<math>\text{\AA}</math>)</b>                               | 5.360040(9)                  | 5.316985(11)                 | 5.301244(8)                  | 5.271584(8)                  | 5.167419(8)                  | 5.28487(1)                   |
| <b>c (<math>\text{\AA}</math>)</b>                               | 11.66093(3)                  | 11.54690(3)                  | 11.50648(2)                  | 11.43367(2)                  | 11.17993(2)                  | 11.51278(3)                  |
| <b>Volume (<math>\text{\AA}^3</math>)</b>                        | 335.019(1)                   | 326.435(2)                   | 323.369(1)                   | 317.737(1)                   | 298.529(1)                   | 321.551(1)                   |
| <b>O(x)</b>                                                      | 0.1455(3)                    | 0.1493(7)                    | 0.1452(6)                    | 0.1476(7)                    | 0.1593(3)                    | 0.1519(3)                    |
| <b>O(y)</b>                                                      | 0.0151(3)                    | 0.0126(9)                    | 0.0135(5)                    | 0.0143(4)                    | 0.0063(4)                    | 0.0127(4)                    |
| <b>O(z)</b>                                                      | 0.2102(2)                    | 0.2111(4)                    | 0.2107(3)                    | 0.2083(2)                    | 0.2110(2)                    | 0.2103(2)                    |
| <b><math>B_{eq}(\text{A})</math> (<math>\text{\AA}^2</math>)</b> | 0.787(12)                    | 0.784(13)                    | 0.662(11)                    | 0.605(9)                     | 0.639(7)                     | 0.793(15)                    |
| <b><math>B_{eq}(\text{W})</math> (<math>\text{\AA}^2</math>)</b> | 0.535(5)                     | 0.707(6)                     | 0.622(5)                     | 0.608(5)                     | 0.753(5)                     | 0.66(7)                      |
| <b><math>B_{eq}(\text{O})</math> (<math>\text{\AA}^2</math>)</b> | 1.29(7)                      | 1.42(9)                      | 1.16(7)                      | 1.24(6)                      | 2.12(8)                      | 0.96(3)                      |
| <b>A-O (<math>\text{\AA}</math>)</b>                             | 2.5723(17)                   | 2.533(5)                     | 2.520(3)                     | 2.510(3)                     | 2.4070(19)                   | 2.5052(19)                   |
| <b>A-O (<math>\text{\AA}</math>)</b>                             | 2.514(2)                     | 2.482(5)                     | 2.475(4)                     | 2.486(3)                     | 2.4037(18)                   | 2.483(3)                     |
| <b>W-O (<math>\text{\AA}</math>)</b>                             | 1.7834(18)                   | 1.792(5)                     | 1.787(4)                     | 1.748(3)                     | 1.7854(19)                   | 1.784(3)                     |
| <b><math>\text{WO}_4</math> BVS</b>                              | 5.802                        | 5.666                        | 5.742                        | 6.277                        | 5.771                        | 5.797                        |
| <b><math>R_{wp}</math></b>                                       | 6.12                         | 6.53                         | 6.51                         | 5.36                         | 4.60                         | 6.50                         |

Table A.7: Refinement parameters of  $\text{NaA}(\text{MoO}_4)_2$  ( $A^{3+} = \text{La}, \text{Eu}, \text{Lu}, \text{Bi}$ ) derived from combined synchrotron X-ray and neutron powder diffraction data to the tetragonal  $I4_1/a$  space group. Refinement parameters for  $\text{NaEu}(\text{MoO}_4)_2$  are derived only from synchrotron X-ray diffraction data. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection.

|                                                                  | $\text{NaLa}(\text{MoO}_4)_2$ | $\text{NaEu}(\text{MoO}_4)_2$ | $\text{NaLu}(\text{MoO}_4)_2$ | $\text{NaBi}(\text{MoO}_4)_2$ |
|------------------------------------------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| <b>Radius (<math>\text{\AA}</math>)</b>                          | 1.16                          | 1.079                         | 0.977                         | 1.17                          |
| <b>a (<math>\text{\AA}</math>)</b>                               | 5.343637(6)                   | 5.247063(6)                   | 5.160527(6)                   | 5.277413(5)                   |
| <b>c (<math>\text{\AA}</math>)</b>                               | 11.733870(16)                 | 11.461738(17)                 | 11.236629(17)                 | 11.580273(16)                 |
| <b>Volume (<math>\text{\AA}^3</math>)</b>                        | 335.054(1)                    | 315.561(1)                    | 299.243(1)                    | 322.523(1)                    |
| <b>O(x)</b>                                                      | 0.1415(7)                     | 0.1460(3)                     | 0.15560(17)                   | 0.1487(4)                     |
| <b>O(y)</b>                                                      | 0.0114(8)                     | 0.0161(3)                     | 0.0042(2)                     | 0.0102(5)                     |
| <b>O(z)</b>                                                      | 0.2082(4)                     | 0.20775(12)                   | 0.20996(12)                   | 0.2093(3)                     |
| <b><math>B_{eq}(\text{A})</math> (<math>\text{\AA}^2</math>)</b> | 0.76(1)                       | 0.909(13)                     | 0.518(12)                     | 1.14(3)                       |
| <b><math>B_{eq}(\text{W})</math> (<math>\text{\AA}^2</math>)</b> | 0.435(11)                     | 0.547(10)                     | 0.50(3)                       | 0.73(3)                       |
| <b><math>B_{eq}(\text{O})</math> (<math>\text{\AA}^2</math>)</b> | 1.14(5)                       | 1.75(4)                       | 1.167(16)                     | 0.45(6)                       |
| <b>A-O (<math>\text{\AA}</math>)</b>                             | 2.564(5)                      | 2.5102(16)                    | 2.4093(13)                    | 2.505(3)                      |
| <b>A-O (<math>\text{\AA}</math>)</b>                             | 2.521(5)                      | 2.4921(15)                    | 2.4064(11)                    | 2.487(4)                      |
| <b>Mo-O (<math>\text{\AA}</math>)</b>                            | 1.7750(5)                     | 1.7297(16)                    | 1.7791(12)                    | 1.781(3)                      |
| <b><math>\text{MoO}_4</math> BVS</b>                             | 5.716                         | 6.459                         | 5.652                         | 5.630                         |
| <b><math>R_{wp}</math></b>                                       | 7.98                          | 3.54                          | 3.33                          | 4.53                          |

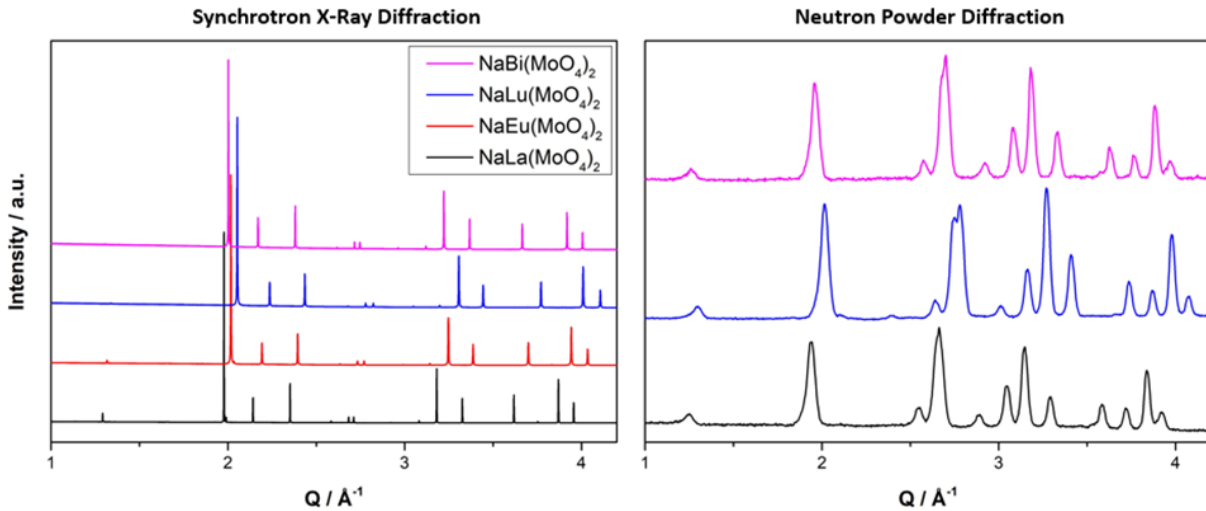


Figure A.13: (Left) Synchrotron X-ray and (right) neutron powder diffraction patterns of  $\text{NaA}(\text{MoO}_4)_2$  ( $A^{3+} = \text{La}, \text{Eu}, \text{Lu}, \text{Bi}$ ). The  $\text{NaEu}(\text{MoO}_4)_2$  sample was not analysed using neutron powder diffraction due to the large neutron absorption cross section of Eu. Each diffraction pattern has been offset vertically for visibility.



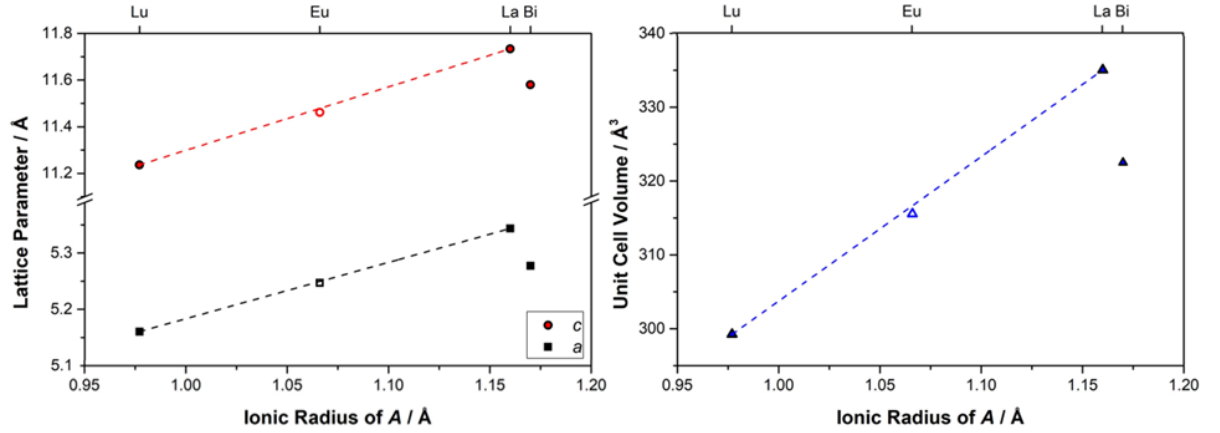


Figure A.14: Unit cell parameters of the  $\text{NaA}(\text{MoO}_4)_2$  ( $A^{3+} = \text{La, Eu, Lu, Bi}$ ) series derived from combined X-ray and neutron powder diffraction Rietveld refinements. For  $\text{NaEu}(\text{MoO}_4)_2$ , only the synchrotron X-ray diffraction dataset was refined (indicated with hollow symbols). Where not apparent, the errors are smaller than the symbols. The dashed lines have been drawn the guide the eyes.

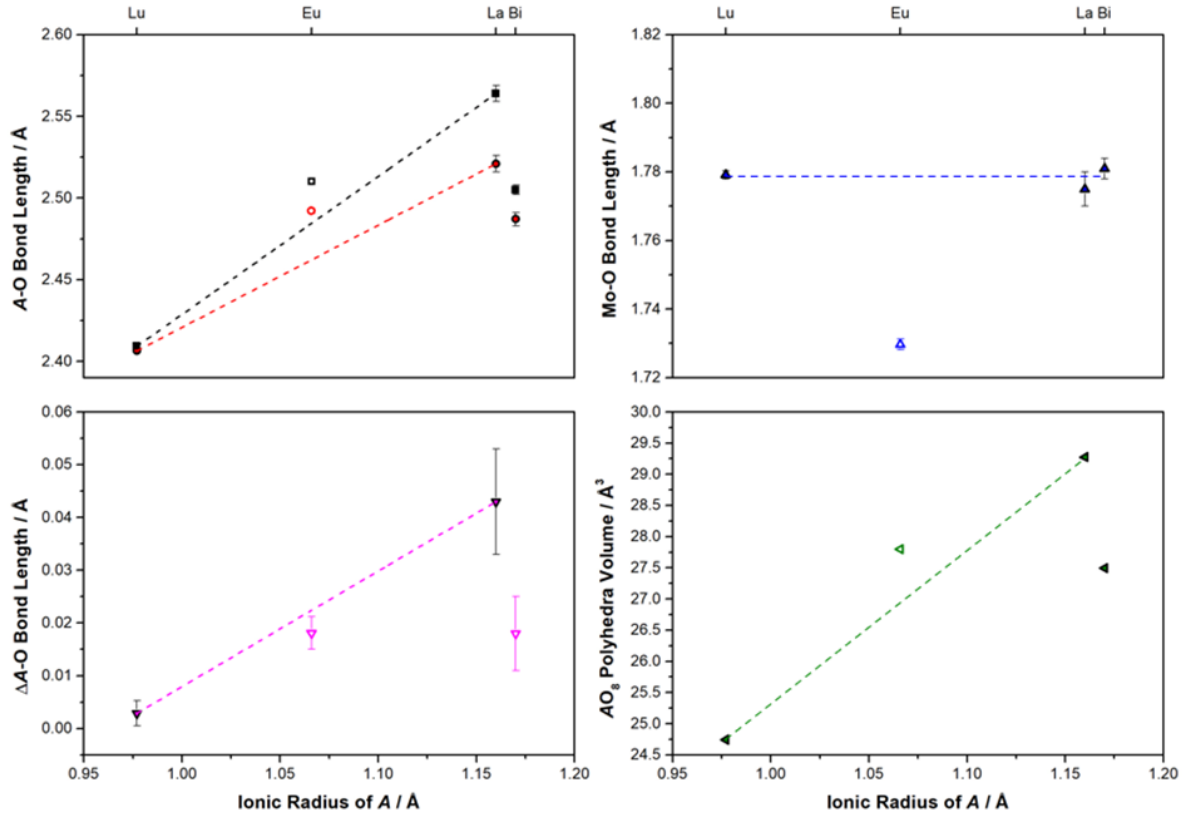


Figure A.15: (Top left) The  $A$ -O, (top right)  $B$ -O, (bottom left) difference between the unique  $A$ -O distances, and (bottom right)  $\text{AO}_8$  polyhedra volume of the  $\text{NaA}(\text{MoO}_4)_2$  ( $A^{3+} = \text{La, Eu, Lu, Bi}$ ) series derived from combined X-ray and neutron powder diffraction Rietveld refinements. For  $\text{NaEu}(\text{MoO}_4)_2$ , only the synchrotron X-ray diffraction dataset was refined (indicated with hollow symbols). Where not apparent, the errors are smaller than the symbols. The dashed lines have been drawn the guide the eyes.

Table A.8: Refinement parameters of  $\text{NaBi}(\text{WO}_4)_2$  from the neutron pair distribution function fits to the tetragonal  $I4_1/a$ , tetragonal  $I\bar{4}$ , and monoclinic  $I2/b$  space groups. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection.

| Space Group                     | $\text{NaBi}(\text{WO}_4)_2$ |                       |           |
|---------------------------------|------------------------------|-----------------------|-----------|
|                                 | $I4_1/a$                     | $I\bar{4}$            | $I2/b$    |
| $a$ (Å)                         | 5.2739(3)                    | 5.2757(2)             | 5.269(2)  |
| $b$ (Å)                         | = $a$                        | = $a$                 | 5.281(2)  |
| $c$ (Å)                         | 11.4830(10)                  | 11.4747(6)            | 11.477(3) |
| $\gamma$ (°)                    | = 90                         | = 90                  | 90.38(6)  |
| Vol. (Å <sup>3</sup> )          | 319.39(4)                    | 319.37(3)             | 319.3(2)  |
| $\text{Bi}^{3+}$ $y$            | = 5/8                        | = 0.5                 | 0.6286(3) |
| $\text{W}^{6+}$ $y$             | = 1/8                        | = 0                   | 0.1274(4) |
| O(1) $x$                        | 0.1536(2)                    | 0.3457(4)             | 0.1566(6) |
| O(1) $y$                        | 0.0104(2)                    | 0.2460(3)             | 0.5018(5) |
| O(1) $z$                        | 0.2104(2)                    | 0.1680(2)             | 0.2095(2) |
| O(2) $x$                        | --                           | 0.8474(4)             | 0.2717(4) |
| O(2) $y$                        | --                           | 0.2322(3)             | 0.3968(7) |
| O(2) $z$                        | --                           | 0.00880(2)            | 0.4614(2) |
| $B_{eq}$ (A) (Å <sup>2</sup> )  | 0.38(2)                      | 0.93(2)               | 0.67(2)   |
| $B_{eq}$ (W) (Å <sup>2</sup> )  | 1.1(2)                       | 0.74(2)               | 0.48(2)   |
| $B_{eq}$ (O) (Å <sup>2</sup> )  | 1.2(2)                       | 1.1(2)                | 0.79(2)   |
| A-O (Å)                         | 2.487(2)                     | (Na) 2.525(2)         | 2.575(4)  |
| A-O (Å)                         | 2.473(2)                     | (Na) 2.485(2)         | 2.514(4)  |
| A-O (Å)                         | --                           | (Bi) 2.470(2)         | 2.422(4)  |
| A-O (Å)                         | --                           | (Bi) 2.451(2)         | 2.413(4)  |
| $\text{AO}_8$ (Å <sup>3</sup> ) | 27.0                         | (Na) 27.9 / (Bi) 26.3 | 27.1      |
| W-O (Å)                         | 1.793(2)                     | 1.780(2)              | 1.823(4)  |
| W-O (Å)                         | --                           | 1.798(2)              | 1.760(4)  |
| BVS ( $\text{WO}_4$ )           | 5.66                         | 5.58                  | 5.70      |
| $R_{wp}$ (%)                    | 18.2                         | 9.96                  | 9.46      |

## A.4 Chapter 5: Local Structure Studies of Photocatalysts

Supporting information includes different space group representations of the monoclinic Fergusonite-type structure, Rietveld refinement parameters for  $\text{BiVO}_4$ , lattice parameters from the APS data, Landau mean-field theory fits to the monoclinic  $\gamma$  angle, photos of the rapidly-actuating pneumatic thermal reactor, synchrotron diffraction patterns of  $\text{PbO} + \text{WO}_3$  showing the melting of  $\text{PbO}$ , and DFT calculations on the geometry-optimised structure of  $\text{PbWO}_4$ .

Table A.9: Tabulated potential space group selections of  $\text{BiVO}_4$ . Atomic coordinates are written outside of the 0.0–1.0 range to highlight the relationship between the space groups. The high temperature tetragonal  $I4_1/a$  phase is also displayed to show its relationship.

| Sample       | $\text{BiVO}_4$ |          |          |          |
|--------------|-----------------|----------|----------|----------|
| Space Group  | $C2/c$          | $I2/a$   | $I2/b$   | $I4_1/a$ |
| $a$ (Å)      | 7.24787         | 5.09120  | 5.19070  | 5.105    |
| $b$ (Å)      | 11.69410        | 11.69410 | 5.09120  | = $a$    |
| $c$ (Å)      | 5.09120         | 5.19070  | 11.69410 | 11.577   |
| $\alpha$ (°) | = 90            | = 90     | = 90     | = 90     |
| $\beta$ (°)  | 134.2621        | 90.36    | = 90     | = 90     |
| $\gamma$ (°) | = 90            | = 90     | 90.36    | = 90     |
| $A x$        | = 0             | = $1/4$  | = 0      | = 0      |
| $A y$        | 0.6334          | 0.6334   | = $1/4$  | = $1/4$  |
| $A z$        | = $1/4$         | = 0      | 0.6334   | = $5/8$  |
| $B x$        | = 0             | = $1/4$  | = 0      | = 0      |
| $B y$        | 0.1298          | 0.1298   | = $1/4$  | = $1/4$  |
| $B z$        | = $1/4$         | = 0      | 0.1298   | = $1/8$  |
| $O(1) x$     | -0.146          | 0.494    | 0.146    | 0.143    |
| $O(1) y$     | 0.202           | 0.202    | 0.494    | -0.001   |
| $O(1) z$     | 0.348           | 0.146    | 0.202    | 0.203    |
| $O(2) x$     | -0.283          | 0.375    | 0.283    | --       |
| $O(2) y$     | 0.446           | 0.446    | 0.375    | --       |
| $O(2) z$     | 0.092           | 0.283    | 0.446    | --       |

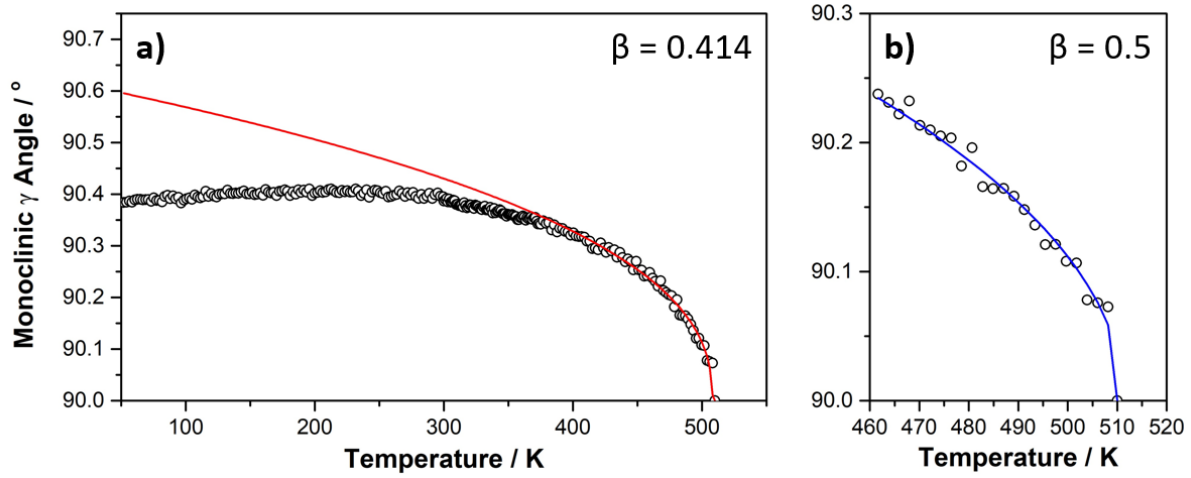


Figure A.16: The monoclinic  $\gamma$  angle from the variable temperature Rietveld refinements of  $\text{BiVO}_4$  upon heating. (a) The monoclinic  $\gamma$  angle fitted over the temperature 400-510 K (shown with the whole temperature to highlight the anomalous behaviour at low temperature). (b) The fit performed in a range 50 K below  $T_c$  with  $\beta = 0.5$ .

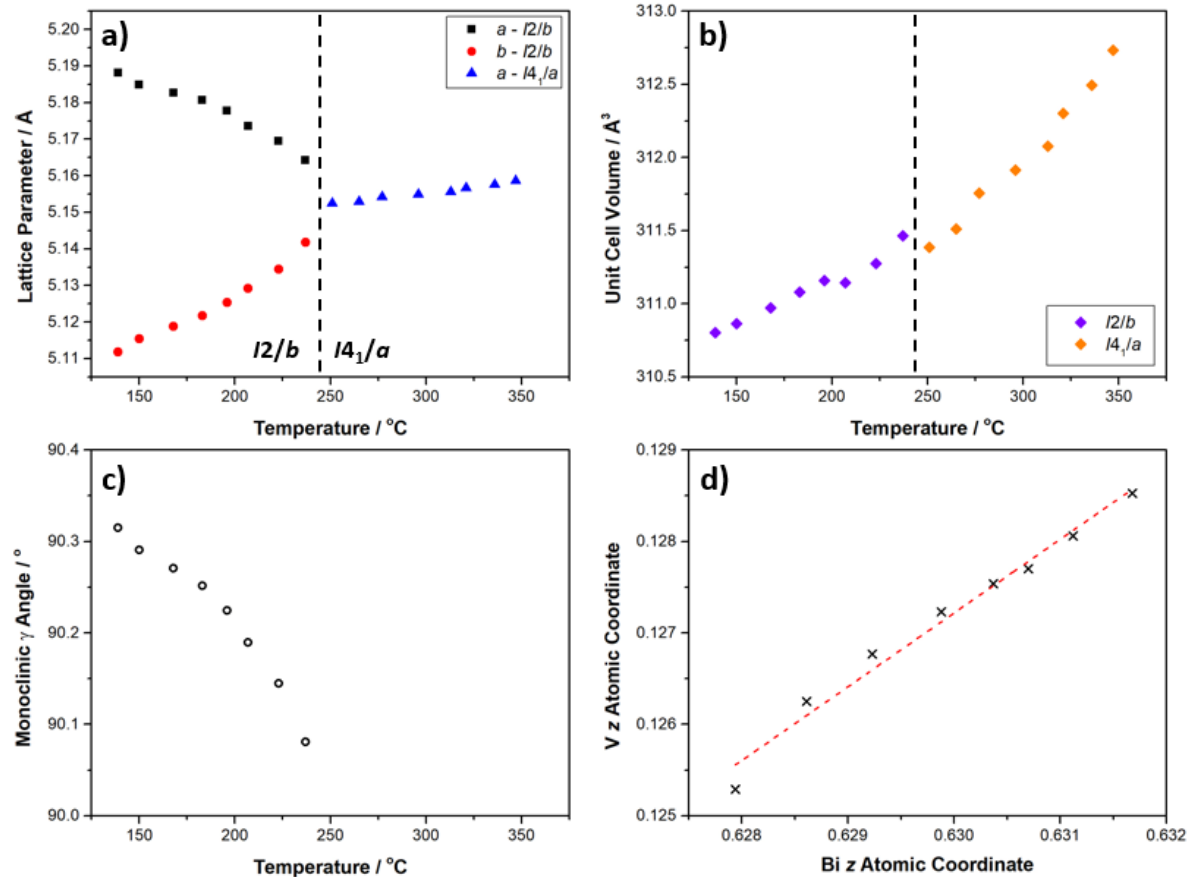


Figure A.17: Rietveld refinements for the synchrotron X-ray powder diffraction variable temperature dataset of  $\text{BiVO}_4$ , with (a) the  $a$  and  $c$  lattice parameters, (b) the unit cell volume, (c) the monoclinic  $\gamma$  angle, and (d) the  $z$  atomic coordinates of  $\text{Bi}^{3+}$  and  $\text{V}^{5+}$  plotted against each other. The black dashed lines represent the temperature of the  $I2/b \rightarrow I4_1/a$  phase transition, and the red dashed line is a linear fit.

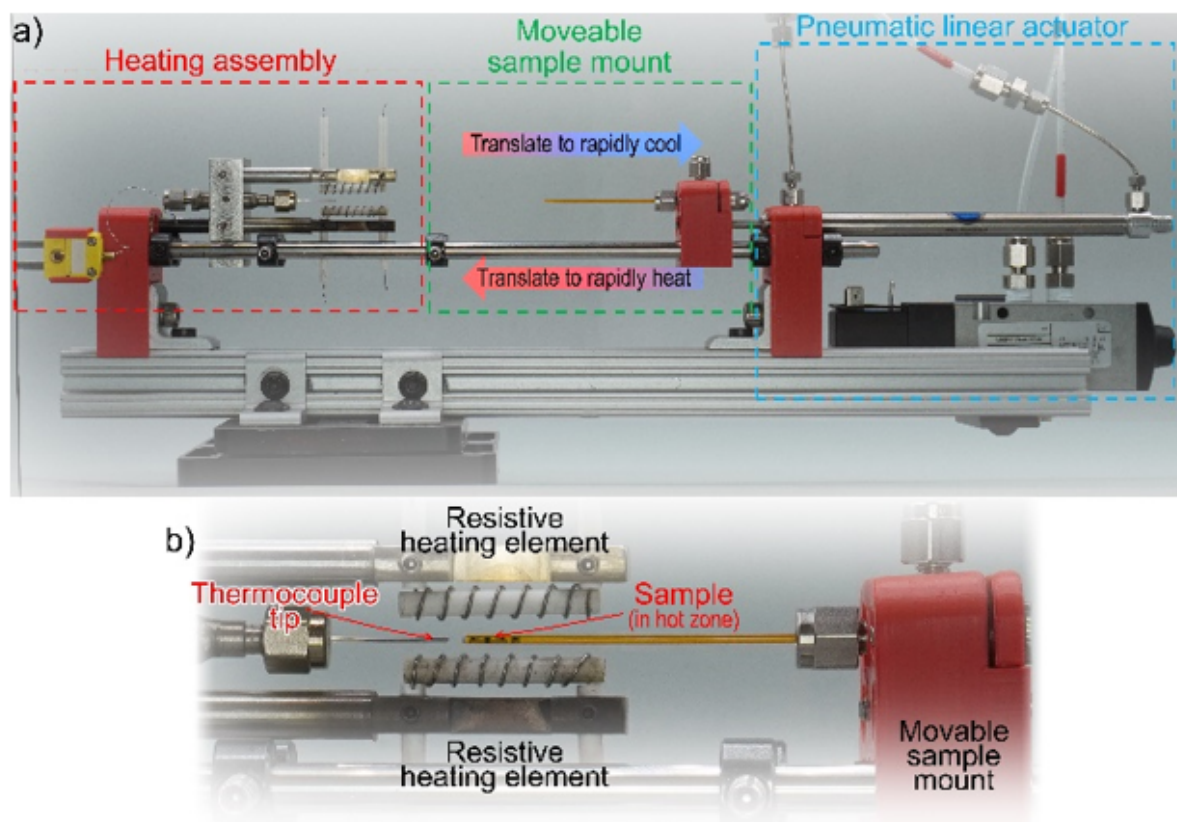


Figure A.18: (a) A photo of the rapidly-actuating pneumatic thermal reactor furnace indicating the heating assembly, the movable sample fixture, and the pneumatic linear actuator. (b) An expanded view of the sample in the hot zone. For clarify, the heat shields are not shown.

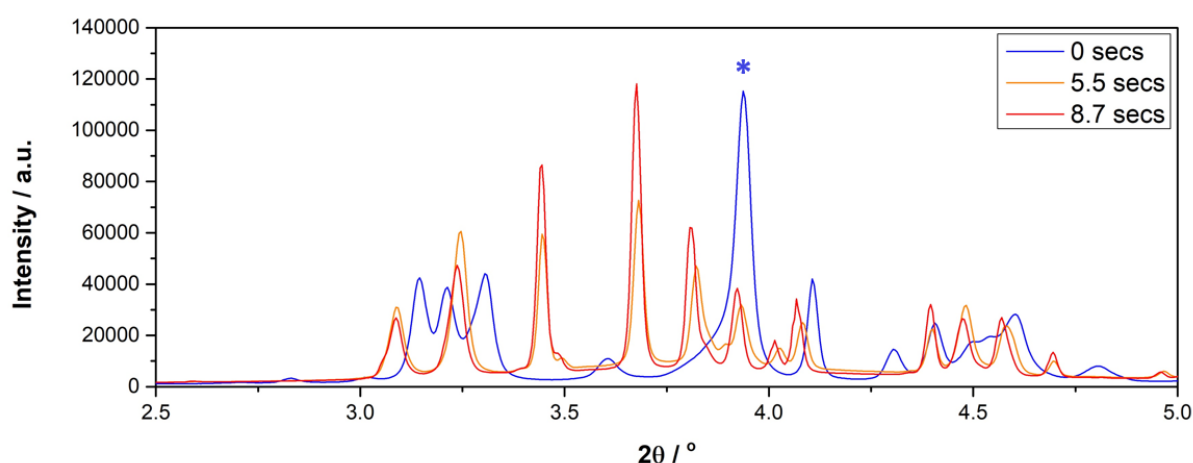


Figure A.19: Synchrotron X-ray diffraction patterns of a sample of  $\text{PbO} + \text{WO}_3$  in the hot zone of the rapidly-actuating pneumatic thermal reactor. Three patterns are displayed: after 0 seconds (blue), after 5.5 seconds (orange), and after 8.7 seconds (red). The blue asterisk indicates the prominent reflection associated with the  $\text{PbO}$  phase, which disappears after 5.5 seconds. This is accompanied by an increase in diffuse scattering.

Table A.10: Comparison of the unit cell parameters and distortion of the  $\text{PbO}_8$  polyhedra in  $\text{PbWO}_4$ , assuming a monoclinic  $I2/b$  structure obtained by small box fitting against neutron pair distribution data measured at 115 K, with the geometry-optimised structure obtained using density functional theory calculations. The number in parentheses beside each entry indicates the estimated standard deviation of the last digit(s) shown. Note that these are underestimated as they do not consider the errors of the data collection.

|                                       | <b>NPDF<br/>115 K</b> | <b>DFT<br/>(PBEsol)</b> | <b>DFT<br/>(AM05)</b> |
|---------------------------------------|-----------------------|-------------------------|-----------------------|
| <b><math>a</math> (Å)</b>             | 5.45406(14)           | 5.441                   | 5.461                 |
| <b><math>b</math> (Å)</b>             | 5.45406(14)           | 5.441                   | 5.460                 |
| <b><math>c</math> (Å)</b>             | 12.0078(5)            | 11.874                  | 11.971                |
| <b><math>\gamma</math> (°)</b>        | 90.02(2)              | 89.99                   | 90.004                |
| <b>Vol. (Å<sup>3</sup>)</b>           | 357.193(8)            | 351.621                 | 356.97                |
| <b>Pb-O(1) (Å)</b>                    | 2.597(3)              | 2.597                   | 2.5939                |
| <b>Pb-O(1) (Å)</b>                    | 2.6055(19)            | 2.615                   | 2.6224                |
| <b>Pb-O(2) (Å)</b>                    | 2.609(3)              | 2.638                   | 2.5935                |
| <b>Pb-O(2) (Å)</b>                    | 2.658(19)             | 2.647                   | 2.6223                |
| <b>Pb-O<sub>av.</sub> (Å)</b>         | 2.617                 | 2.624                   | 2.6080                |
| <b><math>\Delta\text{AO}_8</math></b> | $6.65 \times 10^{-4}$ | $4.46 \times 10^{-4}$   | $2.41 \times 10^{-4}$ |

## A.5 Chapter 6: Safe Storage of Radioactive Waste

Supporting information includes synchrotron X-ray diffraction and X-ray pair distribution function data for  $\text{CsReO}_4$ .

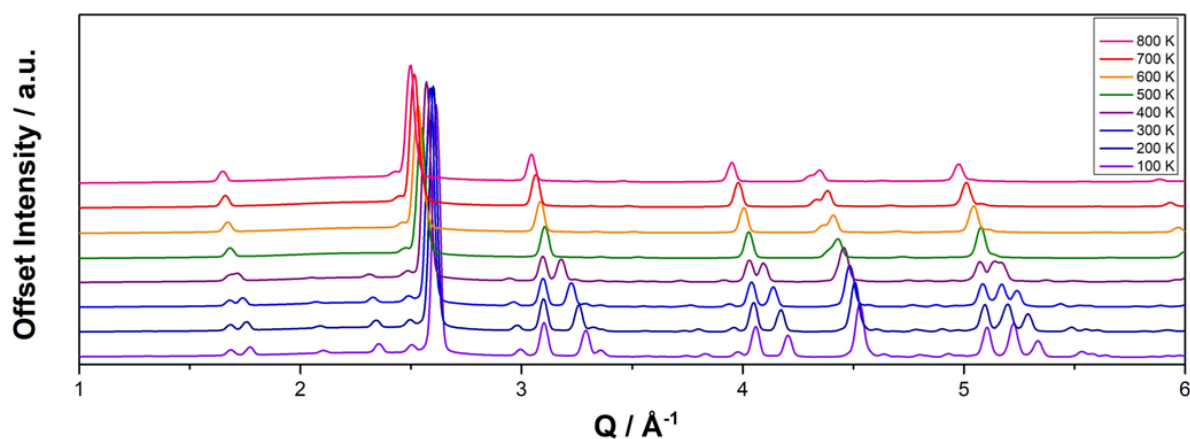


Figure A.20: Synchrotron X-ray diffraction patterns of  $\text{CsReO}_4$  from 100–800 K in 100 K steps. The patterns have been offset vertically to enhance visibility.

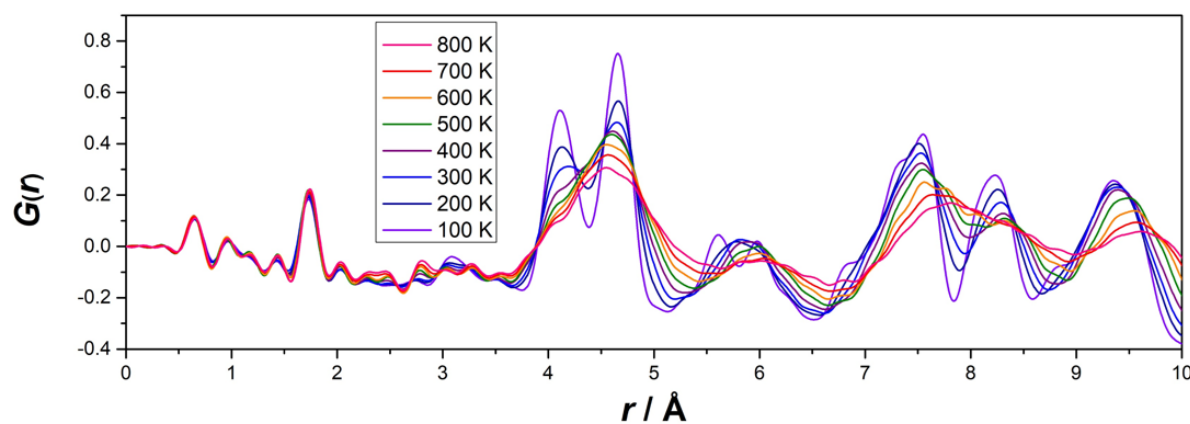


Figure A.21: X-ray pair distribution function data for  $\text{CsReO}_4$  from 100–800 K in 100 K steps.

## A.6 Chapter 7: Adventures Outside of Metal Oxides

Supporting information includes neutron powder diffraction data for a mixed-phase sample of  $\text{CsMnF}_4$ .

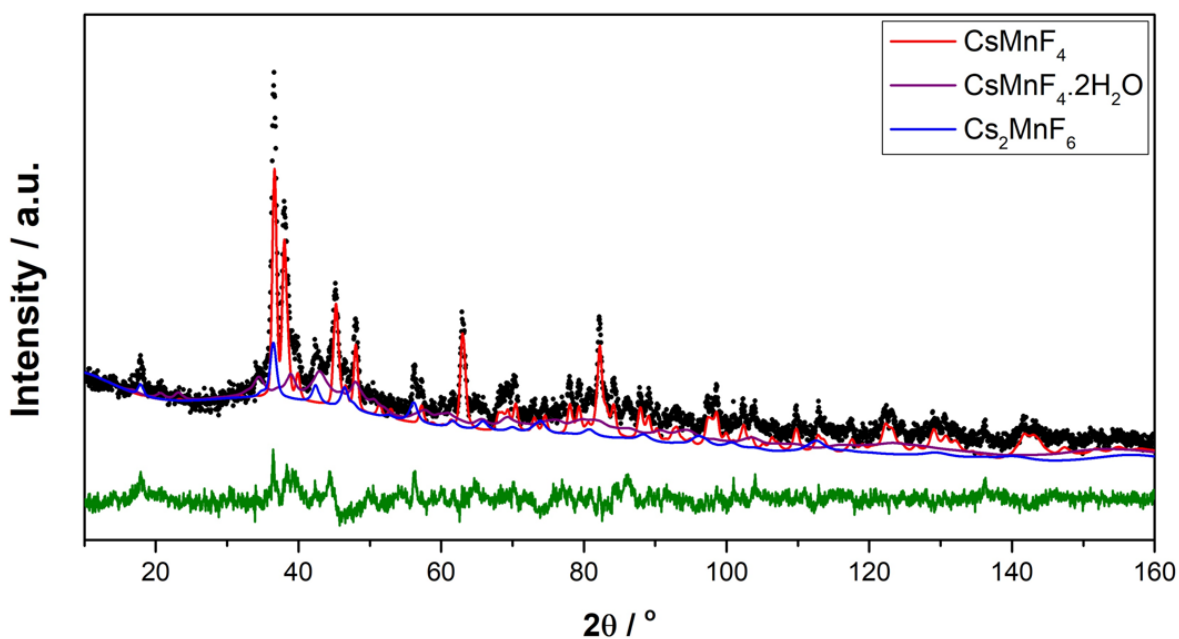


Figure A.22: Neutron powder diffraction pattern of an impure sample of  $\text{CsMnF}_4$  collected at room temperature.