Phase Behaviour and Mixed Ionic-Electronic Conductivity of Ba₄Sb₂O₉

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Abstract

The 6H-type perovskite phase Ba₄Sb₂O₉, which decomposes in air below 600 K, is found to survive to room temperature in a CO₂-free atmosphere. It shows substantial mixed protonic, oxide ionic and electronic conductivity. However, compared to Ba₄Nb₂O₉ and Ba₄Ta₂O₉, Ba₄Sb₂O₉ shows higher ionic conductivity due to the relatively easy reducibility of Sb⁵⁺, but lower electronic conductivity due to the predominantly n-type conductivity provided by the Sb⁵⁺/Sb³⁺ redox couple which leads to reduced hole concentration under oxidising conditions.

Variable temperature synchrotron x-ray and neutron powder diffraction studies carried out in...
situ under controlled atmospheres reveal a strong monoclinic distortion below 1150 K. The hexagonal $\rightarrow$ monoclinic transition is slow, does not show second-order behaviour, is strongly dependent on atmosphere, and coincides with the loss of $\sim$0.4 molecules of H$_2$O per formula unit of Ba$_4$Sb$_2$O$_9$. All of this suggests an important structural role for protons or hydroxide ions in the monoclinic phase.

**Introduction**

The development and implementation of new materials for use in solid oxide fuel cells (SOFCs) and oxygen separation has been a focus of research for some decades. Of particular importance has been the search for materials which are efficient and offer high conductivity while at the same time being stable over a range of temperatures and atmospheric conditions. The discovery of many new niobium and tantalum containing oxides such as La(Nb,Ta)O$_4$, Ba$_3$Ca$_{1+x}$(Nb,Ta)$_{2-x}$O$_{9-3x/2}$, HLa(Nb,Ta)$_2$O$_7$·0.5H$_2$O$^7$ and La$_3$(Nb,Ta)O$_7$ is interesting in that, while in most cases the Nb and Ta analogues are isostructural, better conductivity properties are observed for the more reducible Nb$^{5+}$ cation. Antimony oxides, where Sb$^{5+}$ has the same 5+ valence as Nb and Ta, and a similar ionic radius (0.60 Å for Sb$^{5+}$ vs 0.64 Å for Nb$^{5+}$ and Ta$^{5+}$), would seem promising due to its relatively easy reducibility to Sb$^{3+}$. Fast protonic transport in the low-temperature range is well known for Sb-containing inorganic acids, salts and composites, as for their Nb- and Ta-containing analogues. However, apart from some reports of doped systems such as SrCo$_{1-x}$Sb$_x$O$_{3-\delta}$, double perovskites containing Sb$^{5+}$ in the $B$-sites and BiSb$_2$$_{-\delta}$, there has been remarkably little work into the potential of antimony oxides as oxygen ionic, intermediate-temperature protonic or mixed ionic conductors.

We recently reported the structural phase diagrams and conductivity of Ba$_4$Nb$_2$O$_9$ and Ba$_4$Ta$_2$O$_9$. Both show significant mixed protonic, oxide ionic and electronic conductivity. The two materials share the same low-temperature $\alpha$ structure, which is isomorphic to that of Sr$_4$Ru$_2$O$_9$. However, upon heating in normal atmospheres, they undergo reconstructive phase transitions to completely different structures. At 1473 K, $\alpha$-Ba$_4$Nb$_2$O$_9$ transforms into $\gamma$-Ba$_4$Nb$_2$O$_9$, a unique structure.
type with a supercell that is yet to be solved, while at 1513 K $\alpha$-Ba$_4$Ta$_2$O$_9$ transforms into a 6H-perovskite. Ba$_4$Sb$_2$O$_9$ adopts a similar high-temperature structure (6H-perovskite) to Ba$_4$Ta$_2$O$_9$ with ideal hexagonal symmetry ($P6_3/mmc$). However, while 6H-Ba$_4$Ta$_2$O$_9$ undergoes a series of symmetry-lowering transitions to a stable room temperature monoclinic $P2_1/c$ phase, Ba$_4$Sb$_2$O$_9$ decomposes reversibly in air below 600 K, with the decomposition products bearing no resemblance to the low-temperature $\alpha$ (Sr$_4$Ru$_2$O$_9$-type) form of Ba$_4$Nb$_2$O$_9$ and Ba$_4$Ta$_2$O$_9$.

Here, we demonstrate that a stable monoclinically distorted room temperature phase for Ba$_4$Sb$_2$O$_9$ does exist, but only under controlled atmosphere (CO$_2$-free) conditions. We also report conductivity measurements which show that hydration plays an important role in the structure and dynamics of Ba$_4$Sb$_2$O$_9$, making this phase a new addition to the growing family of mixed ionic-electronic conducting barium oxides.

**Experimental Methods**

Pure polycrystalline samples of Ba$_4$Sb$_2$O$_9$ were prepared by solid-state reaction in air from BaCO$_3$ and Sb$_2$O$_3$ (99.99% purity or greater). Prior to weighing, BaCO$_3$ was dried at 1000 K overnight. The stoichiometric mixture was ground in an agate mortar and pestle, calcined at 1073 K for 4 h, then reground and calcined at 1273 K for 12 h. The sample was then reground and calcined for a further 12 h at 1273 K. Room-temperature and *in situ* high-temperature x-ray powder diffraction (XRD) data were collected on a Panalytical X’Pert Pro diffractometer using Cu K$_\alpha$ radiation. The sample appeared to be pure on the basis of these data, pending the higher-resolution synchrotron XRD and neutron powder diffraction experiments described below. For further confirmation, it was found to have a 2:1 ratio of Ba:Sb by energy-dispersive X-ray analysis (EDXA), performed in conjunction with imaging using a Phillips XL-30 scanning electron microscope (SEM) with a tungsten filament operating at 20 keV, a spot size setting of 5 and a working distance of 11 mm.

Variable-temperature synchrotron XRD (S-XRD) data were collected at the Powder Diffraction beamline of the Australian Synchrotron using a wavelength $\lambda = 0.68933$ Å. Samples were
placed on a 10 mm wide platinum strip with ethanol to ensure an even coating and heated in an AntonPaar2000 furnace under air and under dynamic vacuum. Data were collected in 25 K steps from room temperature up to 1123 K and back down on cooling.

Variable-temperature neutron powder diffraction (NPD) data were collected on the instrument Echidna at the OPAL reactor (Lucas Heights, Australia) using a wavelength $\lambda = 2.4395$ Å. Samples were placed in 9 mm diameter sealed vanadium cans and heated with a cylindrical niobium element under vacuum. Complete data sets were collected over 1 h each in 50 K steps from room temperature to 1173 K.

Rietveld-refinements against S-XRD and NPD data were carried out using the GSAS program$^{21}$ with the EXPGUI interface.$^{22}$

After ball-milling of the powder, ceramic samples of $\text{Ba}_4\text{Sb}_2\text{O}_9$ were prepared for conductivity measurements by uniaxial pressing of disk- and bar-shaped green compacts at 250-280 MPa and sintering them at 1773 K for 4 h in air, using closed alumina containers filled with $\text{Ba}_4\text{Sb}_2\text{O}_9$ powder. In order to minimize hydration and carbonation at low temperatures, the samples were cooled down with a rate of 5 K/min. The density of the sintered $\text{Ba}_4\text{Sb}_2\text{O}_9$ ceramics were 4.3-4.5 g/cm$^3$, which corresponds to 73-76% of the theoretical density calculated from the structural data at 1023 K.$^{20,23}$ Note that the latter value an only be used as a rough approximation at room temperature due to phase transitions on cooling.$^{20,23}$ Attempts to increase density of $\text{Ba}_4\text{Sb}_2\text{O}_9$ ceramics by sintering at higher temperatures failed owing to liquid phase formation, leading to embrittlement and even partial melting; increasing sintering time at 1473-1673 K did not result in higher density values. The Ba:Sb cation concentration ratio in the sintered $\text{Ba}_4\text{Sb}_2\text{O}_9$ ceramics, determined by inductively-coupled plasma (ICP) spectroscopic analysis, was found equal to $2.01 \pm 0.02$, which corresponds to the nominal cation composition within the limits of experimental error.

Experimental procedures and equipment used for thermogravimetric analysis (TGA), temperature-programmed desorption (TPD), AC impedance spectroscopic studies in humid and dry atmospheres, and determination of ion transference numbers by the modified electromotive force (EMF) method have been described elsewhere.$^{18,24,25}$ Powdered samples for TGA were prepared by grind-
ing of sintered ceramics. For the impedance spectroscopy and EMF measurements, porous Pt electrodes were deposited onto the surface of Ba$_4$Sb$_2$O$_9$ bars or disks and annealed at 1323 K during 15 min. In order to minimize any influence of non-electrolytic permeation in the EMF cells, where the oxygen chemical potentials at the electrodes may be shifted due to sample porosity, relatively thick (3-4 mm) disks were used for these tests. The EMF measurement results presented below were well reproducible and independent of the gas flow rates supplied onto the electrodes, thus validating that the permeation effects can be neglected. The reproducibility error of the transference numbers was ±0.02. The total (ionic + electronic) conductivity, $\sigma$, was calculated from the impedance spectra collected on cooling from 1273 K down to 973 K, with subsequent heating up to 1273 K and reproducibility check. Reproducibility was validated over the entire measuring cycle in dry and humid atmospheres. The criterion for equilibration after a change in temperature, oxygen partial pressure or water vapor pressure included the relaxation of the sample resistance or concentration cell EMF less than 0.5% during 30 min. Typical examples of the conductivity relaxation curves are presented in Figure 1.

![Figure 1](image_url)

Figure 1: Typical relaxation behaviour of the total conductivity of Ba$_4$Sb$_2$O$_9$ ceramics, after heating up to 1273 K in dry air and argon. The water vapor partial pressure in the flowing dry gases, continuously measured by a Jumo humidity transducer, was $5 \times 10^{-4}$ atm. The oxygen partial pressure in flowing Ar, measured by an electrochemical oxygen sensor, was $2 \times 10^{-5}$ atm.
Results and Discussion

Low-temperature Structural Characterisation and Phase Transition

The high-temperature 6H-perovskite structure for Ba$_4$Sb$_2$O$_9$ had been found to decompose slowly below 600 K in air.$^{23}$ In order to obtain a diffractogram of the pure phase, we pre-annealed the sample at 1273 K in a CO$_2$-free atmosphere prior to collecting temperature-dependent in situ S-XRD and NPD data under vacuum. The data showed clear evidence for the 6H-perovskite phase down to room temperature, with a previously unobserved monoclinic peak splitting (Figure 2). The 6H-perovskite phase of Ba$_4$Ta$_2$O$_9$ follows a $P6_3/m \rightarrow P2_1/c$ (hexagonal $\rightarrow$ monoclinic) symmetry-lowering path on cooling from 1273 K to room temperature, with a doubling of the $c$-axis. In this case, no evidence was found for a doubling of $c$, and a direct lowering of symmetry from $P6_3/m \rightarrow P2_1/m$ in the equivalent unit cell was found to give the best fit to experimental data.

NPD data were used for Rietveld refinement of atomic positions, due to its greater relative sensitivity to oxygen atoms in the presence of the heavy metals Ba and Sb. The final Rietveld refinement fit of monoclinic 6H-Ba$_4$Sb$_2$O$_9$ to NPD data is shown in Figure 3. Refinement data and structural parameters are summarised in Table 1. The final refined room-temperature structure is shown in Figure 4.

There are a small number of unindexed peaks, the most prominent of which are very close to the strongest peaks (the (240)/(042) doublet) of the 6H phase. We were unable to adequately account for these with any known potential impurity phase in the Ba-Sb-O system (including carbonates), nor with any hypothetical analogues of the $\alpha$ or $\gamma$ phases from the Ba$_4$Nb$_2$O$_9$ and Ba$_4$Ta$_2$O$_9$ systems.$^{17,18,30}$ Given that all these phases present their strongest peaks in this region, which corresponds to the spacing between planes of perovskite A-site Ba cations, these unindexed peaks may be due to a defective variant of 6H-Ba$_4$Sb$_2$O$_9$ with stacking faults along the $c$ axis in the Sb$_2$O$_9$ face-sharing dimers.

Bond-valence sum (BVS)$^{10}$ calculations indicate that the Ba3 cation is substantially over-bonded (BVS = 3.374). This follows a trend of increasing over-bonding with increasing effective
Figure 2: Synchrotron x-ray diffractograms ($\lambda = 0.68933$ Å) for Ba$_4$Sb$_2$O$_9$ annealed under air. The monoclinic peak splitting can be clearly seen in the room-temperature pattern, as can the monoclinic $\rightarrow$ hexagonal transition at higher temperatures. An impurity peak is indicated by arrows.

Figure 3: Rietveld-refined fit of 6H-Ba$_4$Sb$_2$O$_9$ against 298 K NPD data ($\lambda = 2.4395$ Å). Crosses are observed data, solid line is the calculated fit, and the lower solid line is the difference curve.
Figure 4: Structure of monoclinic (P2₁/m) 6H-Ba₄Sb₂O₉ at 298 K, Rietveld-refined against NPD data. Ba atoms are drawn as grey spheres, BaO₆ octahedra as grey polyhedra, and Sb₂O₉ face-sharing bi-octahedral dimers as yellow polyhedra.

ionic radius⁹ of B in the series Ba₃BSb₂O₉: BVS = 2.18 for B = Mg,⁳³,³⁴ BVS = 2.67 for B = Ca, and BVS = 2.82 for B = Sr.²⁶ This is due to increasing size mismatch between the BO₆ and SbO₆ octahedra. In the present B = Ba case, Sb₂O₉ dimers are so strained and distorted by this size mismatch that the phase decomposes readily at lower temperatures.

In order to further investigate the decomposition of the Ba₄Sb₂O₉ phase, we collected in situ temperature-dependent S-XRD data under both air and dynamic vacuum to compare the evolution of the lattice parameters and observe any effect on the monoclinic → hexagonal transition. Under both air and vacuum, no structural changes other than thermal expansion were seen. To determine the transition temperature we plotted the monoclinic β angle vs. temperature (Figure 6). Extrapolation suggests a transition temperature under air of ~1150 K and under vacuum of 1800 K, i.e., significantly shifted to a higher temperature. Such a dramatic influence of atmospheric conditions on a structural transition is not unprecedented; for example, reducing p(O₂) shifts the transition between brownmillerite and oxygen-deficient perovskite phases in strontium ferrites and cobaltites towards higher temperatures.²⁸ Reducing conditions have also been found to lead to the forma-
Table 1: Structural details for 6H-Ba$_4$Sb$_2$O$_9$ at 298 K from Rietveld refinement against NPD data. Space group: monoclinic $P2_1/m$ (No. 14); $a = 6.0959(4)$ Å, $b = 16.10240(6)$ Å, $c = 6.1295(5)$ Å and $\beta = 119.832(9)\,^\circ$. GOF = 7.531 for 53 refined parameters. $R_p = 0.1341$, $wR_p = 0.1752$, $R(F^2) = 0.1988$. Superscript symbols indicate constraints.

<table>
<thead>
<tr>
<th>atom</th>
<th>$x (a)$</th>
<th>$y (b)$</th>
<th>$z (c)$</th>
<th>$100U_{iso}$ (Å$^2$)</th>
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<td>0</td>
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<td>0.1075(14)</td>
<td>0.638(5)</td>
<td>4.10(3)</td>
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<td>0.214(4)</td>
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<td>0.25</td>
<td>0.082(6)</td>
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<td>0.532(6)</td>
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<td>0.8416(8)</td>
<td>0.655(5)</td>
<td>2.8(5)</td>
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</table>

A unusual feature of this transition (under both air and vacuum) is the slow, almost linear evolution of $\beta$ towards $120^\circ$. If it involved only a cooperative rotation of Sb$_2$O$_9$ dimers and BaO$_6$ octahedra, such a transition ought to be second-order in nature. The experimentally observed behavior instead suggests a slow, kinetically limited equilibrium between these two structures, which can be influenced by more than just thermal energy. The same set of experiments on 6H-Ba$_4$Ta$_2$O$_9$ revealed a similar retardation of the transition to higher temperatures as shown in Figure 6, from approximately 1050 K under air to 1700 K under vacuum. Note that we were able to heat to 1723 K due to Ba$_4$Ta$_2$O$_9$ being stable at higher temperatures than Ba$_4$Sb$_2$O$_9$.

The discovery of a stable room-temperature form of Ba$_4$Sb$_2$O$_9$ allows us to amend and complete the phase diagram of Ba$_3$BSb$_2$O$_9$ ($B =$ Ba, Mg, Ca and Sr), as shown in Figure 6. The behavior of Ba$_4$Sb$_2$O$_9$ is still anomalous compared to the other compounds in the series, probably due to the massive size mismatch between the effective ionic radii of Ba$^{2+}$ (1.35 Å) and Sb$^{5+}$ (0.60 Å) in 6-fold coordination. Instead of following the symmetry-lowering transitions $P6_3/mmc \rightarrow C2/c \rightarrow P\overline{1}$ as for $B =$ Mg, Ca and Sr, Ba$_4$Sb$_2$O$_9$ transforms from $P6_3/m$ to monoclinic $P2_1/m$ symmetry at quite a high temperature ($\sim 1150$ K). Additionally, in situ NPD data down to 3 K confirm that no further symmetry-lowering transition occurs below room-temperature.
Figure 5: Rietveld-refined (against synchrotron XRD data) monoclinic β angle for 6H-Ba₄Ta₂O₉ (black squares) compared to 6H-Ba₄Sb₂O₉ (red circles), heated from 298 to 1723 K. Data collected under air are shown with filled symbols, while data collected under vacuum is shown with open symbols. Extrapolating the trend to 120° gives a monoclinic → hexagonal transition temperatures for 6H-Ba₄Ta₂O₉ (Ba₄Sb₂O₉) of ~1050 K (1150 K) under air and 1700 K (1800 K) under vacuum.

This behaviour and the influence of vacuum on these transitions, suggest that it has more in common with Ba₄Ta₂O₉ and Ba₄Nb₂O₉ than with the other members of the Ba₃BSb₂O₉ series.

Figure 6: Updated thermodynamic phase diagram²⁰ for Ba₃BSb₂O₉, B = Ba, Mg, Ca, and Sr, as a function of temperature and effective ionic radius (IR) of the B²⁺ cation. Open markers represent fully Rietveld-refined structures, and closed markers represent phase transitions determined by variable-temperature XRD (T < 500 K) or differential scanning calorimetry (DSC) (T > 500 K).
Figure 7: Thermogravimetric curves of \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) collected on heating (5 K/min) and cooling (2 K/min) in flowing dry air. The inset shows temperature regime used for the TGA measurements.

**Hydration Behaviour**

TGA showed that as-prepared \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) behaves very similarly to \( \text{Ba}_4\text{Ta}_2\text{O}_9 \) and \( \text{Ba}_4\text{Nb}_2\text{O}_9 \), irrespective of the different phase relations in the intermediate and low temperature ranges in these systems.\(^{18,20,23}\) Namely, significant weight losses related to dehydration and \( \text{CO}_2 \) desorption are observed at 370—670 K and 870—1100 K (Figure 7). TPD analysis confirmed that no traces of \( \text{CO}_2 \) could be detected in helium flowing over the as-prepared \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) powder on heating up to 800 K. The weight variations in this low-temperature range originate, therefore, predominantly from dehydration processes. The corresponding amount of water is approximately 0.4 molecules per \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) formula unit. In the range 870—1100 K, both \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) were found to desorb, but the amount of \( \text{CO}_2 \) (total 0.01-0.06 molecules per formula unit) was much smaller than that reported for \( \text{Ba}_4\text{Nb}_2\text{O}_9 \) prepared in air.\(^{31}\) This small amount was dependent on sample pre-history and particle size, indicative of surface carbonation rather than \( \text{CO}_2 \) incorporation into the \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) structure, as reported for \( \text{Ba}_4\text{Nb}_2\text{O}_9 \) by Bezjak \textit{et al.}\(^{31}\) Substantial amounts of water were found to desorb from \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) up to 1100—1150 K when the weight stabilised. The lat-
ter trend suggests significant protonic conduction, as for the hydrated $\text{Ba}_4\text{Ta}_2\text{O}_9$ and $\text{Ba}_4\text{Nb}_2\text{O}_9$ phases.\textsuperscript{18}

It should be noted that the dehydration behaviour observed by TGA (Figure 7) exhibits a definite correlation with the phase transition in $\text{Ba}_4\text{Sb}_2\text{O}_9$. Specifically, the monoclinic $\rightarrow$ hexagonal transition $\text{Ba}_4\text{Sb}_2\text{O}_9$ at $\sim 1150$ K coincides with the completion of the last major dehydration step. This may indicate that the incorporated water hinders the formation of the high-symmetry phase of $\text{Ba}_4\text{Sb}_2\text{O}_9$; and it is only upon dehydration that the structure can transform. This is a potential explanation for the observation that the monoclinic $\rightarrow$ hexagonal transition does not show normal second-order behaviour, and is strongly dependent on atmospheric conditions. Comparison to the TGA and structural data for 6H-$\text{Ba}_4\text{Ta}_2\text{O}_9$ reveals a similar result,\textsuperscript{18} where the transition temperature also coincides with the completion of one of the dehydration steps at $\sim 1050$ K.

![Figure 8: Typical impedance spectra of $\text{Ba}_4\text{Sb}_2\text{O}_9$ ceramics with porous Pt electrodes in various atmospheres. The water vapor partial pressure in flowing wet argon and air was $3.5 \times 10^{-2}$ atm. In dry gases, the water vapor content was approximately $5 \times 10^{-4}$ atm.](image)

**Transport Properties**

Impedance spectra of $\text{Ba}_4\text{Sb}_2\text{O}_9$ ceramics (Figure 8) are similar to those of $\text{Ba}_4\text{Ta}_2\text{O}_9$ and $\text{Ba}_4\text{Nb}_2\text{O}_9$,\textsuperscript{17,18} consisting of one semicircle with a small electrode tail at low frequencies. However, contrary to $\text{Ba}_4\text{Ta}_2\text{O}_9$ and $\text{Ba}_4\text{Nb}_2\text{O}_9$, the bulk resistivity of $\text{Ba}_4\text{Sb}_2\text{O}_9$ displays a strong dependence on hu-
 midity, even at elevated temperatures such as 1273 K. Increasing the water vapor partial pressure leads to higher conductivity, unambiguously indicating a significant protonic contribution. An increase in the total conductivity is also observed when oxygen partial pressure increases. The latter tendency is quite common for many oxide materials with mixed protonic, oxygen ionic and p-type electronic transport under oxidizing conditions, for example, 6H-type Ba$_4$Ta$_2$O$_9$ or cubic perovskite SrCe(Y)O$_{3.8}$.\textsuperscript{18,27}

![Figure 9: Temperature dependences of the total conductivity of Ba$_4$Sb$_2$O$_9$ ceramics in dry and wet atmospheres. The water vapor partial pressure in flowing wet argon and air was $3.5 \times 10^{-2}$ atm.]

These trends are clearly visible in the Arrhenius curves of the total conductivity (Figure 9). The change in the conductivity activation energy, $E_a$, observed at 1070—1120 K correlates with the dehydration behaviour on heating (Figure 7). Above 1120 K the proton concentration in the lattice becomes low and the relative role of oxygen ionic conductivity increases, in accordance with the simplified reaction (in Kröger-Vink notation):

$$2 \text{OH}_o^+ \rightarrow \text{H}_2\text{O(gas)} + \text{O}_o^x + \text{V}_o^m$$  (1)

Below 1070—1120 K the concentration of protons is higher, and $E_a$ seems to be essentially de-
terminated by their migration activation energy and hydration enthalpy. As a result, the total conductivity activation energy is weakly dependent on oxygen pressure and decreases with increasing humidity from 88—101 kJ/mol in dry atmospheres down to 36—40 kJ/mol under wet conditions (Table 2). These changes are much larger compared to those induced by decreasing oxygen pressure.

![Figure 10: Comparison of the total conductivity of \( \text{Ba}_4\text{Sb}_2\text{O}_9 \), 6H-\( \text{Ba}_4\text{Ta}_2\text{O}_9 \) and \( \gamma\)-\( \text{Ba}_4\text{Nb}_2\text{O}_9 \) ceramics in dry air.](image)

When compared with 6H-\( \text{Ba}_4\text{Ta}_2\text{O}_9 \) and \( \gamma\)-\( \text{Ba}_4\text{Nb}_2\text{O}_9 \), the conductivity of the high-temperature 6H polymorph of \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) is clearly more similar to its Ta-containing analogue with the same structural type (Figure 10).

The ion transference numbers \( (t_i) \) of \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) (Figure 11), are higher than those of both 6H-\( \text{Ba}_4\text{Ta}_2\text{O}_9 \) and \( \gamma\)-\( \text{Ba}_4\text{Nb}_2\text{O}_9 \). As the \( t_i \) values are equal to the ratio of the sum of partial oxygen-anionic and protonic conductivities and total conductivity, this difference shows that the relatively low total conductivity of \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) is associated with lower electronic transport compared to 6H-\( \text{Ba}_4\text{Ta}_2\text{O}_9 \) and \( \gamma\)-\( \text{Ba}_4\text{Nb}_2\text{O}_9 \). The ionic conductivity of \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) is substantially high (Figure 12A). The level of ionic conduction in \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) is quite similar to that in 6H-\( \text{Ba}_4\text{Ta}_2\text{O}_9 \), suggesting that the similar structure of the high-temperature polymorphs of these compounds is
Table 2: Apparent activation energies for the total conductivity of $\text{Ba}_4\text{Sb}_2\text{O}_9$ in dry and wet atmospheres.

<table>
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<tr>
<th>Atmosphere</th>
<th>$p(\text{O}_2)$, atm</th>
<th>$p(\text{H}_2\text{O})$, atm</th>
<th>$T$, K</th>
<th>$E_a$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry air</td>
<td>0.21</td>
<td>$5 \times 10^{-4}$</td>
<td>1073—1273</td>
<td>180</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>973—1073</td>
<td>88</td>
</tr>
<tr>
<td>Wet air</td>
<td>0.20</td>
<td>$3.5 \times 10^{-2}$</td>
<td>1073—1273</td>
<td>107</td>
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<td></td>
<td></td>
<td></td>
<td>973—1073</td>
<td>36</td>
</tr>
<tr>
<td>Dry argon</td>
<td>$2 \times 10^{-5}$</td>
<td>$5 \times 10^{-4}$</td>
<td>1073—1273</td>
<td>215</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>973—1073</td>
<td>101</td>
</tr>
<tr>
<td>Wet argon</td>
<td>$2 \times 10^{-5}$</td>
<td>$3.5 \times 10^{-2}$</td>
<td>1073—1273</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>973—1073</td>
<td>40</td>
</tr>
</tbody>
</table>

Figure 11: Ion transference numbers of $\text{Ba}_4\text{Sb}_2\text{O}_9$, averaged under the oxygen partial pressure range 0.21-1.0 atm and water vapor partial pressure range 0.01-0.02 atm.
Figure 12: Comparison of the ionic and electronic contributions to the conductivity of Ba₄M₂O₉ (M= Sb, Nb, Ta) phases, averaged under dry oxygen/air gradient: A, total ionic (oxygen anionic and protonic); B, electronic. Data on 6H-Ba₄Ta₂O₉ and α-Ba₄Nb₂O₉ are taken from previous works.¹⁷,¹⁸
the main factor governing their transport properties. Some slight differences may be ascribed, primarily, to an easier reducibility of \(\text{Sb}^{5+}\) compared to \(\text{Ta}^{5+}\). The structural phase transition leads to local distortions hampering ionic transport, the role of which increases with decreasing temperature. As a result, the ionic contribution to total conductivity of \(\text{Ba}_4\text{Sb}_2\text{O}_9\) becomes lower as temperature decreases, contrary to \(6\text{H-Ba}_4\text{Ta}_2\text{O}_9\) where no local distortions were revealed in this temperature range. Note that qualitatively similar behaviour was reported for uranium-antimony oxide phases. \(^{32}\)

The relatively easy reducibility of \(\text{Sb}^{5+}\), shifting the electron-hole equilibrium towards \(n\)-type charge carriers, also leads to a low hole concentration and to lower electronic transport under oxidising conditions in comparison with \(\text{Ba}_4\text{Ta}_2\text{O}_9\) (Figure 12B). The incorporation of the \(\text{Sb}^{5+}/\text{Sb}^{3+}\) redox couple, which usually provides \(n\)-type electronic conductivity in antimonates, \(^{32}\) therefore seems a promising strategy to suppress electron-hole transport in protonic and mixed conductors. In fact, the electronic transport in \(\text{Ba}_4\text{Sb}_2\text{O}_9\) becomes similar to that in \(\alpha\)-\(\text{Ba}_4\text{Nb}_2\text{O}_9\) with a heavily distorted structure.

Another important trend is the correlation between ionic and electronic transport. This is reflected in quite similar activation energies and in the very weak dependence of the transference numbers on temperature at 1023—1273 K (Figures 11 and 12), also observed for \(\text{Ba}_4\text{Ta}_2\text{O}_9\) and \(\text{Ba}_4\text{Nb}_2\text{O}_9\). \(^{17,18}\) Exact microscopic mechanisms responsible for such tendency require further analysis. At first glance, however, this correlation may be qualitatively explained by the competing reactions of water and oxygen incorporation on cooling:

\[
\text{H}_2\text{O} + \text{O}_0^x + \text{V}_o^- \rightarrow 2\text{OH}_o^-
\]

\[
\frac{1}{2}\text{O}_2 + \text{V}_o^- \rightarrow \text{O}_0^x + 2\text{h}^-
\]

which lead to the formation of mobile charge carriers, namely protons and electron holes. Similar competing processes of charge carrier generation should occur if the incorporation of oxygen and water involves any interstitial positions.
Conclusions

{$\text{Ba}_4\text{Sb}_2\text{O}_9$} represents a new addition to the range of barium oxide based materials that show significant mixed ionic-electronic conductivity, including $\text{Ba}_4\text{Nb}_2\text{O}_9$ and $\text{Ba}_4\text{Ta}_2\text{O}_9$. Compared to those compounds, it shows higher ionic conductivity due to the easier reducibility of $\text{Sb}^{5+}$, but lower electronic conductivity due to reduced hole concentration under oxidising conditions. Having previously attempted to optimise the conductivity properties by studying the $\text{Ba}_4\text{Nb}_{2-x}\text{Ta}_x\text{O}_9$ solid-solution,\textsuperscript{30} adding $\text{Ba}_4\text{Sb}_2\text{O}_9$ to this family adds a further dimension to the phase space available to produce a single phase material with optimised mixed ionic-electronic conductivity properties.

We have shown that $\text{Ba}_4\text{Sb}_2\text{O}_9$ is stable down to room-temperature in a CO$_2$-free atmosphere, and undergoes a symmetry lowering phase transition from high-temperature hexagonal $P6_3/m$ to monoclinic $P2_1/m$ at 1150 K. This is similar to the phase transition observed in 6H-$\text{Ba}_4\text{Ta}_2\text{O}_9$. Under reducing conditions (such as dynamic vacuum), this transition is shifted to a much higher temperature of approximately 1800 K. The evolution of the cell parameters in $\text{Ba}_4\text{Sb}_2\text{O}_9$ (and 6H-$\text{Ba}_4\text{Ta}_2\text{O}_9$) through this transition is highly first-order, rather than second-order as would be expected for a conventional displacive symmetry-lowering.\textsuperscript{20} These results, combined with the TGA data, suggest that this symmetry lowering transition is intimately linked to the removal of hydrated water from the unit cell, presumably through steric factors. Further work is needed to determine the local positions of incorporated hydroxide ions, which do not appear to be long-range ordered.

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References


