

Complex 5d magnetism in a novel $S = \frac{1}{2}$ trimer system, the 12L hexagonal perovskite $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$

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Supporting Information Placeholder

ABSTRACT: The 12L hexagonal perovskite $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ has been synthesized for the first time and characterized using high-resolution neutron and synchrotron x-ray diffraction as well as physical properties measurements. The structure contains Ir_3O_{12} linear face-sharing octahedral trimer units, bridged by corner-sharing BiO_6 octahedra. The average electronic configurations of Ir and Bi are shown to be $4+(d^5)$ and $4+(s^1)$ respectively, the same as for the $S = \frac{1}{2}$ dimer system $\text{Ba}_3\text{BiIr}_2\text{O}_9$ which undergoes a spin-gap opening with a strong magnetoelastic effect at $T^* = 74$ K. Anomalies in magnetic susceptibility, heat capacity, electrical resistivity and unit cell parameters indeed reveal an analogous effect at $T^* \approx 215$ K in $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$. However, the transition is not accompanied by the opening of a gap in spin excitation spectrum, because antiferromagnetic coupling among $s = \frac{1}{2}$ Ir^{4+} (d^5) cations leads to the formation of a $S = \frac{1}{2}$ doublet within the trimers, vs. $S = 0$ singlets within dimers. The change in magnetic state of the trimers at T^* leads to a structural distortion, the energy of which is overcompensated for by the formation of $S = \frac{1}{2}$ doublets. Extending this insight to the dimer system $\text{Ba}_3\text{BiIr}_2\text{O}_9$ sheds new light on the more pronounced low-temperature anomalies observed for that compound.

INTRODUCTION

Systems that exhibit quantum cooperative phenomena due to coupling between magnetic, electronic, and orbital degrees of freedom have attracted a great deal of interest in recent years.¹ An interesting class of quantum cooperative system is the low-dimensional antiferromagnetic (AFM) dimer systems, where interactions between neighbouring electronic spins result in a gap opening between the singlet ground state and the excited triplet state.² Examples include TlCuCl_3 ,³ $\text{Ba}_3\text{Cr}_2\text{O}_8$,⁴ CuIr_2S_4 ,⁵ and, most recently, $\text{Ba}_3\text{BiRu}_2\text{O}_9$ ⁶ and $\text{Ba}_3\text{BiIr}_2\text{O}_9$.⁷ The spin-gap openings at $T^* = 176$ K and 74 K, respectively, in these last two phases is accompanied by a large negative thermal volume expansion (1% in the case of $\text{Ba}_3\text{BiIr}_2\text{O}_9$), in a remarkably strong magnetoelastic coupling effect.

$\text{Ba}_3\text{BiRu}_2\text{O}_9$ and $\text{Ba}_3\text{BiIr}_2\text{O}_9$ ^{8,9} are members of isostructural series of 6H-type hexagonal perovskites $\text{Ba}_3\text{RRu}_2\text{O}_9$ or $\text{Ba}_3\text{RIr}_2\text{O}_9$ ($R = \text{Y}$, rare earth).¹⁰⁻¹⁴ In the $R =$ lanthanoid phases, magnetic properties are mostly associated with $4f$ ions. 6H-type perovskites consist of face-sharing bi-octahedral $M_2\text{O}_9$ dimers that share vertices with RO_6 octahedra, with high-coordinate Ba^{2+} cations on the A sites. Direct M - M distances within the $M_2\text{O}_9$ dimers are relatively short at ~ 2.5 Å, allowing for the possibility of direct metal-metal bonding. The oxidation states of M and R are coupled, with $R^{3+}/M^{4.5+}$ and R^{4+}/M^{4+} being the most common combination (R^{4+}/M^{4+} typically has the smaller unit cell). The unit cell volumes of $\text{Ba}_3\text{BiRu}_2\text{O}_9$

and $\text{Ba}_3\text{BiIr}_2\text{O}_9$ are comparable to other B^{4+}/M^{4+} 6H-type perovskites, suggesting that the oxidation state of Bi is +4.

Bi^{4+} is a highly unusual oxidation state, corresponding to an unstable $[\text{Xe}]4f^{14}5d^{10}6s^1$ electronic configuration, and is seldom observed in the solid state; nominally Bi^{4+} oxides normally disproportionate into $\text{Bi}^{3+}/\text{Bi}^{5+}$, as has been shown to occur in, e.g., BaBiO_3 .¹⁵⁻²⁰ However, in the case of $\text{Ba}_3\text{BiRu}_2\text{O}_9$ and $\text{Ba}_3\text{BiIr}_2\text{O}_9$, we could find no evidence for $\text{Bi}^{3+}/\text{Bi}^{5+}$ disproportionation in our detailed high-resolution neutron and synchrotron x-ray diffraction studies, either above or below their magnetoelastic spin-gap transitions at T^* . We also saw no evidence for local disproportionation (peak broadening or anisotropic atomic displacement parameters), noting that BiO_6 octahedra are distributed on a pseudo-hexagonal lattice that could frustrate long-range ordering; or for charge transfer from Bi to M (i.e., $\text{Bi}^{4+}/M^{4+} \rightarrow \text{Bi}^{3+}/M^{4.5+}$). Considering that no spin-gap or structural transition is observed for any other $\text{Ba}_3\text{RRu}_2\text{O}_9$ or $\text{Ba}_3\text{RIr}_2\text{O}_9$ compound, it is reasonable to conclude that Bi in this unusual and unstable oxidation state plays a crucial role in the magnetoelastic spin-gap transitions. However, the exact mechanism remains unclear.

In order to shed more light on this, in the present study we investigated an analogue to $\text{Ba}_3\text{BiIr}_2\text{O}_9$ featuring Ir_3O_{12} face-sharing octahedral trimers in place of Ir_2O_9 dimers. The series of 12L-type hexagonal perovskites $\text{Ba}_4\text{RRu}_3\text{O}_{12}$ and $\text{Ba}_4\text{RIr}_3\text{O}_{12}$ had been reported for a wide range of $R =$ lanthanoid,²¹⁻²⁵ but not for $R = \text{Bi}$. We were unable to prepare

Ba₄BiRu₃O₁₂, but did succeed in producing high-quality samples of Ba₄BiIr₃O₁₂ for the first time. Ba₄BiIr₃O₁₂ shows evidence for a transition at ~215 K analogous to that observed in Ba₃BiIr₂O₉, but orders of magnitude weaker in terms of both the magnetic and structural effects. The results help narrow down the possible mechanisms for these transitions by distinguishing the roles of Ir–Ir direct bonding and Bi⁴⁺ instability.

EXPERIMENTAL

Pure polycrystalline samples of 12L perovskite-type Ba₄BiIr₃O₁₂ were prepared by conventional solid-state reaction in air from BaCO₃, Bi₂O₃ and Ir metal (99.99% purity or greater). Prior to weighing, BaCO₃ was dried at 1000 K overnight. The stoichiometric mixture with a 10% excess of Bi₂O₃ was ground with an agate mortar and pestle, made into pellets and calcined at 873 K for 16 h. The sample was then reground, pelleted and calcined at 1173 K for 48 h. Reaction progress and sample purity were monitored by conventional x-ray powder diffraction (XRD) collected on a Panalytical X'Pert Pro diffractometer using non-monochromated Cu K_α radiation. Attempts to prepare the Ru analogue Ba₄BiRu₃O₁₂ by the same method (using both RuO₂ and Ru metal as reagents) were unsuccessful, instead producing a mixture of the dimer Ba₃BiRu₂O₉ and BaRuO₃.

Room-temperature time-of-flight neutron powder diffraction (NPD) data were collected on the instrument HRPD at the ISIS facility, UK. The sample was placed in a 4 mm diameter vanadium can. Variable-temperature NPD data were collected on the instrument Echidna at the OPAL reactor (ANSTO, Lucas Heights, Australia) between 3 and 350 K at a wavelength of $\lambda = 2.4395$ Å. The sample was placed in a 6 mm diameter vanadium can and data collected in a closed-cycle cryofurnace.

Low-temperature synchrotron XRD (S-XRD) data were collected at the Powder Diffraction (PD) beamline of the Australian Synchrotron between 130 and 250 K at a wavelength of $\lambda = 0.82460$ Å (calibrated against a LaB₆ standard). Samples were placed in unsealed 0.3 mm diameter quartz capillaries, which were cooled in a liquid nitrogen cryostream.

Rietveld-refinements against NPD data were carried out using the GSAS²⁶ program with the EXPGUI²⁷ front-end. Scale factors, zero-shifts, background functions, and a single Lorentzian broadening term on top of the standard pseudo-Voigt peak shape functions for the instruments were refined. Data from the HRPD backscattering bank was used to refine structural parameters, which are presented in Table 1. Atomic displacement parameters (ADPs) were constrained to be equal for atoms of the same species. Metal–oxygen and short metal–metal bond lengths are presented in Table 2. The final Rietveld fit is shown in Figure 1, and the structure in Figure 2. The corresponding CIF file is available as deposited data.

TABLE 1. Structural parameters and bond valence sums²⁸ (BVS) for Ba₄BiIr₃O₁₂ at room temperature, refined against NPD (HRPD, ISIS) data. Space group *C2/m*, $a = 10.23625(14)$, $b = 5.90149(7)$, $c = 29.9970(4)$ Å, $\beta = 93.6407(11)^\circ$, $V = 1808.44(4)$ Å³.

Atom	x (a)	y (b)	z (c)	U_{iso} (100Å ²)	BVS
Ba1	0.3356(2)	0	0.5391(7)	0.58(9)	1.66
Ba2	0.3500(2)	0	0.3794(6)	0.58(9)	2.03

Ba3	0.0023(2)	0	0.2820(7)	0.58(9)	1.98
Ba4	0.3295(2)	0	0.7993(6)	0.58(9)	2.01
Ba5	0.0096(2)	0	0.1266(7)	0.58(9)	2.18
Ba6	0.3224(2)	0	0.9480(7)	0.58(9)	2.01
Bi1	0.3328(18)	0	0.6695(5)	0.90(10)	3.69
Bi2	0	0	0	0.90(10)	3.56
Ir1	0	0	0.500000	0.73(6)	4.08
Ir2	0.0144(14)	0	0.4121(4)	0.73(6)	5.12
Ir3	0.3193(14)	0	0.2505(4)	0.73(6)	4.59
Ir4	0.3387(13)	0	0.1675(4)	0.73(6)	4.66
Ir5	0.3506(12)	0	0.0792(4)	0.73(6)	4.60
O1	0.1577(2)	0	0.4606(5)	1.00(6)	2.09
O2	0.1190(18)	0	0.6375(5)	1.00(6)	1.97
O3	0.4543(2)	0	0.2982(7)	1.00(6)	2.08
O4	0.8245(2)	0	0.7994(7)	1.00(6)	2.30
O5	0.4961(2)	0	0.1324(7)	1.00(6)	2.26
O6	0.8005(19)	0	0.9654(7)	1.00(6)	2.02
O7	0.4293(15)	0.7234(3)	0.4516(4)	1.00(6)	2.10
O8	0.3879(14)	0.7244(2)	0.6196(4)	1.00(6)	2.09
O9	0.2654(12)	0.7531(2)	0.7174(4)	1.00(6)	2.16
O10	0.0919(14)	0.7327(3)	0.7897(4)	1.00(6)	2.16
O11	0.2356(16)	0.7317(3)	0.8791(5)	1.00(6)	2.07
O12	0.0484(14)	0.7396(3)	0.9459(4)	1.00(6)	2.42

TABLE 2. Bi–O, Ir–O and Ir–Ir bond lengths for Ba₄BiIr₃O₁₂ at room temperature, as refined against NPD (HRPD, ISIS) data. Labels (a–d) of intertrimer Ir–Ir bonds refer to Figure 2.

Bond	Distance (Å)	Bond	Distance (Å)
Bi1–O2	2.334(3)	Ir4–O4	1.998(3)
Bi1–O3	2.327(3)	Ir4–O5	1.979(3)
Bi1–O8 (×2)	2.305(16)	Ir4–O10 (×2)	1.981(18)
Bi1–O9 (×2)	2.189(17)	Ir4–O11 (×2)	2.065(18)
Bi2–O6 (×4)	2.232(2)	Ir5–O5	2.114(3)
Bi2–O12 (×4)	2.311(13)	Ir5–O6	1.979(2)
Ir1–O1 (×2)	2.061(18)	Ir5–O11 (×2)	2.087(2)
Ir1–O7 (×4)	2.058(15)	Ir5–O12 (×2)	1.932(16)
Ir2–O1	1.999(3)	Ir1–Ir2 (×2)	2.651(11)
Ir2–O2	1.953(3)	Ir3–Ir4	2.512(16)
Ir2–O7 (×2)	2.009(17)	Ir4–Ir5	2.659(18)
Ir2–O8 (×2)	1.943(15)	Selected intertrimer bonds	
Ir3–O3	1.925(3)	Ir2–Ir3 (a)	5.930(17)
Ir3–O4	2.032(3)	Ir2–Ir3 (b×2)	5.913(15)
Ir3–O9 (×2)	2.003(16)	Ir2–Ir2 (c×4)	5.908(18)
Ir3–O10 (×2)	2.076(17)	Ir2–Ir2 (d×2)	5.90149(7)

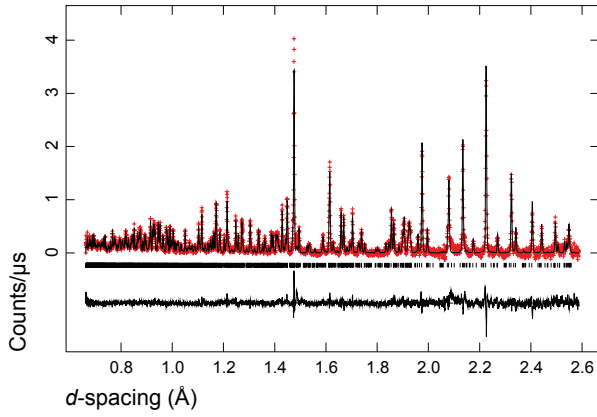


Figure 1. Observed (crosses), calculated (upper line) and difference (lower line) profiles for the final Rietveld fit of the structure of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ to NPD data (backscattering bank of HRPD, ISIS). $R_p = 0.0695$, $wR_p = 0.0691$, $\chi^2 = 1.925$ for 70 variables.

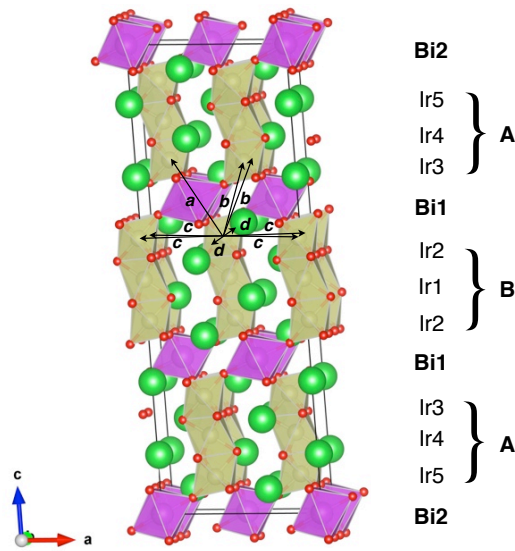


Figure 2. Room-temperature structure of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ as refined against NPD (HRPD, ISIS) data. BiO_6 octahedra are purple, Ir_3O_{12} face-sharing tri-octahedra are yellow, Ba atoms are green. Labels on selected longer Ir–Ir distances correspond to those listed in Table 2.

Rietveld refinements against low-temperature S-XRD data were also carried out using GSAS and EXPGUI. Due to the relatively poor sensitivity of the X-ray data to light oxygen atoms in the presence of heavy Ba, Bi and Ir atoms, it was not possible to reliably refine their structural parameters. We therefore used the model refined against NPD (HRPD, ISIS) data, and refined only lattice parameters in addition to a scale factor, zero-shift, background function, and a single Lorentzian broadening term on top of the standard pseudo-Voigt peak shape function for the instrument. The final Rietveld fit to 250 K data, *i.e.*, above the transition, is shown in Figure 3.

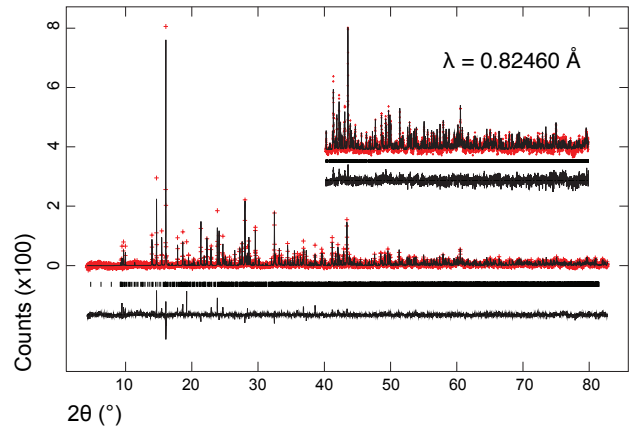


Figure 3. Observed (crosses), calculated (upper line) and difference (lower line) profiles for the final Rietveld fit to 250 K S-XRD data (PD, AS). $R_p = 0.0328$, $wR_p = 0.0445$, $\chi^2 = 1.828$. The inset shows the high-angle region with an expanded y-axis.

The temperature dependence of the lattice parameters obtained by Rietveld refinement between 3 and 350 K is shown in Figure 4. Data points from 130 to 250 K are from S-XRD data (highest resolution); other data points are from NPD (Echidna, OPAL).

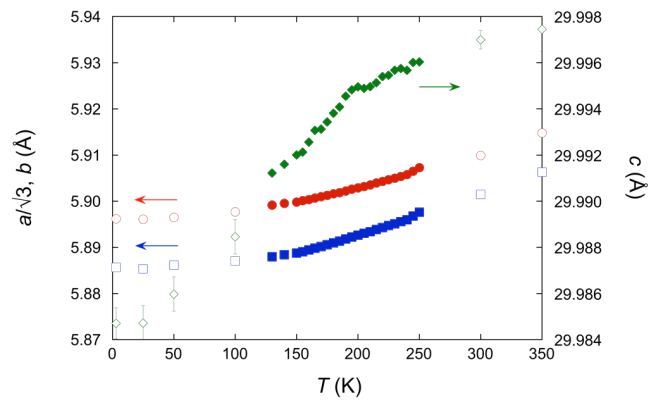


Figure 4. Temperature dependence of the lattice parameters for $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ between 3 and 350 K, from Rietveld-refinement against S-XRD (closed symbols) and NPD (open symbols) data. Error bars are smaller than symbols where not shown.

Physical properties (magnetic susceptibility and heat capacity) were measured using a Quantum Design PPMS. Magnetic susceptibility data (Figure 5) were collected from 350 to 2 K in an applied magnetic field of 50 kOe using the vibrating sample magnetometer (VSM) technique. Unfortunately it was not possible to collect useful data in lower fields due to the magnetically sparse nature of the system combined with the relatively high molar mass. For the same reason, attempts to collect useful AC-susceptibility measurements were unsuccessful.

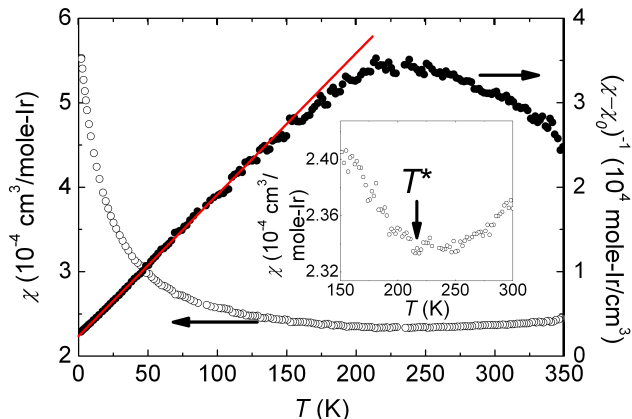


Figure 5. Temperature dependence of the molar susceptibility and its reciprocal.

Heat capacity (Figure 6) was measured using a relaxation technique on approximately 10 mg sample extracted from sintered pellets. Electrical resistivity data were collected using standard 4-probe technique on the same sample that was used for heat capacity measurements.

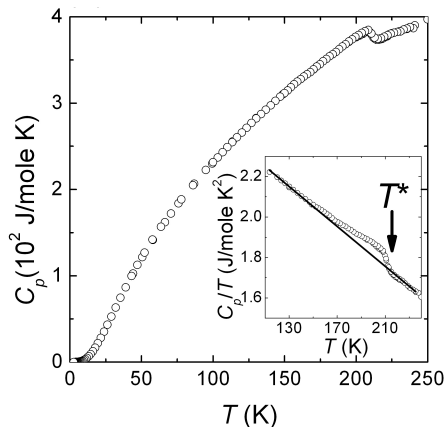


Figure 6. Temperature dependence of the specific heat, C_p .

RESULTS AND DISCUSSION

The 12L-type perovskite $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ consists of face-sharing tri-octahedral Ir_3O_{12} trimers that share vertices with BiO_6 octahedra, with Ba^{2+} cations in the high-coordinate perovskite A sites. Direct Ir–Ir distances within the Ir_2O_9 trimers are relatively short at ~ 2.6 Å, allowing for the possibility of direct metal–metal bonding.

A comparison of the unit cell parameters across the isostructural 12L-type series $\text{Ba}_4R\text{Ir}_3\text{O}_{12}$, $R =$ lanthanoid or lanthanum²² (Figure 7), shows that $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ has more in common with the $R = \text{Tb}$, Pr and Ce compounds than with those based on the other lanthanoids. Shimoda *et al.*²² used comparisons of average R –O bond lengths to the predictions of Shannon’s effective ionic radii²⁹ to demonstrate that the difference between the two series is due to $R = \text{Tb}$, Pr and Ce adopting 4+ valence states (meaning that the average valence state of Ir is also 4+), while the other lanthanoids adopt 3+ valence states (meaning that the average valence state of Ir is 4.33+). In the case of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$, our data (Table 2) yield a mean Bi–O bond length of 2.27(5) Å, very close to the average (2.29 Å) of Shannon’s radii for Bi^{3+} (2.43 Å) and Bi^{5+} (2.16 Å). BVS (Table 1) for the two Bi sites are calculated as 3.69 (Bi1) and 3.56 (Bi2). All these results indicate that the

apparent valence state of Bi is closer to 4+ than to 3+. This is the same highly unusual nominal valence state for Bi that we found in $\text{Ba}_3\text{BiIr}_2\text{O}_9$ ⁷ and $\text{Ba}_3\text{BiRu}_2\text{O}_9$.⁶ Again, S-XRD and high-resolution NPD data show no evidence for symmetry lowering or short-range disorder, at any temperature, that could indicate the $\text{Bi}^{3+}/\text{Bi}^{5+}$ disproportionation normally found in “ Bi^{4+} ” oxides such as BaBiO_3 .¹⁶ Crystallographically, therefore, $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ at room temperature is a perfect trimer analogue to the dimer compound $\text{Ba}_3\text{BiIr}_2\text{O}_9$.

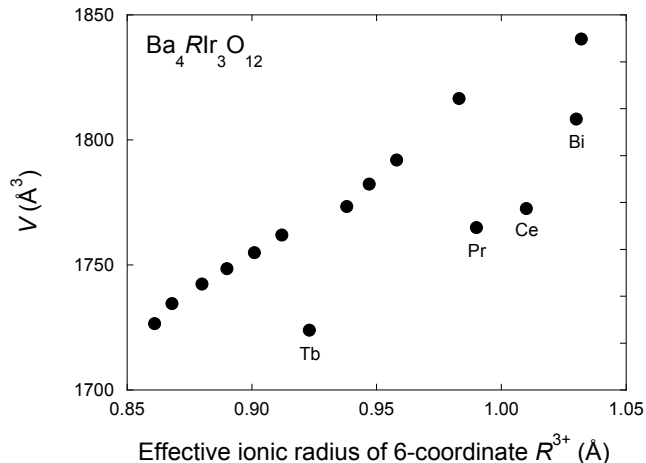


Figure 7. Effective ionic radii²⁹ of R^{3+} ($R = \text{Bi}$, Y, lanthanoid) cations in 6-fold coordination vs. unit cell volume (in the equivalent $C2/m$ cell of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$) for the 12L perovskite series $\text{Ba}_4R\text{Ir}_3\text{O}_{12}$ at room temperature. Error bars are smaller than symbols. Adapted from Shimoda *et al.*²², from which all data points except $R = \text{Bi}$ (this work) are taken.

Figure 4 shows the temperature dependence of the lattice parameters obtained from Rietveld refinements against S-XRD data between 150 and 250 K. A small but statistically significant anomaly is observed in the c axis at the same temperature as the physical properties anomalies, reminiscent of the c axis negative thermal expansion observed at T^* in $\text{Ba}_3\text{BiIr}_2\text{O}_9$.⁷ However, the anomaly is far smaller: 0.003%, vs. 1.0% for $\text{Ba}_3\text{BiIr}_2\text{O}_9$ (or 0.3% for $\text{Ba}_3\text{BiRu}_2\text{O}_9$).⁶ Similarly, magnetic susceptibility (Figure 5) and heat capacity (Figure 6) show features at ~ 200 K, but they are not nearly as pronounced as for the 6H compounds. Because the standard deviations on refined bond lengths are two orders of magnitude larger than on lattice parameter (see Tables 1 and 2), the lattice effect cannot be unambiguously ascribed to a change in the nature of Ir–Ir bonds as for $\text{Ba}_3\text{BiIr}_2\text{O}_9$.⁷ The small discrepancy between T^* observed by heat capacity vs. diffraction measurements may be partly explained by the first-order nature of the transition (noting that diffraction data were collected on cooling and heat capacity data on warming). It should also be noted that the relatively coarse data collection steps in the low temperature S-XRD measurements limit the accuracy with which T^* can be estimated. For this reason, coupled with the more accurate thermometry of the helium cryostat used for heat capacity measurements, we use the value for T^* obtained from the latter measurement in the following discussion.

Figure 5 shows the temperature dependence of the molar susceptibility χ as a function of temperature. The overall magnetic susceptibility is weakly temperature dependent, with a very shallow minimum at $T^* = 215$ K (see the inset). Below 150 K,

the susceptibility is well described by a modified Curie-Weiss law:

$$\chi(T) = \frac{N_A g^2 \mu_B^2 J(J+1)}{3k_B(T - \theta_{CW})} + \chi_0 \quad (1)$$

where θ_{CW} , J , g , k_B and χ_0 are the Curie-Weiss characteristic temperature, angular momentum, Landé g -factor, Boltzmann constant and temperature-independent contribution to susceptibility, respectively. A least square fit, performed below 150 K, (Figure 5) yielded an effective moment $\mu_{\text{eff}} = g\mu_B(J(J+1))^{0.5} = 0.22(2) \mu_B/\text{Ir}$, $\theta_{CW} = -15(1)$ K and $\chi_0 = 2.0(2) \times 10^{-4}$ emu/mole Ir. The effective moment is much lower than the spin-only value expected for an $S = 1/2$ ion ($1.73 \mu_B$), and much lower than value observed in $\text{Ba}_3\text{BiIr}_2\text{O}_9$ in its non-dimerized state ($0.9 \mu_B/\text{Ir}$).

Analyzing the structure of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$, we find that the exchange scheme for this compound may be complex. Because the structure consists of two crystallographically inequivalent trimers, A(Ir3–Ir4–Ir5) and B(Ir2–Ir1–Ir2), there are three possible nearest-neighbor exchanges, J_{12} , J_{34} and J_{45} ; two next-nearest neighbor exchanges within each trimer, J_{22} and J_{35} ; and generalized interdimer interactions J_{AA} , J_{BB} and J_{AB} (Figure 2). In principle, all of these interactions determine the magnetic response of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$. However, for simplicity we will assume that the nearest-neighbor exchange dominates and may be generalized by one J , representing an average of J_{12} , J_{34} and J_{45} .

Antiferromagnetic exchange within trimers of $s = 1/2$ ions should lead to different magnetic behavior in the high- and low-temperature regimes. At high temperatures, well above $|J|$, a single-ion like response is expected due to thermal fluctuations dominating over magnetic exchange, and simple Curie-Weiss like behavior should be observed. In the low temperature limit, well below $|J|$, a doublet within each trimer is formed. Antiferromagnetic exchange then gives rise to a collective $S = 1/2$ configuration formed by all three moments *per* trimer. At temperatures comparable to $|J|$, a crossover between these two regimes should be then observed.

The experimentally observed behavior of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ is, however, slightly different to the picture described above. Compared to $3d$ counterparts, magnetism in this $5d$ Ir^{4+} system is much weaker due to its much more extended d orbitals, causing strong hybridization with ligands and much more pronounced spin-orbit coupling.³⁰ This results in much lower effective moments than expected for systems where J is a “good” quantum number. In $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ we observe, near T^* , a transition from a weakly temperature-dependent paramagnet, with a positive temperature coefficient ($T > 220$ K), to a paramagnetic region with Curie-Weiss-like magnetic susceptibility due to the presence of weak fluctuating magnetic moments. The values of the effective moment *per* Ir in $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ ($0.22 \mu_B/\text{Ir}$) are much lower than in $\text{Ba}_3\text{BiIr}_2\text{O}_9$ ($0.9 \mu_B/\text{Ir}$) which may indicate that in the former compound, a doublet $S = 1/2$ ground state develops below T^* within magnetic Ir_3O_{12} trimers. The slightly negative characteristic Curie-Weiss temperature $\theta_{CW} = -15$ K then reflects then weak antiferromagnetic exchange among these doublets (J_{AA} , J_{AB} and J_{BB}).

A similar model has been proposed to describe the magnetism of $\text{Ba}_4\text{CeIr}_3\text{O}_{12}$.²⁵ However, no signature of a T^* -like transition was reported in that compound, and its effective moment was much closer to the theoretical value expected for a $S = 1/2$ doublet (almost $1.7 \mu_B/\text{trimer}$, vs. $0.4 \mu_B/\text{trimer}$ for $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$).

Figure 6 shows the temperature dependence of the heat capacity C_p as a function of temperature. Below $T^* \sim 215$ K, an anomaly starts to develop with a maximum at 210 K, extending down to about 150 K. As we were not able to find suitable non-magnetic counterpart compound, we have estimated the heat capacity associated with the T^* transition on the assumption that the C_p/T associated with the crystal lattice is a linear function of T in the range 115–270 K (inset in Figure 6). The estimated entropy associated with this transition is very small: only about $1.1 \text{ J K}^{-1} \text{ mole}^{-1}(\text{Ir})$, compared to $R \ln 2 = 5.75 \text{ J K}^{-1} \text{ mole}^{-1}$ expected for an $S = 1/2$ system undergoing a long-range magnetic ordering transition.

Figure 8 shows the electrical resistivity as a function of temperature. The overall character of the resistivity is typical of semiconductors, with ρ increasing as temperature decreases. The T^* transition is apparent as a kink in $\rho(T)$ and a rapid change in $d\rho/dT$ (shown in the inset). In general, the temperature dependence of the resistivity for semiconductors can be described by one of three models: an Arrhenius law, Mott’s variable-range hopping expression or the nearest-neighbor hopping of small polarons. Above T^* , $\rho(T)$ is well described by the variable range hopping model³¹:

$$\log \rho = a + bT^{\frac{-1}{1+n}} \quad (3)$$

where a and b are model parameters and n is the effective dimensionality of hopping. This model was developed for materials where the conduction is mediated by localized states *via* thermally induced hopping. A least-square fits yields $a = -8.1$, $b = 52 \text{ } \Omega \text{ cm K}^{3.2}$ and $n = 2.2$. A rapid change of resistivity at T^* suggests a change in the electronic structure of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$, *i.e.*, an increase of the band gap or a reduction in charge-carriers concentration or mobility.

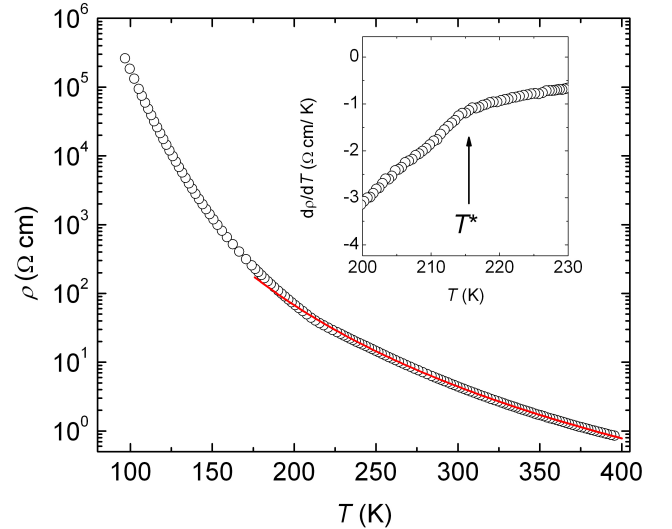


Figure 8. Temperature dependence of the electronic resistivity ρ . Solid line is a fit to Eq. (3). The inset shows the temperature derivative of resistivity vs. temperature in the vicinity of T^* .

The results and analysis presented above provide new information about the character of the T^* transition in the dimer system $\text{Ba}_3\text{BiIr}_2\text{O}_9$ ⁷ as well as in this new trimer system $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$. $\text{Ba}_3\text{BiIr}_2\text{O}_9$ undergoes a pronounced magnetoelastic transition associated with opening of a gap in the spin-excitation spectrum at $T^* = 74$ K, to which the $T^* = 215$ K transition in $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ appear to be analogous. Our observations for $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ on cooling through T^* can be summarized as follows: i) a change from non-Curie-Weiss and very

weakly temperature-dependent susceptibility above T^* , to Curie-Weiss behaviour with a low effective moment due to the formation of $S = \frac{1}{2}$ trimers below T^* ; ii) a release of structural/magnetic entropy; iii) an anomalous thermal lattice expansion; and iv) a change in the electrical structure, apparent as an anomaly in the electrical resistivity. Taken together, these findings present a picture of a transition based on magneto-crystalline coupling between lattice and magnetic degrees of freedom. According to this model, the transition results in a gain of magnetic energy (due to the formation of antiferromagnetically coupled $S = \frac{1}{2}$ trimers), which overcompensates for the loss of elastic energy arising from the structural distortion. Above T^* , magnetic susceptibility is very weakly temperature-dependent with a positive temperature coefficient, suggesting that there is very strong exchange within trimers, but that $S = \frac{1}{2}$ ground state doublets have not been able to form. This suppression of doublet formation above T^* could be explained by geometric frustration, due to competing antiferromagnetic exchange among the trimers.³² Table 2 lists the intertrimer Ir–Ir distances from Ir2, the peripheral site of trimer B (see Figure 2). Because the trimers are triangularly disposed relative to each other, there are a total of 9 intertrimer Ir–Ir bonds from Ir2, all between 5.91 and 5.93 Å and therefore all closely competing. Below T^* , the frustration is overcome, producing the observed small structural anomaly in the c axis (along which the Ir–Ir–Ir intratrimer bonds are aligned), and the moments within trimers form $S = \frac{1}{2}$ doublets so that weak antiferromagnetic coupling among them starts to become apparent in magnetic susceptibility. In this model, the T^* transition is analogous to that seen in $\text{Ba}_3\text{BiIr}_2\text{O}_9$.

It should be pointed out that this model is almost certainly an oversimplification, and that there remain some experimental observations that it does not fully or satisfactorily explain. In particular, it offers no insight into the cause of the strongly reduced effective moment of $0.22(2) \mu_{\text{B}}/\text{Ir}$ compared to the expected spin-only value of $1.73 \mu_{\text{B}}/\text{Ir}$ despite the excellent fit to the Curie-Weiss law at low-temperatures. We have therefore considered several other possible models, described below. Although these models are in fact less complete in terms of their ability to explain our data, it is possible that the true nature of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ incorporates aspects of each.

One alternative model is that for $T > T^*$, no localised spins at all are present, resulting in an almost temperature-independent magnetic susceptibility. Below T^* , charge carriers are localised into trimers that bear local magnetic moments with doublet ground state. However, this scenario predicts a metallic state above T^* , which is contrary to our observations.

The final model that could potentially explain all experimentally observed phenomena is the onset of charge order in the form of a so-called charge density wave (CDW), a well known precondition to high-temperature superconducting states, such as occurs in BaBiO_3 ³³ which, like $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$, contains Bi in the unusual nominal oxidation state of 4+. In that compound, “ Bi^{4+} ” is known to disproportionate into Bi^{3+} and Bi^{5+} , and this seems to play a critical role in the CDW state. In $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ (and $\text{Ba}_3\text{BiIr}_2\text{O}_9$) the structural distortion at T^* could be a hallmark of charge ordering in Bi sublattice; however, in both cases we found no evidence for satellite reflections or lattice strain in our diffraction patterns below T^* .

CONCLUSIONS

We have synthesized the 12L hexagonal perovskite $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ for the first time by conventional solid-state reaction. This compound contains face-sharing octahedral Ir_3O_{12} trimers, related to the Ir_2O_9 dimers in the spin-gap compound $\text{Ba}_3\text{BiIr}_2\text{O}_9$, and we observe anomalies in lattice constants, magnetic susceptibility, heat capacity and electrical resistivity in the proximity of $T^* = 215$ K that mirror those seen at $T^* = 74$ K in $\text{Ba}_3\text{BiIr}_2\text{O}_9$. By analogy to the dimer system, which shares the same electronic state of Ir and Bi, we can explain our experimental observations by the formation of $S = \frac{1}{2}$ doublets within trimers at T^* . However, different magnetic ground states are predicted for antiferromagnetically coupled dimers ($S = 0$ singlet) and trimers ($S = \frac{1}{2}$ doublet), which explains the gapless magnetic susceptibility in $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ compared to the spin-gap opening seen in $\text{Ba}_3\text{BiIr}_2\text{O}_9$. Similarly to the dimer compound, the $5d$ states appear to be strongly hybridized with surrounding orbitals, resulting in very low experimentally observed effective magnetic moments. Finally, while this model is internally consistent, it is most likely incomplete and does not explain all aspects of our experimental observations, notably the strongly reduced moments *per* Ir. Future investigations of the magnetic excitation spectrum of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$, using computational first principles methods (density functional theory) as well as experimental inelastic neutron scattering, should provide further insights into the strong coupling between magnetism and structure in these materials, leading to a more complete model for the unusual low-temperature behavior of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$.

ASSOCIATED CONTENT

Supporting Information. Crystallographic information file (CIF) for the room-temperature structure of $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ as Rietveld-refined against NPD data (HRPD, ISIS). This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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ABBREVIATIONS

ADP, atomic displacement parameter; AFM, antiferromagnetic; BVS, bond valence sums; CDW, charge-density wave; HT, high temperature; LT, low temperature; NPD, neutron powder diffraction; NTE, negative thermal expansion; S-XRD, synchrotron x-ray powder diffraction; VSM, vibrating sample magnetometer; XRD, x-ray powder diffraction

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TOC Graphic: Ba₄BiIr₃O₁₂ consists of Ir₃O₁₂ linear face-sharing octahedral trimer units bridged by corner-sharing BiO₆ octahedra. Antiferromagnetic coupling among $s = \frac{1}{2}$ Ir⁴⁺ (d^5) cations leads to the formation of $S = \frac{1}{2}$ doublets within the trimers. The onset of magnetic order is accompanied by anomalies in magnetic susceptibility, heat capacity, electrical resistivity and unit cell parameters; however, long-range magnetic order is not observed because interactions between the trimers are geometrically frustrated.

