High-Pressure Synthesis of 5d Cubic Perovskite BaOsO$_3$ at 17 GPa: Ferromagnetic Evolution over 3d to 5d Series


ABSTRACT: In continuation of the series of perovskite oxides that includes 3d$^4$ cubic BaFeO$_3$ and 4d$^4$ cubic BaRuO$_3$, 5d$^4$ cubic BaOsO$_3$ was synthesized by a solid-state reaction at a pressure of 17 GPa, and its crystal structure was investigated by synchrotron powder X-ray diffraction measurements. In addition, its magnetic susceptibility, electrical resistivity, and specific heat were measured over temperatures ranging from 2 to 400 K. The results establish a series of 5d$^4$ cubic perovskite oxides, which can help in the mapping of the itinerant ferromagnetism that is free from any complication from local lattice distortions for transitions from the 3d orbital to the 5d orbital. Such a perovskite series has never been synthesized at any d configuration to date. Although cubic BaOsO$_3$ did not exhibit long-range ferromagnetic order unlike cubic BaFeO$_3$ and BaRuO$_3$, enhanced feature of paramagnetism was detected with weak temperature dependence. Orthorhombic CaOsO$_3$ and SrOsO$_3$ show similar magnetic behaviors. CaOsO$_3$ is not as conducting as SrOsO$_3$ and BaOsO$_3$, presumably due to impact of tilting of octahedra on the width of the t$_{2g}$ band. These results elucidate the evolution of the magnetism of perovskite oxides not only in the 5d system but also in group 8 of the periodic table.

INTRODUCTION

Transition metal oxides, which are electronically and magnetically active, are emerging as functional materials for a broad range of scientific and practical applications owing to their high-temperature superconductivity, multiferroicity, metal–insulator transitions, and spintronics.$^{1-9}$ Transition metal oxides that exhibit a variety of solid states have been fabricated; however, the electronic properties of these oxides are extraordinarily rich, and hence it has been challenging to map out even their primary magnetic properties, given the limited number of material parameters available. Establishing a series of transition metal oxides that can aid in the mapping of the properties of these materials would be a significant step in comprehensively understanding the chemistry of not only solid-state transition metal oxides but also nanoscaled magnetic and electronic oxides as well as other materials.

Recent studies of transition metal oxides have focused on perovskite-based 5d oxides since the properties of the correlated 5d electrons seem to be fundamentally different from those of the electrons of 3d oxides$^{1-4}$ such as iron, manganese, and copper oxides,$^{5-9}$ which have been widely used in various applications. The major differences in the magnetic properties of 3d and 5d oxides are primarily caused by the fact that the 5d orbital is spatially more extended than the 3d orbital. This strengthens the hybridization between the 5d and oxygen 2p orbitals. In addition, the spin–orbit (SO) interaction of the 5d atoms is stronger than that of the 3d atoms because the SO coupling is roughly proportional to the fourth power of the effective nuclear charge (atomic number)$^{10,11}$ Indeed, a delicate balance between the nearly comparable magnitudes ($\sim 0.5-2$ eV)$^{1-4}$ of the on-site Coulomb repulsion, $U$, and the bandwidth, $W$, and the magnitude of the SO interaction in 5d perovskite-based oxides

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may drive distinguishable phenomena such as the unconventional insulating state of SrIrO$_3$ (5d$^4$)$_{1−4}$ and the Slater-like transition of NaOsO$_3$ (5d$^3$)$_{12−15}$. To the best of our knowledge, the SO coupling constant for even free 3d and 5d ions has not yet been experimentally determined.$^{11}$ Therefore, an experimental evaluation of the nature of d electrons for orbitals ranging from 3d to 5d would be significant for further developing perovskite-based 5d oxides that are fundamentally different from 3d oxides.

In this study, we focused our attention on a perovskite-based 5d oxide, namely, 5d$^4$ BaOsO$_3$. The large crystal field of a 5d atom usually stabilizes the low-spin (LS) configuration; thus, 5d$^0$ and 5d$^6$ oxides do not have unpaired 5d electrons, exhibiting only a nonmagnetic state. Perovskite-based 5d$^1$ and 5d$^2$ oxides, such as Re$^{5+}$,$^{16}$ Re$^{5+}$,$^{17}$ and Os$^{6+}$,$^{18}$ oxides, are rare. In addition, their synthesis is usually very challenging. Several 5d$^4$ and 5d$^5$ oxides as well as 5d$^3$ oxides have been synthesized and characterized.$^{1−4,19−21}$ Unlike 5d$^4$ and 5d$^5$ oxides, 5d$^3$ oxides exhibit a minor SO interaction owing to their configuration.$^{12−15,22}$ We therefore focused our attention on the 5d$^4$ and 5d$^5$ electrons. In practice, a number of perovskite-based d$^4$ and d$^5$ oxides, which cover 3d to 5d orbitals, have been synthesized. These include Sr$_2$TrO$_4$ (d$^4$ Tr = Fe$^{4+}$,$^{23}$ Ru$^{4+}$,$^{24}$ d$^5$ Tr = Co$^{3+}$,$^{25}$ Rh$^{3+}$,$^{26}$ Ir$^{4+}$,$^{4}$ and SrTrO$_3$ (d$^4$ Tr = Fe$^{4+}$,$^{27}$ Ru$^{4+}$,$^{28}$ Os$^{4+}$,$^{29,30}$ d$^5$ Tr = Co$^{3+}$,$^{31}$ Rh$^{4+}$,$^{32}$ Ir$^{4+}$,$^{33}$). However, in these oxides, octahedral TrO$_6$ distortion and tilting seem to have a significant effect on the features of the d electrons, as was suggested for the Sr and Ca series of oxides.$^{27−30}$ Very recently, cubic 3d$^4$ BaFeO$_3$,$^{34}$ and cubic 4d$^4$ BaRuO$_3$,$^{35}$ were synthesized, establishing a new distortion-free perovskite series. Both these cubic perovskite oxides have the same space group, Pm$ar{3}$m, with all the atoms located at special positions: Ba(0, 0, 0), Tr(1/2, 1/2, 1/2), and O(1/2, 1/2, 0). Therefore, if cubic 5d$^4$ BaOsO$_3$ is added to the series, the nature of the d electrons should be known for 3d to 5d orbitals without there being significant influence from a local lattice distortion.

In this study, we were able to synthesize cubic 5d$^4$ BaOsO$_3$ to complete the series of d$^4$ perovskite oxides that includes 3d$^4$ cubic BaFeO$_3$ and 4d$^4$ cubic BaRuO$_3$ by a solid-state reaction at a pressure of 17 GPa. The results of crystal structure investigations through X-ray diffraction (XRD) analyses indicated that the space group of the oxide was the same as that of BaFeO$_3$ and BaRuO$_3$, namely Pm$ar{3}$m. This series of cubic perovskite oxides with valence orbitals ranging from 3d to 5d can aid in the mapping of the evolution of d magnetism that is free from complications from local lattice distortions. Such a textbook-like perovskite series has never been synthesized for any group of the periodic table.

### EXPERIMENTAL PROCEDURES

Polycrystalline CaOsO$_3$, SrOsO$_3$, and BaOsO$_3$ were synthesized by a solid-state reaction under high-pressure and high-temperature conditions. Polycrystalline CaOsO$_3$ and SrOsO$_3$ were synthesized in a belt-type high-pressure apparatus operated at the National Institute for Materials Science, Japan. This apparatus could maintain a pressure of up to 6.5 GPa at 1000 °C for 1 h in the same high-pressure apparatus. Next, a powder of 6H BaOsO$_3$ was placed into a smaller Pt capsule and heated in a Kawai-type multianvil high-pressure apparatus operated at Gakushuin University, Japan.$^{30}$ The reaction conditions were a temperature of 1600 °C, a reaction time of 30 min, and a pressure of 17 GPa. The capsule was then quenched to room temperature, and the pressure within was released.

The three polycrystalline compounds, CaOsO$_3$, SrOsO$_3$, and BaOsO$_3$, were studied through powder XRD analyses, which were performed at room temperature using monochromatic Cu Ka radiation, to confirm the quality of the compounds. A Rigaku diffractometer was employed for the purpose. To investigate the crystal structures of the compounds in detail, the compounds were studied through synchrotron powder XRD (SRXD) measurements at room temperature, which were performed using a large Debye–Scherer camera at the BL15XU beamline of SPring-8, Japan.$^{37,38}$ The wavelength of the monochromatic radiation was 0.6529 Å, determined using a standard material. The obtained SRXD patterns were analyzed by the Rietveld method using the software programs RIETAN-FP$^{39}$ and VESTA.$^{40}$

The temperature dependence of the electrical resistivity, $\rho(T)$, of the materials was measured between 2 and 400 K by the four-probe method using a physical properties measurement system from Quantum Design, Inc. Electrical contacts were formed on a bar-shaped pellet, cut from each final product, using silver paste and Au wires. The gauge current was 0.1 or 0.2 mA. The specific heats ($C_p$) were measured using the same apparatus and a relaxation-time method over temperatures ranging from 2 to 300 K. The direct current (DC) magnetic susceptibility ($\chi$) was measured in the zero-field cooling (ZFC) and field cooling (FC) modes over temperatures ranging from 2 to 400 K. A magnetic property measurement system from Quantum Design, Inc., was used for the measurements. The applied magnetic field was 50 kOe. The isothermal magnetization $M(H)$ at 2 and 300 K was measured using the same apparatus for magnetic fields ranging from ~50 to 50 kOe. A loosely ground powder of each compound was used for the magnetic measurements.

The electronic states of the perovskites CaOsO$_3$, SrOsO$_3$, and BaOsO$_3$ were studied by a first-principles method. The electronic densities of states (DOS) of the compounds were calculated by the generalized gradient approximation (GGA) method,$^{41}$ which is based on the density functional theory.$^{41}$ The WIEN2K software package, which is based on the highly precise full-potential linearized augmented-plane-wave method, was used for the calculations.$^{42}$

### RESULTS

The synthesis of perovskite compounds with the 5d$^4$ configuration, CaOsO$_3$, SrOsO$_3$, and BaOsO$_3$, under ambient-pressure and high-pressure conditions (pressure of up to 6.5 GPa) was reported by Chamberland et al. in 1973$^{29}$ and 1978.$^{30}$ The compounds CaOsO$_3$ and SrOsO$_3$ crystallize into an orthorhombic GdFeO$_3$-type structure with the space group Pnma, while BaOsO$_3$ crystallizes into the six-layer hexagonal (6H) BaTiO$_3$ structure. In addition, BaOsO$_3$ crystallizes into a body-centered cubic polymorph with a lattice parameter of 9.373(1) Å, which was reported to be a K$_2$SbO$_3$-type compound.$^{30}$ The cubic perovskite BaOsO$_3$ had not been synthesized previously.

In the present study, the synthesis of the orthorhombic perovskites CaOsO$_3$ and SrOsO$_3$ was performed, and the structure and electromagnetic properties of these compounds were studied. Although their properties have been investigated to some extent in earlier works, a detailed study was lacking. In
addition, we found that 6H BaOsO₃ transforms into a cubic polymorph on heating at 17 GPa. As a result, a new series of the cubic perovskite d⁴ BaTrO₃ (Tr = Fe⁴⁺, Ru⁴⁺, and Os⁴⁺ [this work]) was established. This series could be useful for studying the evolution of the electromagnetic properties of perovskites over a transition from the 3d orbital to the 5d orbital because the cubic structure is free from local lattice distortions that often have an effect on electromagnetic properties. The cubic perovskite series could help in the mapping of the fundamental d⁴ properties for a transition from the 3d orbital to the 5d orbital. Such a cubic perovskite series has never been able to date, not only in the d⁴ configuration but also in other d configurations.

First, the crystal structure of BaOsO₃ was studied by SXRD analysis. Figure 1 shows a refined SXRD pattern of reasonable quality of BaOsO₃. A cubic perovskite structure model was used to refine the pattern. The R factors of the refinement were lower than 5.8%, indicating a reasonable quality. The crystal picture drawn from the refined solution is shown in Figure 1. As a result of the refinement, the possibility of the formation of a KSB₉O₃-type polymorph could be rejected. In addition, a trivial amount of impurity was detected; this was presumably Os with the weight fraction of 2.9%. Details of the refinement are listed in Table 1. We emphasize that the refinement of occupation factors of the Ba and Os sites gave values equal to the unity within standard deviations.

Structures of SrOsO₃ and CaOsO₃ could be refined in the GdFeO₃-type model with space group Pnma. While a reasonable structural model was obtained for CaOsO₃, the OsO₆ octahedron was highly distorted in SrOsO₃. The careful analysis of the SXRD pattern of SrOsO₃ showed that reflections with intensities above 0.2% could be indexed in space group Imma with the same lattice parameters. The refinement in the Imma model gave similar R indexes (Rwp = 3.33%, Rp = 1.83%, Rb = 3.74%, and Rf = 2.30%) in comparison with the Pnma model (Rwp = 3.31%, Rp = 1.80%, Rb = 3.76%, and Rf = 2.60%).

The appearance of extremely weak superstructure reflections (<0.2%) could originate from additional octahedral tilt along the "pseudo-cubic" a axis. Extremely weak superstructure reflections originating from ordering of oxygen atoms and the presence of heavy Sr and Os cations could prevent accurate localization of the O2 atom in the Pnma model. Therefore, we used constraints, z(O2) = 1 − x(O2) and B(O2) = B(O1), during the refinement of SrOsO₃ in the Pnma model. The refined structural parameters for SrOsO₃ and CaOsO₃ are listed in Tables 2 and 3, respectively. The lattice parameters of SrOsO₃ and CaOsO₃ are comparable to those reported previously.

![Figure 1. Observed (crosses) and calculated (solid line) synchrotron X-ray powder diffraction patterns of BaOsO₃ at room temperature, as well as the differences between them. The small markers at the bottom denote the simulated peak positions. The lower marks are for an impurity phase, which is 2.9 wt% Os. Inset shows the structure inferred after refinement.](image)

### Table 1. Structural Parameters of Cubic BaOsO₃ at Room Temperature

<table>
<thead>
<tr>
<th>site</th>
<th>WP</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.271(8)</td>
</tr>
<tr>
<td>Os</td>
<td>1b</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.032(6)</td>
</tr>
<tr>
<td>O</td>
<td>3c</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.37(6)</td>
</tr>
</tbody>
</table>

*WP, Wyckoff position. The occupancy factor was fixed at 1 for all atoms. The space group is Pm3m (No. 221). Z = 1, a = 4.02573(1) Å, and V = 65.2430(1) Å³. The R indexes were Rwp = 5.79%, Rp = 3.68%, Rb = 5.54%, and Rf = 3.77%.*

SrOsO₃ and CaOsO₃ are comparable to those reported previously. Figures 2 and 3 show the refinement fits. We emphasize that the (110) cubic reflection was split into three strong reflections in SrOsO₃, thus excluding tetragonal and rhombohedral symmetries. All reflections of SrOsO₃ could only be indexed in an orthorhombic symmetry with the lattice parameters. We also emphasize that in SrOsO₃, the a parameter is smaller than the c parameter (a < b/√2 < c) for both Imma and Pnma models in comparison with CaOsO₃ (c < b/√2 < a). Exchange of the a and c parameters in SrOsO₃ gave similar refinement results, but expected positions of a few very weak reflections did not match with the experimental positions, thus confirming the order of the lattice parameters. The same order of the lattice parameters was observed in SrRuO₃ and SrIrO₃ (a < b/√2 < c). Note that sometimes the a and c parameters of SrRuO₃ and SrIrO₃ were erroneously exchanged in the literature.

Small amounts of impurities (Os in SrOsO₃ and Os in Ca₂Os₂O₇ in CaOsO₃) were detected in SrOsO₃ and CaOsO₃.
It is worth noting that Os is paramagnetic at temperatures as low as 0.66 K and eventually becomes superconductive.45 Thus, the presence of small amounts of Os by mass fraction should have a negligible impact on electromagnetic characterization at temperatures greater than 2 K. In addition, the mass fraction of CaOsO3, in the Ca-based compound was ~0.07%, suggesting that the impurity had little impact on the measurements, although it does drive a metal–insulator transition at 327 K.46

In the AOsO3 series (A = Ca, Sr, and Ba), the decrease of the size of the A cations results in the appearance of additional tilting and the increase of tilt angles to adjust for smaller A cations while keeping almost rigid and regular OsO6 octahedra. BaOsO3 has ideal OsO6 octahedra without tilts (the tilt system is $a^0a^0a^0$, and the Os–O–Os bond angles are 180°). SrOsO3 has the $a^0b^0b^0$ tilt system (the inset of Figure 2, with negligible tilt along the $Pnma$ b axis), and the Os–O–Os bond angles are 165.7° and 169.5°. CaOsO3 has the $a^0b^0b^0$ tilt system (the inset of Figure 3, with noticeable tilt along the $Pnma$ b axis), and the Os–O–Os bond angles are 151.7° and 152.0°. The tilt angles can be estimated from the fractional coordinates of the O1 and O2 atoms and the lattice parameters: in-phase tilt angle $\phi_{O2} = \arctan(1 + 2x_{O2} - 2z_{O2})$, out-of-phase tilt angles $\phi_{O2} = \arctan(2\gamma_{O2})$ and $\phi_{O1} = \arctan(2\gamma_{O1})$ [for our coordinates in space group $Pnma$], and $\phi_{lattice} = \arccos(\sqrt{2a^2/(ab)})$ for $c < b/\sqrt{2}.a$.47 Values of $\phi_{O2}$, $\phi_{O1}$, and $\phi_{lattice}$ were very close to each other for CaOsO3 and SrOsO3 (Table 4) indicating that the OsO6 octahedra were very rigid. It is interesting that $\phi_{O2}$ was just 1.7° in SrOsO3 in comparison with SrRuO3 ($\phi_{O2} = 5.9°$) and CaOsO3 ($\phi_{O2} = 9.6°$) (see Table S1, Supporting Information).

The local structure distortion was evaluated on the basis of the bond valence sums (BVSs, where $BVS = \sum_{i=1}^{N} vi = \exp[\{(R_{vi} - 1)/B\}, N$ is the coordination number, $B = 0.37, R_{O}(O_{3+}) = 1.811, R_{O}(Fe^{3+}) = 1.780$, and $R_{O}(Ba^{2+}) = 2.29$, which are listed in Table 4.48 The BVSs for the Ba atoms in BaOsO3, BaRuO3, and BaFeO3 are far greater than the expected value of 2.00.48 The high degree of overbonding suggests the presence of significant internal stress. In addition, the tolerance factor is slightly higher than 1.00, even though BaOsO3, BaRuO3, and BaFeO3 all have a cubic perovskite lattice.51 These results thus suggest that the internal bonds of BaOsO3, BaRuO3, and BaFeO3 are under certain stresses, which may account for the extreme conditions required to synthesize the compounds.

**Table 4. Comparison of the Lattice and Structural Parameters of the Perovskite Oxides**

<table>
<thead>
<tr>
<th></th>
<th>CaOsO3</th>
<th>SrOsO3</th>
<th>BaOsO3</th>
<th>BaRuO3</th>
<th>BaFeO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>space group</td>
<td>$Pnma$</td>
<td>$Pnma$</td>
<td>$Pm3m$</td>
<td>$Pm3m$</td>
<td>$Pm3m$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.57439(3)</td>
<td>5.55925(1)</td>
<td>4.02573(1)</td>
<td>4.0059(2)</td>
<td>3.97106(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.77067(4)</td>
<td>7.88779(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.44525(3)</td>
<td>5.59801(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>8.187</td>
<td>9.558</td>
<td>7.398</td>
<td>6.230</td>
<td></td>
</tr>
<tr>
<td>Tr-O1 (Å)</td>
<td>2.003(1) x 2</td>
<td>1.9875(9)</td>
<td>2.0129(1) x 6</td>
<td>2.0029(1)</td>
<td>1.9856(1)</td>
</tr>
<tr>
<td>Tr-O2 (Å)</td>
<td>1.9784(4)</td>
<td>1.9803(9)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tr-O2 (Å)</td>
<td>2.037(4) x 2</td>
<td>1.9811(9)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tr-O1-Tr (deg)</td>
<td>151.7(1) x 2</td>
<td>165.7(1)</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Tr-O2-Tr (deg)</td>
<td>152.0(2) x 4</td>
<td>169.5(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BVS at A-site</td>
<td>1.90 (III), 2.04 (III)</td>
<td>2.09 (III)</td>
<td>2.63 (III)</td>
<td>2.73 (III)</td>
<td>2.92 (III)</td>
</tr>
<tr>
<td>BVS at B-site</td>
<td>3.55</td>
<td>3.77</td>
<td>3.48</td>
<td>3.80</td>
<td>3.44</td>
</tr>
<tr>
<td>tolerance factor $t$</td>
<td>0.95</td>
<td>0.99</td>
<td>1.05</td>
<td>1.05</td>
<td>1.07</td>
</tr>
<tr>
<td>$\phi_{O2}$ (deg)</td>
<td>9.6</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\phi_{O1}$, $\phi_{lattice}$ (deg)</td>
<td>14.6, 13.6, 14.5</td>
<td>7.1, 7.1, 8.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The BVSs for Sr and Os in SrOsO$_3$ are nearly comparable with the expected values. In addition, the tolerance factor is close to 1.00. But SrOsO$_3$ has an orthorhombic distortion similar to SrRuO$_3$, which also has $t \approx 1.00$. Because this type of octahedral distortion usually has a large impact on the correlated d electrons, it is essential to carefully investigate the magnetic and electrical properties of the CaOsO$_3$, SrOsO$_3$, and BaOsO$_3$.

All the compounds exhibited negligible thermal hysteresis in the $\rho(T)$ curves on warming and cooling over temperatures ranging from 2 to 400 K (Figure 4). CaOsO$_3$ showed semiconductor-like $\rho(T)$ values (i.e., $d\rho/dT < 0$) over the entire temperature range. The $\rho$ value at room temperature was $\sim 16.9 \ \Omega \ \text{cm}$, which was approximately 3 orders of magnitude more than what is expected for a metallic oxide. On cooling, $\rho$ increased gradually to 28 $\Omega \ \text{cm}$ at 80 K and 102 $\Omega \ \text{cm}$ at 2 K. However, neither the Arrhenius conduction model [$\ln \rho(T) \propto T^{-1}$] nor the variable range hopping [$\ln \rho(T) \propto T^{-1/4}$] one$^5$ fits the $\rho(T)$ values for CaOsO$_3$. Thus, the semiconductor-like behavior is possibly affected by the complex scattering, which involves grain boundaries and undetected disorder. A simple explanation could be that CaOsO$_3$ is in the vicinity of a Mott insulating regime, as has been hypothesized in the case of Sr$_2$IrO$_4$.$^{1-2}$ Further studies involving a high-quality single crystal are required in order to fully characterize the $\rho(T)$ behavior of CaOsO$_3$.

In contrast to CaOsO$_3$, SrOsO$_3$ remained metallic until the lowest temperature (2 K). The value of $\rho$ at room temperature was 7.85 m$\Omega$ cm, and it decreased gradually upon cooling to 5.66 m$\Omega$ cm at 2 K. The $\rho(T)$ curve for temperatures lower than 250 K followed the power law relation, $\rho(T) = \rho_0 + A_T T^2$, to a high degree. This relation is usually indicative of Fermi liquid-like behavior when $\rho_0$ and $A_T$ are constant. A least-squares analysis yielded $\rho_0 = 5.67 \ \text{m}\Omega \ \text{cm}$ and $A_T = 0.796 \ \text{m}\Omega \ \text{cm} \ K^{-2}$. The $\rho_0$ value was unusually larger than that for a normal metal, suggesting additional scattering by the grain boundaries and undetected disorders, for instance. In addition, the residual resistivity ratio, $\rho_{300}/\rho_0$ was 1.24; this was much smaller than what is expected for a metallic material.$^*$

The $\rho(T)$ curve for BaOsO$_3$ showed a broad upturn at a temperature of approximately 60 K; the conductivity of the compound changed from metal-like to non-metal-like upon cooling. Note that this change was not accompanied by thermal hysteresis, indicating that a first-order phase transition was unlikely. Regardless of the change, $\rho(T)$ remained very low over the entire temperature range, suggesting that the charged-carrier density was altered little over the upturn. Analyzing the metallic conduction behavior using the formula for Fermi liquids yielded $\rho_0 = 17.43 \ \text{m}\Omega \ \text{cm}$ and $A_T = 0.441 \ \text{m}\Omega \ \text{cm} \ K^{-2}$. The $\rho_0$ value was approximately three times larger than that of SrOsO$_3$, suggesting that additional scattering at such as grain boundaries might be significant. Indeed, the nonmetallic behavior for temperatures lower than approximately 30 K followed well the variable-range hopping model, indicating that disorder scattering has greater impact on the conduction at the low temperatures. Alternatively, a possible pseudogap nature is responsible for the weak upturn, as was argued for similar features observed for SrRuO$_3$ and 9R-BaRuO$_3$. The delicate transport issue needs to be investigated using a single crystal BaOsO$_3$.

The temperature dependence of $\chi$ was measured for all the compounds, as shown in Figure 5a. It was found that the temperature did not have a significant effect on $\chi$, unlike a localized spin system. In addition, a long-range ferromagnetic order as found for cubic BaRuO$_3$ and BaFeO$_3$ were not obvious above 2 K. This was true for all the compounds and the entire temperature range. Although a small rise in $\chi$ upon cooling at low temperatures was observed, magnetic ordering accompanied by the metallic to nonmetallic change at approximately 60 K was not, unlike in the case of NaOsO$_3$.$^{12}$

![Figure 4](image_url)  
Figure 4. Temperature dependence of $\rho$ of AOsO$_3$ (A = Ba, Sr, and Ca). Inset: an expanded view of the $\rho(T)$ data for BaOsO$_3$.

![Figure 5](image_url)  
Figure 5. (a) Temperature dependence of $\chi$ for AOsO$_3$, measured at 50 kOe during cooling (A = Ba, Sr, and Ca) and (b) a $\chi^{-1}$ vs T plot of the data. The solid lines denote the least-squares fits to the data.
To quantitatively analyze the magnetic properties of the compounds, the 1/χ vs T plots of all the compounds were fit to the Curie–Weiss (CW) law; these are the solid curves in Figure Sb. The analytical formula used was χ = Nk_bμ_eff^2/(3k_b(T − Θ_W)) + χ_0, where N is the Avogadro constant, μ_eff is the effective Bohr magneton, k_b is the Boltzmann’s constant, Θ_W is the Weiss temperature, and χ_0 is the temperature-independent term. When we assumed that Θ_W = 0, a least-squares fit of the data for temperatures greater than 200 K yielded Θ_W = −1911(9) K and μ_eff = 3.037(7) μ_B for BaOsO_3, Θ_W = −1028(1) K and μ_eff = 2.659(1) μ_B for SrOsO_3 and Θ_W = −682(3) K and μ_eff = 2.302(4) μ_B for CaOsO_3. It appeared that the values of the magnetic parameters Θ_W and μ_eff for BaOsO_3 were greater than those for CaOsO_3. We note that the spin-only value for S = 1 (Os^3+, t_{2g}) gave μ_eff = 2(S(S + 1))^{1/2} of 2.83 μ_B, which was slightly lower than that for BaOsO_3 and slightly higher than that for SrOsO_3 and CaOsO_3. Therefore, contribution of itinerant electrons should be carefully evaluated to correctly analyze the observed magnetism. It should be kept in mind, however, that the applicability of the Curie–Weiss law to an itinerant system such as cubic BaOsO_3 is not justified theoretically, although in practice one can obtain useful results. Thus, we report the analysis results for future reference. In addition, SO interactions might have an impact on 5d magnetism, a quantitative analysis that takes into account theoretical considerations should be attempted. The values of the magnetic parameters for BaOsO_3 are listed in Table S.

To investigate the magnetic properties of the compounds further, the isothermal magnetization of the compounds was measured at 2 and 300 K, as shown in Figure 6. The measured magnetization curves indicated that the compounds did not exhibit a significant degree of magnetization upon cooling. In addition, magnetic hysteresis was not obvious in any of the curves; therefore no long-range magnetic order was established over the temperature and composition ranges investigated. The curvature of the magnetization curves at 2 K for the compounds may reflect the nature of the possible enhanced paramagnetism and magnetic impurity contributions. Further analysis is left for future study.

Figure 7 shows a comparison of the total DOS for electronic states around the Fermi energies (E_F) of BaOsO_3, SrOsO_3, and CaOsO_3 estimated by taking into consideration the SO interaction in the first-principles calculations. In all compounds, the E_F level is located very near the peak structure, suggesting the presence of magnetic instabilities. As stated previously, the 5d orbital is spatially more extended than the 3d orbital, strengthening hybridization between the 5d and oxygen 2p orbitals. The high degree of hybridization in 5d oxides, which is greater than that in 3d and 4d oxides, significantly broadens the DOS structure around the E_F level in general. In addition, the 5d t_{2g} band is slightly broadened from the Ca to Ba compositions; CaOsO_3 is not as conducting as SrOsO_3 and BaOsO_3, presumably due to the impact of tilting of octahedra on the width of the t_{2g} band as can be seen in Figure 7a. Although strong hybridization is generally not conducive to magnetic instabilities, the observed χ_0 was approximately 3.6–3.9 times larger than the Pauli paramagnetic susceptibilities estimated theoretically from the total DOS at E_F for the Ca to Ba compositions. The enhanced χ_0 of the cubic perovskite BaOsO_3 might indicate proximity to itinerant ferromagnetism.

### Table 5. Comparison of the Curie–Weiss and C_p Parameters of the Perovskite Oxides

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CaOsO_3</th>
<th>SrOsO_3</th>
<th>BaOsO_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curie–Weiss Parameters without χ_0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ_0 (μ_B)</td>
<td>2.302(4)</td>
<td>2.659(1)</td>
<td>3.037(7)</td>
</tr>
<tr>
<td>C (emu mol⁻¹ Oe⁻¹ K)</td>
<td>0.663(2)</td>
<td>0.884(1)</td>
<td>1.153(5)</td>
</tr>
<tr>
<td>Θ_W (K)</td>
<td>−682(3)</td>
<td>−1028(1)</td>
<td>−1911(9)</td>
</tr>
<tr>
<td>χ_0 (emu mol⁻¹ Oe⁻¹)</td>
<td>0 (fixed)</td>
<td>0 (fixed)</td>
<td>0 (fixed)</td>
</tr>
<tr>
<td>Curie–Weiss Parameters with χ_0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ_0 (μ_B)</td>
<td>0.685(6)</td>
<td>0.586(2)</td>
<td>0.403(1)</td>
</tr>
<tr>
<td>C (emu mol⁻¹ Oe⁻¹ K)</td>
<td>0.0586(9)</td>
<td>0.0429(3)</td>
<td>0.0203(1)</td>
</tr>
<tr>
<td>Θ_W (K)</td>
<td>0 (fixed)</td>
<td>0 (fixed)</td>
<td>0 (fixed)</td>
</tr>
<tr>
<td>χ_0 (10⁻⁶ emu mol⁻¹ Oe⁻¹)</td>
<td>4.74(4)</td>
<td>5.18(1)</td>
<td>4.51(3)</td>
</tr>
</tbody>
</table>

### Figure 6. Isothermal magnetization at 2 and 300 K for AOsO_3 (A = Ba, Sr, and Ca).

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where $N_A$ is Avogadro’s constant and $T_D$ and $T_E$ are the Debye and Einstein temperatures, respectively. The scale factors, $n_D$ and $n_E$, corresponded to the number of vibrational modes per formula unit in the Debye and Einstein models, respectively. Fitting the curves yielded a $T_D$ of 710(13) K, $T_E$ of 173(5) K, $n_D$ of 3.25(4), and $n_E$ of 2.24(6) for BaOsO$_3$; the values for SrOsO$_3$ and CaOsO$_3$ were very similar (these are listed in Table 5). The Einstein term, which was linearly added to the Debye term, dramatically increased the quality of the fit in all the cases, suggesting that the phonon DOS at frequencies corresponding to 300 K or lower resulted in a much more complex DOS structure than that for the Debye model for all the compounds.

The inset shows an alternative plot of the data in the form of $C_p(T)/T$ vs $T^2$. The plots for all the compounds are displayed together for comparison. The linear trend of the plots indicates that the Debye approximation may characterize the temperature dependence of $C_p$ for low temperatures. The least-squares analysis using the formula $C_p(T) = \beta T^2 + \gamma$, where $\beta$ and $\gamma$ are a constant and the Sommerfeld coefficient, respectively, yielded $\beta = 2.19(2) \times 10^{-4} \text{ J mol}^{-1} \text{ K}^{-2}$ and $\gamma = 16.8(1) \text{ mJ mol}^{-1} \text{ K}^{-2}$ for BaOsO$_3$; $\beta = 0.98(4) \times 10^{-4} \text{ J mol}^{-1} \text{ K}^{-2}$ and $\gamma = 27.3(2) \text{ mJ mol}^{-1} \text{ K}^{-2}$ for SrOsO$_3$; and $\beta = 2.15(1) \text{ J mol}^{-1} \text{ K}^{-2}$ and $\gamma = 18.1(1) \text{ mJ mol}^{-1} \text{ K}^{-2}$ for CaOsO$_3$. The values of $T_D$ calculated from the $\beta$ values are listed in Table 5. Although $\rho$ in the case of CaOsO$_3$ does not show a metallic temperature dependence, the $\gamma$ value of 18.06 $\text{ mJ mol}^{-1} \text{ K}^{-2}$ is substantially high and so are those for BaOsO$_3$ and SrOsO$_3$, implying the presence of a nontrivial electronic DOS at the $E_F$ level. This disagreement suggests that the nonmetallic conduction of CaOsO$_3$ is possibly due to scattering by disorder including polycrystalline nature such as grain boundaries. The $\gamma$ value of SrOsO$_3$ is approximately 1.5 times higher than those of BaOsO$_3$ and CaOsO$_3$, this may account for the fact that $\rho$ for SrOsO$_3$ is the lowest over the entire temperature range.

The observed $\gamma$ values were compared with the theoretically determined ones (Table 5). The comparison clearly indicated that the observed values were approximately 2.2 (Ca), 2.9 (Sr), and 2.2 (Ba) times greater than their theoretically determined counterparts. This increase is likely coupled with the enhanced magnetic susceptibility of the compounds and suggests that a magnetic instability in the compounds has an impact on their bulk properties. In addition, the $\gamma$ increase is indeed present in cubic BaOsO$_3$. This proves that the octahedral distortion does not have a significant effect on the increase in $\gamma$.

### DISCUSSION AND CONCLUSIONS

Previously, body-centered cubic K$_2$SO$_3$-type BaOsO$_3$ with a lattice parameter of 9.373(1) Å had been synthesized under ambient pressure; $^{29,30}$ the calculated crystal density, $d_{calc}$, had been 9.088 g cm$^{-3}$. In this study, we were able to successfully synthesize cubic BaOsO$_3$ perovskite. Synthesis via heating under high pressure (6–6.5 GPa) resulted in 6H BaOsO$_3$. Note that the previously reported lattice parameters for BaOsO$_3$ of $a = 10.031(2)$ Å and $c = 4.632(1)$ Å ($d_{calc} = 9.270$ g cm$^{-3}$) indicate a two-layer hexagonal (2H) structure than a 6H one $^{29,30}$ In general, a series of transitions are caused in the perovskite structure with a change in density; each transition leads to a gain in crystal density in compounds such as BaIrO$_3$ $^{54}$ BaRuO$_3$ $^{49}$ and BaFeO$_3$. $^{50}$ In the present study, three-layer cubic (3C) BaOsO$_3$ was achieved at a $d_{calc}$ of 9.557 g cm$^{-3}$, confirming a part of the common sequence K$_2$SO$_3$-type.
$2H \rightarrow 9R \rightarrow 4H \rightarrow 6H \rightarrow 3C$, with the total gain in $d_{\text{calc}}$ being 5.2%.

In stark contrast to CaOsO$_3$ and SrOsO$_3$, BaOsO$_3$ has an ideal perovskite structure that is free of OsO$_6$ octahedral distortions and the buckling of the octahedral connections. In CaOsO$_3$ and SrOsO$_3$, the longer Os=O bonds in each octahedron are slightly longer than the shortest bonds (3.0% and <1%, respectively). On the other hand, in BaOsO$_3$, all Os-O bonds are of equal length. The bond angles for the interoctahedral Os=O=Os bonds are ~152° and ~165–170° for CaOsO$_3$ and SrOsO$_3$, respectively, whereas it is 180° for BaOsO$_3$. This variation in the bonds and tilts usually results in a significant difference in the magnetic and electrical properties, as has been found in the case of the compounds ARuO$_3$ and AFeO$_3$, where A = Ca and Sr. For example, CaRuO$_3$ is metallic with increased paramagnetism for temperatures as low as 30 mK, while SrRuO$_3$ is a ferromagnetic metal at metallic with increased paramagnetism for temperatures as low as 30 mK, while SrRuO$_3$ is a ferromagnetic metal at.

The 10D$_{Q}$ energy, which is normally $\sim$1 eV for 3d$^4$ and $>$3 eV for 4d$^4$ and 5d$^4$, can be increased by physically squeezing the crystal. Indeed, the HS state of CaFeO$_3$ transforms into the LS state on the application of a pressure of $\sim$30 GPa, indicating that the 10D$_{Q}$ energy is greater than the magnitude of the Hund’s coupling under this condition. Cubic BaFeO$_3$, however, may not exhibit a comparable spin-state transition within an experimentally feasible pressure range. Therefore, a comparison of the magnetic and electrical properties of the LS configuration of cubic BaFeO$_3$ with those of cubic BaRuO$_3$ and BaOsO$_3$ has never been made.

In cubic BaFeO$_3$, the SO interaction is negligible. Thus, the total angular momentum, $J$, can be approximated by the total spin angular momentum, $S$, which is equal to 2. Indeed, the ordered magnetic moment of 3.5 $\mu_B$ per Fe is close to the expected value of 4 $\mu_B$ for $S = 2$. While cubic BaRuO$_3$ undergoes a ferromagnetic transition at 60 K with an ordered magnetic moment of 0.8 $\mu_B$ per Ru, the moment is however far below the expected spin-only moment of 2 $\mu_B$ per Ru ($t_{2g}^4 e_g^0$), implying that S does not approximate J well. The interaction between the total orbital angular momentum, $L$, and $S$ (LS coupling) or that between the individual angular momentums, $j$ and $j$ (jj coupling), has a nontrivial effect on the magnetism.

The SO interaction should increase for a move from 3d to 5d, although a quantitative estimation of the same is yet to be performed. When the SO interaction is significant in a cubic perovskite, the degenerated 3 $t_{2g}$ states should split into energetically lower 4 $J_{\text{eff}} = 3/2$ states and higher 2 $J_{\text{eff}} = 1/2$ states. In this situation, the $J_{\text{eff}} = 3/2$ band is filled by d$^4$ electrons, resulting in the appearance of an electrically insulating state. However, cubic BaOsO$_3$ does not show such insulating behavior and is thus inconsistent with the $J_{\text{eff}}$ picture. The strong disagreement suggests that an intermediate state between the $jj$ coupling and the LS coupling is much closer to the true state of cubic BaOsO$_3$. The $\rho$ vs $T$ curve for BaOsO$_3$ shows a broad upturn in the low-temperature region; this can be assumed to indicate that, over these temperatures, BaOsO$_3$ is in the vicinity of the metal-to-insulator boundary. If this is true, chemical substitutions and physical squeezing may be effective in placing BaOsO$_3$ into an unusual insulating state where the SO interaction is significant.

Finally, the crystal structure and magnetic and electrical properties of BaOsO$_3$ synthesized at a pressure of 17 GPa were investigated by SXRD analyses. The $\chi$, $\rho$, and $C_p$ values of the synthesized compound were also measured. Thus, a series of d$^4$ cubic perovskite oxides was established, which mapped out the evolution of itinerant ferromagnetism that was free from any complications from local lattice distortions for a transition from over the 3d orbital to the 5d orbital. Such a perovskite series has not been achieved at any d configuration to date. The d$^4$ cubic BaOsO$_3$ exhibited enhanced paramagnetism to 2 K, while the d$^4$ cubic BaFeO$_3$ and BaRuO$_3$ were found to be itinerantly ferromagnetic at temperatures of 111 and 60 K, respectively. Cubic BaOsO$_3$ is possibly a nearly ferromagnetic metal rather than a paramagnetic metal, although it does not show a magnetically long-range order, as evidenced by its high Ch values greater than the expected Pauli paramagnetic suscept-

![Figure 9](image.png)

**Figure 9.** Magnetic transitions and tolerance factors of the d$^4$ perovskite oxides ATrO$_3$ (A = Ca, Sr, and Ba; Tr = Fe, Ru, and Os). $T_c$ of AFeO$_3$ peaks out at tolerance factor of 1.17.
ibility and owing to the fact that its $\chi$ value is greater than the expected value from the DOS at $E_f$. In addition, its DOS structure was indicative of magnetic instabilities. The SO interaction of the 5d electrons should be stronger than those of the 3d and 4d ones; however, establishing an unusual insulating state in which the SO interaction plays a significant role is not sufficient. Therefore, the jj coupling does not adequately describe all the properties of BaOsO$_3$. Further theoretical and quantitative studies of the SO interaction, $U$, and $W$ in cubic perovskite BaOsO$_3$ are needed for characterizing the ferromagnetic evolution from 3d to 5d in group 8 elements. It should be noted that the local lattice distortion introduced in orthorhombic SrOsO$_3$ and CaOsO$_3$ did not markedly alter their magnetic properties, in contrast to the comparable orthorhombic/tetragonal Ru and Fe perovskite oxides. It is possible that an isoelectric compound with reduced structural dimensionality, such as layered Ba$_2$OsO$_4$$_6$, would lie on the boundary between metallic and unusually gapped states, if it is synthesized.

**ASSOCIATED CONTENT**

Supporting Information

Comparison of the lattice and structural parameters of the perovskite oxides. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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