High-pressure synthesis, crystal structure, and magnetic properties of KSbO₃-type 5d oxides K₀.₈₄OsO₃ and Bi₂.₉₃Os₃O₁₁

Yahua Yuan¹,², Hai L Feng¹,², Youguo Shi³, Yoshihiro Tsujimoto⁴, Alexei A Belik⁵, Yoshitaka Matsushita⁶, Masao Arai⁷, Jianfeng He¹,², Masahiko Tanaka⁸ and Kazunari Yamaura¹,²

¹ Superconducting Properties Unit, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
² Graduate School of Chemical Sciences and Engineering, Hokkaido University, North 10 West 8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan
³ Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
⁴ Materials Processing Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
⁵ International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
⁶ Materials Analysis Station, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
⁷ Computational Materials Science Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
⁸ Synchrotron X-ray Station at SPring-8, National Institute for Materials Science, Kohto 1-1-1, Sayo-cho, Hyogo 679-5148, Japan

E-mail: YUAN.Yahua@nims.go.jp and YAMAURA.Kazunari@nims.go.jp

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Abstract

5d Solid-state oxides K₀.₈₄OsO₃ (Os⁵.¹₆⁺; 5d².₈₄) and Bi₂.₉₃Os₃O₁₁ (Os⁴.₄₀⁺; 5d³.₆₀) were synthesized under high-pressure and high-temperature conditions (6 GPa and 1500–1700 °C). Their crystal structures were determined by synchrotron x-ray diffraction and their 5d electronic properties and tunnel-like structure motifs were investigated. A KSbO₃-type structure with a space group of Im-3 and Pn-3 was determined for K₀.₈₄OsO₃ and Bi₂.₉₃Os₃O₁₁, respectively. The magnetic and electronic transport properties of the polycrystalline compounds were compared with those obtained theoretically. It was revealed that the 5d tunnel-like structures are paramagnetic with metallic charge conduction at temperatures above 2 K. This was similar to what was observed for structurally relevant 5d oxides, including Bi₃Re₃O₁₁ (Re⁴.₃₃⁺; 5d².₆₆) and Ba₂Ir₂O₉ (Ir⁴.₆₆⁺; 5d³.₃₃). The absence of long-range magnetic order seems to be common among 5d KSbO₃-like oxides, regardless of the number of 5d electrons (between 2.6 and 4.3 per 5d atom).

Keywords: high-pressure synthesis, osmium oxide, KSbO₃-type, KO₅Os₃, Bi₃Os₃O₁₁

1. Introduction

Crystalline KSbO₃-type [1] or comparable-type solid-state oxides are attractive for their possible applications in ionically...
conductive and electrocatalytic materials [2–5]. This prospect may be related to the presence of tunnel motifs in the crystal structure of these oxides [6]. Furthermore, structurally related La4Ru6O18 has received considerable attention because of its role in novel electronic transport in non-Fermi-liquids [7, 8]. The KSbO3-type family of solid-state oxides is currently an emergent subject in the field of inorganic chemistry. They can be used to develop advanced technologies for energy-related applications and to help understand correlated electron properties.

The KSbO3-type family of oxides consists of several compositional variants have been synthesized and characterized by the similar tunnel motifs, such as the following:

- **AMOO3**: KSbO3 [1], KlIrO3 [9], BaOsO3 [10], KBiO3 [4, 11], AgBiO3 [12];
- **A3MO4**: La2Ir3O11 [13], Bi3Ru3O11 [3], La3Ru3O11 [7, 14], Bi3OsO3 [15, 16], Bi3Mn1.8Te1.1O11 [17], Bi3Re3O11 [18], Bi3CrSb2O11 [19], Bi3LaMSb3O11 (M = Cr, Mn, Fe) [19], NaBi2Sb2O11 [20];
- **A3MO4:O2**: Sr2ReO4 [18];
- **A3MO4:O19**: La2Re6O19 [18], Pb6Re6O19 [18], Ba4Os6O18Cl [21], La4Os6O19 [21], Sr4Ru6ClO18 [22], and La4Ru6O19 [7, 8].

Most of these examples were synthesized at ambient pressure, while high-pressure heating led to successful syntheses of additional compounds, which include NaOsO3 [15], Bi3Mn1.8Te1.1O11 [17, 23, 24], Bi3Ge3O10.5 [25], Ba2Ir3O9 [26], and Bi3Cr2.91O11 [27].

Our recent studies have focused on the synthesis of solid-state osmium oxides in order to develop 5d electronic properties and 5d materials for possible advancements in the field of spintronics and related scientific devices [28–31]. During our attempted syntheses of compositionally new osmium oxides under high-pressure and high-temperature conditions, an additional oxide K0.84OsO3 was synthesized (at 6 GPa).

The polycrystalline compounds K0.84OsO3 was studied by using synchrotron x-ray diffraction and magnetic and charge transport measurements. The refined crystal structure indicated that the crystalline oxide has a KSbO3-type structure and shares a tunnel structural motif with a related Os oxide Bi2.93Os3O11 [15, 16]. Herein, we report the synthesis, crystal structure, and primary electrical and magnetic properties of the newly synthesized KSbO3-type oxide K0.84OsO3 and compare those with the properties of the structurally comparable oxide Bi2.93Os3O11.

## 2. Materials and methods

Polycrystalline K0.84OsO3 was synthesized by a solid-state reaction method in a belt-type high-pressure and high-temperature apparatus (Kobe Steel, Japan), in which a pyrophyllite cell was used to produce a quasi-hydrostatic environment at an elevated pressure [32]. The starting materials Os (99.95%, Heraeus Materials Technology) and KO2 (O2: 45.6%, yellow powder, Sigma-Aldrich) were mixed at a molar ratio of 1:2 in a glove box under argon. The mixture was sealed in a platinum capsule, followed by heating in a compressed pyrophyllite cell at 1500 °C for 1 h. The capsule pressure was maintained at 6 GPa during the heating process. The capsule was then quenched to ambient temperature within a minute by cutting off the electric power supply before releasing the pressure. The final product was a dense pellet of part of it was ground in an agate mortar and pestle. The powder was then rinsed in an ultrasonic water bath multiple times to remove any residue. The high-pressure method is helpful in reducing the risk of human exposure to possible presence of toxic OsO4 during the synthesis.

Polycrystalline Bi2.93Os3O11 was similarly prepared using fine powders of Bi2O3 (99.999%, Kojundo Chem. Lab, Japan) and Os2O3 (Os-83%, Alfa Aesar) in the high-pressure apparatus. A small amount of an oxygen source (KClO4, 99.5%, Kishida Chem) was added to a stoichiometric mixture of the starting materials. The elevated pressure was maintained at 6 GPa during the heating process at 1700 °C for 1 h. Residues in the final product (including KCl) were removed in a water bath.

The final products were characterized by synchrotron x-ray diffraction (SXRD) using a large Debye–Scherrer camera at the beam line BL15XU in the SPring-8 synchrotron radiation facility, Japan [33]. The diffraction profiles were collected at room temperature between 2θ of 3° and 81° at 0.003° intervals using a monochromatized beam (λ=0.65 298 Å or 0.40 025 Å). The wavelength was confirmed by measurements of a standard material (CeO2). Each powder was placed into a Lindemann glass capillary (inner diameter: 0.1 mm) and rotated during the measurements. The SXRD profiles were analyzed by a Rietveld method using the program RIETAN- FP [34].

The dc magnetic susceptibility (χ) of the compound was measured in the Magnetic Property Measurement System (MPMS, Quantum Design) between 2 and 395 K in an applied magnetic field of 10 kOe. Each powdered compound was loosely gathered in a sample holder and cooled to the temperature limit. The magnetic field was then applied to the holder. The holder was gradually warmed to 395 K (zero-field cooling, ZFC), followed by cooling in the field (field cooling, FC). The isothermal magnetization of the compounds was also measured in the apparatus with a magnetic field range between −70 and 70 kOe at 5 K. The specific heat Cψ of a piece of the physically compressed bulk material was measured in the Physical Property Measurement System (PPMS, Quantum Design) between 2 and 300 K. In the apparatus, the electrical resistivity (ρ) of a pellet piece was measured by a 4-terminal method using platinum wires and a silver paste.

The K content of polycrystalline K0.84OsO3 was determined by inductively coupled plasma spectrometry. Water-rinsed fine powder was used in the analysis and the average K content was found to be 0.837(7) in accordance with the formula unit.

First-principles calculations of the electronic state of the stoichiometric hosts KOsO3 and Bi2OsO11 were performed by a generalized gradient approximation [35] of the density functional theory. The WIEN2k program [36] was used, which was based on the full-potential augmented plane-wave method. The muffin–tin radii were chosen to be 2.4 atomic
unit (au) for K, 2.2 au for Bi, 1.9 au for Os, and 1.6 au for O atoms. The spin–orbit interaction was included as a perturbation to the scalar-relativistic equations. The cut-off wave vector $K$ was fixed at $RK = 8$, where $R$ is the smallest muffin–tin radius (i.e. 1.6 au). The Brillouin zone integration was approximated by the tetrahedron method with 294 $k$ points in an irreducible zone for KO$_3$O$_7$ and 76 $k$ points for Bi$_3$Os$_3$O$_{11}$. We assumed that K atoms occupy the K1 site for KOsO$_3$ and Bi atoms occupy Bi1 (8e) and Bi2 (4b) sites for Bi$_3$Os$_3$O$_{11}$ to avoid fractional occupation.

### 3. Results and discussion

The crystal structure of K$_{0.84}$OsO$_3$ was characterized well by a cubic model with a space group of $Im-3$, similar to KBiO$_3$ and AgBiO$_3$ [4, 11, 12]. Figure 1 shows the SXRD pattern for K$_{0.84}$OsO$_3$ at room temperature. Rietveld analysis conducted on the pattern with the cubic model resulted in a well-refined profile with $R$ indices below 7%. The refined cubic lattice parameter was $a = 9.47164(1)$ Å, which is smaller than the corresponding cubic parameters of KBiO$_3$ (10.0194(6) Å) and AgBiO$_3$ (9.7852(2) Å). The smaller ionic radius (0.575 Å) for O in the octahedral environment than that of Bi(V) (0.76 Å) may account for this observation [37]. We concluded that a reasonable fit was established; the final structural parameters, including the refined atomic coordinates, are listed in table 1. Although the true chemical composition was slightly under-stoichiometric (K$_{0.84}$OsO$_3$), we analyzed the pattern without considering the small amount of K deficiencies that we were unable to refine. However, the thermal parameters for all atoms remained within a reasonable level regardless of the K deficiencies. The small amount of deficiencies may have been distributed almost equally over the three crystallographic K sites, minimizing impact on the analysis.

The refined crystal structure is illustrated in the inset of figure 1. The structural view indicates that an Os atom bonding has formed. It can be noted that the ionic size difference is unlikely to affect the observation.

![Figure 1](image1.png)  
**Figure 1.** Rietveld analysis of the SXRD pattern for K$_{0.84}$OsO$_3$ at room temperature. Markers and solid lines show the observed and calculated profiles, respectively, and the difference is shown at the bottom of the figure. The expected Bragg reflections are marked by the small bars; and the reflections analyzed under partial profile relaxation are marked in purple color [34]. The proposed crystal structure is presented in the inset, in which Os and O atoms are drawn as large red and small blue balls, respectively. K atoms are not shown for clarity.

| Table 1. Structural parameters of K$_{0.84}$OsO$_3$. |
|---------------------------------------------------|
| **Atom** | **Site** | **g** | **x** | **y** | **z** | **B (Å$^2$)** |
| K1 | 16f | 0.5 | 0.3429(2) | =x | =x | 1.65(9) |
| K2 | 16f | 0.213 | 0.2818(5) | =x | =x | 1.4(2) |
| K3 | 2a | 0.296 | 0 | 0 | 0 | 1.4(4) |
| Os | 12e | 1 | 0.5 | 0.14 047(3) | 0 | 0.237(4) |
| O1 | 12d | 1 | 0.3482(7) | 0 | 0 | 1.6(1) |
| O2 | 24 g | 1 | 0.3597(5) | 0.2935(4) | 0 | 0.74(7) |

Note. The space group is $Im-3$ (no. 204), $a = 9.47164(1)$ Å, $Z = 12$, $V = 849.718(2)$ Å$^3$, and $d_{\text{cal}} = 6.90$ g cm$^{-3}$. $R$ Indices were $R_{\text{wp}} = 3.35\%$, $R_{\text{fl}} = 2.47\%$, $R_B = 6.58\%$, and $R_F = 5.57\%$. The bond distances of Os–O in the OsO$_3$ octahedra were $d($Os–O$) = 1.972(6)$ Å ($x2$), $d($Os–O$) = 1.954(6)$ Å ($x2$), and $d($Os–O$) = 1.966(6)$ Å ($x2$). BVS(Os) = +4.63. In which BVS = $\sum_{\nu=1}^{N} x_{\nu} \nu = \exp (R_{\nu}=d_{\nu}) / B, N$ is the coordination number, $B = 0.37$ and $R_{\text{wp}}($Os$^{3+}) = 3.35\%$ [38] (BVS, bond valence sum).

![Figure 2](image2.png)  
**Figure 2.** Rietveld analysis of the SXRD pattern for Bi$_{2.93}$Os$_3$O$_{11}$ at room temperature. Markers and solid lines show the observed and calculated profiles, respectively, and the difference is shown at the bottom. The expected Bragg reflections are marked by the small bars; and the reflections analyzed under partial profile relaxation are marked in purple color [34]. The proposed crystal structure is presented in the inset, in which Os and O atoms are drawn as large red and small blue balls, respectively. K atoms are not shown for clarity.
isostructural to Bi$_3$Mn$_3$O$_{11}$ [24]; fractional atomic coordinates for Bi$_3$Mn$_3$O$_{11}$ were tested in early refinements. The Bi$_1$ atom was found to be disordered as in Bi$_3$Mn$_3$O$_{11}$ [24] and Bi$_3$GaSb$_2$O$_{11}$ [39]. Eventually, a refinement with an occupation factor ($g$) of 1/3 for Bi$_1$ and 1 for Bi$_2$ resulted in a negative thermal parameter ($B$) for O$_1$; however, the $B$(O$_1$) was positive when we allowed the refinement of $g$(Bi$_1$) and $g$(Bi$_2$). A small amount of vacancies was therefore suggested at these sites; the refined composition was Bi$_2.93$Os$_3$O$_{11}$. The under-stoichiometric composition may be connected to the presence of a small amount of impurities in the compound. We also note that splitting of Bi$_2$ from the ideal 4$b$ site (0,0,0) to 8$e$ site ($\times$, $\times$, $\times$) resulted in slightly better $R$ factors at $x$=0.0029(4). Note that the shortest Os–Os distance is 2.5653 Å, comparable with the Os–Os distance in K$_{0.84}$OsO$_3$. Details of the refinement are summarized in table 2.

The OsO$_6$ framework of Bi$_2.93$Os$_3$O$_{11}$ is tunnel-like, similar to K$_{0.84}$OsO$_3$, as shown in the inset of figure 2. The Bi atoms are not shown in the structural views for clarity. When assuming an ionic picture of the compounds, the formal Os valence should be +5.16 for K$_{0.84}$OsO$_3$ and +4.33 for Bi$_2.93$Os$_3$O$_{11}$. This reflects the difference in the average Os–O bond distance of 1.964(8) Å and 1.992(1) Å for K$_{0.84}$OsO$_3$ and Bi$_2.93$Os$_3$O$_{11}$, respectively. It is also reasonable to expect that the Os–Os distance in K$_{0.84}$OsO$_3$ is longer than that of Bi$_2.93$Os$_3$O$_{11}$ owing to Coulomb repulsion between the positive charges; the observed Os–Os distance is indeed 3.7% longer than that of Bi$_2.93$Os$_3$O$_{11}$. Nevertheless, the bond valence sum (BVS) was +3.37, +2.93, and +4.19, for which BVS = $\sum_{i}^{N} \nu_{i} = \exp[(R_{0}-d_{i})/B]$. $N$ was the coordination number, $B=0.37$, $R_{0}$(Os$^{5+}$) = 1.868 [38].

![Figure 3](image1.png)

**Figure 3.** Temperature dependence of $\rho$ of polycrystalline K$_{0.84}$OsO$_3$ and Bi$_2.93$Os$_3$O$_{11}$. 

![Figure 4](image2.png)

**Figure 4.** Temperature dependence of $\chi$ for polycrystalline K$_{0.84}$OsO$_3$ and Bi$_2.93$Os$_3$O$_{11}$ in a magnetic field of 50 kOe. Solid and open symbols represent data measured in FC and ZFC conditions, respectively. The dashed lines indicate the theoretically calculated $\chi$ for stoichiometric hosts KOsO$_3$ and Bi$_3$Os$_3$O$_{11}$ for comparison. The inset shows the isothermal magnetizations of the compounds at 5 K.

### Table 2. Structural parameters of Bi$_{2.93}$Os$_3$O$_{11}$.

| Atom | Site | $g$ | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|------|------|-----|-----|-----|-----|--------------|
| Bi1  | 24$h$| 0.3255(6) | 0.3890(7) | 0.3844(9) | 0.3736(4) | 0.39(2) |
| Bi2  | 8$e$ | 0.4887(9) | 0.0029(4) | =x | =x | 0.53(1) |
| Os   | 12$g$| 0.38 677 (5) | 0.75 | 0.25 | 0.161(4) |
| O1   | 8$e$ | 0.1501(5) | =x | =x | 0.04(1) |
| O2   | 12$f$| 0.5823(9) | 0.25 | 0.25 | 0.36(1) |
| O3   | 24$h$| 0.6018(6) | 0.2426(5) | 0.5343(6) | 0.13(7) |

Note. The space group is Pn-3 (no. 201) at origin choice 2, $Z=4$, $a=9.35993(2)$ Å, and $V=820.007(4)$ Å$^3$. $R$ Indices were $R_p$=6.42%, $R_s$=4.03%, $R_B$=3.52%, and $R_F$=1.75%. The bond distances of Os–O in the OsO$_6$ octahedra were $d$(Os–O$_3$)=1.991(4) Å (×2), $d$(Os–O$_2$)=1.991(5) Å (×2), $d$(Os–O$_3$)=1.994(4) Å (×2). BVS(Os) Were +3.37, +2.93, and +4.19, for which BVS = $\sum_{i}^{N} \nu_{i} = \exp[(R_{0}-d_{i})/B]$. $N$ was the coordination number, $B=0.37$, $R_{0}$(Os$^{5+}$) = 1.868 [38].

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A compound can still be characterized according to this type. In contrast, a piece of polycrystalline Bi\textsubscript{2.93}Os\textsubscript{3}O\textsubscript{11} shows a weak temperature dependence and a $\rho$ of $\sim$0.21 ohm cm at room temperature. However, this feature is not consistent with what is expected for a semiconducting oxide with an energy gap. Note that polycrystalline Bi\textsubscript{3}Os\textsubscript{3}O\textsubscript{11} synthesized without a high pressure process shows a $\rho$ of $\sim$0.001 ohm cm at room temperature [16], being remarkably lower than what was observed for the polycrystalline Bi\textsubscript{2.93}Os\textsubscript{3}O\textsubscript{11}. The true conductivity of Bi\textsubscript{2.93}Os\textsubscript{3}O\textsubscript{11} is possibly masked by polycrystalline nature such as resistive grain boundaries and impurities. Additional studies on single crystals of the oxides are necessary to reveal true nature of electric transport.

Attempts to grow crystals of the oxides under high-pressure and high temperature conditions have been unsuccessful so far.

The magnetic properties of polycrystalline oxides K\textsubscript{0.84}OsO\textsubscript{3} and Bi\textsubscript{2.93}Os\textsubscript{3}O\textsubscript{11} were studied and compared. Figure 4 shows the temperature dependence of $\chi$ for the oxides, revealing weakly temperature-dependent paramagnetic features over the temperature range. Any possible magnetic transition was unlikely over the measurements. Although a broad and small bump is seen at approximately $\sim$50 K for K\textsubscript{0.84}OsO\textsubscript{3}, any corresponding anomalies were not obvious in the $\rho$ and $C_p$ measurements (shown later). The inset shows the isothermal magnetizations of the oxides at low temperature (5 K) and only quasi-linear behaviors with trivial magnetizations were observed. Therefore, we

![Figure 5. Temperature dependence of $C_p$ of polycrystalline (a) K\textsubscript{0.84}OsO\textsubscript{3} and (b) Bi\textsubscript{2.93}Os\textsubscript{3}O\textsubscript{11}. The solid line represents the fitting curve. A linear fit of the low-temperature measurements of the $C_p/T$ versus $T^2$ plot is shown for (c) K\textsubscript{0.84}OsO\textsubscript{3} and (d) Bi\textsubscript{2.93}Os\textsubscript{3}O\textsubscript{11}, respectively.](image)
where materials [40]. The analytical formula was

$$\frac{C_p(T)}{T^3} = n_D \times 9N_A k_B \left( \frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^{x}}{(e^x - 1)^2} dx + n_E \times 3N_A k_B \left( \frac{T_E}{T} \right)^2 \frac{e^{T/E}}{\left( e^{T/E} - 1 \right)^2},$$

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 $n_E$, correspond to the number of vibrational modes per formula unit in the Debye and Einstein models, respectively. The fitting curves yielded the following: $T_D$ of 628(7) K, $T_E$ of 150(2) K, $n_D$ of 2.88(3), and $n_E$ of 1.25(3) for K$_{0.84}$OsO$_3$, and $T_D$ of 650(7) K, $T_E$ of 110(2) K, $n_D$ of 3.63 (2), and $n_E$ of 1.34(3) for Bi$_{2.93}$Os$_3$O$_{11}$. The Einstein term added to the Debye term increased the quality of fitting, suggesting a possibility that the phonon density of state (DOS) forms a rather complex structure over the whole temperature range. However, analysis on the $C_p/T^3$ versus $T$ plots (not shown) indicated that anomalous Einstein contributions, which are indicative of lattice rattling, were not obvious (unlike related oxides) [40]. Further analysis of the phonon modes is needed to clarify the phonon DOS structure of both the compounds.

The low-temperature measurements of the $C_p/T$ versus $T^2$ plot for each compound were analyzed by an approximated Debye model (figures 5(c) and (d)), which was $C_p/T = \beta T^2 + \gamma$, where $\beta$ and $\gamma$ are a constant and the Sommerfeld coefficient, respectively. The fit of the plots yielded $\beta = 3.03(9) \times 10^{-4}$ J (one mole of osmium atoms (mol-Os))$^{-1}$ K$^{-2}$ and $\gamma = 16.8(2)$ mJ mol-Os$^{-1}$ K$^{-2}$ for K$_{0.84}$OsO$_3$; and $\beta = 7.00(9) \times 10^{-4}$ J mol-Os$^{-1}$ K$^{-2}$ and $\gamma = 1.6(2)$ mJ mol-Os$^{-1}$ K$^{-2}$ for Bi$_{2.93}$Os$_3$O$_{11}$. The $T_D$ for K$_{0.84}$OsO$_3$ and Bi$_{2.93}$Os$_3$O$_{11}$ were calculated from $\beta$ of 315(4) K and 250(1) K, respectively. It appeared that the $\gamma$ for Bi$_{2.93}$Os$_3$O$_{11}$ is nearly one tenth of the $\gamma$ for K$_{0.84}$OsO$_3$; we therefore carefully investigated the electronic state of the compounds by a theoretical method.

Figures 6(a) and (b) show the theoretically predicted electronic DOS structure for the stoichiometric hosts K$_{0.84}$OsO$_3$ and Bi$_{2.93}$Os$_3$O$_{11}$, respectively. The total DOS was found to consist of mainly Os and O contributions and little from K/Bi. Both compounds have a nontrivial electronic DOS at the Fermi level ($E_F$). Therefore, the hosts are expected to be metallic. The estimated $\gamma$ for KOsO$_3$ from the DOS at $E_F$ is 15.6 mJ mol-Os$^{-1}$ K$^{-2}$, which is nearly comparable to the observed $\gamma$ for K$_{0.84}$OsO$_3$ (16.8(2) mJ mol-Os$^{-1}$ K$^{-2}$). However, the estimated $\gamma$ for Bi$_{2.93}$Os$_3$O$_{11}$ is 9.7 mJ mol-Os$^{-1}$ K$^{-2}$, which is much larger than the observed $\gamma$ for Bi$_{2.93}$Os$_3$O$_{11}$ (1.6(2) mJ mol-Os$^{-1}$ K$^{-2}$). This disagreement between the expected and observed $\gamma$ for the compounds is possibly owing

![Figure 6. Electronic DOS of stoichiometric hosts of (a) K$_{0.84}$OsO$_3$ and (b) Bi$_{2.93}$Os$_3$O$_{11}$. The vertical line indicates $E_F$.](image-url)
to a steep change of DOS in the vicinity of $E_F$ with lowering the Bi stoichiometry. This phenomenon has been previously discussed for related Os oxides [41]. Although we need to carefully investigate possible contributions from spin-polarization and spin–orbit interactions over the DOS structure, opening a full gap at $E_F$ for Bi$_{2.93}$Os$_3$O$_{11}$ seems unlikely.

4. Conclusions

Materials with 5$d$ electrons may show characteristic features owing to radially extended valence orbitals and large spin–orbit couplings of 5$d$ electrons over 3$d$ electrons. For example, a perovskite-type oxide, NaOsO$_3$, shows a Slater-like transition [30, 31] and a LiNbO$_3$-type oxide, LiOsO$_3$, shows a ferroelectric-like transition in the metallic state [29]. The results led to the reasonable expectation that KOsOs$_3$ if synthesized, also shows characteristic features of 5$d$ electrons. Nevertheless, K$_2$SbO$_3$-type crystalline $\text{K}_{0.84}$OsO$_3$ shows only a weak temperature-dependent paramagnetic feature. In addition, K$_2$SbO$_3$-type Bi$_{2.93}$Os$_3$O$_{11}$ was also synthesized under high-pressure and high-temperature conditions. The Os–O network in this system was found to form a similar tunnel motif to that of $\text{K}_{0.84}$OsO$_3$. Although the formal valence of Os decreased from +5.16 (K) to +4.40 (Bi), the observed magnetic and electronic properties did not change significantly.

In contrast to the remarkable 5$d$ properties of related compounds NaOsO$_3$ [30, 31] and LiOsO$_3$ [29], $\text{K}_{0.84}$OsO$_3$ and Bi$_{2.93}$Os$_3$O$_{11}$ seem to have less characteristic 5$d$ properties above 2 K. Both compounds showed rather weak temperature-dependent paramagnetism and metallic transports. Disorders such as K/Bi vacancies and the polycrystalline nature of the compounds (including grain boundaries and impurities) could possibly complicate the observed 5$d$ properties. Nevertheless, the magnetic and electronic properties are quite similar to what was observed for structurally relevant 5$d$ oxides, including Bi$_2$Re$_2$O$_7$ (Re$^{4.33+}$, 5$d$ 2.66$^0$) [18] and Ba$_2$Ir$_2$O$_9$ (Ir$^{4.66+}$, 5$d$ 4.33$^0$) [26], regardless of the number of 5$d$ electrons. The absence of a long-range magnetic order seems to be common among the tunnel-like structures of 5$d$ oxides. Further studies on high-quality single crystals of newly synthesized K$_2$SbO$_3$-type material K$_{0.84}$OsO$_3$ may reveal the 5$d$ characteristic features and help establish a comprehensive picture of the 5$d$ electronic system.

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