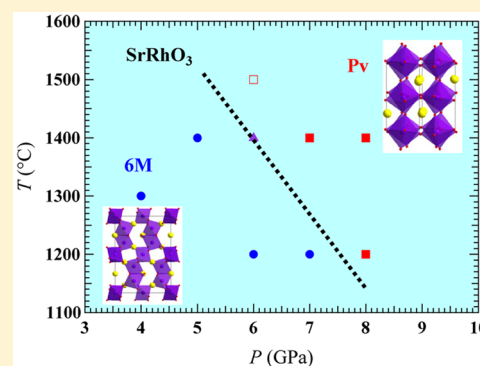


High-Pressure Synthesis, Crystal Structure, and Magnetic and Transport Properties of a Six-Layered SrRhO_3 Yan Li,^{†,‡} Jinguang Cheng,^{‡,§,⊥} José Antonio Alonso,^{‡,||} John B. Goodenough,^{‡,⊙} and Jianshi Zhou^{*,‡}[†]College of Materials Science and Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, China[‡]Materials Science and Engineering Program, University of Texas at Austin, Austin, Texas 78712, United States[§]Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China^{||}Instituto de Ciencia de Materiales de Madrid, Cantoblanco, E-28049 Madrid, Spain[⊥]School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

S Supporting Information

ABSTRACT: A SrRhO_3 polytype with six-layered (6M) structure was synthesized under high pressure and high temperature. The crystal structure was obtained by refining X-ray powder diffraction with the monoclinic space group $C2/c$ with lattice parameters $a = 5.5650(1)$ Å, $b = 9.5967(2)$ Å, $c = 14.0224(4)$ Å, and $\beta = 92.846(2)^\circ$. It is isostructural with SrIrO_3 synthesized under ambient pressure and consists of dimers of the face-shared $\text{Rh}(2)\text{O}_6$ octahedra connected by their vertices to the corner-shared $\text{Rh}(1)\text{O}_6$ octahedra along the c axis with a stacking of SrO_3 layers in the sequence of CCHCCH, where C and H denote cubic and hexagonal closed packing, respectively. With increasing pressure, the 6M SrRhO_3 transforms to an orthorhombic perovskite (Pv) phase, having $a = 5.5673(1)$ Å, $b = 5.5399(2)$ Å, $c = 7.8550(2)$ Å in the space group $Pbnm$. A pressure–temperature phase diagram shows that the 6M–Pv phase boundary moves to lower temperatures with increasing pressure.

Both the 6M and the Pv phases of SrRhO_3 were characterized by magnetic susceptibility, resistivity, and thermopower; they are all metals with an enhanced and temperature-dependent magnetic susceptibility; no long-range magnetic order has been found. The polytype structures are normally found in ABO_3 oxides with the geometric tolerance factor $t > 1$. SrRhO_3 represents another example (in addition to SrIrO_3) where the polytype 6M structure can be stabilized with a $t < 1$.



■ INTRODUCTION

The AMO_3 oxides with perovskite (Pv) and Pv-related structures have been intensively studied for application in modern technologies and the interest of fundamental science. A tolerance factor, defined as $t \equiv (A-O)/\sqrt{2} (M-O)$, determines the mismatch between the A–O and M–O equilibrium bond lengths in the three-dimensional (3D) framework of corner-shared octahedra. A $t < 1$ places a compressive stress on the A–O bond that is accommodated by a cooperative rotation of the corner-shared octahedra in the Pv structure; the cooperative rotations about the cubic $[110]$ and $[001]$ axes give rise to the orthorhombic symmetry with the space group $Pbnm$, which is the most popular structure in the Pv oxides. On the other hand, a $t > 1$ can be accommodated by adding layers of the face-shared octahedra along with the corner-shared octahedra layers in polytype structures.¹ The polytypes can have a variety of stackings of close-packed AO_3 layers, which can have either cubic ($abcabc\dots$) or hexagonal ($abab\dots$) stacking. The smaller M cations occupy the octahedral interstitial sites between the AO_3 layers. In the ideal Pv structure, there is only cubic stacking of the AO_3 layers, and the $\text{MO}_{6/2}$ octahedra share only corners in three dimensions; this

ideal Pv structure is labeled 3C, since the unit cell requires three AO_3 layers and the structure is cubic. If all the AO_3 layers are hexagonal-close-packed, the $\text{MO}_{6/2}$ octahedra share faces to form one-dimensional (1D) columns parallel to the hexagonal c axis; this 2H structure is found in CsNiF_3 and BaNiO_3 , for example, where $(t - 1)$ is large. It is also possible to have a mixed cubic (C) and hexagonal (H) stacking, where t is large but close to 1. As t approaches 1 from $t > 1$, the polytypes are normally found in the sequence $2H \rightarrow 9R$ (CHHCHHCHH) $\rightarrow$ $4H$ (CHCH) $\rightarrow$ $6H$ (CCHCCH) $\rightarrow$ $3C$. Since the cubic stacking has a higher density than that of the hexagonal stacking in AMO_3 oxides, high-pressure synthesis favors the polytypes with a larger number of C layers in the order of $9R$ to $4H$ to $6H$ to $3C$. (For a review, see ref 1.) Recently, we identified a new high-pressure sequence $9R \rightarrow 5H \rightarrow 6H \rightarrow 3C$ in BaIrO_3 ;² the appearance of $5H$ BaIrO_3 instead of the commonly found $4H$ polytype is due to a subtle balance between strong Ir–Ir bonding and Coulombic repulsion across the shared octahedral-site faces along the c -axis.

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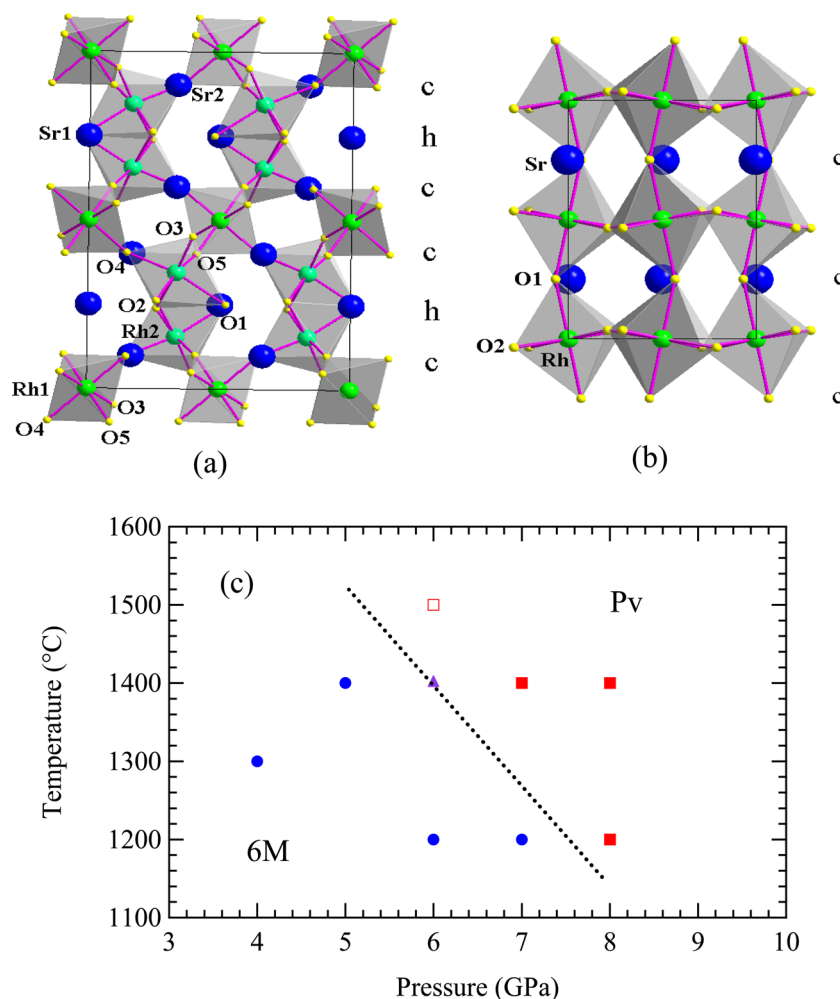


Figure 1. Projection of the crystal structure of (a) 6M-SrRhO₃ along $[1\ 0\ 0]$ direction and (b) Pv-SrRhO₃ along $[0\ 1\ 0]$ direction. (c) Temperature–pressure phase diagram for the 6M to Pv transformation: (●) 6M phase, (■) Pv phase, (▲) mixed phase. (□) Yamaura et al.⁷

Many Pv AMO₃ oxides that can not be made at atmospheric pressure can be stabilized under high pressure, for example, (Ca,Sr)CrO₃^{3,4} and BiMnO₃.⁵ Several compounds have also been found to transform to the Pv structure from a structure with a lower density than that of the Pv phase, for example, RMnO₃ (R = Ho, ..., Ln).⁶ Moreover, by incorporating an oxygen-releasing agent, for instance KClO₄, in the high-pressure cell, higher oxidation states can be stabilized in the MO_{6/2} octahedral site, which leads to a number of new perovskites. For example, by employing KClO₄ under 6 GPa and 1500 °C, Yamaura et al.⁷ were able to stabilize Rh⁴⁺ in a new orthorhombic Pv SrRhO₃, which is a Fermi-liquid metal with enhanced Pauli paramagnetism. Its inverse magnetic susceptibility exhibited an unusual quadratic temperature dependence, that is, $\chi^{-1}(T) \propto T^2$. Density-functional calculations indicated that Pv SrRhO₃ is near a quantum critical point with the physical properties substantially affected by quantum critical fluctuations.⁸ Several novel Rh⁴⁺ oxides with the Pv-related structures, including bi- and trilayered Sr_{n+1}Rh_nO_{3n+1} ($n = 2, 3$)^{9,10} as well as Pv¹¹ and post-Pv CaRhO₃,¹² were subsequently obtained by using a similar synthetic procedure. CaRhO₃, after CaMO₃ (M = Ir, Pt, Ru), becomes the fourth known oxide that is quenchable to ambient condition with a post-Pv structure. These postperovskites form an important family for earth sciences as an analogue to the

post-Pv phase of MgSiO₃ in the lowermost mantle of earth. As for BaRhO₃ with larger $t = 1.064$, Siegrist et al.¹³ have reported two hexagonal polytypes, the 9R and 4H, prepared under 1175 °C and 6–6.5 GPa. Therefore, the high-pressure and high-temperature (HPHT) synthesis is an important approach in obtaining new compounds with Pv-related structures.

Here, we report the HPHT synthesis of a new six-layered polytype of SrRhO₃, which is isostructural with the 6H phase of SrIrO₃ made under ambient pressure.¹⁴ Since the structure has a monoclinic distortion, we denoted it as 6M. The 6M SrRhO₃ transforms to the orthorhombic Pv phase at elevated temperatures and pressures in accord with the expected sequence of polytypes made under high pressure. We established a pressure–temperature phase diagram of SrRhO₃ based on HPHT experiments. As discussed below, the polytype 6M phase of SrRhO₃ is formed, although a $t < 1$ holds. This finding contradicts the established Pv to polytypes transition as a function of the t factor in the literature. The puzzle could be caused by the strong tendency of forming face-shared RhO₆ octahedra. A similar situation was found in SrIrO₃. We give a detailed description of the crystal structure of the 6M SrRhO₃, based on results of refinement of the powder XRD, and discuss the relationship of the bonding structure and the orbital occupation. These samples have been characterized by

measurements of magnetic susceptibility, resistivity, and thermopower.

EXPERIMENTAL DETAILS

The precursor of SrRhO_3 for the HPHT experiments was prepared by conventional solid-state reaction. Thoroughly mixed SrCO_3 and Rh powders in a 1:1 ratio were pressed into pellets and sintered at 1000 °C for 24 h and then at 1200 °C for 48 h with an oxygen flow. The HPHT experiments were performed in a Walker-type, multianvil pressure module. Ceramcast 584 (5% Cr_2O_3) octahedra cured at 1000 °C were used as the pressure medium. Starting materials for the HPHT experiment were contained in a Pt capsule ($\phi = 1.68$ mm and $L \approx 3.0$ mm). The Pt capsule was put into a BN sleeve and then inserted into a cylindrical graphite heater, both ends of which were stuffed with a molybdenum foil and a steel ring. Other spaces were filled with pyrophyllite plugs. To produce a high oxygen pressure in the Pt capsule for SrRhO_3 , we used a thin yttrium-stabilized ZrO_2 pellet (~ 0.3 mm) to separate the precursor and the oxygen source, KClO_4 , with the volume ratio of ~ 1 . Such a split-cell arrangement prevents the sample from mixed with KCl and the sample pellet after the synthesis can be used for physical property measurements. In a typical HPHT experiment, an octahedron was first compressed to the desired pressure by eight truncated tungsten carbide cubes with a truncated edge length (TEL) = 8 mm. Then, the sample was subjected to a heating treatment at temperatures between 1000 and 1400 °C for 30 min before quenching to room temperature. Finally, the pressure was released slowly. In the present study, we performed HPHT experiments in the pressure range of $4 \leq P \leq 8$ GPa.

The high-pressure products were first checked with powder X-ray diffraction (XRD) at room temperature with a Philips X'pert diffractometer (Cu $K\alpha$ radiation). The XRD data were collected by a step scan from 15 to 120° in 2θ in increments of 0.02° and a counting time of 10 s at each step. The XRD patterns were refined with the Rietveld method by using the FullProf program.¹⁵ Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were performed on three samples in a commercial apparatus (JEOL JSM-5610 equipped with INCA Energy, Oxford Instruments). Magnetic properties were measured with a SQUID magnetometer (Quantum Design) in the temperature range of 2–750 K. A four-probe method was used to measure the resistivity, and a homemade apparatus was employed to measure the thermopower.

RESULTS

1. The Temperature–Pressure Phase Diagram of SrRhO_3 . The XRD pattern of the as-sintered precursor for the synthesis of SrRhO_3 shows a mixture of $\text{Sr}_6\text{Rh}_5\text{O}_{15}$ and SrRh_2O_4 , indicating that Rh^{4+} cannot be stabilized at ambient pressure. The high oxygen pressure maintained in the high-pressure cell is thus essential to stabilize the Rh^{4+} cation and obtain novel rhodium oxides.⁷ The XRD pattern of a sample synthesized at 6 GPa and 1400 °C was found to be totally different from that of the Pv phase reported by Yamaura et al.,⁷ but it was very similar to that of the ambient 6M phase of SrIrO_3 .¹⁴ By using the structural model of 6M- SrIrO_3 given by Longo et al.,¹⁴ almost all of the XRD peaks can be indexed very well. However, Rietveld refinement to the XRD data shows a large discrepancy at certain reflections corresponding to the Pv SrRhO_3 . After the orthorhombic Pv phase was introduced as a second phase,⁷ the Rietveld refinement converged very well, which indicated that the obtained sample actually consists of $\sim 80\%$ the 6M phase and $\sim 20\%$ the Pv phase. This result is consistent with that of Yamaura et al.,⁷ who prepared the Pv phase at 6 GPa and 1500 °C. We believe that the 6M polytype must be a low-temperature phase of SrRhO_3 and that 1400 °C is close to the boundary temperature to separate these two phases under 6 GPa. Therefore, we performed a number of

HPHT experiments to obtain pure phases of both products and to construct a pressure–temperature phase diagram in Figure 1c. The phase relationship between 6M and Pv polytypes of SrRhO_3 was determined for $4 \leq P \leq 8$ GPa and $1200 \leq T \leq 1400$ °C. The XRD patterns of SrRhO_3 obtained at different HPHT conditions are given in Figure S1. The 6M SrRhO_3 can be synthesized at lower pressures or temperatures, and the Pv phase was obtained at higher pressures or temperatures.

The SEM photos and a typical EDS spectrum in Figure S2 indicated that the samples with the 6M and Pv phase are well-sintered with the grain size ~ 10 μm . EDS measurements at several positions of three samples, namely, one 6M and two Pv phases, yield an average Sr/Rh molar ratio of 0.94(2):1, and no other metal elements were identified.

2. Crystal Structure. The 6M- SrRhO_3 . The XRD pattern of the sample obtained at 6 GPa and 1200 °C is shown in Figure 2a, which can be indexed in a monoclinic unit cell with $a =$

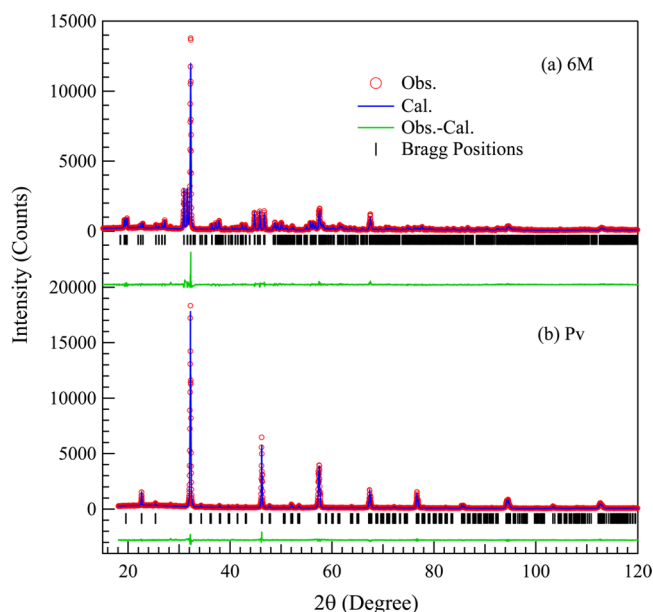


Figure 2. Rietveld refinements on the XRD pattern of (a) 6M- SrRhO_3 obtained at 6 GPa and 1200 °C and (b) Pv- SrRhO_3 obtained at 8 GPa and 1400 °C.

5.5650(1) Å, $b = 9.5967(2)$ Å, $c = 14.0224(4)$ Å, and $\beta = 92.846(2)^\circ$. The crystal structure was refined from the powder XRD data with the space group $C2/c$ of ambient SrIrO_3 as a starting model. Sr atoms are placed at 4e (0, y , 1/4) and 8f (x , y , z) positions; Rh1 is at 4a (0, 0, 0) and Rh2 at 8f sites; and five independent positions for oxygen atoms, O1 at 4e, O2–O5 are at 8f positions. The goodness of the fit to the XRD data is illustrated in Figure 2a; the final atomic parameters and the main interatomic distances and angles after the refinement are listed in Tables 1 and 2. The crystal structure of the 6M SrRhO_3 is shown in Figure 1a; it consists of dimers of face-shared $\text{Rh}(2)\text{O}_6$ octahedra linked by their vertices to single corner-shared $\text{Rh}(1)\text{O}_6$ octahedra along the c axis. Alternatively, it can be described as a stacking of layers of corner-shared (C) and face-shared (H) RhO_6 octahedra in the sequence CCHCCH along the c axis.

Rh–O distances for the two Rh atoms vary in the range from 1.91 Å for Rh2–O3 to 2.25 Å for Rh2–O1. The longest Rh2–O1 bond is due to a strong distortion in the face-shared $\text{Rh}(2)\text{O}_6$ octahedra. The average Rh1–O distance, 2.00 Å, is

Table 1. Atomic Coordinates and Isotropic Thermal Factors B_{iso} [Å²] for 6M-SrRhO₃ from Powder XRD Data^a at 295 K

atom	site	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso}
Sr1	4e	0.0	0.0029(6)	0.25	1.26(14)
Sr2	8f	0.0095(6)	0.6666(5)	0.0986(2)	1.97(9)
Rh1	4a	0.0	0.0	0.0	1.44(12)
Rh2	8f	0.9841(5)	0.6642(4)	0.8448(2)	1.45(6)
O1	4e	0.0	0.525(3)	0.25	2.4(2)
O2	8f	0.244(3)	0.260(2)	0.2618(11)	2.4(2)
O3	8f	0.817(3)	0.397(2)	0.0486(12)	2.4(2)
O4	8f	0.939(3)	0.147(3)	0.4040(11)	2.4(2)
O5	8f	0.331(4)	0.411(2)	0.0999(13)	2.4(2)

^aDiscrepancy factors: $R_p = 9.10\%$, $R_{\text{wp}} = 12.1\%$, $R_{\text{exp}} = 6.92\%$, $\chi^2 = 3.03$, $R_{\text{Bragg}} = 8.45\%$. Space group $C2/c$, $a = 5.5650(1)$ Å, $b = 9.5967(2)$ Å, $c = 14.0224(4)$ Å, $\beta = 92.846(2)^\circ$, $V = 747.96(3)$ Å³, $Z = 12$.

Table 2. Main Interatomic Distances (Å) and Angles (deg) of 6M-SrRhO₃ from Powder XRD Data at 295 K

RhO ₆ octahedra		SrO ₁₂ cuboctahedra	
Rh1–O3 (×2)	2.106(17)	Sr1–O1 (×2)	2.791(2)
Rh1–O4 (×2)	1.97(2)	Sr1–O2 (×2)	2.819(17)
Rh1–O5 (×2)	1.925(20)	Sr1–O2 (×2)	2.740(17)
⟨Rh1–O⟩	2.000	Sr1–O3 (×2)	3.552(17)
Rh2–O1	2.25(2)	Sr1–O4 (×2)	2.60(2)
Rh2–O2	2.045(16)	Sr1–O5 (×2)	2.428(19)
Rh2–O2	2.035(17)	⟨Sr1–O⟩	2.822
Rh2–O3	1.908(17)	Sr2–O1	2.523(16)
Rh2–O4	2.01(3)	Sr2–O2	2.926(17)
Rh2–O5	2.08(2)	Sr2–O2	2.501(16)
⟨Rh2–O⟩	2.055	Sr2–O3	2.874(19)
⟨Rh–O⟩	2.028	Sr2–O3	2.401(18)
Rh2–Rh2	2.673(3)	Sr2–O3	2.903(19)
Rh2–O1–Rh2	72.7(8)	Sr2–O4	3.27(2)
Rh2–O2–Rh2	81.9(7)	Sr2–O4	2.501(17)
Rh1–O3–Rh2	147.4(7)	Sr2–O4	3.077(17)
Rh1–O4–Rh2	155.0(1)	Sr2–O5	3.04(2)
Rh1–O5–Rh2	151.2(9)	Sr2–O5	3.372(19)
		Sr2–O5	2.55(2)
		⟨Sr2–O⟩	2.828

consistent with the ionic radii sum for Rh⁴⁺ (0.60 Å) and O^{2−} (1.40 Å). In comparison with Rh(1)O₆ octahedra, however, the Rh(2)O₆ octahedra show a significant expansion with an average Rh2–O distance of 2.06 Å. This is presumably due to the strong metal–metal bonding across the shared face within the Rh(2)₂O₉ dimer, as evidenced by the short Rh2–Rh2 distances, 2.673(3) Å, which are even shorter than the separation of 2.69 Å found in the Rh metal.

The Sr–O distances for the two Sr atoms vary in the range of 2.40 Å for Sr2–O3 to 3.55 Å for Sr1–O3; for Sr1, there are 10 short and 2 long bonds, whereas for Sr2 there are 5 short and 7 long bonds. The average Sr–O distances for both polyhedra are very similar; that is, ⟨Sr1–O⟩ = 2.82 Å and ⟨Sr2–O⟩ = 2.83 Å.

The Pv-SrRhO₃. Figure 2b shows the XRD pattern of the Pv phase prepared at 8 GPa and 1400 °C; it can be refined very well in the space group *Pbnm* with the Sr atom at 4c (*x*, *y*, 1/4), the Rh atom at 4b (1/2, 0, 0), and two kinds of O atoms at 4c and 8d (*x*, *y*, *z*) sites. The lattice parameters, $a = 5.5673(1)$ Å, $b = 5.5399(2)$ Å, and $c = 7.8550(2)$ Å, are in excellent agreement with those reported by Yamaura et al.⁷ of $a = 5.5394(2)$ Å, $b = 7.8539(3)$ Å, and $c = 5.5666(2)$ Å of the *Pnma* setting. Tables 3

Table 3. Atomic Coordinates and Isotropic Thermal Factors B_{iso} [Å²] for Pv-SrRhO₃ from Powder XRD Data^a at 295 K

atom	site	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso}
Sr	4c	0.9985(13)	0.00275(3)	0.25	1.51(5)
Rh	4b	0.5	0.0	0.0	1.22(3)
O1	4c	0.065(4)	0.498(2)	0.25	1.9(3)
O2	8d	0.714(2)	0.279(3)	0.0369(19)	1.9(3)

^aDiscrepancy factors: $R_p = 6.61\%$, $R_{\text{wp}} = 9.24\%$, $R_{\text{exp}} = 6.94\%$, $\chi^2 = 1.77$, $R_{\text{Bragg}} = 4.57\%$. Space group *Pbnm*, $a = 5.5673(1)$ Å, $b = 5.5399(2)$ Å, $c = 7.8550(2)$ Å, $V = 242.267(9)$ Å³, $Z = 4$.

and 4 list the final atomic parameters and the main interatomic distances and angles. As shown in Figure 1b, the crystal

Table 4. Main Interatomic Distances (Å) and Angles (deg) of Pv-SrRhO₃ from Powder XRD Data at 295 K

RhO ₆ octahedra		SrO ₁₂ cuboctahedra	
Rh–O1 (×2)	1.997(4)	Sr–O1	2.957(11)
Rh–O2 (×2)	1.973(15)	Sr–O1	2.633(12)
Rh–O2 (×2)	2.029(13)	Sr–O1	3.14(2)
⟨Rh–O⟩	2.000	Sr–O1	2.44(2)
Rh–O1–Rh	159.11(16)	Sr–O2(×2)	2.693(15)
Rh–O2–Rh	157.7 (6)	Sr–O2(×2)	2.769(15)
O1–Rh–O2	88.2(9)	Sr–O2(×2)	2.469(15)
O1–Rh–O2	89.9(9)	Sr–O2(×2)	3.244(15)
O1–Rh–O2	88.7(9)	⟨Sr–O⟩	2.793

structure consists of a 3D network of corner-shared RhO₆ octahedra with large Sr cations in the interstitial positions. The orthorhombic distortion arises from cooperative rotations of the RhO_{6/2} octahedra about [110] and [001] cubic axes, which results in the deviation from ideal Rh–O–Rh angles of 180°; that is, Rh–O1–Rh = 159.1(2)° and Rh–O2–Rh = 157.7(6)°. Moreover, the RhO_{6/2} octahedra are not rigid, with O–Rh–O angles 88.2°, 89.9°, and 88.7°, deviating from 90°. It has been demonstrated thoroughly in the R³⁺M³⁺O₃ perovskites that the O–M–O angle α reduced from 90° subtends the orthorhombic *b* axis, converting from $b > a$ to $a > b$.¹⁶ Such a crossover has been argued to occur for $\delta = (90^\circ - \alpha)$ as small as 1°. Thus, a $\delta = 1.3^\circ$ for the O2–Rh–O2 angle seems to be in accordance with the observed $a > b$ in the Pv SrRhO₃. The average Rh–O distance, 2.00 Å, is the same as that of ⟨Rh1–O⟩ in the 6M phase, and it is also consistent with the ionic radii sum for Rh⁴⁺ and O^{2−}. The Sr–O distances vary from 2.44(2) to 3.24(2) Å, with an average of 2.79 Å, smaller than those of 6M phase. There are eight short and four long Sr–O bonds. The tolerance factor calculated from the average Sr–O and Rh–O bond lengths is $t = 0.986$.

3. Magnetic Properties. Figure 3 summarizes the magnetic properties of the Pv and 6M SrRhO₃, including the temperature dependence of magnetic susceptibilities $\chi(T)$ and its inverse $\chi^{-1}(T)$, as well as the magnetization curves $M(H)$ at 5 K. The $\chi(T)$ of 6M-SrRhO₃ was measured with $H = 5$ T due to the small sample mass, while the Pv phase was measured with $H = 1$ T. For both samples, $\chi(T)$ was recorded with increasing temperatures after zero field cooling (ZFC) and field cooling (FC); there is no difference for ZFC- and FC- $\chi(T)$ curves, and no long-range magnetic ordering was observed down to 2 K. Interestingly, their $\chi(T)$ curves exhibit distinct behaviors. The $\chi(T)$ of the Pv phase is higher than that of the 6M phase and displays a broad hump centered around 150 K, which results in

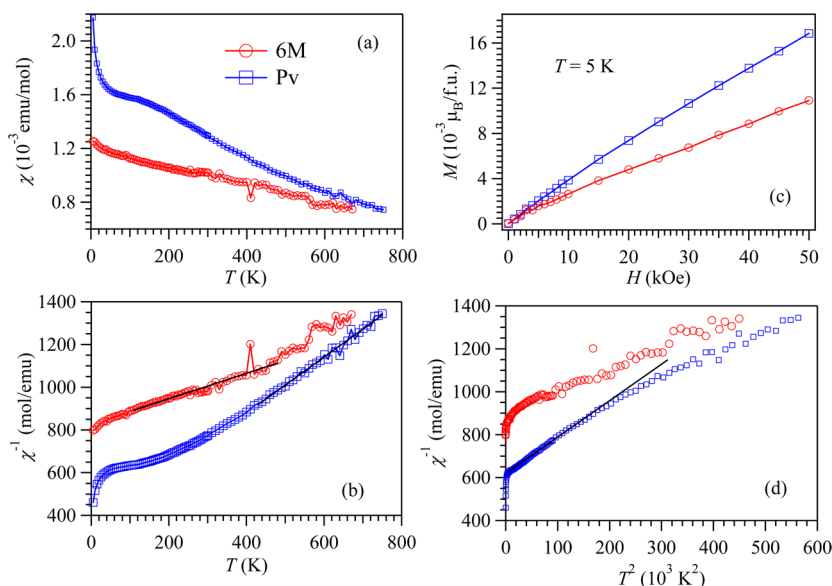


Figure 3. Temperature dependence of the magnetic susceptibility $\chi(T)$ and its inverse $\chi^{-1}(T)$, as well as magnetization curve $M(H)$ at 5 K for SrRhO₃ polytypes.

an unusual linear behavior in the plot of χ^{-1} versus T^2 (below 400 K) similar to that reported by Yamaura et al.⁷ As shown in Figure 3d, however, our measurements of $\chi(T)$ in a much extended temperature range up to 750 K show that such a quadratic temperature dependence of $\chi^{-1}(T)$ becomes invalid for $T > 400$ K; above 400 K a linear behavior of $\chi^{-1}(T)$ is restored in Figure 3b. Fitting the curve to a Curie–Weiss (CW) law at $T > 400$ K yields an effective moment $\mu_{\text{eff}} = 2.47 \mu_{\text{B}}/\text{Rh}^{4+}$, and a CW temperature $\theta_{\text{CW}} = -272$ K. In contrast, the $\chi^{-1}(T)$ of the 6M phase follows basically the CW behavior over a wide temperature range, Figure 3b; fitting $\chi^{-1}(T)$ to a CW law in the temperature range of 100–500 K gives a $\mu_{\text{eff}} = 3.65 \mu_{\text{B}}/\text{Rh}^{4+}$, and $\theta_{\text{CW}} = -1378$ K. The fitting curves are shown in Figure 3b as the solid lines. For both cases, the obtained μ_{eff} is much larger than the calculated spin-only value of $1.73 \mu_{\text{B}}$ for Rh⁴⁺ with $S = 1/2$. Fitting $\chi(T)$ of a narrow band metal to a CW law normally gives rise to a larger μ_{eff} than the spin-only value and an unphysically large Weiss constant. The $\chi^{-1}(T)$ for both Pv and 6M phases are not linear over a broad temperature range, which indicates that either the effect of spin–orbit coupling is strong in these phases or quantum critical fluctuations play a significant role.⁸ The competition between interatomic and intraatomic exchange interactions suppresses the spin ordering. Increase of the C layers in the polytypes usually enhances the interatomic exchange interaction as demonstrated in BaRuO₃.¹⁷ Therefore, a strong interatomic exchange interaction is expected in Pv SrRhO₃, which brings the oxide at the verge of a magnetic transition. The $M(H)$ curves of both polytypes increase almost linearly with increasing magnetic fields, and no remanence was observed; the magnetic moments of Rh^{IV} at $T = 5$ K and $H = 5$ T are very tiny, $0.011 \mu_{\text{B}}$ and $0.017 \mu_{\text{B}}$ for the 6M and Pv SrRhO₃, respectively.

4. Transport Properties. The temperature dependence of electrical resistivity $\rho(T)$ and thermopower $S(T)$ for the SrRhO₃ polytypes are shown in Figures 4 and 5, respectively. As shown in Figure 4, both samples show a metallic conductivity in the whole measured temperature range, and the 6M phase shows a larger resistivity than the Pv phase. The

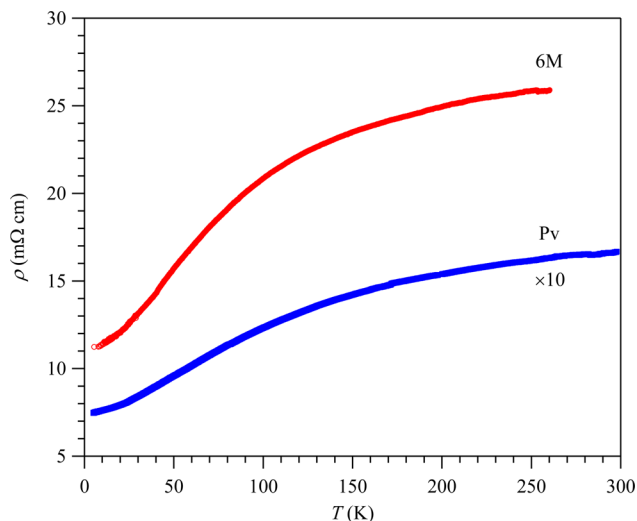


Figure 4. Temperature dependence of resistivity $\rho(T)$ for SrRhO₃ polytypes.

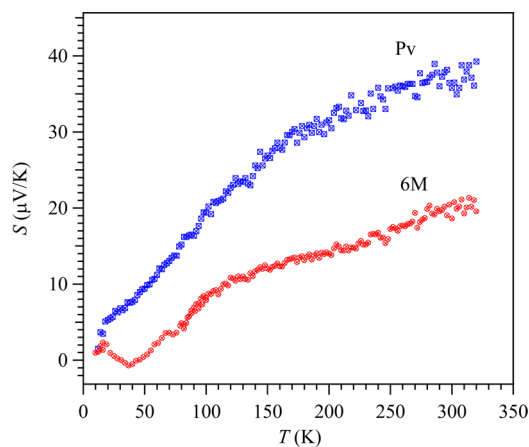


Figure 5. Temperature dependence of thermopower $S(T)$ for SrRhO₃ polytypes.

$\rho(T)$ data at low temperatures can be described with the power-law behavior, $\rho(T) = \rho_0 + AT^n$. The Pv phase follows the Fermi-liquid behavior with $n = 2$,⁷ whereas the 6M phase shows a non-Fermi-liquid behavior with $n \approx 1.60(2)$, implying that the 6M phase might approach a magnetic instability. A similar situation has also been observed in the 6M SrIrO_3 , in which the observed non-Fermi-liquid behavior $\rho \sim T^{3/2}$ and the enhanced specific heat $C/T \sim -\ln T$ have been attributed to the close proximity to a ferromagnetic quantum critical point (QCP).¹⁸ The importance of magnetic correlations on the transport properties as a function of structural evolution has been well-illustrated in our previous studies on the BaIrO_3 polytypes involving four kinds of structural phases, that is, $9R \rightarrow 5H \rightarrow 6H \rightarrow 3C$.¹⁹ The electronic bandwidth derived from the Ir 5d states is expected to increase gradually with an increasing fraction of corner-shared octahedra. As such, the ground state of BaIrO_3 evolves gradually from the weak ferromagnetic insulator with $T_c = 180$ K in the 9R phase, to a ferromagnetic metal with $T_c = 50$ K in the 5H phase, to an exchange-enhanced paramagnetic metal near a QCP in the 6H phase, and finally to a Pauli paramagnetic metal in the 3C phase. Similarly, the 6M SrRhO_3 with a narrower bandwidth than that of Pv phase is likely located closer to a magnetic transition. However, a strong spin-orbit coupling suppresses magnetic ordering. As shown in Figure 5, $S(T)$ for both samples is positive and increases with temperature, in line with the metallic behavior of $\rho(T)$ and a nearly fully occupied π^* band. The thermopower $S(T)$ for both 6M and Pv phases of SrRhO_3 is generally consistent with that described by the Mott diffusive formula for a metal. The low-temperature anomaly starting at ~ 100 K in the 6M phase appears to be due to an enhancement with negative sign. The enhancement could be caused by either the phonon-drag effect or quantum critical fluctuations as a quantum critical point is approached. Since the maximum of the enhancement occurs at ~ 40 K, it is more likely due to the phonon-drag effect.

DISCUSSIONS

As pointed out in the Introduction, pressure can induce a 6H to 3C transition for AMO_3 compounds with a $t > 1$. When the ionic radius of XII Sr^{2+} (1.44 Å), VI O^{2-} (1.40 Å), and VI Rh^{4+} (0.60 Å) is used,²⁰ t of SrRhO_3 is calculated to be 1.004. Then, the 6M/Pv transformation seems to be consistent with the general expectation. However, the obtained Pv phase is orthorhombic rather than cubic, which implies $t < 1$. As illustrated in Figure S3, the calculated tolerance factors for the series of SrMO_3 (M = transition metals) perovskites are overestimated if the 12-fold coordinated ionic radius for XII Sr^{2+} (1.44 Å) is used, leading to a $t > 1$ for all the cubic perovskite except for SrMoO_3 , and they should crystallize in polytype structures. In reality, some of them are with the cubic structure, and others are with the orthorhombic structure. This observation means that the effective ionic radius for Sr^{2+} in these SrMO_3 perovskites should be smaller than 1.44 Å. Especially in the orthorhombically distorted perovskites, the structural distortion has reduced the effective coordination number of Sr^{2+} from 12 to 10 or even 8 with reducing t . In this case, a more reasonable estimation of t should be made by using the experimentally determined average $\langle \text{Sr-O} \rangle$ and $\langle \text{M-O} \rangle$ bond lengths. This gives $t = 0.986$ for the Pv SrRhO_3 as shown above. Therefore, in addition to SrIrO_3 , SrRhO_3 has a $t < 1$ but undergoes a 6M to Pv transformation under high pressure.

As pointed out by Longo et al.¹⁴ for 6M SrIrO_3 , this unusual stability of the 6M polytype in SrMO_3 (M = Rh, Ir) with $t < 1$

should be attributed to the low-spin t^5e^0 configuration and the larger radial extension of the 4d and 5d orbitals relative to that of the 3d orbitals. A strong M–M bonding stabilizes the dimers of the 6M phase via half-filled a_1^1 orbitals of the $e_\pi^4 a_1^1 e_\sigma^0$ configuration in the trigonal site symmetry. Displacement of the M2 cations forming dimers leaves the M1 ions without a partner for bonding, so the M1 cations occupy sites where a smaller site distortion does not completely quench the orbital angular momentum so that the $yz \pm izx$ orbital in the O4–M1–O5 plane remains half-filled. Thus, the appearance of a 6M structure with a tolerance factor $t < 1$ can be understood, and the pressure-induced 6M–Pv phase transition is consistent with the volume contraction. The observed crystallographic densities of the 6M and Pv polytypes are 6.35 and 6.54 g/cm³ for SrRhO_3 and 8.58 and 8.86 g/cm³ for SrIrO_3 , respectively. They represent an increase in density of 3.0% and 3.3% from the 6M polytype to Pv phase for SrRhO_3 and SrIrO_3 , respectively.

The ideal hexagonal 6H structure is found where an ABX_3 has a $t > 1$, for example, RbNiF_3 and TiNiF_3 .²¹ The 6H polytypes transform to the cubic 3C perovskite under high pressure. However, the monoclinic distortion of the 6M phases of SrRhO_3 and SrIrO_3 indicates that a compressive stress on the A–O bond due to an M–O versus A–O bond-length mismatch remains due to a strong M–M bonding. The argument is supported by the observation that the monoclinic distortion of 6M SrIrO_3 decreases from $\beta = 93.184(4)^\circ$ to $\beta = 91.319(2)^\circ$ in BaIrO_3 .² However, a reduced monoclinic distortion in 6M BaIrO_3 indicates that the M–M bonding also plays an important role in creating the compressive stress on the A–O bond. We also note that with increasing pressure, the 9R BaRuO_3 made at ambient condition transforms to the 4H polytypes at 3 GPa and to the 6H phase at 5 GPa and finally to the cubic 3C phase at 18 GPa;¹⁷ both the 4H and 6H phases have hexagonal symmetry with space group $P6_3/mmc$. Interestingly, Zhao et al.²² have reinvestigated the structural evolution of the $\text{Ba}_{1-x}\text{Sr}_x\text{RuO}_3$ system and shown that the 6H phase is stabilized for $0 \leq x \leq 0.3$, whereas the 6M structure is found for $0.4 \leq x \leq 0.6$. The 6M phase found in $\text{Ba}_{1-x}\text{Sr}_x\text{RuO}_3$ ($0.4 \leq x \leq 0.6$) has the same space group, $C2/c$, as that in SrIrO_3 and SrRhO_3 . The distortion from the 6H to the 6M structure in the $\text{Ba}_{1-x}\text{Sr}_x\text{RuO}_3$ system also increases as the average A-cation size decreases. Taking the 1:2 B-site ordered 6H $\text{Ba}_3(\text{MSb}_2)\text{O}_9$ (M = Mg, Ca, Sr)^{23,24} as another example, the symmetries are also lowered successively from hexagonal $P6_3/mmc$ to monoclinic $C2/c$, and then to triclinic $P\bar{1}$ on going from VI Mg^{2+} (0.72 Å) through VI Ca^{2+} (1.00 Å) to VI Sr^{2+} (1.18 Å), as the bond-length mismatch with VISb^{5+} (0.60 Å) increases. The 1:2 B-site ordered 6H $\text{Ba}_3(\text{MRu}_2)\text{O}_9$ oxides with M = Li, Na, Mg, Ca, Sr, Ti, Fe, Co, Ni, Cu, Zn, Cd, In, Sb, Y, Bi, La–Ln²⁵ form a wide family. The hexagonal space group $P6_3/mmc$ was found for all compounds except two oxides with M = Sr and Bi. The relatively large ionic radius of VISr^{2+} and VIIBi^{3+} , makes these two oxides crystallized in the monoclinic $C2/c$ phase.

Among the known SrMO_3 (M = 3d, 4d, and 5d transition metals) oxides, SrRhO_3 and SrIrO_3 are the only two compounds that adopt a monoclinic distortion of the 6H structure at lower pressures and transform to an orthorhombic $Pbnm$ Pv rather than the cubic 3C perovskite under higher pressures. Rietveld refinements on their crystal structures revealed great similarities: for example, in the 6M polytypes, the $M(2)\text{O}_{6/2}$ octahedra are expanded with a low valence sum

relative to the $M(1)O_{6/2}$ octahedra; the M2–M2 distances are short, implying strong metal–metal bonding; and the M2–O1 bond lengths are stretched due to highly distorted octahedra in the dimers. Similar features have also been observed recently in the 6M $Ba_{0.4}Sr_{0.6}RuO_3$ with a monoclinic distortion.²² These features include (1) the average distance of Ru2–O, 2.109 Å, is much larger than that of Ru1–O with 2.00 Å; (2) the Ru2–Ru2 distance, 2.596(2) Å, is shorter than the separation of 2.65 Å found in ruthenium metal; and (3) the Ru2–O1 bond length, 2.319 Å, is the longest among the Ru–O bonds.

The high-pressure phase of both $SrRhO_3$ and $SrIrO_3$ has the orthorhombic $Pbnm$ Pv structure, which is consistent with the $t \approx 0.98 < 1$, as calculated from the average Sr–O and Rh/Ir–O bond lengths. The same Pv structure is also found in $SrRuO_3$, which can be prepared at ambient pressure. With the $Pbnm$ setting, all of them show the lattice parameters $a > b$, which continuously evolves to $b > a$ with decreasing average size of A-site cation by Ca^{2+} doping. The crossover occurs at $\sim 30\%$,²⁶ $\sim 10\%$,²⁷ and $\sim 15\%$ Ca^{2+} doping in $SrRuO_3$, $SrRhO_3$, and $SrIrO_3$, respectively. Such a lattice-parameter anomaly has been demonstrated thoroughly in the $R^{3+}M^{3+}O_3$ (R = rare earth and Y; M = 3d transition metals and Ga) perovskites arising from an intrinsic octahedral-site distortion.¹⁶ It consists of a deviation from 90° of the O–M–O angle subtending the site-rotations with increasing A-site cation radius above 1.11 Å for most $R^{3+}M^{3+}O_3$ perovskites; the $MO_{6/2}$ octahedra are not rigid, and b decreases while a increases until they cross. We have seen this distortion in Pv phases of both $SrRhO_3$ and $SrIrO_3$. Examination of the evolution of the lattice parameters a and b in the $Sr_{1-x}Ca_xMO_3$ (M = Ru²⁶ and Rh²⁷) system indicates that such an intrinsic octahedra-site distortion has already taken place for $CaMO_3$.

The metallic conductivity of the Pv $SrRhO_3$ with Fermi-liquid behavior;⁷ that is, $\rho \sim T^2$, can be expected for the low-spin $4d^5$ configuration; the covalent bonding between oxygen 2p orbital and the spatially extended 4d orbital gives Rh: t_{2g} –O: $2p_\pi$ –Rh: t_{2g} interactions that are strong enough to transform localized t_{2g} orbitals into itinerant π^* orbitals.²⁸ The π^* bands are five-sixths filled to give a p-type conduction as confirmed by $S(T)$ in Figure 5.

In the 6M phase, we should expect the Rh–Rh bonding in the dimers to split the half-filled a_1 molecular orbital into filled bonding and empty antibonding states, so we are left to consider only Rh1: t_{2g} –O–O–Rh1: t_{2g} interactions. As demonstrated in the double perovskite $Sr_2MgMoO_{6-\delta}$, for example, t_{2g} orbital interatomic interaction via a two- O^{2-} -ion bridge can be strong enough to give rise to an itinerant-electron behavior, but the π^* bands of the Rh1 sites would be significantly narrower than those of the perovskite phase, where the interaction between cation M is bridged through a single O^{2-} ion. The bandwidth and therefore the conductivity of the 6M phase should be much reduced relative to that of the Pv phase as shown in Figure 4. Moreover, the observation of non-Fermi-liquid behavior indicated that the 6M phase might approach a QCP from the itinerant-electron side. In this region we should expect to find stronger evidence of strong-correlation fluctuations in the paramagnetic state. A temperature-dependent $\chi(T)$ is typical of a metallic phase containing strong-correlation fluctuations on the approach to a QCP from the itinerant-electron side. The anomalous $\chi^{-1} \sim T^2$ behavior at $T < 400$ K in the Pv $SrRhO_3$ seems related to the spin–orbit coupling effect. The competition between interatomic exchange coupling and intraatomic coupling normally causes the $\chi(T)$

deviated from a CW behavior such as the systematic change of $\chi(T)$ observed in the $BaRuO_3$ polytypes.¹⁷

CONCLUSION

In summary, a new 6M polytype of $SrRhO_3$ can be stabilized in narrow ranges of temperature (1200–1400 °C) and pressure (4–7 GPa). It is metallic and shows an enhanced Pauli paramagnetism. The 6M polytype is a distorted version of the 6H polytype structure, which is normally found in oxides $A^{2+}M^{4+}O_3$, especially for M = 4d and 5d transition metals, $Ba_3(CaSb_2)O_9$, and $Ba_3(M'Ru_2)O_9$ (M' = Sr, Bi) with a t slightly less than 1. A strong M–M bonding in these oxides prefers layers of face-shared octahedra that are intergrown with the corner-shared layers along the c -axis. High-pressure synthesis converts the 6M phase of $SrRhO_3$ into the $Pbnm$ Pv structure, because pressure favors the phase with a higher density.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00864.

XRD patterns, SEM photos, and EDS spectrum of $SrRhO_3$, and the calculated tolerance factors of $SrMO_3$ (M = transition metal) perovskites (PDF)

Accession Codes

CCDC 1550141 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interest.

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