

$\text{Bi}_{2/3}\text{Ce}_{1/3}\text{Rh}_2\text{O}_5$: A new mixed-valent Rh oxide with hitherto unknown structure

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Abstract

The new compound $\text{Bi}_{2/3}\text{Ce}_{1/3}\text{Rh}_2\text{O}_5$ has been discovered. It is currently the only known compound in the Bi–Ce–Rh–O system, and it crystallizes in a previously unknown structure type. The structure was established from single crystal X-ray diffraction data. Interatomic distances indicate the oxidation states as $\text{Bi}_{2/3}^{3+}\text{Ce}_{1/3}^{4+}\text{Rh}_2^{3.33+}\text{O}_5$. The structure indicates no ordering between Rh^{3+} and Rh^{4+} . The lack of charge ordering is consistent with the metallic properties determined from electrical conductivity, Seebeck coefficient, and magnetic susceptibility measurements.

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1. Introduction

Rhodium is commonly found as Rh^{3+} or Rh^{4+} in oxides. Synthesis in air usually gives Rh^{3+} oxides. The synthesis of Rh^{4+} oxides normally needs a larger partial pressure of oxygen [1–4]. However, the existence of electropositive countercations such as Ba^{2+} often enhances the formation of Rh^{4+} even for synthesis under air [5–11].

Several interesting compounds have been found in the Bi–Rh–O system. Pyrochlore-type $\text{Bi}_2\text{Rh}_2\text{O}_{6.8}$ is synthesized easily under air, although it does not contain electropositive cations [12]. It is considered as having 0.8 positive holes per formula unit in a valence band composed of Rh $4d$ –O $2p$ t_{2g}^* , and in fact, a high electrical conductivity of 330 S/cm at 300 K is reported. Another mixed-valent Rh compound, $(\text{Bi}_6\text{O}_5)\text{Rh}_{12}\text{O}_{24}$, reported very recently has the Todolokite structure [13,14]. This structure is related to the rutile and Hollandite structures and has large channels containing Bi_6O_5 chains. In $(\text{Bi}_6\text{O}_5)\text{Rh}_{12}\text{O}_{24}$ there is evidence for charge ordering, consistent with its semiconducting behavior. The perovskite-type structure is found

for BiRhO_3 , which is prepared at high pressure [12]. Apparently, the only compound known in the Ce–Rh–O system is CeRhO_3 with a perovskite-type structure [15].

Our investigations of the Bi–Ce–Rh–O system revealed the existence of the new compound, $\text{Bi}_{2/3}\text{Ce}_{1/3}\text{Rh}_2\text{O}_5$, which occurs in a structure apparently not previously observed.

2. Experimental

Reactants were Bi_2O_3 (99.9%, Baker), CeO_2 nanopowder (99.9%, Aldrich), V_2O_5 (99.9%, Johnson Matthey) and Rh_2O_3 prepared from $\text{RhCl}_3 \times \text{H}_2\text{O}$ (99.9%, Alfa, Aesar) by heating in moist air at 1073 K for 10 h. Appropriate amounts of Bi_2O_3 , CeO_2 , and Rh_2O_3 were mixed by grinding together under ethanol in an agate mortar. This pressed mixture was placed in an alumina boat and heated in air at 1073, 1173, and 1273 K each for 10 h with intermediate grindings. Single crystals of $\text{Bi}_{2/3}\text{Ce}_{1/3}\text{Rh}_2\text{O}_5$ were grown in a flux of 90 wt% Bi_2O_3 and 10 wt% V_2O_5 . An intimate mixture of polycrystalline CeO_2 (0.18 g), Rh_2O_3 powder (0.14 g), Bi_2O_3 (3.5 g), V_2O_5 (0.38 g) was heated to 1373 K under air in a covered alumina crucible. After holding for 10 h, the crucible was cooled to 973 K at a

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rate of 3 K/h. After reaching 973 K, it was cooled to room temperature at a rate of 300 K/h. The flux was dissolved in HNO₃(aq) at 360 K. The product consisted of lustrous black crystals with several hundred micrometers in length. Attempts to substitute La, Nd, Y for Bi or Zr, Hf, Pr, or Tb for Ce failed.

The cationic composition was determined by a CAMECA SX100 electron microprobe analyzer. No vanadium or aluminum could be detected in the crystals. Single crystal X-ray diffraction data were collected on a Bruker SMART APEXII CCD system at 173 K. A standard focus tube was used with an anode power of 50 kV at 30 mA, a crystal to plate distance of 5.0 cm, 512 × 512 pixels/frame, beam center (256.52, 253.16), total frames of 6602, oscillation/frame of 0.50°, exposure/frame of 10.0 s/frame and SAINT integration. A subsequent SADABS correction was applied. The crystal structure was solved with the direct method program SHELXS and refined with full-matrix least-squares program SHELXTL [16]. Further details are given in Tables 1 and 2, and in available cif files.

DC electrical conductivity measurements were conducted by conventional four probe methods over the temperature region 80–300 K. Seebeck coefficient measurements were conducted over the temperature region 120–300 K. Magnetic measurements were made using a Quantum Design Magnetic Property Measurement System. EUTAX software was used to calculate bond valences [17].

Table 1
Crystal data and structure refinement for Bi_{2/3}Ce_{1/3}Rh₂O₅

Empirical formula	Bi _{0.67} Ce _{0.33} O ₅ Rh ₂
Formula weight	471.03
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions	<i>a</i> = 7.1298(9) Å, α = 90° <i>b</i> = 9.9666(12) Å, β = 90° <i>c</i> = 5.1067(6) Å, γ = 90°
Volume	362.88(8) Å ³
<i>Z</i>	4
Density (calculated)	8.622 g/cc
Absorption coefficient	45.119 mm ⁻¹
<i>F</i> (000)	817
Crystal size	0.05 × 0.04 × 0.03 mm ³
Theta range for data collection	4.09–27.48°
Index ranges	−9 ≤ <i>h</i> ≤ 9, −12 ≤ <i>k</i> ≤ 12, −6 ≤ <i>l</i> ≤ 6
Reflections collected	3703
Independent reflections	442 [<i>R</i> (int) = 0.0234]
Completeness to $\theta = 27.48^\circ$	99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3447 and 0.2113
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	442/1/43
Goodness-of-fit on <i>F</i> ²	1.212
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0217, <i>wR</i> ₂ = 0.0508
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0230, <i>wR</i> ₂ = 0.0513
Extinction coefficient	0.0041(3)
Largest diff. peak and hole	2.043 and −2.123 e Å ⁻³

Table 2
Atomic coordinates and displacement factors for Bi_{2/3}Ce_{1/3}Rh₂O₅

	Wyckoff	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) (Å ² × 10 ³) ^a
(Ce,Bi)	4 <i>c</i>	0.7386(1)	0.75	0.2154(1)	6(1)
Rh	8 <i>d</i>	0.5798(1)	0.4410(1)	0.2498(1)	4(1)
O1	8 <i>d</i>	0.3318(7)	0.4493(5)	0.065(1)	7(1)
O2	4 <i>c</i>	0.620(1)	0.25	0.0951(15)	10(2)
O3	8 <i>d</i>	0.4805(7)	0.3801(5)	0.597(1)	6(1)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*^{*ij*} tensor.

3. Results

The structure of Bi_{2/3}Ce_{1/3}Rh₂O₅ is shown in Fig. 1, and some bond distances and angles are given in Table 3. The ratio of Bi-to-Ce on the 4*c* site was confirmed by both chemical analysis and refinement of occupation factors. A notable feature is the zigzag chains of edge-shared Rh octahedra extending along the *c*-axis. The same type of chains exists in other structures such as the α-PbO₂ structure (Fig. 1) [18]. A difference between the Bi_{2/3}Ce_{1/3}Rh₂O₅ and α-PbO₂ structures is the way the chains are connected to each other. The O atoms joining the chains in α-PbO₂ all have a coordination number of three. In the case of Bi_{2/3}Ce_{1/3}Rh₂O₅ some of the O atoms joining the chains have a coordination number of two.

A similarity of the Bi_{2/3}Ce_{1/3}Rh₂O₅ structure to the structures of BaNb₂O₆ and BaTi₄O₉ is shown in Fig. 2 [19–21]. For all three structures, networks of linked octahedra form similar channels for the A cations Ba, Bi, and Ce. The polyhedra around these A cations is shown in Fig. 2. Perpendicular to these channels the A cations form a hexagonal array, although the actual symmetry is orthorhombic in all cases. The way that the octahedra are linked is, however, much different in these three structures. There are no edge-shared chains in BaNb₂O₆. Instead, there are octahedra sharing edges in pairs, which are then linked by corners to form chains along the *a*-axis. In BaTi₄O₉ there are edge-shared chains along the *b*-axis, but with much more edge sharing than in Bi_{2/3}Ce_{1/3}Rh₂O₅. In Bi_{2/3}Ce_{1/3}Rh₂O₅ each octahedron shares just two edges to form the zigzag chains. There are two such zigzag chains in BaTi₄O₉, which share edges with each other so that each octahedron shares six of its 12 edges with other octahedra.

Fig. 3 shows the electrical conductivity of a Bi_{2/3}Ce_{1/3}Rh₂O₅ pellet from 80 to 300 K. The temperature dependence is metal like with a conductivity of 60 S/cm at 300 K. This is a low value for a metal but is typical for Rh oxides showing such temperature dependence [4,22,23]. As shown in the inset, the behavior obeys the equation: $\rho = \rho_0 + AT^2$, indicative of a Fermi liquid. The fitting gives *A* = 0.0734 (10⁻⁶ Ω cm K⁻²). Fig. 3 also shows the temperature dependence of Seebeck coefficients. The small values of ~4–5 μV/K are consistent with the metallic temperature dependence of the electrical conductivity. Fig. 4 shows the

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