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Synthesis and crystal structure of two new cerium rhodium oxides: $Ce_{2/3-x}Rh_2^{3+}O_4$ ($x\sim0.12$) with Ce mixed valency and $Ce^{4+}Rh_2^{3+}O_5$

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The new compounds $Ce_{2/3-x}Rh_2O_4$ ($x\sim0.11$–0.14) and $CeRh_2O_5$ have been prepared. Their structures were determined from single crystal X-ray diffraction data. Electrical and magnetic properties were also evaluated. Based on the structural analysis and physical properties, oxidation states for $CeRh_2O_5$ can be assigned as $Ce^{4+}Rh_2^{3+}O_5$. A small variation in x was detected for $Ce_{2/3-x}Rh_2O_4$ indicating a formula ranging from $Ce_{0.55}^{3.64+}Rh_2^{3+}O_4$ to $Ce_{0.525}^{3.81+}Rh_2^{3+}O_4$.

1. Introduction

Rhodium is commonly found as Rh^{3+} or Rh^{4+} in oxides [1]. Synthesis in air usually results in Rh^{3+}, which takes octahedral coordination. For many years only two structures have been known in R–Rh–O ternary systems (R=rare earth cation). One structure is perovskite-type $RRhO_3$ [2,3]. The other structure is pyrochlore-type $R_2Rh_2O_7$, which requires a high pressure synthesis [4]. Recently, $R_{2/3-x}Rh_2O_4$ phases with a defect $CaFe_2O_4$-type structure were reported [5]. We have now investigated the Ce–Rh–O system in search of new compounds. Although the most common oxidation state for rare earths in oxides is the trivalent state, for Ce we might expect either Ce^{3+} or Ce^{4+}.

2. Experimental

Reactants were CeO_2 nanopowder (99.9%, Aldrich), $Ce(NO_3)_3\cdot 6H_2O$ (99.99%, Aldrich), PbO (99.9%, Aldrich), V_2O_5 (99.9%, Johnson Matthey), NaCl (99.9%, Mallinckrodt) and Rh_2O_3 prepared from $RhCl_3\times H_2O$ (99.9%, Alfa Aesar) by heating in moist air at 1073 K for 10 h. Single crystals of $CeRh_2O_5$ were grown in a flux of 66 mol% PbO and 33 mol% V_2O_5. An intimate mixture of polycrystalline CeO_2 (0.046 g), Rh_2O_3 (0.034 g), PbO (0.41 g), V_2O_5 (0.17 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 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 HNO_3(aq) at 360 K. For synthesis of the polycrystalline materials, appropriate amounts of CeO_2 (or $Ce(NO_3)_3\cdot 6H_2O$) 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 973, 1073, 1173, and 1373 K each for 10 h with intermediate grindings. Black powders resulted. The addition of NaCl as a flux was also tried. Single crystals of $Ce_{2/3-x}Rh_2O_4$ were grown in a mixture of $Ce(NO_3)_3\cdot 6H_2O$ (0.037 g), Rh_2O_3 (0.044 g), and NaCl (0.5 g). The mixed powder was heated to 1273 K under air in a covered alumina crucible for 20 h. It was then cooled to room temperature at a rate of 300 K/h. The product consisted of lustrous black crystals about 0.1 mm in length.

The cationic compositions of the obtained single crystals were determined with a CAMECA SX100 electron microprobe analyzer. Single crystal X-ray diffraction data were collected on a Bruker SMART APEXII CCD system at 173 or 213 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. Crystal structures were solved using the direct method program SHELXS and refined with the full-matrix least squares program SHELXTL [6]. Further details are given in Tables 1–3 and is available in cif files. X-ray powder diffraction patterns were obtained with a RIGAKU MINIFLEX II with Cu$K\alpha$ radiation and a graphite monochromator. VALENCE software was used to calculate bond valences [7].

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Table 1
Crystal data and structure refinement for $CeRh_2O_5$ and $Ce_{0.55}Rh_2O_4$.

Empirical formula	$CeRh_2O_5$	$Ce_{0.55}Rh_2O_4$
FW	425.94	347.59
T (K)	173(2)	213(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*
Unit cell dimensions (Å)	$a=7.1440(6)$	$a=9.014(13)$
	$b=9.8169(9)$	$b=3.055(5)$
	$c=5.0983(5)$	$c=10.812(16)$
Volume (Å^3)	357.55(6)	297.7(8)
Z	4	4
Density (calculated) (g/m^3)	7.913	7.754
Absorption coefficient (mm^{-1})	21.527	19.172
$F(0\,0\,0)$	752	617
Crystal size (mm^3)	$0.04 \times 0.03 \times 0.02$	$0.08 \times 0.01 \times 0.01$
Theta range (deg)	4.15–26.98	2.94–29.24
Index ranges	$-9 \leq h \leq 9$	$-11 \leq h \leq 11$
	$-12 \leq k \leq 12$	$-4 \leq k \leq 4$
	$-6 \leq l \leq 6$	$-14 \leq l \leq 14$
Reflections collected	3580	2503
Independent reflections	413 [$R_{int}=0.0200$]	454 [$R_{int}=0.0385$]
Completeness to theta (%)	99.8 at 27.48°	95.0 at 29.24°
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.6727 and 0.4797	0.8314 and 0.3092
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	413/0/41	454/0/44
Goodness-of-fit on F^2	1.071	1.028
Final R indices [$I > 2\text{sigma}(I)$]	$R_1=0.0197$, $wR_2=0.0575$	$R_1=0.0230$, $wR_2=0.0480$
R indices (all data)	$R_1=0.0199$, $wR_2=0.0577$	$R_1=0.0322$, $wR_2=0.0507$
Extinction coefficient	0.0133(8)	–
Largest diff. peak and hole (e Å^{-3})	1.470 and -1.094	1.342 and -1.244

Table 2
Atomic coordinates and displacement factors for $CeRh_2O_5$.

	Wyckoff	x	y	z	U_{eq} (Å$^2 \times 10^{-3}$)[a]
Ce	4*c*	0.7354(1)	3/4	0.1987(1)	4(1)
Rh	8*d*	0.5812(1)	0.4409(1)	0.2493(1)	4(1)
O1	8*d*	0.3314(5)	0.4436(4)	0.0638(8)	5(1)
O2	4*c*	0.6216(8)	1/4	0.0801(11)	8(1)
O3	8*d*	0.4829(5)	0.3767(3)	0.5990(7)	6(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

Table 3
Atomic coordinates and displacement factors for $Ce_{0.55}Rh_2O_4$.

	Wyckoff	x	y	z	U_{eq} (Å$^2 \times 10^{-3}$)[a]
Ce[b]	4*c*	0.2353(1)	1/4	0.6609(1)	13(1)
Rh1	4*c*	0.0901(1)	1/4	0.4016(1)	6(1)
Rh2	4*c*	0.4473(1)	3/4	0.3835(1)	7(1)
O1	4*c*	0.3059(6)	1/4	0.3344(4)	7(1)
O2	4*c*	0.4119(6)	3/4	0.5714(4)	7(1)
O3	4*c*	0.5371(7)	3/4	0.2115(4)	13(1)
O4	4*c*	0.8811(6)	1/4	0.4736(4)	7(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U^{ij} tensor.
[b] The occupancy factor for Ce is 0.554(2).

DC electrical conductivity measurements were conducted by a two probe method or four probe method. Seebeck coefficient measurements were conducted over the temperature region 120–300 K. Magnetic measurements at 1.0 T were made using Quantum Design PPMS. Band structure calculations were performed using the linear muffin-tin orbital (LMTO) method with the atomic sphere approximation (ASA) including the combined correction (CC). The LMTO-ASA code used in the calculations was developed in Stuttgart by Andersen et al. [8]. Interstitial space was filled with empty spheres. The *k*-space integrations employed the tetrahedron method using irreducible *k*-points within the Brillouin zone. The number of *k*-points included in the calculations is 196. The Perdew–Wang generalized gradient approximation was used to treat the effects of exchange and correlation [9].

3. Results

Our investigation of the ternary Ce–Rh–O system shown in Fig. 1 revealed the existence of two new ternary compounds, $CeRh_2O_5$ and $Ce_{2/3-x}Rh_2O_4$ ($x\sim0.11$–0.14). In the case of $CeRh_2O_5$ lustrous reddish black crystals several hundred micrometers in length were obtained (Fig. 2). Microprobe analysis of these crystals indicated that impurity elements from the flux or crucible were less than 1%. The structure of $CeRh_2O_5$ is shown in Fig. 3(a), and some bond distances and angles are given in Table 4. This structure is the same as recently reported for $Bi_{2/3}Ce_{1/3}Rh_2O_5$ [10], which has a slightly higher unit cell volume than $CeRh_2O_5$. As shown in Fig. 4(a), Ce cations in the channels have a coordination number of seven. The bond valence sums for Rh and Ce were calculated to be 3.19 and 3.82, respectively, suggesting the formula $Ce^{4+}Rh_2^{3+}O_5$. We used a bond valence parameter, $l_0=1.800$ for Rh^{3+}, which was deduced recently [11]. A notable feature of the $CeRh_2O_5$ structure is the zigzag chains of edge-shared Rh octahedra extending along the *c*-axis. The same type of chains exist in other structures such as the α-PbO_2 structure [12]. However, this type of zigzag chain has not been observed in other rhodate structures.

The observed electrical conductivity for a single crystal of $CeRh_2O_5$, 4×10^{-8} S/cm at 300 K, indicates that this oxide is a semiconductor. This is consistent with a fully occupied Rh 4d t_{2g} band for Rh^{3+} with LS configuration and supports the formula $Ce^{4+}Rh_2^{3+}O_5$ (Fig. 5). Numerous attempts to synthesize polycrystalline $CeRh_2O_5$ were not successful. Various different temperatures,