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Undulating Layers in a New Rhodate Network: Structure of $Bi_{1.4}CuORh_5O_{10}$

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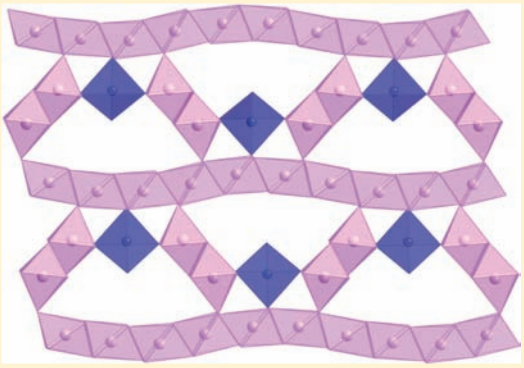
Supporting Information

ABSTRACT: A new rhodate, $Bi_{1.4}CuRh_5O_{11}$, with an hitherto unknown channel structure containing undulating layers of RhO_6 octahedra sharing corners and edges has been discovered and its structure refined from single crystal X-ray diffraction data. The channels contain Bi^{3+}, Cu^{2+}, and some O strongly bound to Cu. The Cu coordination is distorted square planar. Mixed Rh^{3+}/Rh^{4+} valency leads to significant electrical conductivity.



INTRODUCTION

Known rhodates contain Rh^{3+}, Rh^{4+}, or a mixture of these oxidation states, and the coordination of Rh is always octahedral in these oxides.[1] Our recent investigations of Bi containing rhodates led to the discovery of $(RE_{1-y}Bi_y)_{2/3-x}$ Rh_2O_4 (RE = rare earth), $Bi_{2/3}Ce_{1/3}Rh_2O_5$, $Bi_{0.78}Li_2Rh_6O_{12}$, $Bi_{0.75}Sc_{2.18}Rh_{4.92}O_{12}$, and $Bi_{0.68}Be_2Rh_6O_{12}$ and synthesis of single crystals of $Bi_6Rh_{12}O_{29}$.[2−5] Previously, $BiRhO_3$, $Bi_2Rh_2O_{6.8}$, $Bi_6Rh_{12}O_{29}$, and $Ba_{1.21}Bi_{0.33}Rh_8O_{16}$ had been known.[6−9] The known Cu containing rhodates are $CuRhO_2$ and $CuRh_2O_4$.[10] Apparently, the only known ternary Bi/Cu oxide is Bi_2CuO_4.[11] Our continuing exploratory investigation of rhodates has now produced a new rhodate containing Bi and Cu.

EXPERIMENTAL SECTION

Reagents were Bi_2O_3 (99.9% Baker), V_2O_5 (99.9%, Aldrich), CuO (99.9% Aldrich), and Rh_2O_3 prepared from $RhCl_3 \cdot xH_2O$ (99.9%, Alfa Aesar) by heating in moist air at 1073 K for 10 h. Single crystals were grown in a 75% Bi_2O_3−25% V_2O_5 flux. An intimate mixture of $2CuO/Rh_2O_3$ was added to an 11-fold excess by weight of flux. This was heated to 1373 K in air using a platinum crucible. After holding for 10 h, the crucible was cooled to 973 K at a rate of 5 K/h. After reaching 973 K, it was cooled to room temperature at a rate of 200 K/h. The flux was dissolved in HNO_3 (aq) at 363 K, and the black crystals obtained were needle shaped (Figure 1). Chemical analysis by energy dispersive spectroscopy (EDS) did not detect vanadium in the crystals.

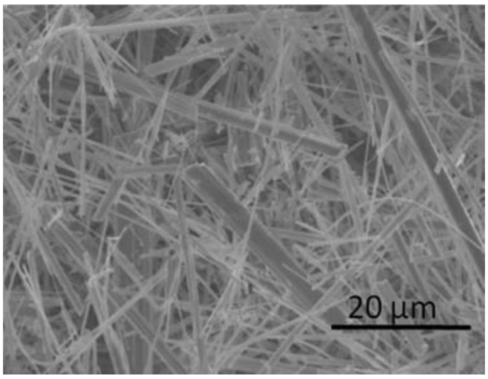


Figure 1. Scanning electron micrograph showing the morphology of $Bi_{1.4}CuORh_5O_{10}$ single crystals.

Single crystal X-ray diffraction data were collected at room temperature using a four circle diffractometer (Rigaku AFC 7R). No superlattice reflections were detected when scanning for diffraction intensities between various reciprocal lattice points along a*, b*, c*, a* + b*, a* + c*, and b* + c*. An initial structure model was obtained by the charge-flipping method using SUPERFLIP.[12] All atoms were placed on a mirror plane in earlier stages of the refinement with reliability factors of $R_{obs}(F)$ = 0.1197 and $wR_{all}(F^2)$ = 0.2354. Highly unusual displacement

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Table 1. Crystallographic Summary

empirical formula	$Bi_{1.4}CuORh_5O_{10}$
formula weight	1048.7
T (K)	295
wavelength (Å)	0.710 69
crystal system	monoclinic
space group	$C2/m$
a (Å)	17.310(3)
b (Å)	3.0775(9)
c (Å)	16.009(3)
b (°)	95.903(15)
V (Å^3)	848.3(3)
Z	4
D (calculated) (g cm^{-3})	8.209
absorption coefficient (mm^{-1})	41.14
F (000)	1832.8
crystal size (mm)	0.12 × 0.01 × 0.01
θ range (deg)	2.56−40.01
index ranges	$-30 \le h \le 30, -5 \le k \le 0, -28 \le l \le 28$
reflns collected	5983
independent reflns	2993
max and min transmission	0.680 and 0.557
refinement method	full matrix least-squares on F^2
data/restraints/params	2993/0/110
GOF on F^2	1.83
final R indices [$I > 2\sigma(I)$]	$R_{obs}(F) = 0.0524$, $wR_{obs}(F^2) = 0.1162$
R indices (all data)	$R_{all}(F) = 0.0986$, $wR_{all}(F^2) = 0.1219$
largest diff. peak and hole	7.77 and −4.91 e Å^3

parameters were observed for Bi, Cu, and O11. Moving some Bi atoms off the mirror plane resulted in a dramatic drop of reliability factors to $R_{obs}(F) = 0.0612$ and $wR_{all}(F^2) = 0.1352$. Further reduction of reliability factors was attained for the final model (Table 1), in which Cu and O11 were also moved to positions off the mirror plane. The program package JANA2006[13] was used for least-squares refinements and other calculations. Crystallographic results are summarized in Tables 1 and 2. Refinement of occupation factors gives a formula of $Bi_{1.4}CuRh_5O_{11}$. Selected interatomic distances are given in Table 3. Further details are in an available cif file in the Supporting Information.

Table 2. Atomic Coordinates, Occupation Factors (g), and Displacement Factors (U) for $Bi_{1.4}CuORh_5O_{10}$

atom	site	x	y	z	g	U^a × 100 Å^2
Bi1	8j	0.3473(1)	0.139(3)	0.3660(4)	0.25(1)	1.22(8)
Bi2	8j	0.3499(1)	0.146(2)	0.1543(3)	0.256(9)	1.21(7)
Bi3	4i	0.3481(3)	0	0.3500(1)	0.20(2)	1.8(3)
Bi4	4i	0.3505(2)	0	0.1714(7)	0.21(2)	1.5(2)
Rh1	2a	0	0	0	1	0.37(3)
Rh2	4i	0.69155(5)	0	0.43930(6)	1	0.522(19)
Rh3	4i	0.02614(5)	0	0.33642(5)	1	0.365(18)
Rh4	4i	0.52864(5)	0	0.16876(6)	1	0.431(18)
Rh5	4i	0.6891(5)	0	0.04604(6)	1	0.535(19)
Rh6	2d	0	0.5	0.5	1	0.42(3)
Cu	8j	0.1977(1)	0.0821(6)	0.2429(1)	0.5	0.44(5)
O1	4i	−0.0445(5)	0	0.4279(5)	1	0.53(13)
O2	4i	0.2092(5)	0	0.3615(6)	1	0.93(16)
O3	4i	0.575(5)	0	0.4078(5)	1	0.43(13)
O4	4i	−0.0360(5)	0	0.1160(5)	1	0.46(13)
O5	4i	0.5700(5)	0	0.0506(5)	1	0.47(13)
O6	4i	0.4710(5)	0	0.2726(5)	1	0.44(13)
O7	4i	0.8064(5)	0	0.0389(6)	1	0.82(15)
O8	4i	0.0871(5)	0	0.2318(5)	1	0.57(13)
O9	4i	0.8075(5)	0	0.4748(5)	1	0.73(15)
O10	4i	0.2064(5)	0	0.1285(6)	1	0.95(15)
O11	8j	0.2993(7)	0.545(8)	0.2539(8)	0.5	1.9(3)

[a] U_{eq} for Bi, Cu, and Rh, which were refined anisotroptically. U_{iso} for O.

Table 3. Selected Interatomic Distances (Å)

Rh1−O	2.018(8) × 2	2.071(5) × 4		
Rh2−O	2.023(6) × 2	2.028(8)	2.030(9)	2.062(6) × 2
Rh3−O	2.002(9)	2.031(5) × 2	2.047(5) × 2	2.070(9)
Rh4−O	2.025(9)	2.035(5) × 2	2.049(5) × 2	2.091(8)
Rh5−O	2.030(6) × 2	2.046(9)	2.061(6) × 2	2.070(8)
Rh6−O	2.027(5) × 4	2.064(9) × 2		
Cu−O	1.87(1)	1.904(9)	1.922(8)	2.09(2)

■ RESULTS AND DISCUSSION

The structure of $Bi_{1.4}CuORh_5O_{10}$ is shown in Figure 2. This is a framework of RhO_6 octahedra sharing corners and edges. There are undulating layers perpendicular to the a axis and tunnels along the b axis. The Rh−O framework with a composition of Rh_5O_{10} (or RhO_2) is well ordered. However, there is considerable disorder with respect to the contents of the channels ($Bi_{1.4}CuO$). A reasonable structural model in space group $C2/m$ could be obtained only with all of these channel atoms in partially occupied sites. The disorder of the Bi and Cu is shown in Figure 3, where the horizontal lines are the mirror planes of space group $C2/m$. The pairs of Cu and O atoms are both in sites that are $^1/_2$ occupied. The Cu−Cu distance in the pair is 0.505 Å, and the O−O distance in the pair is 0.277 Å. These distances are so short that only one Cu atom and one O atom can be present in each pair. The Bi atoms occur as triplets where the central Bi is on the mirror plane. The refined Bi occupancy parameters (Table 2) are such that they sum to about 70% of a Bi atom in each triplet. If each triplet were occupied by one Bi atom, the formula would be $Bi_2CuORh_5O_{10}$. This would dictate some reduction of Cu below 2+ or Rh below 3+, which is not likely for an oxide prepared in air. The Bi−Bi distances in each triplet of about 0.5 Å dictate that each Bi triplet can actually contain no more than one Bi atom. Thus locally, the mirror plane symmetry of space group $C2/m$ must be violated by Cu, Bi, and the channel O. One can envisage a structure where only one Cu site and one channel O site for each pair would be occupied, and this site would then be fully occupied. Attempts to refine such a structure in space group $C2$ were unsuccessful. Even when the space group $C2$ was taken at the beginning of the refinement for the determination of the initial model by the direct method, the refined structure possessed strong $C2/m$ pseudosymmetry and reliability factors were only very slightly improved despite the increase in number of parameters. Although there must be some short-range correlations of the displacements of Cu, Bi, and channel O off the mirror planes of space group $C2/m$, such correlations have apparently not led to a destruction of the $C2/m$

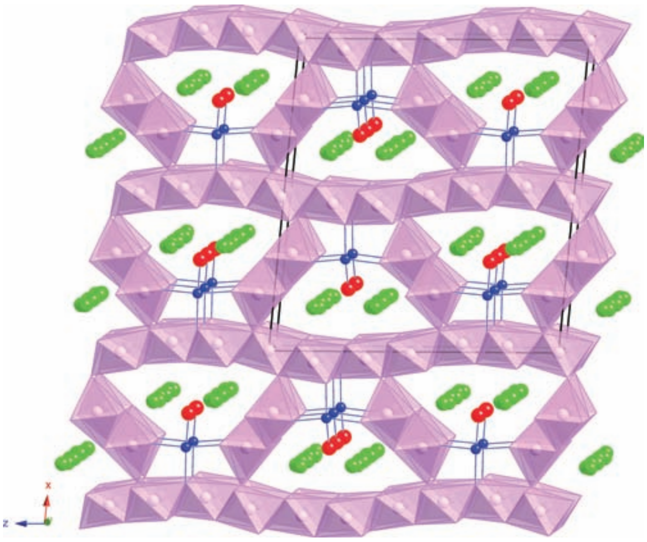

Figure 2. Undulating layers and tunnels in $Bi_{1.4}CuORh_5O_{10}$ shown as RhO_6 octahedra (purple). Channel atoms are Bi (green), Cu (blue), and O (red). The unit cell is outlined (black line).

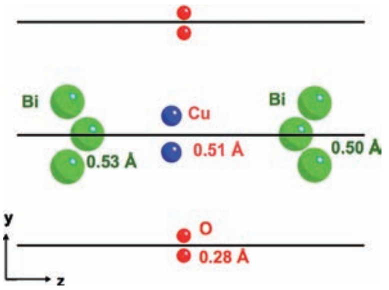

Figure 3. The channel contents with respect to the mirror planes shown as horizontal lines with interatomic distances shown. These distances are so short that a maximum of 1 atom can be present for each doublet and triplet. The Cu sites (blue) and the O sites (red) are each $^1/_2$ occupied. The left and right Bi triplets appear to be related by symmetry, but they are not.

lattice symmetry. A likely explanation is that the disorder associated with partial occupancy of Bi sites has destroyed the necessary long-range correlations required for an ordered C2 structure. In Figure 2, one Cu atom and one channel O atom have been eliminated in each pair. Because there is a bond between this Cu atom and this O atom, their positions are interrelated. The way in which Cu and O atoms were eliminated from Figure 2 gives a Cu−O distance of 2.092 Å for these channel atoms. This then gives an average distance for the four Cu−O bonds of 1.93 Å and a bond valence sum for Cu of 1.99. The coordination of Cu (Figure 4) shows a small distortion of a square planar arrangement in the direction of tetrahedral. Each channel contains two strings of Bi atoms.

There is the appearance that each tunnel has a mirror plane perpendicular to the *z*-axis (Figure 5). However, the mirror planes in the tunnels do not line up. They are displaced along the *z*-axis by about 0.7 Å. Changing β to 90° would line up these mirror planes, but this does not lead to extended mirror planes perpendicular to the *z*-axis because the RhO_2 sheets have no semblance of a mirror plane perpendicular to the *z*-axis. The linkage of the octahedra prohibits any such mirror plane.

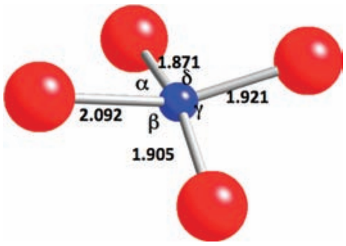

Figure 4. Coordination of Cu (blue) to O (red): Cu−O−Cu angles: α = 90.5°, β = 89.3°, γ = 94.4°, and δ = 94.1°.

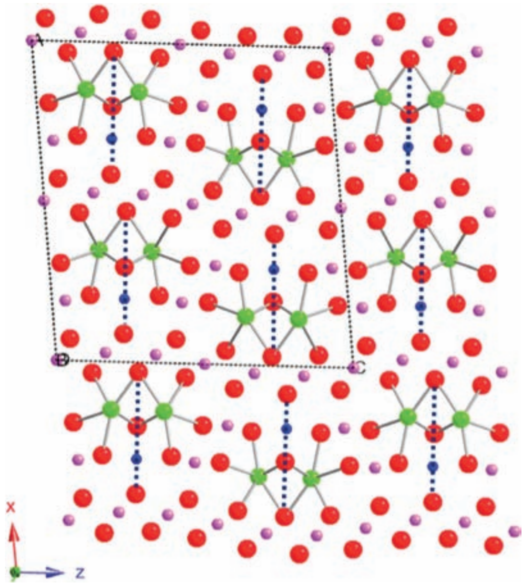

Figure 5. The $Bi_{1.4}CuORh_5O_{10}$ structure showing the "mini-mirror planes" as vertical dashed lines. These planes could not become extended mirror planes even with adjustment of the β angle.

Table 4. Bond Valence Sums (BVS)[a] for Rh and Cu with Average Bond Distances

	distance (Å)	BVS
Rh1−O	2.053	3.03
Rh2−O	2.038	3.16
Rh3−O	2.038	3.16
Rh4−O	2.047	3.08
Rh5−O	2.050	3.06
Rh6−O	2.039	3.14
Cu−O	1.947	1.99

[a] VALENCE software was used to calculate bond valences.[14] A bond valence parameter of l_0 = 1.800 was used for Rh^{4+}, which was deduced recently.[15]

Thus, these mini-mirror or pseudomirrors are not associated with pseudo-orthorhombic symmetry.

The undulating RhO_2 layers are also out of phase with each other. They displace by about 0.7 Å along the *z*-axis on going from one layer to the next. The 0.7 Å displacements of the "mini-mirrors" and the RhO_2 layers are directly related to the definition of the peak position in the layers. One can define this maximum by the highest O atom in the top of the RhO_2 layer or the highest

O atom in the bottom of this layer. These 2 O atoms are displaced from each other along the *z*-axis by about 0.7 Å, thereby causing the 0.7 Å displacement of adjacent layers and the 0.7 Å displacement of the "mini-mirrors."

If one assumes oxidation states of Bi^{3+} and Cu^{2+}, the average oxidation state of Rh is 3.16+. This then suggests that the Rh is mostly Rh^{3+} but that a small amount of Rh^{4+} is present. This is not surprising because heating a 1:1 mixture of Bi_2O_3 and Rh_2O_3 in air results in $Bi_2Rh_2O_{6.8}$ with Bi^{3+} and an average Rh oxidation state of 3.8+.[7] Bond valence sum calculations (Table 4) show that the value for Rh is always slightly above 3.0. This is then supportive of some oxidation of Rh^{3+} in $Bi_{1.4}CuORh_5O_{10}$. Electrical conductivity on a crystal of $Bi_{1.4}CuORh_5O_{10}$ was measured using two probes, which then gives a lower limit of conductivity because contact resistance is unknown (Figure 6). The observed value of 0.3 S/cm at room temperature is high enough to be consistent with a partially filled Rh $4dt_{2g}$ band.

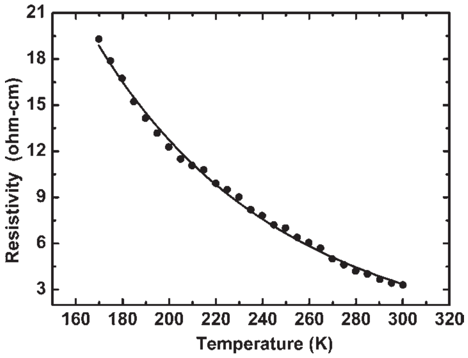

Figure 6. Electrical resistivity (two-probe) versus temperature plot for $Bi_{1.4}CuORh_5O_{10}$.

Channel structures are well-known for rhodates as shown in Figure 7. Some of these structures are also known for oxides of Mn.[17] However, the networks in $Bi_{1.4}CuORh_5O_{10}$ and $Bi_{2/3}Ce_{1/3}Rh_2O_5$ (Figure 6f) are found only for rhodates. For a network with a MO_2 composition and octahedral M cations, the average coordination of O must be three. Thus, the coordination number of O for the RhO_2 networks shown in Figure 7 is 3. However, the Rh_2O_5 network for $Bi_{2/3}Ce_{1/3}Rh_2O_5$ has some O in 2-fold coordination and some in 3-fold coordination, giving an average coordination number of 2.4. In the structure of $Bi_{1.4}CuORh_5O_{10}$, the coordination of O3 and O5 is four, and the coordination of O2 and O10 is two. All other O atoms have coordination number of three, and the average O coordination in this structure is three, as it must be for the RhO_2 network stoichiometry. Thus, the network of $Bi_{1.4}CuORh_5O_{10}$ is unique among rhodates in having undulating layers and some O in a coordination greater than as well as less than three.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic information files (CIF) of $Bi_{1.4}CuORh_5O_{10}$ from single-crystal refinements.

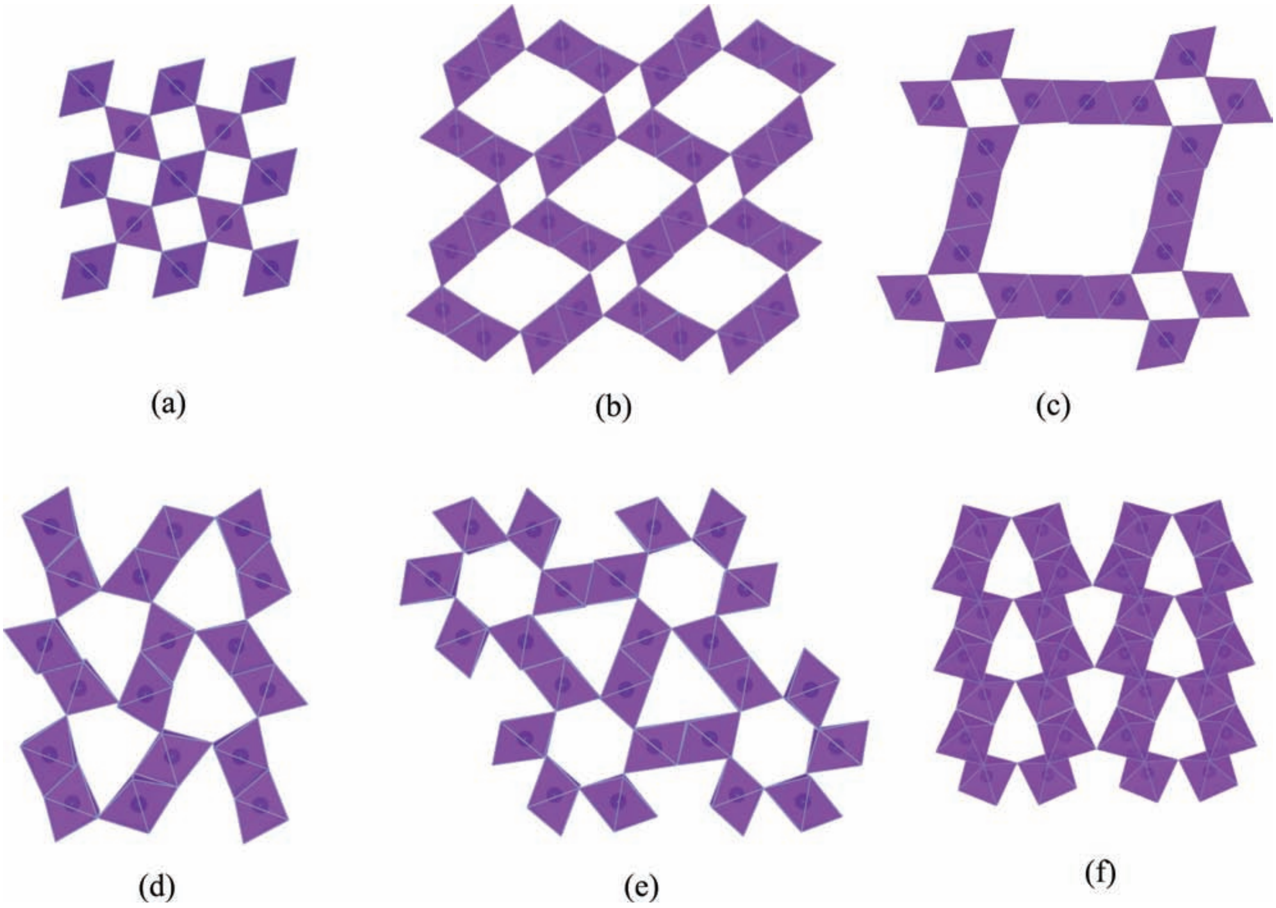

Figure 7. Known octahedral framework structures with channels in rhodium oxides:[2,4,5,16] (a) rutile RhO_2; (b) hollandite, $Ba_{1.72}Rh_8O_{16}$; (c) todorokite, $Bi_6Rh_{12}O_{29}$ (= $(Bi_6O_5)Rh_{12}O_{24}$); (d) $CaRh_2O_4$; (e) $Bi_{0.68}Be_2Rh_6O_{12}$; (f) $Bi_{2/3}Ce_{1/3}Rh_2O_5$.

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