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Synthesis and Structure of a New High-Pressure Form of Rh_2O_3*

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A new high-pressure form of Rh_2O_3 has been prepared at 65 kbar and 1200°C. Four-probe resistivity measurements made on a single crystal show Rh_2O_3 II to be a semiconductor with a room-temperature resistivity of 130 Ω cm and an activation energy of 0.16 eV.

Rh_2O_3 II is orthorhombic with $a = 5.1686 \pm 3$, $b = 5.3814 \pm 4$, $c = 7.2426 \pm 4$ Å, $Z = 4$, $D_{\text{obsd}} = 8.28$ gm/cc, $D_c = 8.36$ gm/cc, and space group, *Pbna*. Although the unit cell is similar to that of an orthorhombic perovskite, the structure, refined by least squares, is similar to that of corundum in that it contains pairs of RhO_6 octahedra which share faces. However, only two edges of each octahedra are shared with other octahedra. The structure may also be described as containing layers of the corundum structure cut parallel to $(10\bar{1}1)$, and stacked together to form the Rh_2O_3 II structure.

In the study of the crystal structures of ABO_3 phases, much attention has been given to criteria for the formation of the corundum and perovskite structures. Recently, Megaw (*1*) discussed the similarities between the lithium niobate structure, which is directly related to that of corundum, and that of perovskite. In this note, we report a new high-pressure phase of rhodium sesquioxide, Rh_2O_3 II, which has a unit cell similar to that of orthorhombic perovskite, but a structure related to that of corundum.

In these experiments, finely divided Rh_2O_3 produced by heating $RhCl_3$ in air at 800°C was placed in a Pt capsule and heated at 1200–1500°C for 1 hr at 65 kbar and quenched rapidly. Oxygen analysis of the resultant metallic-gray crystals of Rh_2O_3 II by a catalytic fusion method indicated 19% O. The calculated oxygen content of Rh_2O_3 is 18.9%. Resistivity measurements using a four-probe technique (*2*) showed a room-temperature resistivity of 130 Ω cm and an activation energy of 0.16 eV.

An X-ray diffraction pattern taken using a Hägg–Guinier camera with a KCl internal standard is given in Table I. The unit cell dimensions, refined by a least-squares technique, are $a = 5.1686 \pm 3$; $b = 5.3814 \pm 4$; and $c = 7.2426 \pm 4$ Å. The calculated density, 8.36 gm/cc, compares reasonably well to the measured density, 8.28 gm/cc. Comparison of the unit cell volume of 201.45 Å^3 for 4-formula units to 208.03 Å^3 for ambient-pressure, low-temperature rhombohedral Rh_2O_3 (*3*) and 205.56 Å^3 for the ambient-pressure, high-temperature, orthorhombic Rh_2O_3 reported by Wold et al. (*3*), indicates percentage volume changes $\Delta V/V_1$ of 3.2% and 2.0%, respectively. The space group determined by precession photographs of a single crystal was found to be $Pbna\text{–}D_{2h}^{14}$, in contrast to the space group $Pbnm\text{–}D_{2h}^{16}$ found for the orthorhombic perovskite $GdFeO_3$ (*4*, *5*).

Reid and Ringwood (*6*) recently predicted the existence of a perovskite-type Fe_2O_3 at pressures of 600–1200 kbar in shock wave experiments by McQueen and Marsh (*7*). Reid and Ringwood based their conclusion on an extrapolated zero-pressure density of 5.96 gm/cm^3, which is 14% higher than that of α-Fe_2O_3 (hematite). We originally thought that the Rh_2O_3 system might be analogous to the Fe_2O_3 system since both Rh_2O_3 I and hematite have the corundum structure and the high-pressure phases appeared to have the orthorhombic perovskite structure. However, we were suspicious of the large difference between the density changes in the

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TABLE I

POWDER DIFFRACTION PATTERN OF Rh_2O_3 II

Index	d_{obsd}	d_{calcd}	I_{obsd}
0 0 2	3.621	3.621	20
1 1 1	3.314	3.314	30
0 2 0	2.691	2.691	70
1 1 2	2.598	2.597	100
2 0 0	2.584	2.584	70
0 2 1	2.521	2.522	5
2 1 0	2.330	2.330	5
1 2 1	2.266	2.267	5
1 0 3	2.187	2.187	5
0 2 2	2.161	2.160	2
2 0 2	2.103	2.104	5
1 1 3	2.027	2.027	5
1 2 2	1.990	1.993	2
2 2 0	1.864	1.864	80
0 0 4	1.811	1.811	30
2 2 1	1.805	1.805	10
0 2 3	1.797	1.797	5
2 2 2	1.657	1.657	10
1 3 1	1.650	1.650	40
1 1 4	1.629	1.629	30
3 1 1	1.600	1.600	5
1 3 2	1.535	1.534	60
0 2 4	1.502	1.502	20
3 1 2	1.494	1.495	80
2 0 4	1.483	1.483	30
2 2 3	1.475	1.475	10
1 3 3	1.387	1.387	5
1 1 5	1.350	1.350	2
0 4 0	1.345	1.345	5
0 4 1	1.322	1.323	5
2 2 4	1.299	1.299	25
4 0 0	1.292	1.292	10

TABLE II

FINAL ATOM PARAMETERS AND INTERATOMIC DISTANCES FOR Rh_2O_3 II[a]

	x	y	z	B
Rh	0.7498(1)	0.0312(2)	0.1058(1)	0.15(4)
0(1)	0.6037(11)	0.1161(10)	0.8494(8)	0.08(8)
0(2)	0.0505(16)	$\frac{1}{4}$	0	0.14(12)

Rh–0(1, 1) $00\bar{1}$	2.055 Å
–0(1, 3) $0\bar{1}0$	2.076
–0(1, 4) 000	2.068
–0(1, 5) $0\bar{1}0$	2.017
–0(2, 1) 100	2.094
–0(2, 5) $0\bar{1}0$	1.985
Rh–0(av.)	2.050
–0(1, 5) $1\bar{1}0$	3.449
–0(1, 6) 100	3.171
–0(1, 8) $0\bar{1}\bar{1}$	3.431
–0(2, 5) $0\bar{1}0$	3.255

[a] The second number within the parentheses for each oxygen atom indicates the symmetry transformation applied to the coordinates of this atom. The numbers, *pqr*, just to the right of the parentheses are the translations applied to the transformed coordinates. For example, 0(2, 5) $0\bar{1}0$ means that symmetry transformation 5 was applied to 0(2) and then −1 was subtracted from the transformed y coordinate. The symmetry transformations are xyz; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $\frac{1}{2} - x, \bar{y}, \frac{1}{2} - z$; $x, \frac{1}{2} - y, \bar{z}$; $\bar{x}, \bar{y}, \bar{z}$; $-\frac{1}{2} + x, -\frac{1}{2} - y, -\frac{1}{2} + z$; $-\frac{1}{2} + x, y, -\frac{1}{2} - z$; $\bar{x}, -\frac{1}{2} + y, z$.

two systems. Using criteria established by Shannon and Prewitt (*8*) relating density changes with changes in coordination, it appeared that Rh_2O_3 II should contain Rh in six-coordination, whereas the high-pressure Fe_2O_3 probably contains Fe in greater than six-coordination.

To resolve this problem, the crystal structure of Rh_2O_3 II was solved using observed structure factors obtained with a Picker single-crystal diffractometer, MoKα X-rays, and a spherically ground Rh_2O_3 II crystal of 0.008-cm radius. Full-matrix least-squares refinement resulted in a discrepancy index $R(R = \Sigma \|F_0| - |F_c\| / \Sigma |F_0|)$ of 0.042. The final atom parameters and interatomic distances are given in Table II.

The Rh_2O_3 II structure is related to that of corundum in that it contains pairs of RhO_6 octahedra which share faces. However, each octahedron shares only two edges with other octahedra rather than three as in corundum. In fact, the structure may be thought of as containing slabs of the corundum structure cut parallel to $(10\bar{1}1)$ which, incidentally, is the most common twinning plane of corundum crystals. These slabs stacked together form the Rh_2O_3 II structure. Figure 1a and b are schematic representations showing the relation between the two structures. Figure 1a is the Rh_2O_3 II structure projected down the a axis. Two unit cells are shown here with only the bonds from the rhodium atoms (small circles) to the oxygen atoms in the shared octahedral face drawn in. The dashed lines from the rhodium atom in the left center of the figure indicate the other three oxygen atoms required to complete the octahedron. The dark motifs represent Rh_2O_3 units centered around $x = \frac{1}{2}$, and the light ones $x = 0$. Figure 1b shows Rh_2O_3 with the corundum structure drawn to emphasize the similar aspects of the two structures. The drawing is projected down the hexagonal a and the direction of the hexagonal c is indicated by the Rh–Rh vector

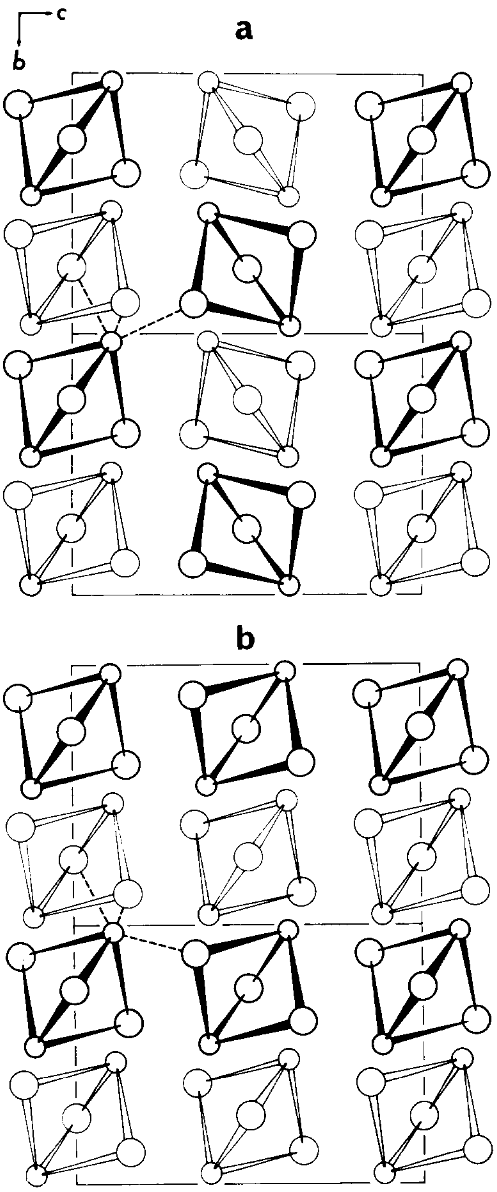

FIG. 1. (a) The Rh_2O_3 II structure projected along the a axis. The small circles are rhodium atoms and the dark motifs are centered around $x = \frac{1}{2}$ and the light ones around $x = 0$.

(b) The Rh_2O_3 I structure (corundum) projected along the hexagonal a. The hexagonal c is defined by the vector between rhodium pairs sharing a common octahedral face.

across the shared octahedral faces. In both figures the columns on the left and right of each drawing are essentially identical. The center columns are related by a twofold axis at $\frac{1}{4}, y, \frac{1}{2}$ in Fig. 1a. That is, if this operation is applied to the center column of the structure in Fig. 1a, the structure in Fig. 1b will result. Note that five of the six oxygen atoms coordinating Rh remain the same, but the sixth is different. This causes the greater distortion of the octahedra in the corundum-type structure.

The average Rh–O distance predicted for six-coordinated Rh^{3+} using effective ionic radii (*9*) is 2.045 Å. From Table II the observed average is seen to be 2.050 Å. The Rh–Rh distance is 2.80 Å, somewhat shorter than the 2.90 Å predicted for Rh_2O_3 I by Prewitt, Shannon, Rogers, and Sleight (*10*).

Summary and Conclusions

A new form of Rh_2O_3 has been synthesized which has a structure similar to that of corundum but a diffraction pattern much like that of orthorhombic perovskite. Although the new structure is denser than the Rh_2O_3 corundum structure, the oxygen atoms are not obviously more perfectly close packed than in the corundum structure although the RhO_6 octahedra are less distorted.

It is possible that ilmenite and lithium niobate equivalents of the Rh_2O_3 II structure will be found and that possibly some other phases previously thought to be orthorhombic perovskite actually have this structure.

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