

## The Preparation and Crystal Structure of a BaRhO<sub>3</sub> Polytype

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Received December 8, 1980; in final form February 16, 1981

Barium rhodium oxide, BaRhO<sub>3</sub>, was prepared at 1175°C and 60–65 kbar by the reaction of BaO<sub>2</sub> and RhO<sub>2</sub>. A hexagonal black platelet obtained in the reaction product was found to possess a four-layer stacking sequence in space group *P6<sub>3</sub>/mmc* having hexagonal unit cell parameters  $a = 5.744(1)$ ,  $c = 9.642(1)$  Å. The structure was determined from 707 independent reflections of which 224 were considered observed. Averaging equivalent reflections yielded 132 unique observed reflections. Refinement of the structure by least-squares methods gave a conventional *R* value of 4.4%. The structure consists of a four-layer stacking sequence of close-packed BaO<sub>3</sub> layers containing tetravalent rhodium in all the octahedral oxygen interstices. The compound was found to be isostructural with previously reported BaMO<sub>3</sub> phases. This is the first single-crystal refinement of the 4*H* polytype using a four-circle diffractometer.

### Introduction

The preparation of BaRhO<sub>3</sub> was attempted by the reaction of BaCO<sub>3</sub> and Rh<sub>2</sub>O<sub>3</sub> at ambient pressure under oxidizing conditions. The product obtained appeared to have a 4*H* structure (high-temperature BaMnO<sub>3</sub> polytype) based on close-packed BaO<sub>3</sub> layers. The product was always obtained in the form of a microcrystalline powder and exact structural information could not be obtained. Attempts to isolate single crystals of BaRhO<sub>3</sub> in flux-growth experiments always yielded a different phase. The ambient-pressure product and the crystal growth phases were observed to react with aqueous HCl to generate chlorine gas. This reaction was believed to proceed by a redox process involving Rh<sup>4+</sup> and the chloride ion of the acid. The Ba/Rh/O phases appeared to be strongly oxidizing and could be represented by the

general formula BaRhO<sub>3-x</sub>, where  $x$  lies between 0.1 and 0.45.

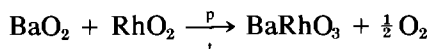
In order to obtain a stoichiometric product in the form of the single crystals, an attempt was made utilizing the high-temperature/high-pressure experiment. This method had been used previously to yield other unstable or metastable phases in single-crystal form. The results of these experiments with BaRhO<sub>3</sub> and the characterization of the product are presented.

### Experimentation

#### Preparation

The synthesis of BaRhO<sub>3</sub> was performed in a tetrahedral anvil apparatus under the following conditions: 1175°C and 60–65 kbars for 2 hr, then quenched to room temperature prior to the release of the applied pressure. The reaction can be ex-

pressed by the chemical equation:



The source of BaO<sub>2</sub>, reagent grade, was A. D. Mackay, and RhO<sub>2</sub> was obtained from K & K (as a black amorphous reagent). Since RhO<sub>2</sub> decomposes at 850°C, an excess of oxidizing agent in the form of BaO<sub>2</sub> was used to insure the stabilization of the high oxidation state of rhodium. The results of these experiments yielded large single crystals (0.4 × 0.4 × 0.1 mm) of a black product in the form of chunks and hexagonal plates. This massive product was stable to dilute HCl and the excess BaO and BaO<sub>2</sub> could be removed by this acid treatment.

#### Crystallographic Studies

The X-ray powder diffraction analysis of the product indicated a layer-type ABO<sub>3</sub> phase suggesting that the major phase was possibly a 6H polytype. Further crystallographic studies, however, indicated the presence of two (or more) polytypes in the product. Precession data taken on several single crystals showed the presence of a six-layer phase with rhombohedral and not hexagonal symmetry. For these reasons, we believe the major phase to be an 18R product and not a 6H polytype. A structure refinement on this phase is planned.

A large hexagonal plate was studied by the precession method and was found to possess hexagonal symmetry with a four-layer stacking sequence. Cone axis data confirmed this suspicion ( $c > 9.41 \text{ \AA}$ ). The space group was found to be  $P6_3/mmc$ ,  $P6_3mc$ , or  $P6\bar{3}2c$  and the unit cell parameters from the precession data suggested  $a = 5.766$  and  $c = 9.645 \text{ \AA}$ .

An energy-dispersive analysis of the crystal utilizing a scanning electron microscope confirmed the presence of Ba ( $L\alpha$ ,  $L\beta$ , and  $L\gamma$ ) and Rh ( $L\alpha$ , and  $L\beta$ ).

#### Structure Determination

The space group was assumed to be  $P6_3/mmc$  (#194) and the unit cell parameters were determined in a PICK-II least-squares refinement program using 24 reflections within the angular range  $45 < 2\theta < 53^\circ$ ; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using MoK $\alpha$  radiation ( $\lambda = 0.70930 \text{ \AA}$ ). The unit cell parameters were found to be  $a = 5.744(1)$  and  $c = 9.642(1) \text{ \AA}$ , where the figures in parentheses represent the standard deviations in the last reported figure. The calculated volume is  $275.54 \text{ \AA}^3$ , giving a calculated density, with  $Z = 4$ , of  $6.95 \text{ g cm}^{-3}$ .

No attempt was made to grind the hexagonal plate into a sphere since all previous experiments on crystals of this shape yielded only circular disks. The hexagonal plate ( $0.22 \times 0.29 \times 0.09 \text{ mm}$ ) (volume =  $4.97 \times 10^{-6} \text{ cm}^3$ ) was used for data collection. Precise dimensions of the crystal were determined with a microscope utilizing high magnification. These data were used in an absorption correction program written by N. W. Alcock and B. Lee for a crystal of general shape.

Diffraction intensities were measured using Zr-filtered MoK $\alpha$  radiation at a takeoff angle of  $1.5^\circ$  with the diffractometer operating in the  $\omega$  scan mode. Ten-second background counts were taken at both ends of a  $1.4^\circ \theta - 2\theta$  offset corrected for dispersion. Of the 707 data collected in the angular range  $2\theta < 54^\circ$ , 224 were considered observable according to the criterion  $|F_0| > 3.0\sigma_F$ , where  $\sigma_F$  is defined as  $0.02 |F_0| + [C + k^2 B]^{1/2}/2 |F_0| L_p$ ; the total scan count is  $C$ ,  $k$  is the ratio of scanning time to the total background time, and  $B$  is the total background count. Three reflections were systematically monitored as standards during the experiment; the maximum variation in intensity observed was never greater than  $\pm 3\%$  over the data collection period.

Intensity data were corrected for Lorentzian and polarization effects, and absorption corrections were carried out using the computer program already cited. The corrected data were then averaged using a program written by L. Fingers and using the hexagonal transformation for determining equivalent reflections. This generated 132 independent reflections.

### Structure Refinement

The study of the precession photographs indicated a four layer stacking sequence of BaO<sub>3</sub> layers with Rh located in octahedral interstices. Since this system was previously observed for the (high-temperature form) BaMnO<sub>3</sub> (1) and BaCrO<sub>3</sub> (2) systems, it was decided to attempt the structure refinement based on this particular polytype of BaMO<sub>3</sub> composition. The most probable space group for these hexagonal polytypes is taken as *P6<sub>3</sub>/mmc*.

A full-matrix refinement (3) using the positional parameter for five atoms, a  $1/\sigma^2$  weighting scheme, zero-valent scattering factors for Ba, Rh, and O (4), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion yielded a residual  $R = 0.11$  and a weighted residual  $R_w = 0.22$ . The final anisotropic refinement, based on a data:parameter ratio of 8.7 with the 15 independently varied parameters, yielded  $R$

$= 0.044$  and  $R_w = 0.071$  for the observed data.

Table I presents the positional and anisotropic temperature parameters from the final anisotropic refinement. Except for two ripples at the periphery of the Ba(1) atoms, the difference Fourier map was essentially flat and equivalent to 0.2 of an oxygen atom or less.

An illustration of the structure is given in Fig. 1. The figure was prepared using ORTEP (5). Bond lengths and angles calculated in the ORFFEE program are given in Table II. The table of observed and calculated structure factors comprises Table III.

### Results and Discussions

There exists only a few binary and ternary oxides of rhodium (IV). Most of these phases have been formed and crystallized under high-pressure conditions. The amorphous binary oxide, RhO<sub>2</sub>, is crystallized with the rutile structure at 3000 atm and at higher pressures (6).

More recently ternary oxides of Rh (IV) have been reported to crystallize with the pyrochlore-type structure. These publications include the derivatives Ti<sub>2</sub>Rh<sub>2</sub>O<sub>7</sub> (7), Bi<sub>2</sub>Rh<sub>2</sub>O<sub>7</sub> (8), Sc<sub>2</sub>Rh<sub>2</sub>O<sub>7</sub>, and Sm<sub>2</sub>Rh<sub>2</sub>O<sub>7</sub> (9).

No structural determination has ever been carried out on any of these rhodium

TABLE I  
ATOMIC PARAMETERS FOR BaRhO<sub>3</sub> (4H)

Atom	Position	x	y	z	$B_{11}^a$	$B_{22}^a$	$B_{33}^a$	$B_{12}^a$
Ba(1)	2a	0	0	0	0.73(8)	0.70	0.56(2)	0.35
Ba(2)	2c	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.54(7)	0.52	0.16(2)	0.26
Rh(1)	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.6137(1)	0.36(7)	0.31	0.08(2)	0.16
O(1)	6g	$\frac{1}{2}$	0	0	2.25(40)	1.11(40)	0.65(14)	0.88
O(2)	6h	-0.1799	-0.3598(16)	$\frac{1}{4}$	0.15(26)	-0.34(30)	0.45(11)	0.07

<sup>a</sup> Thermal parameters are multiplied by 100. The  $B$ 's are defined by the general temperature factor exp  $[-\frac{1}{4} B_{11} h^2 a^{*2} + B_{22} k^2 b^{*2} + B_{33} l^2 c^{*2} + 2B_{12} hka^*b^* + 2B_{13} hla^*c^* + 2B_{23} klb^*c^*]$ . For Ba and Rh atoms,  $B_{22}$  and  $B_{12}$  were not refined since  $B_{11} = B_{22}$ , and  $B_{12} = \frac{1}{2} B_{11}$ . For oxygen, the  $x$  parameter was not refined since  $x = \frac{1}{2}y$ ; and  $B_{12} = \frac{1}{2} B_{22}$ .

TABLE II  
 BOND LENGTHS AND ANGLES IN BaRhO<sub>3</sub> (4H)

Distance (Å)		Angle (°)	
Ba(1)–O(1)	6@ 2.872(1)	O(1)–O(1)	4@ 2.872(1)
Ba(1)–O(2)	6@ 3.002(5)	O(1)–O(2)	4@ 2.891(3)
		O(1)–O(2)	2@ 2.926(1)
Ba(2)–O(1)	6@ 2.926(1)	O(2)–O(2)	2@ 2.644(14)
Ba(2)–O(2)	6@ 2.875(5)	O(2)–O(1)	2@ 2.875(5)
		O(2)–O(1)	2@ 2.891(3)
		O(2)–O(2)	2@ 3.100(14)
Rh(1)–O(1)	3@ 1.988(1)	Rh–O(2)–Rh	81.43(31)
Rh(1)–O(2)	3@ 2.014(6)	Rh–O(1)–Rh	180.0
Rh–Rh	2.628(3)		
Rh–O(1)–Rh	3.976(2)		

(IV) phases but recently a mixed rhodium (III)/rhodium (IV) compound has been prepared and its structure was determined (10). The ionic formulation of the derivative is given as  $Pb_3^{2+}Rh_3^{4+}Rh_4^{3+}O_{15}^{2-}$ . Previously, the preparation of  $Pb_2Rh_2O_7$  was shown to contain trivalent rhodium and tetravalent lead atoms (11). Table IV lists the Rh–O distances for many of the trivalent and tetravalent derivatives.

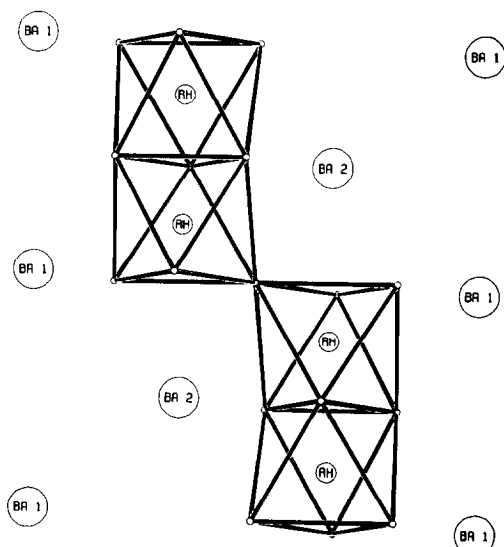


FIG. 1. The projection of the hexagonal (110) plane for BaRhO<sub>3</sub> (4H).

The calculated values for  ${}^{VI}Rh^{3+}$ –O and  ${}^{VI}Rh^{4+}$ –O distances are 2.05 and 2.00 Å, respectively (12). The observed  ${}^{VI}Rh$ –O distance in BaRhO<sub>3</sub> is 2.001 Å which is consistent with the tetravalent state for rhodium as expected.

The packing sequence for the four-layer structure is ABAC, where A layers have metal atoms at 00z, B layers at  $\frac{2}{3}\frac{1}{3}z'$ , and C layers at  $\frac{1}{3}\frac{2}{3}z'$ . The Zhdanov notation for this packing sequence is 2(2), space group  $P6_3/mmc$ . This particular structure type has been reported for BaMnO<sub>3</sub> (high-temperature phase) (1), BaCrO<sub>3</sub> (2), h.p. BaRuO<sub>3</sub> (15), SrMnO<sub>3</sub> (16, 17), and BaIrO<sub>3</sub> (18). The reported structure refinement on this BaRhO<sub>3</sub> phase is the first single-crystal determination utilizing a four-circle diffractometer.

The high pressure used in the preparation is considered to be most essential in stabilizing the high oxidation state of rhodium and in the formation of single crystals. Previous experiments at lower pressures of oxygen indicate the formation of a 4H derivative, but one possessing a much larger unit cell, indicative of a Rh(III) product of possible nonstoichiometric composition BaRhO<sub>3-x</sub>.

The observation that another polytype is

TABLE III  
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR BaRhO<sub>3</sub> (4H)

h	k	l	FOBS	FCAL	h	k	l	FOBS	FCAL	h	k	l	FOBS	FCAL	h	k	l	FOBS	FCAL
0	0	2	183	208	-2	2	3	1826	1806	-3	1	11	916	890	-4	4	9	321	324
0	0	4	1024	937	-2	2	4	924	969	-4	1	0	250	248	-5	0	0	101	92
0	0	6	562	567	-2	2	5	1088	1146	-4	1	1	80	68	-5	0	1	68	25
0	0	8	2312	2042	-2	2	6	1222	1287	-4	1	2	319	784	-5	0	2	579	540
0	0	10	332	335	-2	2	8	174	177	-4	1	3	1181	1166	-5	0	3	981	952
0	0	12	319	269	-2	2	9	413	401	-4	1	4	613	638	-5	0	4	577	594
-1	0	0	453	417	-2	2	10	396	379	-4	1	5	735	754	-5	0	5	632	632
-1	0	2	1161	1135	-2	2	11	1068	991	-4	1	6	803	835	-5	0	6	616	620
-1	0	3	1643	1670	-3	0	0	2604	2396	-4	1	7	237	249	-5	0	7	188	202
-1	0	4	833	910	-3	0	2	159	153	-4	1	8	213	210	-5	1	0	1898	1818
-1	0	5	905	994	-3	0	3	45	68	-4	1	9	249	256	-5	1	2	92	93
-1	0	6	1033	1086	-3	0	4	174	161	-4	1	10	217	221	-5	1	3	47	44
-1	0	7	325	331	-3	0	5	91	53	-4	2	0	2729	2711	-5	1	4	149	138
-1	0	8	255	248	-3	0	6	409	433	-4	2	2	108	93	-5	1	5	76	37
-1	0	9	319	311	-3	0	8	1384	1459	-4	2	4	517	538	-5	1	6	365	366
-1	0	10	277	280	-3	0	10	315	315	-4	2	6	426	448	-5	1	8	1157	1207
-1	0	11	1031	959	-3	1	0	213	216	-4	2	8	1597	1592	-5	2	0	251	243
-1	0	12	255	233	-3	1	1	66	71	-4	2	10	267	274	-5	2	1	87	94
-2	1	0	3076	2990	-3	1	2	854	841	-4	4	0	102	124	-5	2	2	747	736
-2	1	2	175	171	-3	1	3	1407	1385	-4	4	1	181	137	-5	2	3	978	994
-2	1	4	178	161	-3	1	4	763	806	-4	4	2	1016	998	-5	2	4	526	542
-2	1	6	477	508	-3	1	5	812	876	-4	4	3	1288	1266	-5	2	5	648	644
-2	1	8	1616	1633	-3	1	6	858	901	-4	4	4	667	678	-5	2	6	756	779
-2	1	10	344	337	-3	1	7	242	264	-4	4	5	836	853	-5	2	7	269	256
-2	2	0	86	110	-3	1	8	224	194	-4	4	6	913	958	-5	2	8	212	212
-2	2	1	319	248	-3	1	9	271	293	-4	4	7	166	131	-6	1	0	156	154
-2	2	2	1629	1554	-3	1	10	231	228	-4	4	8	168	165	-6	1	1	52	53
0	0	2	183	208	-2	2	3	1826	1806	-3	1	11	916	890	-4	4	9	321	324
0	0	4	1024	937	-2	2	4	924	969	-4	1	0	250	248	-5	0	0	101	92
0	0	6	562	567	-2	2	5	1088	1146	-4	1	1	80	68	-5	0	1	68	25
0	0	8	2312	2042	-2	2	6	1222	1287	-4	1	2	319	784	-5	0	2	579	540
0	0	10	332	335	-2	2	8	174	177	-4	1	3	1181	1166	-5	0	3	981	952
0	0	12	319	269	-2	2	9	413	401	-4	1	4	613	638	-5	0	4	577	594
-1	0	0	453	417	-2	2	10	396	379	-4	1	5	735	754	-5	0	5	632	632
-1	0	2	1161	1135	-2	2	11	1068	991	-4	1	6	803	835	-5	0	6	616	620
-1	0	3	1643	1670	-3	0	0	2604	2396	-4	1	7	237	249	-5	0	7	188	202
-1	0	4	833	910	-3	0	2	159	153	-4	1	8	213	210	-5	1	0	1898	1818
-1	0	5	905	994	-3	0	3	45	68	-4	1	9	249	256	-5	1	2	92	93
-1	0	6	1033	1086	-3	0	4	174	161	-4	1	10	217	221	-5	1	3	47	44
-1	0	7	325	331	-3	0	5	91	53	-4	2	0	2729	2711	-5	1	4	149	138
-1	0	8	255	248	-3	0	6	409	433	-4	2	2	108	93	-5	1	5	76	37
-1	0	9	319	311	-3	0	8	1384	1459	-4	2	4	517	538	-5	1	6	365	366
-1	0	10	277	280	-3	0	10	315	315	-4	2	6	426	448	-5	1	8	1157	1207
-1	0	11	1031	959	-3	1	0	213	216	-4	2	8	1597	1592	-5	2	0	251	243
-1	0	12	255	233	-3	1	1	66	71	-4	2	10	267	274	-5	2	1	87	94
-2	1	0	3076	2990	-3	1	2	854	841	-4	4	0	102	124	-5	2	2	747	736
-2	1	2	175	171	-3	1	3	1407	1385	-4	4	1	181	137	-5	2	3	978	994
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-2	1	8	1616	1633	-3	1	6	858	901	-4	4	4	667	678	-5	2	6	756	779
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-2	2	0	86	110	-3	1	8	224	194	-4	4	6	913	958	-5	2	8	212	212
-2	2	1	319	248	-3	1	9	271	293	-4	4	7	166	131	-6	1	0	156	154
-2	2	2	1629	1554	-3	1	10	231	228	-4	4	8	168	165	-6	1	1	52	53

TABLE IV  
RHODIUM-OXYGEN DISTANCES (Å) FOR SEVERAL  
DERIVATIVES

Compound	Rh(III)-O	Rh(IV)-O	Reference
$\alpha$ -Rh <sub>2</sub> O <sub>3</sub>	2.05	—	13
Rh <sub>2</sub> O <sub>3</sub> (II)	2.05	—	14
RhO <sub>2</sub>	—	2.02	6
Pb <sub>2</sub> Rh <sub>2</sub> O <sub>7</sub>	2.02 (for $x = 0.343$ )	—	11
Pb <sub>3</sub> Rh <sub>7</sub> O <sub>18</sub>	2.05 (two sites)	2.00	10
BaRhO <sub>3</sub>	—	2.001	This work

also formed in the high-pressure/high-temperature reaction is of significance. The precession photographs show a six-layer stacking sequence but the overall symmetry is rhombohedral which means that the true packing sequence must be at least 18 layers. The structure determination on 4H BaRhO<sub>3</sub> would suggest that face sharing of octahedral RhO<sub>6</sub> plays an important part in the stabilization of the structure. This information will be useful in developing suitable structural models for the 18-layer rhombohedral polytype.

### Acknowledgments

We wish to acknowledge the financial support from the UConn Research Foundation and NSF INT-7717719. Computations were carried out at the University of Connecticut Computer Center.

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