Short Communications

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The crystal structure of Rh_2O_3.

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The structure of the hexagonal form of Rh_2O_3 has been refined using powder methods. The space group is $R\bar{3}c$, and it has the corundum structure with $a_H = 5{\cdot}127 \pm 0{\cdot}001$, $c_H = 13{\cdot}853 \pm 0{\cdot}004$ Å, $x(O) = 0{\cdot}295 \pm 0{\cdot}010$ and $z(Rh) = 0{\cdot}348 \pm 0{\cdot}001$.

Rhodium sesquioxide has been found in two forms. A hexagonal form having the corundum structure with $a_R = 5.47$ Å and $\alpha = 55°40'$ was identified first (Lunde, 1927). It transforms into an orthorhombic form described by Wold, Arnott & Croft (1963) when heated above 750°C. In this note X-ray powder diffraction results for the hexagonal form are presented.

The lattice parameters were obtained from photographs taken in a 114·6 mm Debye–Scherrer camera, and the integrated intensities of the reflexions in Table 1 were measured using a powder diffractometer. All measurements were made at 23°C with Fe $K\alpha$ radiation. Our sample, a grey powder of reagent grade Rh_2O_3, was obtained from Alfa Inorganics, Beverly, Mass., U.S.A. It was reported to contain 80·91% Rh and the only impurities which could be detected by X-ray fluorescence were 0·2% Pd, 0·1% Ru and 0·1% Sn. It was apparent from the diffractometer trace that roughly 10% of the oxide was in the orthorhombic form. However when the orthorhombic pattern was subtracted off, all the remaining lines could be assigned indices consistent with the space group $R\bar{3}c$. The overlapping was significant only for the hexagonal reflexions 012, 104, 110, 024, 211, 134 and 1,1,12.

Table 1. *Powder pattern for* Rh_2O_3 (*hexagonal form*)

h	k	l	d_{obs}	d_{calc}	I/I_1
0	1	2	3·68 Å	3·738 Å	53
1	0	4	2·731	2·731	88
1	1	0	2·567	2·564	100
0	0	6	2·309	2·309	11
1	1	3	2·242	2·241	7
2	0	2	2·116	2·114	6
0	2	4	1·870	1·869	37
1	1	6	1·717	1·716	53
2	1	1	1·667	1·666	1
1	2	2	1·633	1·631	7
0	1	8	1·615	1·513	2
2	1	4	1·512	1·510	33
3	0	0	1·482	1·480	30
1	2	5	1·436	1·436	1
2	0	8	1·366	1·365	1
1	0	10	1·321	1·322	16
1	1	9		1·320	
2	2	0	1·281	1·282	15
2	1	7		1·280	
0	3	6	1·245	1·246	16
2	2	3	1·236	1·235	1
3	1	2	1·213	1·213	4

Table 1 (*cont.*)

h	k	l	d_{obs}	d_{calc}	I/I_1
1	2	8	1·205	1·205	1
0	2	10	1·175	1·175	17
1	3	4	1·161	1·160	22
0	0	12	1·154	1·154	1
2	2	6	1·121	1·121	25
0	4	2	1·096	1·096	2
2	1	10	1·068	1·068	36
4	0	4	1·057	1·057	12
1	1	12	1·053	1·053	6
3	2	1	1·014	1·016	1
2	3	2	1·008	1·008	4
1	2	11		1·007	
3	1	8	1·003	1·004	5
3	2	4	0·9773	0·9773	90*

* Estimated from photographs.

We find $a_H = 5.127 \pm 0.001$, $c_H = 13.853 \pm 0.004$ Å, the equivalent rhombohedral parameters being $a_R = 5.485$ Å and $\alpha = 55°44'$. $Z = 6$. The calculated density is 8.02 g.cm^{-3}. In order to find the special position parameters for the oxygen and rhodium ions we used a computer to minimize the residual $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with respect to variations in B, the temperature factor, and u and w, the special position parameters for oxygen and rhodium in the rhombohedral structure factor. These factors were obtained from the integrated intensities using the relation $I \propto j[(1 + \cos^2 2\theta)/(\cos\theta \sin^2\theta)]F^2 \exp[-B(\sin\theta/\lambda)^2]$ where j is the multiplicity of the reflexion. No correction was made for anomalous scattering. Only the 24 lines which were observed, resolved, and did not appreciably overlap orthorhombic lines were used in the calculation. The resulting values are $u(O) = 0{\cdot}295 \pm 0{\cdot}010$, $w(Rh) = 0{\cdot}098 \pm 0{\cdot}001$ and $B = 1{\cdot}2 \pm 0{\cdot}4$, the equivalent hexagonal parameters being $x(O) = 0{\cdot}295 \pm 0{\cdot}010$ and $z(Rh) = 0{\cdot}348 \pm 0{\cdot}001$. The corresponding value of R was 13·4%. Values of u, w, and B in agreement with these could also be obtained by minimizing $\Sigma w(|F_o| - |F_c|)^2$ regardless of whether w was taken as 1, F_o^{-2}, or a function similar to that proposed by Evans (1961). Finally we recalculated R using all 33 observed reflexions and found $R = 13{\cdot}2\%$. The observed and calculated structure factors are listed in Table 2, and those used in the structure determination are marked with a dagger.

The structure may be considered as an arrangement of oxygen anions in hexagonal close packed layers, normal to the c axis, which has been distorted by the presence of small

Table 2. *Structure factors for* Rh_2O_3 *(hexagonal form)*

h	*k*	*l*	F_{obs}	F_{calc}	*h*	*k*	*l*	F_{obs}	F_{calc}
0	1	2	52·0	58·4	2	2	3†	27·9	−11·5
1	0	4	96·2	−108·4	1	3	1†	10·5	−3·5
1	1	0	156·9	127·2	3	1	2†	36·4	40·0
0	0	6†	104·7	−85·8	1	2	8†	19·6	20·1
1	1	3†	35·9	26·5	0	2	10†	98·5	98·5
2	0	2†	35·7	38·2	1	3	4	75·8	−74·9
0	2	4	101·8	−107·1	0	0	12†	66·0	61·8
1	1	6†	135·8	−120·0	3	1	5	—	−3·2
2	1	1†	16·7	8·7	2	2	6†	113·4	−92·1
1	2	2†	37·3	38·0	0	4	2†	32·8	42·5
0	1	8†	28·8	29·3	2	1	10†	88·5	95·0
2	1	4†	87·3	−94·9	4	0	4†	70·8	−66·1
3	0	0†	121·3	135·2	1	1	12	48·8	36·4
1	2	5†	13·9	7·4	3	2	1†	11·8	−6·5
2	0	8†	20·5	19·3	2	3	2	—	26·1
1	0	10	—	112·4	1	2	11	—	5·2
1	1	9	—	15·7	3	1	8†	25·2	24·2
2	2	0	—	100·8	2	2	9	—	−9·1
2	1	7	—	6·5	3	2	4	76·1*	−76·9
0	3	6†	68·3	−75·9					

* Estimated.
† These reflexions were used in the determination of *u*, *w* and *B*.

Table 3. *Cation–cation separations in corundum structure sesquioxides*

Oxide	Cation electron configuration	r_c	r_c/c_H	r_a	r_a/a_H
Al_2O_3	$2p^6$	2·65 Å	0·204	2·79 Å	0·586
Ti_2O_3	$3d^1$ (t_{2g}^1)	2·59	0·190	2·99	0·581
V_2O_3	$3d^2$ (t_{2g}^2)	2·70	0·193	2·88	0·582
Cr_2O_3	$3d^3$ (t_{2g}^3)	2·65	0·195	2·89	0·583
Rh_2O_3	$4d^6$ (t_{2g}^6)	2·72	0·196	3·03	0·590
Fe_2O_3	$3d^5$ $(t_{2g}^3 e_g^2)$	2·900	0·211	2·971	0·590
Ga_2O_3	$3d^{10}$ $(t_{2g}^6 e_g^4)$	2·835	0·211	2·938	0·590

rhodium cations in two thirds of the octahedral interstices. Compared with α-Fe_2O_3 (Blake, Hessevick, Zoltai & Finger, 1966), the cations lie closer to the planes mid-way between the oxygen layers, and the oxygen octahedra are more distorted since Rh^{3+} is a larger ion than Fe^{3+}. Each rhodium ion has 6 oxygen neighbours, three at 2·03 ± 0·03 Å and three at 2·07 ± 0·04 Å. Within an oxygen octahedron the distance between oxygen ions in the same layer is either 2·62 ± 0·09 or 3·14 ± 0·05 Å and the distance between adjacent oxygen ions in different layers is 2·78 ± 0·02 or 2·94 ± 0·02 Å. The separation of a *c*-axis cation pair, r_c, is 2·72 ± 0·02 Å and of a 'basal plane' pair, r_a, is 3·03 ± 0·01 Å. In Table 3 these distances are compared with those found in other sesquioxides with the corundum structure using some of the data of Newnham & de Haan (1962), and Marezio & Remeika (1967).

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