Die Moleküle ordnen sich in Schichten parallel zur *ac*-Ebene an. Innerhalb dieser Schichten besteht eine dichteste Kugelpackung der Molekülschwerpunkte.*

Diese Arbeit wurde von der Deutschen Forschungsgemeinschaft, dem Fonds der Chemischen Industrie und der Badischen Anilin- & Sodafabrik unterstützt. Für diese hochherzige Förderung sprechen wir unseren besten Dank aus.

Literatur

ALLERHAND, A. & GUTOWSKY, H. S. (1965). *J. Amer. Chem. Soc.* **87**, 4092.

---

* Inzwischen wurde die Bullvalenstruktur auch von anderer Seite unabhängig gelöst. Soweit aus der Kurzmitteilung (Johnson, McKechnie, Lin & Paul, 1967) zu ersehen ist, sind beide Ergebnisse identisch.

DOERING, W. VON E. & ROTH, W. R. (1963). *Angew. Chem.* **75**, 27. International Edition **2**, 115.
DUNITZ, J. D., FELDMANN, H. G. & SCHOMAKER, V. (1952). *J. chem. Phys.* **20**, 1078.
GRAHAM, J. D. & SANTEE, E. R. (1966). *J. Amer. Chem. Soc.* **88**, 3453.
HOPPE, W. (1957). *Acta Cryst.* **10**, 750.
HOPPE, W. & PAULUS, E. F. (1967). *Acta Cryst.* **23**, 339.
HUBER, R. (1965). *Acta Cryst.* **19**, 353.
JEFFREY, G. A. & SAX, M. (1963). *Acta Cryst.* **16**, 1196.
JOHNSON, S. M., KCKECHNIE, J. S., LIN, B.T.-S. & PAUL, I. C. (1967). *J. Amer. Chem. Soc.* **89**, 7123.
MERENYI, R., OTH, J. F. & SCHRÖDER, G. (1964). *Chem. Ber.* **97**, 3150.
NEWTON, M. G. & PAUL, I. C. (1966). *J. Amer. Chem. Soc.* **88**, 3161.
ROGERS, M. T. (1947). *J. Amer. Chem. Soc.* **69**, 2544.
SCHRÖDER, G. (1964). *Chem. Ber.* **97**, 3140.
TOLLIN, P., MAIN, P. & ROSSMANN, M. G. (1967). *Acta Cryst.* **20**, 404.

Crystal Structure of a High-Pressure Form of B₂O₃

BY C. T. PREWITT AND R. D. SHANNON

Central Research Department*, E.I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898, *U.S.A.*

B₂O₃ II is a high-pressure phase of boron oxide first reported by Dachille & Roy. Crystals for this work were grown in a tetrahedral anvil at 65 kbar and 1100°C and quenched to room temperature. The crystals are orthorhombic with $a = 4\cdot613 \pm 0\cdot001$, $b = 7\cdot803 \pm 0\cdot002$, $c = 4\cdot129 \pm 0\cdot001$ Å, $Z = 4$, $D_o = 3\cdot14$, $D_c = 3\cdot11$ g.cm⁻³, space group $Ccm2_1$, and are weakly piezoelectric. The structure, which has been refined by least squares, consists of a network of corner-linked $(BO_4)^{5-}$ tetrahedra. Within each tetrahedron there are three long B–O distances of 1·507, 1·506, and 1·512 Å, and one short distance of 1·373 Å. The oxygen associated with the short distance is coordinated by only two boron atoms, whereas the other is coordinated by three boron atoms. Unlike the low-pressure hexagonal form, B₂O₃ I, B₂O₃ II is relatively unaffected by hot water or hot concentrated hydrochloric acid. It can be heated in air to just below its melting point without reverting to the ambient pressure structure. In addition, the density of B₂O₃ II is greater by 27% (3·11 vs. 2·44). Another phase reported by Dachille & Roy was also present in the product from the high-pressure runs. This fine-grained material is cubic with $a = 8\cdot914$ and is probably cubic metaboric acid (γ-HBO₂).

Introduction

The high-pressure form of B₂O₃ was reported by Dachille & Roy (1959) who first synthesized this material in a Bridgman uniaxial device at 35 kbar and 525°C. Dachille & Roy and, subsequently, Mackenzie & Claussen (1961) prepared phase diagrams which show the lower pressure limits for synthesis to be about 20 kbar. Although the compounds produced in both investigations appeared to be identical, there were certain inconsistencies and no attempt was made to solve the crystal structure of the new form.

Because of the uncertainty surrounding the nature of high-pressure B₂O₃ and, indeed, of the whole B₂O₃ system, we grew crystals of the high-pressure phase and

---

solved the crystal structure with X-ray diffraction methods. This paper is a report of this investigation.

Previous work

Without making an exhaustive survey of previous investigations of B₂O₃, it is interesting to trace the history of attempts to synthesize and characterize the crystalline material. Apparently Cole & Taylor (1935) were the first to report diffraction data on a crystalline phase of B₂O₃ which they made by heating H₃BO₃ under vacuum at 200°C and then sintering at higher temperatures up to 290°C. The product was cubic with $a = 10\cdot03$ Å, $D_o = 1\cdot805$ g.cm⁻³, and $D_c = 1\cdot818$ g.cm⁻³. The density of B₂O₃ glass as reported by Cole & Taylor is 1·844 g.cm⁻³, which is higher than the density of this cubic phase. Later authors have discounted the

Cole & Taylor work, however, assuming that their product was not really B_2O_3. Kracek, Morey & Merwin (1938) and McCulloch (1939) independently prepared crystalline forms of B_2O_3 by heating H_3BO_3 in open containers for very long periods at temperatures around 240 °C. Berger (1953) has proposed a structure for this material which is hexagonal with $a = 4.334$, $c = 8.334$ Å, $D_o = 2.44$ g.cm^{-3}, and $D_c = 2.56$ g.cm^{-3}.

An interesting investigation of crystallization phenomena and the effect of high pressure on B_2O_3 has been conducted by Uhlmann, Hays & Turnbull (1967). In this work the 'B_2O_3 crystallization anomaly' was defined. This anomaly is that it has been impossible to grow crystals of B_2O_3 at atmospheric pressure from a dry B_2O_3 melt, even when the melt was seeded with B_2O_3 I crystals.

Since it is possible that both low-pressure forms have legitimate B_2O_3 structures, it may be necessary at some time to alter the following naming conventions. In this paper, the low-pressure hexagonal phase will be called B_2O_3 I and the high-pressure one B_2O_3 II, corresponding to Mackenzie & Claussen's α-B_2O_3 and β-B_2O_3, respectively. The latter convention is not a good one for naming pressure-related polymorphs and is therefore not followed in this paper.

Experimental

The high-pressure experiments were performed in a manner similar to that of Bither, Gillson & Young (1966) and Shannon (1967). Each powdered sample was pressed at 20,000 lb.in^{-2} into a small pellet and placed in a cylindrical Pt capsule. This assembly was placed in the center of a pyrophyllite tetrahedron, pressurized to 65 kbar, held at temperature for 1 hr, and quenched. The Pt capsule was used as its own heater; rapid quenching was achieved by cutting off the power. Since an estimated gradient of 100–300 °C existed from the center to the ends of the capsule, samples were not necessarily homogeneous.

Several starting materials were used. The first was a mixture which had previously been prepared as a possible fluorescent host by Borchardt (1967). This mixture, which consisted of 98% B_2O_3 (Baker purified) and 2% Eu_2O_3 (Lindsay 99.9%), was heated at 700 °C for 4 hr in air. The X-ray powder pattern indicated (1) the major phase to be identical with an unindexed phase reported by Senkovits & Hawley* as B_2O_3 and (2) a minor phase to be $EuBO_3$. This mixture, after pressurizing to 65 kbar at 800 °C was a gray, translucent sintered pellet. An X-ray powder pattern from this pellet showed no trace of the starting materials, $B_2O_3.nH_2O$ and $EuBO_3$; however, many of the strong lines in the powder pattern corresponded to the high-

pressure phase of B_2O_3 reported by Dachille & Roy (1959).

A second source was Baker purified B_2O_3. Thermogravimetric analysis of this 'B_2O_3' showed a 17.3% weight loss from 80–350 °C which was presumably from water of hydration. In an attempt to grow crystals of B_2O_3 II this material was heated at 1200 °C (65 kbar) and quenched. The center of the capsule contained large, transparent, colorless crystals whose X-ray pattern could be indexed as cubic with a cell edge of 8.901 Å. This material is probably cubic metaboric acid (γ-HBO_2) whose reported cell edge is 8.886 Å (Zachariasen, 1963a). These crystals dissolved rapidly in H_2O.

At the cold end of the capsule, transparent colorless crystals, $\frac{1}{2} \times \frac{1}{2}$ mm, of B_2O_3 II were found. These crystals were insoluble in hot water and hot concentrated hydrochloric acid. The density of these crystals, as determined by the displacement method in bromoform, was 3.14. The crystals, observed under a hot stage microscope, showed melting at 525 °C. This observed melting point was confirmed by (1) a high temperature X-ray powder diffraction pattern which showed no change up to a temperature of 525 °C, and (2) an endothermic differential thermal analysis peak at 550 °C. Mackenzie & Claussen (1961) noted melting of B_2O_3 II at 475–520 °C, depending on heating rate. B_2O_3 II was found to be an insulator with a room-temperature resistivity of 2×10^9 ohm-cm, as measured by the four-probe technique described by Bither et al. (1966). Hardness measurements carried out on a Wilson Tukon testing machine with three crystals of B_2O_3 II embedded in 'Lucite'® acrylic resin resulted in values of KHN_{25} of 900–1000 kg.mm^{-2}. Hardness of materials synthesized at high pressures should be greater because of defects introduced in the process. Therefore, these values represent an upper limit to the hardness. Furthermore there is some question as to hardness determined on samples embedded in 'Lucite'®.

A final experiment was performed by heating anhydrous Baker purified B_2O_3 to 1200 °C at 65 kbar and cooling at 100 °C per hr to 400 °C where the specimen was quenched. The entire sample was found to be B_2O_3 II.

Cell dimensions for B_2O_3 II from a least-squares refinement (13 observations) of de Wolff–Guinier photograph data are $a = 4.613 \pm 0.001$, $b = 7.803 \pm 0.002$, $c = 4.129 \pm 0.001$ Å, with $V = 148.64$ Å^3, $Z = 4$, $D_o = 3.14$, $D_c = 3.11$ g.cm^{-3}, and μ(Cu $K\alpha$) = 27.3 cm^{-1}. The space group, determined from precession photographs and a positive test for piezoelectricity, is $Ccm2_1$. Mackenzie & Claussen (1961) reported a monoclinic cell with $a = 4.52$, $b = 4.14$, $c = 4.64$, and $\beta = 120°25'$.

This latter cell can be related to the orthorhombic cell by the transformation

$$\mathbf{a}_o = \mathbf{c}_m$$
$$\mathbf{b}_o = 2\mathbf{a}_m + \mathbf{c}_m$$
$$\mathbf{c}_o = \mathbf{b}_m .$$

---

* ASTM Powder Diffraction File, No. 13–570. This is reported as '99% pure, with water as impurity'. We find that the material in fact contains 39.1 wt.% water. It could be a new form of H_3BO_3 which contains a calculated content of 43.7% water.

Close examination of Weissenberg and precession photographs, plus the refinement results, indicate that the orthorhombic cell is the correct choice.

Crystal structure and refinement

A structure for B_2O_3 II was proposed from consideration of the space group and the probability that the oxygen atoms were in a closest-packed arrangement. To test this hypothesis, all available reflections were collected with a Picker automatic diffractometer, using Ni-filtered Cu $K\alpha$ radiation and a scintillation detector with pulse-height analysis. Each peak was integrated at a scan speed of 1° per minute, with 40-second backgrounds at the extremes of each scan. The intensities were converted to structure factors using a computer program, ACACA, written by Prewitt (1966a) which uses the Wuensch & Prewitt (1965) method for calculating absorption corrections. Although the crystal shape was somewhat irregular, it was approximated by a rectangular prism of dimensions $0.11 \times 0.15 \times 0.23$ mm. At this stage the Zachariasen (1963c) secondary extinction parameter β was calculated for use later in the least-squares refinement. Sigmas for each reflection were computed with the use of

$$\sigma_F = (\text{Lp } T)^{-\frac{1}{2}}[(I+\sigma_I)^{\frac{1}{2}} - I^{\frac{1}{2}}]$$

where L, p, and T are the Lorentz, polarization, and transmission factors, respectively, I is the integrated intensity, and

$$\sigma_I = \left[E + \left(\frac{T_E}{2T_B}\right)^2 (B_1+B_2) + \varepsilon^2 I^2\right]^{\frac{1}{2}}.$$

Here E is the total count plus background, T_E and T_B are peak and background times, B_1 and B_2 are background counts, and ε, set in this case to 0.03, is to account for fluctuations in direct beam intensity. In all, 462 reflections were collected. These reflections and their σ's were subsequently reduced to a unique set of 81 reflections.

After a preliminary structure factor calculation indicated the proposed structure was correct, this structure was refined with a full-matrix, least-squares program written by Prewitt (1966b). In this program the quantity minimized is $\Sigma w||F_o| - |F_c||^2$ and the discrepancy index, R, is equal to $\Sigma ||F_o| - |F_c||/\Sigma |F_o|$. Several cycles of refinement of scale factor, positional parameters, and isotropic temperature factors reduced R to 0.079 but resulted in negative temperature factors for all atoms. At this point the secondary extinction parameter, C, where $F_{corr} = F_o[1 + \beta CI_o]$, was varied, which resulted in reasonable isotropic temperature factors. After further cycles with all parameters varied, including anisotropic temperature factors, the unweighted R for all reflections was 0.028 and the weighted R was 0.034. Examination of structure factors at this stage of refinement showed that the strongest reflections were still affected by extinction. Therefore, another cycle was run in which the twelve reflections for which

$\beta CI_o > 0.25$ were not included. Although the change in positional parameters was negligible, there were small shifts in the orientations of the thermal vibration ellipsoids. Both the unweighted and weighted R's were 0.022 for the reflections included in the last cycle. R for all reflections was 0.031. Atomic scattering factors used for the refinement to this point were the curves for neutral B and O taken from International Tables for X-ray Crystallography (1962). Two more cycles were run with the curve for B^{3+} from International Tables and that for O^{2-} from Tokonami (1965). The latter results were not significantly different from those for which neutral B and O curves were used.

Table 1 gives the final observed and calculated structure factors. Table 2 gives a list of the final refined parameters obtained from the 'neutral scattering factor' cycle with $R=0.022$. Table 3 is a compilation of the magnitudes and orientations of the thermal vibration ellipsoids. The values in Table 3 and the distances and angles in Table 4 were obtained with the Busing, Martin & Levy (1962) program ORFFE.

Table 1. Observed and calculated structure factors

Quantities given are h, k, l, $100 F_o$, and $100 F_c$. Reflections not included in final cycle of refinement are marked with *.

h	k	l	$100F_o$	$100F_c$		h	k	l	$100F_o$	$100F_c$		h	k	l	$100F_o$	$100F_c$
2	0	0	2831	3312*		4	2	1	311	314*		2	0	3	3076	3233
4	0	0	1696	1638		1	3	1	2981	2702*		4	0	3	966	965
1	1	0	1733	1805*		3	3	1	683	689		1	1	3	1671	1670
3	1	0	1360	1356		4	4	1	1775	1820		3	1	3	911	925
5	1	0	48	10		4	4	1	487	482		2	2	3	2224	2281
0	2	0	3311	3426*		1	5	1	1134	1136		4	2	3	529	524
2	2	0	1369	1324		3	5	1	1939	1971		1	3	3	2293	2254
4	2	0	2664	3014*		2	6	1	1060	1095		2	4	3	459	442
1	3	0	3054	3065*		1	7	1	2681	2622*		1	5	3	1888	1875
3	3	0	2510	2555		3	7	1	428	429*		3	5	3	1192	1152
5	3	0	306	306		0	8	1	561	583		2	6	3	886	879
0	4	0	2987	2852*		0	0	2	5665	5659*		1	7	3	1052	1054
2	4	0	1200	1227		2	0	2	2071	2027		0	0	4	515	539
4	4	0	425	417		4	0	2	1055	1034		2	0	4	735	735
1	5	0	2283	2257		1	1	2	721	707		1	1	4	151	141
3	5	0	1957	1991		3	1	2	706	719		3	1	4	276	280
0	6	0	2559	2456		0	2	2	2228	2074*		2	2	4	1718	1773
2	6	0	1511	1499		2	2	2	1122	1096		4	0	4	810	819
4	6	0	138	142		2	2	2	2043	2046		1	3	4	412	414
1	7	0	908	934		1	3	2	1408	1426		0	4	4	1389	1355
3	7	0	518	520		3	3	2	1275	1302						
0	8	0	464	458		0	4	2	2457	2342						
2	8	0	516	522		2	4	2	1030	998						
1	9	0	207	202		4	4	2	1114	1064						
4	0	1	3234	3068*		1	5	2	1403	1438						
1	1	1	841	829		3	5	2	1199	1199						
1	1	1	2894	2718*		0	6	2	2019	1966						
3	1	1	1677	1709		2	6	2	1188	1196						
5	1	1	688	685		1	7	2	1250	1233						
2	2	1	2759	2476*		2	8	2	274	276						

Table 2. Final atom parameters* for B_2O_3 II

Standard deviations are in parentheses.

The temperature factors are the coefficients in the expression
$$\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$$
For O(1), $\beta_{12} = \beta_{23} = 0$.

	B	O(1)	O(2)
x	0.1606 (4)	0.2475 (3)	0.3698 (3)
y	0.1646 (3)	0	0.2911 (1)
z	0.4335 (9)	0.5	0.5802 (8)
β_{11}	0.007 (1)	0.003 (1)	0.0085 (9)
β_{22}	0.0017 (4)	0.0026 (4)	0.0015 (3)
β_{33}	0.007 (1)	0.011 (1)	0.005 (1)
β_{12}	0.0002 (5)	0	0.0006 (3)
β_{13}	−0.0015 (9)	−0.0003 (5)	−0.0001 (6)
β_{23}	−0.0009 (5)	0	−0.0004 (4)
B_{eq}	0.45	0.55	0.49
B_{11}	0.57	0.26	0.72
B_{22}	0.42	0.62	0.37
B_{33}	0.36	0.76	0.37
B_{12}	0.03	0.00	0.08
B_{13}	−0.12	−0.02	−0.01
B_{23}	0.12	0.00	−0.05

Table 3. *Magnitudes and orientations of thermal ellipsoids*

Standard deviations are in parentheses.

		r.m.s. amplitude	Angles with respect to *a*	*b*	*c*
B	r_1	0·06 (1) Å	76 (15)°	58 (17)°	36 (12)°
	r_2	0·076 (8)	59 (18)	142 (19)	69 (19)
	r_3	0·091 (7)	35 (18)	71 (16)	118 (12)
O(1)	r_1	0·06 (1)	2 (5)	90	88 (5)
	r_2	0·089 (7)	90	0	90
	r_3	0·098 (6)	92 (5)	90	2 (5)
O(2)	r_1	0·069 (9)	98 (8)	40 (25)	51 (27)
	r_2	0·072 (7)	80 (8)	127 (26)	39 (27)
	r_3	0·097 (5)	13 (7)	77 (6)	93 (7)

Table 4. *Interatomic distances and interbond angles*

Standard deviations are in parentheses.

B–O(1)	1·373 (3) Å
–O(2)	1·507 (2)
–O(2′)	1·506 (3)
–O(2″)	1·512 (2)
O(ave)	1·475
O(1)–O(2)	2·364 (1)
–O(2′)	2·440 (2)
–O(2″)	2·409 (2)
O(2)–O(2′)	2·428 (2)
–O(2″)	2·394 (1)
O(2′)–O(2″)	2·388 (2)
B–B′	2·569 (5)
–B″	2·664 (3)
–B‴	2·664 (3)
–B⁗	2·592 (3)
O(1)–B–O(2)	110·2 (2)°
–O(2′)	115·8 (2)
–O(2″)	113·1 (2)
O(2)–B–O(2′)	107·4 (2)
–O(2″)	104·9 (2)
O(2′)–B–O(2″)	104·7 (1)
O–B–O (ave)	109·4
B–O(1)—B′	138·6 (3)
B–O(2)—B″	123·8 (2)
B–O(2″)–B‴	123·8 (2)
B–O(2′)–B⁗	118·7 (2)

Symmetry transformations: B′ $(x,\bar{y},z)$, B″ $(\frac{1}{2}+x,\frac{1}{2}-y,z)$, B‴ $(-\frac{1}{2}+x,\frac{1}{2}-y,z)$, B⁗ $(\frac{1}{2}-x,\frac{1}{2}-y,-\frac{1}{2}+z)$, O(2′) $(\frac{1}{2}-x, \frac{1}{2}-y,-\frac{1}{2}+z)$, O(2″) $(-\frac{1}{2}+x,\frac{1}{2}-y,z)$.

Final equivalent isotropic temperature factors (Hamilton, 1959) of 0·45 for B, 0·55 for O(1), and 0·49 for O(2) are comparable to those obtained by Zachariasen (1963a) in cubic metaboric acid and to those of many other boron–oxygen compounds (*e.g.* Clark, Appleman & Christ, 1964). The thermal vibrations are not notably anisotropic. Perhaps the most significant result of the anisotropic refinement is that the major axis of O(1) is approximately parallel to c and almost bisects the B–O(1)–B′ angle (Fig. 1), whereas the major axis of O(2) is approximately normal to the bisector of the B–O(2)–B″ angle. Although the calculated errors for the B ellipsoid are large, the orientation of the major axis is roughly normal to the B–O(1) direction which represents the shortest B–O distance.

Discussion of the structure

Fig. 1 shows a tetrahedral model of the B_2O_3 II structure. Although the refinement started from a point based on closest-packed oxygen atoms, the actual structure is distorted considerably from this arrangement. The tetrahedral linkage is similar to that in wurtzite (ZnS) or $LiGaO_2$ (Marezio, 1965) except that in B_2O_3 II, only two-thirds of the tetrahedra are occupied. Furthermore, interatomic distances and angles (Table 4) show the tetrahedra to be very distorted, with one short B–O(1) distance of 1·373 Å and three long B–O(2) distances of 1·507, 1·506, and 1·512 Å. The average B–O distance is 1·475 Å, exactly that proposed by Zachariasen (1963b) as an average tetrahedral B–O distance. The oxygen associated with the short B–O distance is coordinated by only two boron atoms, whereas the other is coordinated by three borons. If electrostatic bond strengths are taken from Zachariasen's table of bond strength *versus* B–O bond length, the net bond strength is 3·01 around B, 1·96 around O(1), and 2·03 around O(2), thus showing that the distortions are necessary to balance the electrostatic charge in the crystal.

The average O–O distance in the tetrahedra is about 2·40 Å, resulting in B–O(1)–B angles of 138·6 and B–O(2)–B angles averaging 122°. The average tetrahedral O–B–O angle is 109·4°.

It is difficult to tell whether the Berger (1953) B_2O_3 I structure is correct. In the assigned space group, $P3_1$, there is only one equipoint, 3(*a*). Since $Z=3$, there are two B and three O locations. If the structure is tetrahedral, then two oxygen atoms must be coordinated by three boron atoms and the other oxygen by two boron atoms. Berger's structure, based on Guinier and Seeman–Bohlin powder data, does contain such an arrangement, but the B–O distances, which range from 1·31 to 2·15 Å, are not reasonable. Furthermore the data have not been refined and Berger gives no R value.

Marezio (1967) has suggested that, in analogy to the borates and metaboric acids, at least three B_2O_3 structures might be expected, one with BO_4^{5-} tetrahedra, one with BO_3^{3-} triangles, and one or more with mixed tetrahedra and triangles. Since the B_2O_3 II structure definitely consists of tetrahedra, it is possible that the hexagonal structure contains one boron in triangular and one in tetrahedral coordination. This structure would require that two oxygen atoms be coordinated by two boron atoms, and the other by three boron atoms. To carry the analogy further, the Cole & Taylor (1935) cubic material could contain boron in triangular coordination with all the oxygen two-coordinated. The densities of the three compounds are consistent with this picture, with 3·11, 2·56, and 1·82 g.cm⁻³ for B_2O_3

II, B_2O_3 I, and the Cole & Taylor material, respectively. A similar variation in density with coordination occurs in the metaboric acids.*

The structure of B_2O_3 glass has been studied by X-ray (Warren, Krutter & Morningstar, 1936), nuclear magnetic resonance (Bray & Silver, 1960), and infrared (Simon, 1960) techniques. Although some controversy about details exists, there is general agreement that in the glass structure the boron is triangularly coordinated. Since the density of B_2O_3 glass is only slightly larger than that of the cubic B_2O_3, there may be some relation between the two structures. That others have not been able to repeat the Cole & Taylor experiments remains puzzling. Perhaps the starting materials are important. Kracek *et al.* (1938) found that the presence of cubic metaboric acid was necessary to initiate crystallization of B_2O_3 I from B_2O_3 glass.

It is interesting to note that in our relatively short-term experiments, B_2O_3 II melts at 525–550 °C without reverting to B_2O_3 I. The exact melting temperature of B_2O_3 II is in doubt since Mackenzie & Claussen (1961) found 50% glass in a four-day run at 475 °C. However,

---

* After this paper was written, a report of a reinvestigation of B_2O_3 I became available (G. E. Gurr, P. W. Montgomery, C. D. Knutson, and B. T. Gorres, *Crystal Structure of Trigonal B_2O_3*, ACA meeting, Minneapolis, Minnesota, August 20–25, 1967). According to this report, boron is coordinated by three oxygen atoms in B_2O_3 I, thus nullifying the above argument for mixed coordinations in this compound. The possibility still exists that other B_2O_3 phases could be synthesized whose structures consist of mixed coordination geometries. It must be admitted, however, that the existence of only three-coordinated boron in the B_2O_3 I structure does add doubt to the validity of the Cole & Taylor B_2O_3.

the melting point of B_2O_3 II is probably higher than that of B_2O_3 I and considerably higher than that of the cubic material which melts at 294 °C.

The authors wish to acknowledge the help of Mr C. L. Hoover for performing the high-pressure experiments, Dr J. F. Whitney, Miss M. S. Licis and Mr E. P. Moore for assistance in obtaining the X-ray data, and Mr J. L. Gillson for performing the resistivity measurements. We also wish to thank Prof. D. R. Uhlmann and Mr R. L. Mozzi of Massachusetts Institute of Technology for valuable comments on the B_2O_3 system.

References

BERGER, S. V. (1953). *Acta Chem. Scand.* 7, 611.
BITHER, T. A., GILLSON, J. L. & YOUNG, H. S. (1966). *Inorg. Chem.* 5, 1559.
BORCHARDT, H. J. (1967). Paper presented at Sixth Rare Earth Research Conference, Gatlinburg, Tennessee, May 3–5, 1967.
BRAY, P. J. & SILVER, A. H. (1960). *Modern Aspects of the Vitreous State.* Vol. 1, pp. 92–119. New York: Butterworths.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORNL-TN-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
CLARK, J. R., APPLEMAN, D. E. & CHRIST, C. L. (1964). *J. Inorg. Nucl. Chem.* 26, 73.
COLE, S. S. & TAYLOR, N. W. (1935). *J. Amer. Ceram. Soc.* 18, 55.
DACHILLE, F. & ROY, R. (1959). *J. Amer. Ceram. Soc.* 42, 78.
HAMILTON, W. C. (1959). *Acta Cryst.* 12, 609.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
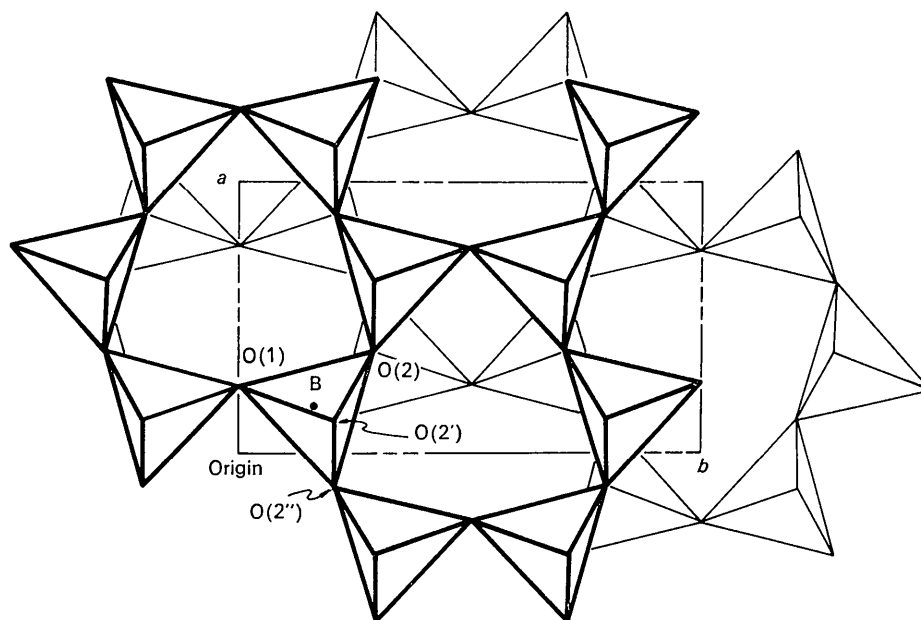
Fig. 1. The B_2O_3 II structure. The direction of c is down, into the page.

KRACEK, F. C., MOREY, G. W. & MERWIN, H. E. (1938). *Amer. J. Sci.* 35A, 143.

McCULLOCH, L. (1939). *J. Amer. Chem. Soc.* 59, 2650.

MACKENZIE, J. D. & CLAUSSEN, W. F. (1961). *J. Amer. Ceram. Soc.* 44, 79.

MAREZIO, M. (1965). *Acta Cryst.* 18, 481.

MAREZIO, M. (1967). Personal communication.

PREWITT, C. T. (1966a). Unpublished computer program for absorption corrections.

PREWITT, C. T. (1966b). Unpublished computer program for crystallographic least-squares refinement.

SHANNON, R. D. (1967). *Inorg. Chem.* 6, 1474.

SIMON, S. (1960). *Modern Aspects of the Vitreous State.* Vol. 1, 120–151.

TOKONAMI, M. (1965). *Acta Cryst.* 19, 486.

UHLMANN, D. R., HAYS, J. F. & TURNBULL, D. (1967). *Phys. Chem. Glasses,* 8, 1.

WARREN, B. H., KRUTTER, H. & MORNINGSTAR, O. (1936). *J. Amer. Ceram. Soc.* 19, 202.

WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* 122, 24.

ZACHARIASEN, W. H. (1963a). *Acta Cryst.* 16, 380.

ZACHARIASEN, W. H. (1963b). *Acta Cryst.* 16, 385.

ZACHARIASEN, W. H. (1963c). *Acta Cryst.* 16, 1139.

The Crystal Structure of ReCl5

BY KENNETH MUCKER, GORDON S. SMITH AND QUINTIN JOHNSON

Lawrence Radiation Laboratory, University of California, Livermore, California, U.S.A.

ReCl5 forms monoclinic crystals with lattice constants: $a=9.24$, $b=11.54$, $c=12.03$ Å; $\beta=109.1°$. The space group is $P2_1/c$, and the unit cell contains eight ReCl5 units. Full-matrix, least-squares refinement of diffractometrically measured X-ray diffraction data resulted in a final R of 9.3% (all reflections). The structure is based on a double-hexagonal closest packing of chlorine atoms, in which rhenium atoms occupy one-fifth of the octahedral holes. Two such octahedra share an edge to form a dimeric Re_2Cl_{10} unit. The Re–Cl bond distances involving bridging Cl average to 2.465 ± 0.013 Å; the average bond length to nonbridging Cl is 2.244 ± 0.012 Å. Rhenium atoms in the Re_2Cl_{10} units are each shifted by about 0.20 Å from the centers of the octahedra in directions away from one another. The packing mode of Cl in ReCl5 contrasts with a hexagonal closest packing of Cl in TaCl5 and a cubic closest packing of Cl in UCl5. Of these, ReCl5 exhibits both the highest density and the smallest interatomic distances.

Introduction

Four compounds in the rhenium–chlorine system are known (Colton, 1965): $ReCl_3$, $ReCl_4$, $ReCl_5$ and $ReCl_6$. The pentachloride is a dark brown to black material, melting at 220°C. It is moisture-sensitive and highly reactive; a few of its chemical reactions have recently been investigated (Cotton, Robinson & Walton, 1967).

Our interest in ReCl5 stems from the variety of crystal structures assumed by the pentachlorides. Examples include: ionic structures – PCl_4^+ and PCl_6^- in PCl_5 (Powell, Clark & Wells, 1940); trigonal, bipyramidal molecules – $SbCl_5$ (Ohlberg, 1959); bridged M_2Cl_{10} dimers – $NbCl_5$ (Zalkin & Sands, 1958); $MoCl_5$ (Sands & Zalkin, 1959); UCl_5 (Smith, Johnson & Elson, 1967); and infinite chains of edge-shared pentagonal bipyramids – $PaCl_5$ (Dodge, Smith, Johnson & Elson, 1967). Five-coordination, we note, is avoided in all except SbCl5. The present investigation shows ReCl5 to be of the bridged-dimer type, but of a different crystallographic variety.

Experimental

Our sample of ReCl5 was kindly provided by Dr D. Brown of the Atomic Energy Research Establishment, Harwell, England. Dr Brown informed us that the material was prepared by the thermal decomposition of $ReCl_6$ in a dry nitrogen atmosphere. Microscopic examination of the sample-tube showed a number of suitably sized crystals. The tube was opened in a dry-box and a half-dozen or so crystals were sealed off in thin-walled glass capillaries for X-ray examination. The reactive nature of ReCl5 was evidenced by the fact that samples left open overnight in the dry-box developed traces of a brown liquid (possibly $ReOCl_4$).

Single-crystal diffraction photographs showed monoclinic symmetry; the systematic extinctions ($h0l$, $l=2n+1$; $0k0$, $k=2n+1$) are those uniquely characterizing the space group $P2_1/c$ (*International Tables for X-ray Crystallography*, 1952). Refined values of the lattice constants are (Mo $K\alpha=0.7107$ Å); $a=9.24$, $b=11.54$, $c=12.03$ Å; $\beta=109.1°$ (probable errors estimated as about 0.3%). The density calculated for eight ReCl5 units per unit cell is 3.98 g.cm^{-3}.

Intensity measurements were carried out on a General Electric XRD-5 diffractometer equipped with a goniostat. The crystal specimen was an irregularly shaped plate, approximately 0.22 mm in length and 0.14×0.07 mm in cross section. The stationary crystal-stationary counter technique (Furnas, 1957) was used; the radiation was Zr-filtered Mo $K\alpha$. A total of 1127 reflections were recorded up to a 2θ-cutoff of 40°. Because of the irregular shape of the crystal and a rather large linear absorption coefficient ($\mu=233$ cm^{-1} for