The Crystal Structure of Boron Oxide

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The crystal structure of B_2O_3 is of particular interest, because it is one of the most difficult inorganic substances to crystallize. Until 1937 the oxide had been known only in the vitreous state. Crystallization was first accomplished by McCulloch [1] and apparently independently also by Kracek, Morey and Merwin [2]. The determination of the crystal structure was, however, first accomplished by the present author in 1950—1951. The results, which have been summarized in a preliminary note [3], are reported in more detail in this paper.

PREPARATION OF CRYSTALLINE B_2O_3

Crystalline B_2O_3 was prepared by the methods of McCulloch [1] and of Kracek, Morey and Merwin [2]. A closer study of the conditions under which crystalline B_2O_3 can be formed gave results, which were in agreement with the report of the latter authors.

The boric acid was dehydrated in open Pyrex glass vessels at about 240° C (McCulloch [1]). After heating for twenty-four hours the preparation was a highly viscous liquid with a water content of nearly 20 mole per cent. The subsequent dehydration and crystallization process then proceeded very slowly. Small spheroidal aggregates of crystalline B_2O_3 — identified as such by powder photographs — appeared at the glass walls after about a week. However, the crystallization of the whole mass, leading to a white stony substance, was in most cases completed only after several months. In a few cases, however, an extremely rapid dehydration, immediately accompanied by crystallization, occurred after heating for about two weeks. This phenomenon is also reported by McCulloch, who speaks of the "volcanic violence" of the reaction. A rapid crystallization could always be effected by seeding a boric acid melt, which still contained water, with a small amount of crystalline B_2O_3.

A simple and relatively rapid method of obtaining crystalline B_2O_3, which does not require any seeds, makes use of the fact that the stable modification of metaboric acid — denoted by Kracek, Morey and Merwin as HBO_2 I — can readily be dehydrated with the formation of crystalline B_2O_3. If a melt of boric acid is kept at about 175° C one obtains a viscous liquid with a slowly increasing precipitation of crystalline HBO_2 I. This phase gives off water forming crystalline B_2O_3 and this process can be accelerated by raising the

temperature to slightly below the melting point of HBO_2 I (236° C). It is probable that the violent reaction mentioned above also takes place via HBO_2 I. The temperature may in these cases have been below the melting point of HBO_2 I.

Single crystals could not be isolated from the products of crystalline B_2O_3 obtained by the above methods. In order to obtain larger crystals experiments were carried out in which boric acid melts containing different amounts of water were heated in sealed Pyrex tubes, enclosed in an autoclave. These experiments were not successful, probably owing to the fact that the autoclave did not permit heating at temperatures above 300° C.

As a consequence, the structure determination had to be carried out from powder data only, which considerably increased the difficulties.

UNIT CELL

All powder photographs were taken with CuK radiation. The reflections in the range $\sin^2\Theta \leq 0.510$ were obtained in a camera of the Guinier type, using monochromatized Cu$K\alpha$ radiation. The range $\sin^2\Theta \geq 0.510$ was covered by means of cameras of the Seeman-Bohlin type.

The crystalline products gave — after separation from small amounts of glassy substance — excellent powder photographs with sharp lines. They could be completely interpreted by means of a hexagonal unit cell with the axial lengths $a = 4.334$ Å and $c = 8.334$ Å. According to Hendricks [4], McMurdie has indexed powder diffraction patterns of crystalline B_2O_3 based on a hexagonal lattice having $a = 4.33$ Å and $c = 8.392$ Å, which is in good agreement with the above result.

The density of the crystalline B_2O_3 was found to be 2.44 g/cm³. McCulloch and Kracek et al. give the values 2.42 and 2.46 g/cm³ respectively. The density calculated on the basis of 3 B_2O_3 per unit cell with a volume of 135.6 Å³ is 2.56 g/cm³.

The intensities of the diffraction lines in the Guinier photograph were obtained from a microphotometer record. Values of $p|F|^2$ were calculated from the intensities by means of an intensity expression derived for Guinier cameras by Hägg (private communication).

The exact intensity expression is rather cumbersome but Hägg has shown that it can be approximated with good accuracy by the following formula, valid for the relative intensities in a given photograph without air absorption (exposure in vacuum):

$$I = C \frac{1 + \cos^2 2\Theta_m \cdot \cos^2 2\Theta}{\sin^2\Theta \cdot \cos\Theta} \cdot \frac{1}{\cos(2\Theta - a)} \cdot e^{-\frac{\mu t}{2\cos(2\Theta - a)}} \left[1 - e^{-\frac{\mu_f h}{\cos(2\Theta - a)}} \right] p|F|^2$$

Here Θ_m = the glancing angle in the monochromator crystal, a = the angle between the beam incident on the plane specimen and the normal of the latter, μ = absorption coefficient of specimen, t = thickness of specimen, μ_f = absorption coefficient of the emul-

sion layer, h = thickness of the emulsion layer. For Kodak x-ray film and CuKα radiation $\mu_r h = 0.13$. The product μt must be determined separately for each specimen.

The intensities of the diffraction lines in the Seeman-Bohlin photographs were visually estimated and based on the relation $I_\beta : I_{\alpha 2} : I_{\alpha 1} = 2 : 5 : 11$ as the relative values for CuK radiation. Values of $p|F|^2$ were calculated from the intensities by means of the intensity expression given by Hägg-Regnström [5]:

$$I = C \frac{1 + \cos^2 2\Theta}{\sin^2\Theta \cdot \cos\Theta} \frac{1}{\sin(2\Theta - a) + \sin a} A_a \cdot A_p \cdot A_f \cdot p|F|^2$$

Provided the experimental conditions are constant all factors preceeding p are functions of Θ only. The intensities and the powder diffraction data are given in Table 1.

SPACE GROUP AND STRUCTURE

Two different methods (a dynamical method and a Giebe-Scheibe method) were tried in order to test the crystalline B_2O_3 for piezoelectricity, but no effect could be detected. Because of the small size of the crystallites this negative result is not conclusive.

Of the absences required in the trigonal and hexagonal space groups only the absence of $00l$ for $l \neq 3n$ or for $l \neq 6n$ (the line observed at $\sin^2\Theta = 0.0761$ may as well be 102 as 003) is compatible with the observed interferences. This makes space groups containing three- or sixfold screw-axes probable.

Among the non-rhombohedral space groups one can immediately exclude the ones which do not contain threefold positions as such a position is necessary for placing the nine oxygen atoms in the cell. Furthermore the space groups $C_{3v}^1 - C3m$, $C_{3v}^2 - C31m$, $C_6^1 - C6$ and $C_{6v}^1 - C6mm$, where all points in the sixfold positions have the same c-coordinate, can be excluded. From spatial considerations six oxygen atoms can not be accomodated in such a position and as a consequence all oxygen atoms have to be placed in positions of lower multiplicity. As a result the a and b coordinates of all oxygen positions are governed by a maximum of two parameters. The contribution of the oxygen atoms to reflections $hk0$ could, therefore, easily be calculated and showed the impossibility of these four space groups.

It can be assumed that the structure of B_2O_3 is either built up of BO_3 triangles or BO_4 tetrahedra or a combination of both of these coordination figures. Among the remaining space groups are some (namely $C_{3i}^1 - C\bar{3}$, $D_{3d}^1 - C\bar{3}1m$, $D_{3d}^3 - C\bar{3}m$, $C_{6h}^1 - C6/m$ and $D_{6h}^1 - C6/m\ mm$) in which practically all positions have such point symmetries, that one can decide whether they can accomodate the centre of a BO_3 triangle or a BO_4 tetrahedron. The orientation of the symmetry elements also indicates the orientation of the coordina-

tion figure in question. The knowledge of the approximate dimensions of a BO_3 triangle and a BO_4 tetrahedron then makes it fairly simple to decide whether the available space or the approximate intensity distribution permit these structures. It was found that they could all be excluded.

The following space groups then remain: C_3^1-C3, $C_3^2-C3_1$ ($=C_3^3-C3_2$), D_3^1-C312, D_3^2-C32, $D_3^3-C3_112$ ($=D_3^5-C3_212$), $D_3^4-C3_12$ ($=D_3^6-C3_22$), $C_{3h}^1-C\bar{6}$, $C_6^4-C6_2$ ($=C_6^5-C6_4$), $D_{3h}^1-C\bar{6}m2$, $D_{3h}^3-C\bar{6}2m$, D_6^1-C62, $D_6^4-C6_22$ ($=D_6^5-C6_42$).

Of these space groups C_3^1-C3, D_3^1-C312, D_3^2-C32, $C_{3h}^1-C\bar{6}$, $D_{3h}^1-C\bar{6}m2$, $D_{3h}^3-C\bar{6}2m$, D_6^1-C62 are less probable as they do not require the absence of $00l$ for $l\neq 3n$. It was also found impossible to base a structure on any of these groups.

The remaining five enantiomorphic pairs all require the absence of $00l\neq 3n$. As it seemed hardly possible to obtain acceptable structures in any of the four more symmetrical of these pairs, the efforts were finally concentrated on $C_3^2-C3_1$ ($=C_3^3-C3_2$), which is contained in the others as a subgroup.

The only position in $C_3^2-C3_1$ is general and threefold. The placing of six boron and nine oxygen atoms on positions of this kind implies the determination by trial-and-error methods of fifteen parameters (of which fourteen are independent). As a result a set of parameters has been found, which give good intensity values as well as an acceptable distribution in space. The parameters are as follows:

O_I	:	0.20,	0.15,	0.00,
O_{II}	:	0.46,	0.79,	0.07,
O_{III}	:	0.51,	0.23,	0.56,
B_I	:	0.54,	0.15,	0.02,
B_{II}	:	0.59,	0.77,	0.26.

Observed and calculated $p|F|^2$ values are given in Table 1.

DISCUSSION OF THE STRUCTURE

The structure of B_2O_3 thus found is built up of two sets (a and b) of BO_4 tetrahedra, reproduced in Fig. 1. The projection of the unit cell is given parallel to [001]. Each type (a and b) of tetrahedra forms a spiral chain, which is seen from Fig. 2, showing a stereoscopic view of the arrangement of the tetrahedra. The spirals are connected in a way that each oxygen atom belongs to two spiral chains. If the function of an oxygen atom is characterized by the types of tetrahedra to which it belongs the oxygen atoms of an a tetrahedron may be

Table 1. Powder diffraction data of $B_2O_3 \cdot CuK$ radiation.

Int.	hkl	$p\|F\|^2_{Obs.}$	$p\|F\|^2_{Calc.}$	$\sin^2\Theta_{Obs.}$	$\sin^2\Theta_{Calc.}$
		Guinier camera			
vw	100	12	34	0.0420	0.0420
m	101	305	234	.0506	.0505
vs	$\begin{Bmatrix}102\\003\end{Bmatrix}$	946	$\begin{Bmatrix}804\\157\end{Bmatrix}$	.0761	$\begin{Bmatrix}.0761\\.0767\end{Bmatrix}$
s	103	762	652	.1188	.1187
w	110	120	192	.1261	.1261
vs +	111	1 000	1 014	.1348	.1346
w +	112	230	177	.1603	.1602
vw	200	66	73	.1686	.1681
w +	$\begin{Bmatrix}201\\104\end{Bmatrix}$	398	$\begin{Bmatrix}79\\401\end{Bmatrix}$	.1780	$\begin{Bmatrix}.1766\\.1784\end{Bmatrix}$
m	$\begin{Bmatrix}202\\113\end{Bmatrix}$	526	$\begin{Bmatrix}561\\54\end{Bmatrix}$	.2024	$\begin{Bmatrix}.2022\\.2028\end{Bmatrix}$
w	203	186	137	.2450	.2448
w +	105	274	239	.2551	.2550
—	114	—	171	—	.2624
w	210	148	98	.2943	.2942
m	$\begin{Bmatrix}211\\204\end{Bmatrix}$	845	$\begin{Bmatrix}494\\226\end{Bmatrix}$	.3034	$\begin{Bmatrix}.3027\\.3044\end{Bmatrix}$
—	006	—	71	—	.3068
w	212	202	305	.3281	.3282
w	115	218	149	.3391	.3391
w	106	295	347	.3488	.3488
w	213	138	274	.3710	.3708
w	$\begin{Bmatrix}300\\205\end{Bmatrix}$	330	$\begin{Bmatrix}171\\215\end{Bmatrix}$	.3797	$\begin{Bmatrix}.3782\\.3811\end{Bmatrix}$
vw	301	102	179	.3873	.3867
m	302	339	378	.4125	.4123
m	$\begin{Bmatrix}214\\116\end{Bmatrix}$	525	$\begin{Bmatrix}478\\65\end{Bmatrix}$	.4307	$\begin{Bmatrix}.4305\\.4328\end{Bmatrix}$
m	303	308	230	.4557	.4549
w	107	176	135	.4604	.4596
vw	206	98	62	.4751	.4748
m	$\begin{Bmatrix}220\\215\end{Bmatrix}$	418	$\begin{Bmatrix}57\\451\end{Bmatrix}$	.5070	$\begin{Bmatrix}.5043\\.5072\end{Bmatrix}$
		Seeman-Bohlin cameras			
m	$\begin{Bmatrix}220a\\215a\end{Bmatrix}$	418	$\begin{Bmatrix}57\\451\end{Bmatrix}$	.5070	$\begin{Bmatrix}.5043\\.5072\end{Bmatrix}$
vw	$\begin{Bmatrix}221a\\304a\end{Bmatrix}$	53	$\begin{Bmatrix}94\\179\end{Bmatrix}$	.5140	$\begin{Bmatrix}.5128\\.5145\end{Bmatrix}$

vw	222a	57	128	.5387	.5383
vw	$\begin{cases}117a\\310a\end{cases}$	118	$\begin{cases}69\\188\end{cases}$	.5462	$\begin{cases}.5436\\.5463\end{cases}$
w +	$\begin{cases}311a_1\\311a_2\end{cases}$	423	$\begin{cases}228\\105\end{cases}$	.5561	$\begin{cases}.5540\\.5566\end{cases}$
w +	$\begin{cases}312a_1\\223a_1\\312a_2\\223a_2\\207a_1\end{cases}$	455	$\begin{cases}185\\126\\85\\58\\136\end{cases}$	.5818	$\begin{cases}.5794\\.5800\\.5823\\.5829\\.5846\end{cases}$
—	$\begin{cases}108a_1\\207a_2\end{cases}$	—	$\begin{cases}9\\61\end{cases}$	—	$\begin{cases}.5864\\.5875\end{cases}$
—	$\begin{cases}108a_2\\305a_1\end{cases}$	—	$\begin{cases}4\\91\end{cases}$	—	$\begin{cases}.5893\\.5902\end{cases}$
—	$305a_2$	—	42	—	.5931
w	$\begin{cases}216a_1\\216a_2\end{cases}$	164	$\begin{cases}198\\91\end{cases}$	.6006	$\begin{cases}.5999\\.6029\end{cases}$
w	$\begin{cases}313a_1\\313a_2\end{cases}$	354	$\begin{cases}289\\133\end{cases}$	.6231	$\begin{cases}.6220\\.6251\end{cases}$
—	$224a_1$	—	109	—	.6395
—	$224a_2$	—	50	—	.6427
vw +	$\begin{cases}118a_1\\400a_1\end{cases}$	148	$\begin{cases}78\\23\end{cases}$	.6708	$\begin{cases}.6703\\.6713\end{cases}$
—	$\begin{cases}118a_2\\400a_2\end{cases}$	—	$\begin{cases}36\\11\end{cases}$	—	$\begin{cases}.6736\\.6747\end{cases}$
—	$401a_1$	—	13	—	.6798
w +	$\begin{cases}314a_1\\401a_2\\306a_1\\314a_2\end{cases}$	370	$\begin{cases}146\\6\\53\\67\end{cases}$	.6830	$\begin{cases}.6815\\.6832\\.6839\\.6849\end{cases}$
—	$306a_2$	—	24	—	.6873
—	$009a_1$	—	25	—	.6891
—	$009a_2$	—	12	—	.6925
—	$402a_1$	—	173	—	.7052
—	$402a_2$	—	80	—	.7087
vw	$\begin{cases}217a_1\\208a_1\\217a_2\end{cases}$	177	$\begin{cases}209\\157\\96\end{cases}$	.7129	$\begin{cases}.7105\\.7122\\.7140\end{cases}$
—	$\begin{cases}208a_2\\225a_1\end{cases}$	—	$\begin{cases}72\\77\end{cases}$	—	$\begin{cases}.7158\\.7161\end{cases}$
—	$225a_2$	—	35	—	.7197
vw	$\begin{cases}109a_1\\109a_2\end{cases}$	93	$\begin{cases}195\\90\end{cases}$	.7311	$\begin{cases}.7310\\.7347\end{cases}$
—	$403a_1$	—	58	—	.7478
—	$403a_2$	—	27	—	.7519
vw	$\begin{cases}315a_1\\315a_2\end{cases}$	14	$\begin{cases}47\\22\end{cases}$	.7599	$\begin{cases}.7580\\.7618\end{cases}$
—	$307a_1$	—	93	—	.7944

vw	$\left.\begin{array}{l}320a_1\\307a_2\\320a_2\end{array}\right\}$	95	$\left.\begin{array}{l}68\\43\\31\end{array}\right\}$	.7984	$\left.\begin{array}{l}.7971\\.7984\\.8011\end{array}\right\}$
—	$321a_1$	—	110	—	.8056
—	$404a_1$	—	42	—	.8074
vw	$\left.\begin{array}{l}321a_2\\226a_1\\404a_2\\226a_2\end{array}\right\}$	104	$\left.\begin{array}{l}51\\39\\19\\18\end{array}\right\}$	.8120	$\left.\begin{array}{l}.8096\\.8097\\.8114\\.8137\end{array}\right\}$
—	$119a_1$	—	17	—	.8150
—	$119a_2$	—	8	—	.8191
vw	$\left.\begin{array}{l}322a_1\\322a_2\end{array}\right\}$	129	$\left.\begin{array}{l}88\\40\end{array}\right\}$	.8321	$\left.\begin{array}{l}.8311\\.8353\end{array}\right\}$
vw	$218a_1$	114	185	.8376	.8381
—	$218a_2$	—	85	—	.8423
vw	$\left.\begin{array}{l}316a_1\\316a_2\\209a_1\end{array}\right\}$	73	$\left.\begin{array}{l}77\\35\\25\end{array}\right\}$	.8551	$\left.\begin{array}{l}.8516\\.8559\\.8569\end{array}\right\}$
—	$209a_2$	—	12	—	.8612
vw	$\left.\begin{array}{l}323a_1\\323a_2\end{array}\right\}$	67	$\left.\begin{array}{l}121\\56\end{array}\right\}$	.8752	$\left.\begin{array}{l}.8737\\.8781\end{array}\right\}$
—	$410a_1$	—	22	—	.8810
—	$405a_1$	—	120	—	.8839
—	$410a_2$	—	10	—	.8854
—	$405a_2$	—	55	—	.8883
vw	$\left.\begin{array}{l}411a_1\\411a_2\end{array}\right\}$	103	$\left.\begin{array}{l}169\\78\end{array}\right\}$	.8922	$\left.\begin{array}{l}.8895\\.8939\end{array}\right\}$

designated by the symbols *aab*, *aab*, *abb* and *ab*. The first two atoms link the tetrahedra within an *a* chain but also connect this chain with a *b* chain. The third atom also serves as a connection between an *a* and a *b* chain but links the tetrahedra of a *b* chain. The fourth atom only connects two different chains.

A formal description of the arrangement in the unit cell is of a certain interest. When projected on (010) the structure is found to be constructed of two-dimensional oxygen layers connected by the boron atoms and indefinitely extended parallel to ($\bar{1}$03). This is also clear from a projection on a plane — close to (102) — perpendicular to ($\bar{1}$03). The two projections are given in Fig. 3 and Fig. 4. A single layer — there are three within the height of the unit cell — may be described as built up of close-packed oxygen spheres. A projection of such a layer on the plane ($\bar{1}$03) is illustrated in Fig. 5, from which the unit area of the layer — marked with dashed lines — is shown to consist of two regions with different densities and extended parallel to [010]. The density
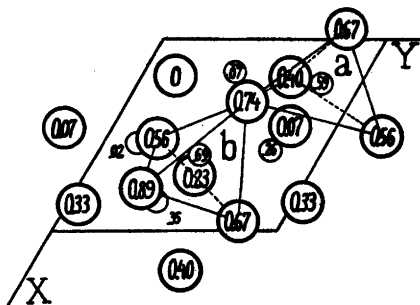
Fig. 1 a. A basal projection of atoms in and about the hexagonal unit of B_2O_3. The large circles are the oxygen atoms. The numbers denote the heights above the basal plane.
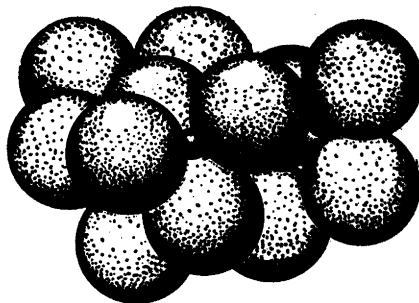
Fig. 1 b. A drawing of the B_2O_3 structure showing how the atoms in the Figure 1a pack together to provide the two sets of tetrahedra.

variation is caused by the gradual change between triangular and quadratic close-packing. Because of the trigonal symmetry the layer is repeated parallel to $(1\bar{1}3)$ and (013).

Calculated from the atomic parameters given in the previous chapter the interatomic distances are found to be:

a tetrahedron	*b* tetrahedron
$O_I' - O_{II}' = 2.49$ Å	$O_I - O_{II} = 2.41$ Å
$O_I' - O_{III}' = 2.37$	$O_I - O_{III} = 2.41$
$O_{II}' - O_{III}' = 3.06$	$O_{II} - O_{III} = 2.37_5$
$O_{II} - O_I' = 2.65$	$O_{III}' - O_I = 2.74$
$O_{II} - O_{II}' = 2.93$	$O_{III}' - O_{II} = 2.96$
$O_{II} - O_{III}' = 2.48$	$O_{III}' - O_{III} = 2.96$
$B_I - O_I' = 1.31$	$B_{II} - O_I = 1.48$
$B_I - O_{II}' = 1.90$	$B_{II} - O_{II} = 1.48$
$B_I - O_{III}' = 1.60$	$B_{II} - O_{III} = 1.37$
$B_I - O_{II} = 1.71$	$B_{II} - O_{III}' = 2.14_5$

The denomination of the different sets of atoms as given in the previous section, is O_I, O_{II}, O_{III} and B_I, B_{II}, respectively. However, in this section a comma is added within each set when moving one step according to the screw axes.
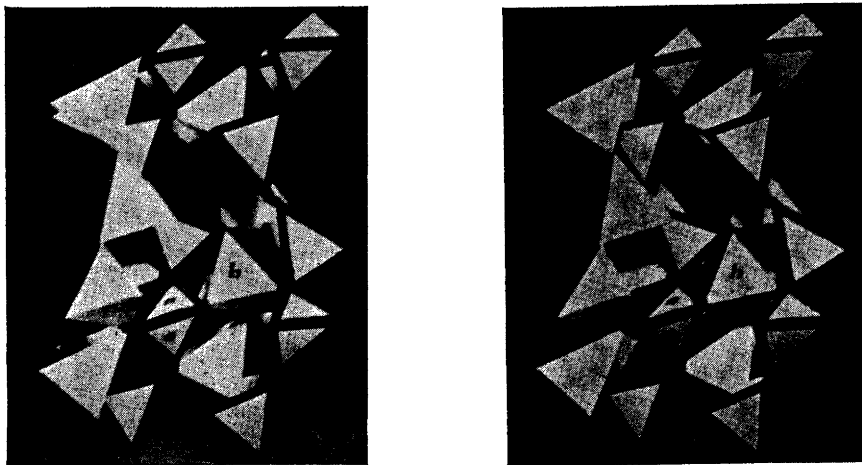
Fig. 2. A stereoscopic view showing the arrangement of the BO_4 tetrahedra of the structure of B_2O_3. Only some tetrahedra near the centre of the model (e.g. the two marked a and b) have the surroundings corresponding to a complete lattice.

Pauling's electrostatic valence rule is fulfilled if the strength of the bond $B-O_I$ is 1 and the strengths of the other $B-O$ bonds are 2/3. In the tetrahedron a these bond strengths are in accord with the short distance $B_I-O'_I$, which has practically the same value as the $B-O$ distance corresponding to
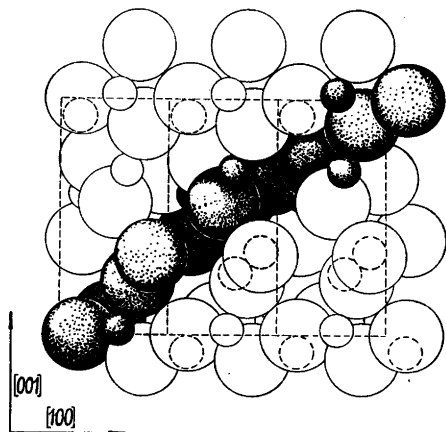
Fig. 3. A projection of the structure on the plane (010) showing oxygen layers extended parallel to the plane ($\bar{1}03$) and connected by boron atoms.
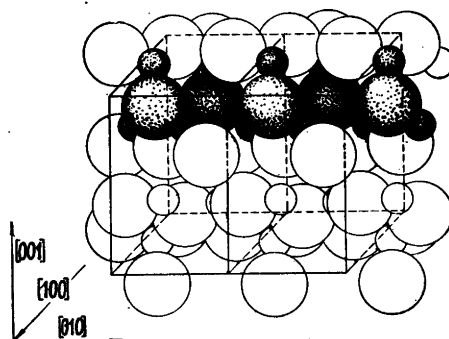
Fig. 4. A projection of the structure on a plane — close to (102) — perpendicular to ($\bar{1}03$).
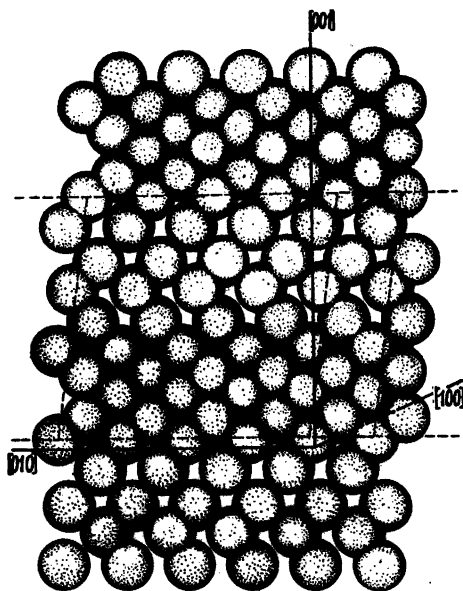
Fig. 5. A projection of one oxygen layer on the plane $(\bar{1}03)$.

the strength 1 in the BO_3 triangles of known borate structures. In tetrahedron b, however, O_I forms part of a highly contracted oxygen triangle with the edges 2.37_5, 2.41 and 2.41 Å, respectively. The boron atom is placed only 0.44 Å from the plane of this triangle. The distance to the fourth oxygen O'_{III} is as long as 2.14_5 Å, and consequently the configuration around B_{II} is actually a hybrid between a triangular and a tetrahedral one. Attempts have been made to adjust the parameters in a way that the boron atom in tetrahedron b could be placed either in the centre of the oxygen triangle or in the centre of the tetrahedron but without success. The distribution of the bond strengths is evidently not so simple as could be supposed from Pauling's rule.

On account of the fact that B_2O_3 tends to crystallize spontaneously from a viscous liquid of partially dehydrated H_3BO_3 in the presence of crystals of cubic HBO_2 (designated HBO_2 I by Kracek, Morey and Merwin), it seems reasonable to suppose that a structural relationship exists between B_2O_3 and HBO_2 I. However, the crystal structure of HBO_2 I has not yet been crystallographically worked out. The monoclinic modification (designated HBO_2 II) has recently been investigated by Zachariasen [6]. Because Kracek, Morey and Merwin did not find that HBO_2 II initiated the spontaneous crystallization of B_2O_3 it is of interest in the present case to establish that the structure is built up of endless chains, the constituents of which are both BO_4 tetrahedra and BO_3 triangles, the latter forming B_2O_5 groups. The marked difference

between the two modifications of the metaboric acid, HBO_2 I and HBO_2 II, in promoting crystallization is in favour of the cubic form HBO_2 I being structurally analogous to B_2O_3.

A study of the structure of B_2O_3 and of α-(β-) SiO_2 — the last of which is a more specialized form of the α-modification only — shows that certain structural analogies exist. The symmetry is trigonal in both cases and the quartz structures are built up of SiO_4 tetrahedra forming spiral chains by coupling of corners. But in quartz the oxygen atoms are only common to two tetrahedra. Two oxygen atoms in one tetrahedron only form links to adjacent tetrahedra in the same chain. The two other oxygen atoms form connections with other chains.

In a recent paper Fajans and Barber [7] make some assumptions as to the structure of boron oxide. From various physical properties said not to be reconcilable with a structure in which a coordinative network extends, they state that boron oxide (both vitreous and crystalline) below about 300° C consists of units of molecular dimensions with a probable composition of B_4O_6. This structure with the groups held together by "weak" forces is said to change gradually with increasing temperature to a "strong" one, approaching more nearly the ideal coordinative type.

These assumptions as regards the molecular structure of B_2O_3 can, however, hardly be understood in the light of the remarkable reluctance of the glass to crystallize. Actually there is experimental evidence from Fourier analysis of vitreous B_2O_3 undertaken by Warren, Krutter and Morningstar [8], which is in complete agreement with Zachariasen's [9] predictions, showing a random network structure to exist. In this each boron is triangularly bonded to three oxygens and each oxygen is bonded to two borons and the interatomic distances found are in good agreement with the bond lengths experimentally derived for BO_3 triangles in known crystalline borates. The reluctance of the oxide to crystallize seems possible to explain by the difficulty to transform one three-dimensional network into another, which difficulty ought to be more pronounced as the coordination number of boron has to change at the same time.

It is not easy to see why a glass, built up according to Fajans and Barber from relatively small and loosely combined B_4O_6 molecules, should not transform quite easily into a crystal with principally the same structure.

SUMMARY

The crystal structure of B_2O_3 has been determined by trial-and-error methods. The unit cell contains three formula units and belongs to the space group $C_3^2 - C3_1$ ($C_3^3 - C3_2$). Dimensions and atomic parameters are given.

The structure is built up of two sets of BO_4 tetrahedra forming interconnected spiral chains of two types running parallel to the trigonal axis. Within each tetrahedron the strength of one B—O bond equals unity and the strengths of the remaining three bonds equals two thirds of unity. A stereoscopic view of the tetrahedral arrangement is given in Fig. 2.

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