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Crystal Structure of $3Bi_2O_3:5B_2O_3$· A New Type of Polyborate Anion $(B_5O_{11})^{7-}$

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Single crystals of $3Bi_2O_3:5B_2O_3$ have been obtained from the melt and subsequent devitrification of the glassy compound, at 450°C during 90 hr. The compound is orthorhombic, space group *Pnma* with two formula units in the cell. The lattice parameters are $a = 6.532$ Å, $b = 7.733$ Å, $c = 18.566$ Å. The structure was solved from a complete set of three-dimensional MoK_α diffractometer data, the final R being 0.097.

The structure is made up of Bi^{3+} cations and O^{2-} and $(B_5O_{11})^{7-}$ anions. The pentaborate anion is formed by two BO_4 tetrahedra and three BO_3 triangles, sharing edges and corners. An oxygen that is not bonded to any boron is in the center of a three-bismuth triangle. Two independent bismuth atoms are present in the structure. Bi(1) has six first-neighbor oxygens with an average Bi–O distance of 2.44 Å and Bi(2) has either six or seven oxygens in the first coordination sphere with an average Bi–O distance of 2.43 or 2.80 Å, respectively.

Introduction

As part of a program aimed at the understanding of the structural principles of anhydrous borates we have undertaken the determination of the crystal structure of $3Bi_2O_3:5B_2O_3$. The only structural information about this compound, from ir spectroscopy (*1*) "implies" the existence of both BO_4 tetrahedra and BO_3 triangle as components of the crystal. Thus, the crystal structure determination should be the best way to corroborate the published information and to obtain more structural knowledge about this compound.

Experimental

Single crystals of $3Bi_2O_3:5B_2O_3$ were grown from the melt of a mixture of Bi_2O_3 and B_2O_3 (3:5 ratio) and subsequent devitrification of the glassy compound at 450°C during 90 hr. The compound was identified by ir spectroscopy (*1*) and X-ray powder diffraction techniques (*2*). The few crystals found were identified as $3Bi_2O_3:5B_2O_3$ after indexing the powder pattern with the cell parameters obtained from oscillation and Weissenberg photographs, which show an orthorhombic symmetry. The final cell parameters were obtained by least-squares refinement of the 2θ values measured with a powder diffractometer using silicon as internal standard. The indexed powder pattern is collected in Table I.

A prismatic crystal of dimensions 0.05 × 0.08 × 0.09 mm was used to measure all reflections included within a sphere in the reciprocal space having $\theta \leqslant 30°$. The intensities were measured in the $\omega/2\theta$ scan mode on a Philips 1100 four-circle diffractometer using MoK_α radiation monochromated by graphite ($\lambda = 0.7107$ Å). The intensities were corrected by Lorentz and polarization factors. Absorption corrections were considered irrelevant for the purpose of this study, despite the high value for the linear absorption coefficient ($\mu = 561.4\ \mathrm{cm}^{-1}$). Crystal data are given in Table II.

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TABLE I

INDEXED POWDER PATTERN: $3Bi_2O_3{:}5B_2O_3$ (CuK_α RADIATION)

d observed (Å)	*d* calculated (Å)	*h k l*	I/I_o (%)[a]
7.1322	7.1388	0 1 1	15
6.1592	6.1622	1 0 1	35
5.3434	5.3424	1 0 2	5
4.6393	4.6416	0 0 4	19
4.4905	4.4927	1 0 3	4
3.8867	3.8847	1 1 3	4
3.5701	3.5694	0 2 2	9
3.3987	3.3987	1 1 4	21
3.2678	3.2663	2 0 0	70
3.2283	3.2282	1 0 5	100
3.0935	3.0944	0 0 6	16
2.9707	2.9709	0 2 4	21
2.9299	2.9307	1 2 3	12
2.8892	2.8886	2 0 3	6
2.6726	2.6712	2 0 4	23
2.6314	2.6298	1 1 6	10
2.5081	2.5089	0 1 7	5
2.4780	2.4781	1 2 5	10
2.4584	2.4575	1 0 7	6
2.4138	2.4160	0 2 6	27
2.3805	2.3796	0 3 3	2
2.3204	2.3208	0 0 8	10
2.2464	2.2464	2 0 6	6
2.1982	2.1978	2 2 4	11
2.1629	2.1627	3 0 1	6
2.1198	2.1200	3 0 2	6
2.0745	2.0741	1 2 7	10
2.0451	2.0445	3 1 2	7
1.9901	1.9899	0 2 8	14
1.9901	1.9897	2 1 7	14
1.9681	1.9672	1 0 9	17
1.9426	1.9424	2 2 6	23
1.8776	1.8784	3 0 5	23
1.8560	1.8566	0 0 10	10
1.8134	1.8140	3 2 3	6

[a] The intensities were measured on powder diffractometer data.

Structure Determination and Refinement

The structure was solved by three-dimensional Patterson and Fourier synthesis using the mean values for the 887 independent reflections; 151 of them were considered as unobserved after the selection criterion: $I_{\text{meas}} \geqslant 3\sigma(I)$.

TABLE II

CRYSTAL DATA

Formula	$3(Bi_2O_3){:}5(B_2O_3)$
Crystal dimensions	0.05 × 0.08 × 0.09 mm
Space group	Orthorhombic: *Pnma*
Cell constants	$a = 6.532(1)$ Å $b = 7.733(1)$ Å $c = 18.566(2)$ Å
Density	$D_{\text{obs}} = 6.38$, $D_x = 6.20$ g cm^{-3}
Molecules per cell	2
Linear absorption coefficient	561.4 cm^{-1}

From the interpretation of the Patterson map, the heavy atoms were located in two different sites, four Bi atoms occupy the 4*c* position (x, $\frac{1}{4}$, z) on the mirror plane, while eight Bi atoms are situated in general positions.

The Bi coordinates were refined by using the full-matrix least-squares method, the light atoms being easily recognized in a ΔF synthesis based on the phases given by the heavy atoms.

There are nine independent oxygens and four independent borons. Six oxygens and three borons occupy the 4*c* sites while one boron and three oxygens are situated in general positions.

The structure was refined by using the full-matrix least-squares method and unit weight for every reflection.

Atomic scattering factors for neutral atoms (*3*) were used. Anomalous dispersion coefficients for Bi atoms were also used (*4*).

Due to the extremely high absorption, individual isotropic thermal motion was assumed. After four refinement cycles, the isotropic thermal parameter of O(1), O(5), O(6), B(2), and B(3) did not stay positive definite. So, the values $U = 607 \times 10^{-5}$ (Å) and $U = 578.10^{-5}$ (Å) were assumed for these oxygen and boron atoms, respectively, and left invariant during three further refinement cycles, yielding a final R value of 0.097.[1] The values for these isotropic temperature factors (Table III) were assumed only for structure factor calculation, but they do not represent

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[1] A table containing the observed and calculated structure factors is available on request from the authors.

TABLE III

FINAL POSITIONAL AND THERMAL PARAMETERS $3Bi_2O_3:5B_2O_3$

	x/a	*y/b*	*c/z*	$U \times 10^5$ (Å)
Bi(1)	0.4594(4)	1/4	−0.1866(1)	607(69)
Bi(2)	−0.0147(3)	0.5171(2)	0.0957(1)	702 (58)
O(1)	0.358(7)	1/4	0.083(2)	607(69)
O(2)	0.483(10)	1/4	−0.043(3)	2684(1457)
O(5)	0.159(7)	1/4	−0.144(2)	607(69)
O(6)	0.725(7)	1/4	0.051(2)	607(69)
O(7)	0.811(7)	1/4	−0.075(2)	178(990)
O(8)	0.615(8)	1/4	0.269(3)	1316(1222)
O(3)	0.177(5)	0.407(5)	−0.003(2)	995(756)
O(4)	0.591(6)	0.414(5)	0.155(2)	1750(868)
O(9)	0.651(5)	0.552(4)	0.265(2)	24(656)
B(1)	0.545(12)	1/4	0.107(4)	658(1614)
B(2)	0.294(11)	1/4	0.011(3)	578(1143)
B(3)	0.667(11)	1/4	−0.024(4)	578(1143)
B(4)	0.619(8)	0.401(7)	0.229(3)	578(1143)

a thermal model for the structure, which had to be selected after absorption correction. But this is not the aim of this study.

The final positional and thermal parameters are listed in Table III.

Description and Discussion of the Structure

The structure consists of Bi^{3+} cations and discrete $B_5O_{11}^{7-}$ anions. The remaining positive charge is compensated by one O^{2-} anion, O(5), not bonded to any boron, and situated in the center of a bismuth triangle, as shown in Fig. 1, which represents a projection of the structure along the crystallographic *a*-axis.

The $B_5O_{11}^{7-}$ polyanions are situated in the mirror planes at $\frac{1}{4}$ and $\frac{3}{4}$ of *b* (Fig. 1).

Figure 2 shows a view of this polyborate anion in which both BO_4 tetrahedra and BO_3 triangles are present as predicted by ir spectroscopy (*1*). In this figure, oxygens and borons are labeled in accordance with Table IV.

This atomic arrangement has been found in other borates, e.g., sodium diborate (*6*) and potasium pentaborate (*7*), although in these compounds the terminal oxygens of the $B_5O_{11}^{7-}$ unit (Fig. 2) are shared with polyborate units to form a three-dimensional network.

The calculated values for the interatomic distances and angles are not very accurate because of the absorption and because of the existence of the very heavy atoms of bismuth. Only the mean values are in accord with those expected for both the BO_4 tetrahedron and BO_3 triangle. Thus, the reported values for sodium diborate (*6*) or potasium pentaborate (*7*) could be applied to the $B_5O_{11}^{7-}$ unit, even

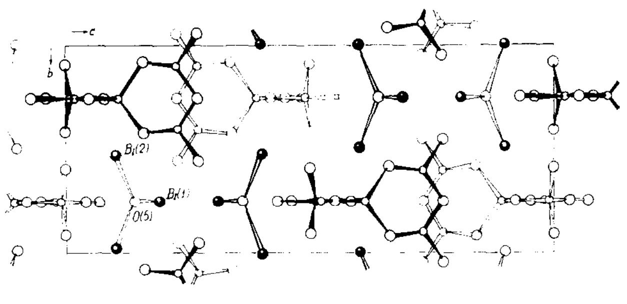

FIG. 1. $3Bi_2O_3:5B_2O_3$. Projection of the structure along (100).

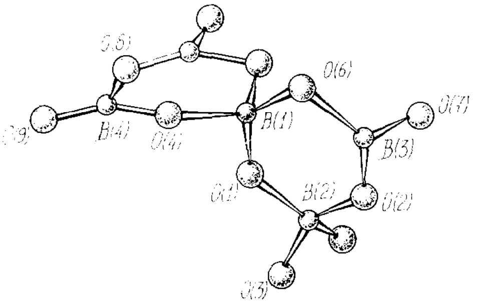

FIG. 2. Conformation of $(B_5O_{11})^{7-}$ anion.

taking into account the possible distortions caused by the sharing of the terminal oxygens.

In Table IVa all the bismuth–neighbor distances less than 3.5 Å are summarized. Bi(1) has six nearest oxygens at distances from 2.12 to 2.68 Å and another four in the range 3.09 to 3.41 Å. Bi(2) has seven nearest oxygens at distances between 2.11 and 2.91 Å and another two at 3.20 and 3.36 Å, giving rise to a total number of nine oxygens around the Bi(2) atom. This distinction between two ranges of distances has been pointed out for several bismuth compounds by Abrahams, Jamieson, and Bernstein (*8*).

The average bismuth–oxygen distances for the first-nearest-neighbor are 2.44 Å for Bi(1)–oxygen and 2.50 Å for Bi(2)–oxygen. In this last case, the average distance becomes 2.43 Å if $O(4)_{xvii}$ is considered as a second-nearest neighbor.

The compound could be formulated either as $Bi_3O(B_5O_{11})$ or as $(Bi_3O)(B_5O_{11})$. In the first case, the existence of Bi^{3+} cations and O^{2-} and $(B_5O_{11})^{7-}$ anions must be assumed. Such a structural formula was given to zinc metaborate (*9*) $Zn_4O(B_6O_{12})$ and bismuth orthoborate (*5*) $Bi_4O_3(BO_3)_2$, in which the existence of oxygen not bonded to any boron has been proven. Contrarily, the (Bi_3O)

TABLE IVa

$3Bi_2O_3:5B_2O_3$ INTERATOMIC DISTANCES

Bi(1)–O(5)	2.12(5) Å	Bi(2)–$O(3)_{iii}$	2.11(4) Å
$O(9)_{i}$	2.23(3)	$O(5)_{iii}$	2.22(3)
$O(9)_{xx}$	2.23(3)	$O(7)_{i}$	2.27(3)
O(2)	2.67(6)	O(3)	2.38(4)
$O(4)_{i}$	2.68(4)	$O(6)_{xi}$	2.80(3)
$O(4)_{xx}$	2.68(4)	$O(9)_{xiv}$	2.82(4)
		$O(4)_{xvii}$	2.91(4)
$B(4)_{i}$	2.86(5)	$B(3)_{i}$	3.19(6)
$B(4)_{xx}$	2.86(5)	O(1)	3.20(3)
O(7)	3.09(4)	$B(2)_{iii}$	3.24(5)
$O(9)_{v}$	3.10(3)	B(2)	3.29(5)
$O(9)_{xxiii}$	3.10(3)	$O(8)_{xiv}$	3.36(4)
B(3)	3.31(7)		
$O(5)_{xiii}$	3.41(4)		

Anion $B_5O_{11}^{7-}$

Tetrahedron B(1)		Tetrahedron B(2)	
B(1)–O(1)	1.30(9) Å	B(2)–O(1)	1.41(8) Å
O(6)	1.56(9)	O(2)	1.59(9)
O(4)	2 × 1.58(6)	O(3)	2 × 1.46(5)
Mean value	1.50(8)	Mean value	1.48(7)

Triangle B(3)		Triangle B(4)	
B(3)–O(2)	1.26(10) Å	B(4)–O(4)	1.40(6) Å
O(6)	1.44(8)	O(8)	1.38(6)
O(7)	1.33(8)	O(9)	1.36(6)
Mean value	1.34(8)	Mean value	1.38(6)

TABLE IVb

$3Bi_2O_3:5B_2O_3$ INTERATOMIC ANGLES; ANION $B_5O_{11}^{7-}$

Tetrahedron B(1)		Tetrahedron B(2)	
O(4)–B(1)–O(4)	107(5)°	O(3)–B(2)–O(3)	113(5)°
O(1)–B(1)–O(6)	120(6)	O(1)–B(2)–O(2)	112(6)
O(4)–B(1)–O(1)	2 × 111(4)	O(1)–B(2)–O(3)	2 × 109(4)
O(4)–B(1)–O(6)	2 × 104(4)	O(2)–B(2)–O(3)	2 × 107(4)
Mean value	109(5)	Mean value	110(5)
Triangle B(3)		**Triangle B(4)**	
O(2)–B(3)–O(6)	122(6)°	O(4)–B(4)–O(8)	125(5)°
O(2)–B(3)–O(7)	119(7)	O(4)–B(4)–O(9)	116(5)
O(6)–B(3)–O(7)	120(6)	O(8)–B(4)–O(9)	118(4)
Mean value	120(6)	Mean value	120(5)
B(1)–O(1)–B(2)	126(6)°	Bi(1)–O(5)–Bi(2)	123(1)°
B(2)–O(2)–B(3)	124(6)	Bi(2)–O(5)–Bi(2)	109(2)
B(1)–O(6)–B(3)	116(5)	Bi(2)–Bi(1)–Bi(2)	56.39(1)
B(1)–O(4)–B(4)	122(4)	Bi(2)–Bi(2)–Bi(1)	61.80(1)
B(4)–O(8)–B(4)	116(5)		

Symmetry code

i. $1-x$	$1-y$	$-z$	xiv. $x-\frac{1}{2}$	y	$\frac{1}{2}-z$
iii. $-x$	$1-y$	$-z$	xvii. $x-1$	y	z
v. $\frac{3}{2}-x$	$y-\frac{1}{2}$	$z-\frac{1}{2}$	xx. $1-x$	$y-\frac{1}{2}$	$-z$
xi. $x-1$	$\frac{1}{2}-y$	z	xxiii. $\frac{3}{2}-x$	$1-y$	$z-\frac{1}{2}$
xiii. $\frac{1}{2}+x$	y	$-\frac{1}{2}-z$			

(B_5O_{11}) would imply the existence of $(Bi_3O)^{7+}$ cations and $(B_5O_{11})^{7-}$ anions.

In our case, since the O(5)-bismuth distances do not differ from the other bismuth–oxygen bond lengths, we think that the $3Bi_2O_3:5B_2O_3$ should be formulated as $Bi_3O(B_5O_{11})$.

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