

# Crystal Growth and Crystal Structure of the Metastable Bismuth Orthoborate $\text{BiBO}_3$

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Single crystals of bismuth orthoborate,  $\text{BiBO}_3$ , were grown from the melt in the system  $\text{Li}_2\text{O}-\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3$ .  $\text{BiBO}_3$  is confirmed to adopt at least two different structural modifications. The modification  $\text{BiBO}_3(\text{I})$  (corresponding to PDF Nr. 28-0169) crystallizes with space group  $P2_1/c$ . The structure consists of  $[\text{Bi}_2\text{O}_{10}]$  groups that are formed by two edge-sharing distorted  $[\text{BiO}_6]$  octahedra and that are interconnected by sharing common corners (oxygen). The  $[\text{Bi}_2\text{O}_{10}]$  groups are further sharing corners with planar  $[\text{BO}_3]$  groups giving a three-dimensional framework.

**Key words:** Bismuth Borate, Crystal Structure, Polymorphism

The phase diagram  $\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3$  determined by Levin and McDaniel in 1962 [1] shows the occurrence of five different crystalline compounds,  $\text{Bi}_{12}\text{BO}_{20}$ , (correctly  $\text{Bi}_{24}\text{B}_2\text{O}_{39}$  [2]),  $\text{Bi}_4\text{B}_2\text{O}_9$ ,  $\text{Bi}_3\text{B}_5\text{O}_{12}$ ,  $\text{BiB}_3\text{O}_6$  and  $\text{Bi}_2\text{B}_8\text{O}_{15}$ . Surprisingly, however, no orthoborate of the type  $\text{M}^{\text{III}}\text{BO}_3$ , known for most of the trivalent metals, had then been reported for bismuth. In 1974, Pottier [3] described a metastable phase, obtained from a melt of composition  $\text{Bi}_2\text{O}_3:\text{B}_2\text{O}_3 = 1:1$ , which was named “ $\text{BiBO}_3$ ”. The polymorphism of this compound with two different modifications, called  $\text{BiBO}_3(\text{I})$  (PDF Nr. 28-0169) and  $\text{BiBO}_3(\text{II})$  (PDF Nr. 27-0320) was also demonstrated. However, no chemical or structural analysis of these crystalline phases has been documented to date in the literature. Recently, the existence of “ $\text{BiBO}_3$ ” was corroborated by Becker [4], and Honma *et al.* [5, 6] reported the occurrence of crystalline phases  $\text{RE}_x\text{Bi}_{1-x}\text{BO}_3$  in crystallized glasses of the systems  $\text{RE}_2\text{O}_3-\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3$  ( $\text{RE} = \text{La, Gd, Sm}$ ).

## Results and Discussion

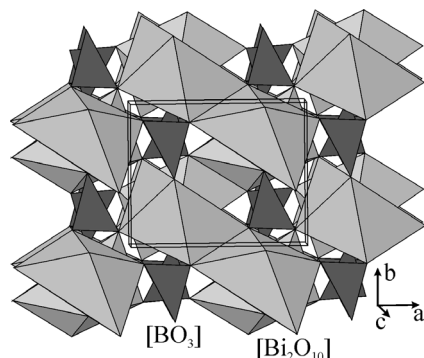
During our own detailed re-investigation of the system  $\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3$  (for crystal growth purposes, *e.g.* [7]) by means of thermal analysis (DTA) and X-ray powder diffraction we found the occurrence of  $\text{BiBO}_3(\text{I})$  as a minor component of double-phased samples within the composition range 40 mole%  $\text{B}_2\text{O}_3$  to 57.5 mole%  $\text{B}_2\text{O}_3$ . However, it was not possible to

Table 1. Fractional atomic coordinates for  $\text{BiBO}_3(\text{I})$  and isotropic displacement parameters.

Atom	Wyckoff position	x	y	z	$U_{\text{iso}}$
Bi	4e	−0.25713(4)	0.23409(7)	0.12288(3)	0.0125(3)
B	4e	0.208(2)	0.2527(18)	0.1092(12)	0.016(2)
O1	4e	0.0693(7)	0.1103(11)	0.1698(6)	0.0175(10)
O2	4e	0.3334(8)	0.1290(12)	0.0299(6)	0.0210(11)
O3	4e	0.2439(8)	0.5214(14)	0.1430(6)	0.0201(13)

obtain single crystals of the compound by crystallization from the melt, since within the given composition range either  $\text{Bi}_4\text{B}_2\text{O}_9$  or  $\text{Bi}_3\text{B}_5\text{O}_{12}$  are the primarily crystallizing compounds. Monophase (plus remaining glass) samples of crystalline  $\text{BiBO}_3(\text{I})$  or  $\text{BiBO}_3(\text{II})$  were finally obtained by crystallization of binary bismuth borate glasses of the compositions 50 mole%  $\text{B}_2\text{O}_3$  to 57.5 mole%  $\text{B}_2\text{O}_3$  at temperatures below 550 °C. Above about 560 °C,  $\text{Bi}_3\text{B}_5\text{O}_{12}$  is obtained by crystallization of these glasses. By heating the glasses at 450 °C for 24 h  $\text{BiBO}_3(\text{II})$  of sub-microscopic particle size is obtained and can easily be identified by means of powder diffraction analysis.  $\text{BiBO}_3(\text{II})$  transforms completely into  $\text{BiBO}_3(\text{I})$  during an additional heating period of 24 h at 450 °C. A partial transformation, however, is also observed after 24 h at room temperature. A back-transformation of  $\text{BiBO}_3(\text{I})$  into  $\text{BiBO}_3(\text{II})$  was not observed. Long-term heating of  $\text{BiBO}_3(\text{I})$  at 450 °C for 6 weeks leads to a transformation into a further, yet unknown crystalline phase, which is under investigation in our group. These obser-

Bi - O1	2.148(5)	O1 - Bi - O2	83.8(2)	O3 - Bi - O1	94.91(17)
Bi - O2	2.190(5)	O1 - Bi - O3	87.02(18)	O1 - Bi - O2	150.8(2)
Bi - O3	2.205(5)	O2 - Bi - O3	92.7(2)	O2 - Bi - O2	68.8(2)
Bi - O3	2.564(5)	O1 - Bi - O3	89.09(17)	O3 - Bi - O2	84.58(18)
Bi - O1	2.591(5)	O2 - Bi - O3	87.8(2)	O3 - Bi - O2	99.30(16)
Bi - O2	2.607(5)	O3 - Bi - O3	176.0(2)	O1 - Bi - O2	124.78(16)
B - O2	1.362(10)	O1 - Bi - O1	81.76(13)	O2 - B - O1	121.2(8)
B - O1	1.381(11)	O2 - Bi - O1	165.26(18)	O2 - B - O3	117.1(8)
B - O3	1.384(11)	O3 - Bi - O1	83.6(2)	O1 - B - O3	121.3(7)

Table 2. Selected interatomic distances [Å] and angles [°] for BiBO<sub>3</sub>(I).Fig. 1. Projection of the BiBO<sub>3</sub>(I) structure along [001]. [Bi<sub>2</sub>O<sub>10</sub>] groups (light grey) and [BO<sub>3</sub>] units (dark grey) are represented as polyhedra (ATOMS [16]).

vations indicate, that both BiBO<sub>3</sub>(II) and BiBO<sub>3</sub>(I) are metastable phases of the system Bi<sub>2</sub>O<sub>3</sub> – B<sub>2</sub>O<sub>3</sub>.

Single crystals of BiBO<sub>3</sub> suitable for structure determination could not be obtained from glass crystallization, but were grown from a melt of the system Bi<sub>2</sub>O<sub>3</sub> – B<sub>2</sub>O<sub>3</sub> – Li<sub>2</sub>O. The colorless crystals (dimensions up to 0.5 × 0.5 × 0.5 mm<sup>3</sup>) consisted of BiBO<sub>3</sub>(I), as it was proven by X-ray powder diffraction. To confirm this modification for the single crystal we used for structure determination, we also calculated a theoretical powder diffraction pattern from our crystal structure data. It agreed perfectly with our own experimental powder diffraction data of BiBO<sub>3</sub>(I) and with PDF Nr. 28-0169.

The crystal structure of BiBO<sub>3</sub>(I) was determined by means of single crystal X-ray diffraction. BiBO<sub>3</sub>(I) crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* (no. 14). Its structure consists of [Bi<sub>2</sub>O<sub>10</sub>] groups that are formed by two distorted [BiO<sub>6</sub>] octahedra sharing a common edge (see Fig. 1). Each of the two bridging oxygen atoms of the group is further part of a planar triangular [BO<sub>3</sub>] unit, while the terminal oxygen atoms of the [Bi<sub>2</sub>O<sub>10</sub>] group belong also to both, one further [Bi<sub>2</sub>O<sub>10</sub>] group and one [BO<sub>3</sub>] triangle. All [BO<sub>3</sub>] groups are oriented with their triangular faces approximately perpendicular to the [101] direction.

The mean B-O distance of 1.376 Å for [BO<sub>3</sub>] fits well into the range of B-O distances found for many other borate structures (see *e.g.* Zobetz [8, 9]). The [BO<sub>3</sub>] triangles are substantially distorted with the B-O2 distance connecting to the [Bi<sub>2</sub>O<sub>10</sub>] group being significantly shorter than the B-O1 and B-O3 distances (see Table 2). Bismuth is positioned off-center within its coordination surrounding with Bi-O distances that vary between 2.148 and 2.607 Å. This indicates the stereochemical activity of the lone pair electrons of trivalent Bi in BiBO<sub>3</sub>(I), that might perhaps also be the reason for the singularity of this new crystal structure type of BiBO<sub>3</sub>(I) among the orthoborates M<sup>III</sup>BO<sub>3</sub> known for trivalent metals.

## Experimental Section

### Synthesis of BiBO<sub>3</sub>(I)

Single crystals of monoclinic BiBO<sub>3</sub> were grown from a melt of composition Bi<sub>2</sub>O<sub>3</sub>:B<sub>2</sub>O<sub>3</sub>:Li<sub>2</sub>O = 49:49:2. A homogenized powder mixture of Bi<sub>2</sub>O<sub>3</sub> (electronic grade, HEK), B<sub>2</sub>O<sub>3</sub> (99.98%, Alfa Aesar) and Li<sub>2</sub>CO<sub>3</sub> (99%, Merck) was heated in a covered platinum crucible to 850 °C and subsequently cooled with a cooling rate of about 3.4 °C/h to 500 °C. Transparent colorless single crystals of the title compound with dimensions up to 0.5 × 0.5 × 0.5 mm<sup>3</sup> were separated mechanically from the sample.

### X-ray data collection, structure solution and refinement

Nonius KappaCCD diffractometer with rotating anode, Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å), graphite monochromator, *T* = 293(2) K. Crystal size: 0.2 × 0.2 × 0.15 mm<sup>3</sup> colorless prism, space group *P*2<sub>1</sub>/*c* (Nr. 14), *a* = 6.585(1), *b* = 5.027(1), *c* = 8.349(1) Å,  $\beta$  = 108.91(1)°, *V* = 261.46(7) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd.}}$  = 6.803 g/cm<sup>3</sup>. Data collection: Collect [10],  $\omega$ - and  $\phi$ -scans,  $\theta$ -range = 4.81–27.45°,  $-8 \leq h \leq 8$ ,  $-6 \leq k \leq 6$ ,  $-10 \leq l \leq 10$ , 10530 reflections collected and averaged to give 590 independent reflections (*R*<sub>int</sub> = 0.066), data reduction: Denzo-SMN [11], multiscan absorption correction (SORTAV [12, 13],  $\mu$  = 67.168 mm<sup>-1</sup>, *T*<sub>min</sub> = 0.0262, *T*<sub>max</sub> = 0.0354, *F*(000) = 448), 46 refined parameters. Final *R* values with  $|I| > 2\sigma(I)$ : *R*(*F*) = 0.0332, *wR*(*F*<sup>2</sup>) = 0.0980, *S* = 1.015.

Structure solution and refinement: SHELXS-97 [14], refinement on  $F^2$  (SHELXL-97 [15]). Further details of the crystal structure investigation are available from the Fachinformations-zentrum Karlsruhe, D-76344 Eggenstein-

Leopoldshafen (Germany), on quoting the depository number CSD-413621, the name of the author(s), and the citation of the paper.

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