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Crystal growth, crystal structure of new polymorphic modification, β-$Bi_2B_8O_{15}$ and thermal expansion of α-$Bi_2B_8O_{15}$

R.S. Bubnova [a], J.V. Alexandrova [b], S.V. Krivovichev [a,b], S.K. Filatov [b,*], A.V. Egorysheva [c]

[a] Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, Makarov Emb 2, 199053 St.Petersburg, Russia
[b] Department of Crystallography, St. Petersburg State University, Universitetskaya nab. 7/9, 199034 St.Petersburg, Russia
[c] Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Leninsky Prospect 31, GSP-1, Moscow 119991, Russia

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ABSTRACT

Single crystals of α- and β-polymorphs of $Bi_2B_8O_{15}$ were grown by Czochralski method from a charge of the stoichiometric composition. The crystal structure of β-$Bi_2B_8O_{15}$ was solved by direct methods from a twinned crystal and refined to $R1=0.081$ ($wR=0.198$) on the basis of 1584 unique observed reflections ($I>2\sigma(I)$). The compound is triclinic, space group $P\bar{1}$, $a=4.3159(8)$, $b=6.4604(12)$, $c=22.485(4)$ Å, $\alpha=87.094(15)^\circ$, $\beta=86.538(15)^\circ$, $\gamma=74.420(14)^\circ$, $V=602.40(19)$ Å^3, $Z=2$. The B–O layered anion of β-$Bi_2B_8O_{15}$ is topologically identical to the anion of α-$Bi_2B_8O_{15}$ but the orientation of neighboring layers is different. Thermal expansion of α-$Bi_2B_8O_{15}$ has been investigated by X-ray powder diffraction in air in temperature range from 20 to 700 °C. It is strongly anisotropic, which can be explained by the hinge mechanism applied to chains of Bi–O polyhedra. While the anisotropy of thermal expansion is rather high, the volume thermal expansion coefficient $\alpha_V=40\times10^6\,^\circ C^{-1}$ for α-$Bi_2B_8O_{15}$ is close to those of other bismuth borates.

1. Introduction

The growing interest to the bismuth borates is due to the discovery of nonlinear optical properties of BiB_3O_6 [1,2]. This fact made it possible to use it in nonlinear optics for producing solid-state ultraviolet lasers. Bismuth borates are luminophores with a high radiation resistance and can exhibit stimulated Raman scattering. Thus, they have a good potential for being used as laser radiation converters.

Stable phase equilibria in the Bi_2O_3–B_2O_3 were determined experimentally in [3] and the metastable equilibria were reported in [4]. Phase transition in $Bi_2B_8O_{15}$ was discovered in [3] and later confirmed in [5]. The temperature of phase transition is determined as 696 °C and the melting temperature is 715 °C. Crystal growth experiments of low-temperature α-$Bi_2B_8O_{15}$ polymorph from stoichiometric melt and by the Czochralski method were described in [6] and [7], respectively. First X-ray diffraction data for both modifications were reported in [3], and the unit cell parameters and symmetry were determined for α-$Bi_2B_8O_{15}$ in [6]. The crystal structure of low-temperature modification, α-$Bi_2B_8O_{15}$, was reported in [5,8]. The polymorph crystallizes in the monoclinic system, space group $P2_1$, $a=4.314$, $b=22.150$, $c=6.469$ Å, $\beta=105.49^\circ$, $Z=2$. Narrow region of homogenous solid solutions has been revealed based on α-$Bi_2B_8O_{15}$ [7] and crystal structure of the α-$Bi_2B_8O_{15}$ $(Bi_2O_3)_{0.06}$ solid solution was refined, although authors have not refined the position of the excess Bi atoms [7]. Although crystal structures for most of the homometallic compounds in the Bi_2O_3–B_2O_3 system have already been reported; the crystal structure of β-modification of $Bi_2B_8O_{15}$ has not been known. Its powder X-ray diffraction pattern, symmetry and unit cell parameters were previously reported [5] as following: triclinic, space group $P\bar{1}$, $a=6.055$, $b=7.704$, $c=8.016$ Å, $\alpha=100.90^\circ$, $\beta=105.43^\circ$, $\gamma=103.71^\circ$.

In this work, we describe the crystal growth of β- and α-$Bi_2B_8O_{15}$ by the Czochralski method, the results of structure determination for β-$Bi_2B_8O_{15}$, and thermal expansion of α-$Bi_2B_8O_{15}$.

2. Experimental

2.1. Crystal growth

Single crystals of the low- and the high-temperature phases $Bi_2B_8O_{15}$ were grown by the Czochralski method from a stoichiometric mixture of Bi_2O_3 (99.999%) and H_3BO_3 (99.999%). The melt had high viscosity and a tendency to glass formation and liquid–liquid phase separation [3,4], which determined the conditions for crystal growth. Crystals were grown in a resistance furnace in a platinum crucible 90 cm^3 volume. To ensure the homogeneity of

* Corresponding author.
E-mail address: filatov@crystalspb.com (S.K. Filatov).

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the melt, the powdered compound previously obtained by solid-phase synthesis was loaded into the crucible. Supercooling temperature was the only growth condition that differed in the case of the low- and the high-temperature modifications. It was in the range 2–4 K for high-temperature phase and 20 K for low-temperature phase $Bi_2B_8O_{15}$ (i.e. at the temperature below the phase transition). The other conditions were the same for α- and β-modifications. Initially, polycrystalline tablets from pre-synthesized $Bi_2B_8Oi_5$ powder were made and one of the tablets was then used as a seed. The crystals were grown at the constant temperature. The pulling rate was 0–0.2 mm/h, the rotation velocity was 1.5–6 rpm. The axial temperature gradient above the melt was 0.8 K/cm. In both cases, bulky conglomerates of crystals were obtained and consisted of thin colorless plates < 0.5 mm thickness and with the maximal size up to 2 cm^2.

Powder samples of β-$Bi_2B_8O_{15}$ were prepared from mixed stoichimetric amounts of Bi_2O_3 (99.999%) and H_3BO_3 (99.9%). The mixture was pressed to form tablets, which were sintered at 680 °C for 3 h. The ceramic samples β-$Bi_2B_8O_{15}$ were heat treated at temperatures near to phase transition (below and above). The ratio of the polymorphic phases changes (depending on the treatment time and temperature); and at 710 °C β-$Bi_2B_8O_{15}$ completely transformed into the α-phase. On cooling, α-$Bi_2B_8O_{15}$ transformed into β-phase at 675 °C, evidencing that the phase transition is reversible and is of the first order.

2.2. Crystal-structure determination

The crystal chosen for data collection was examined with optical microscope and mounted on a glass fiber. Data were collected by means of a STOE IPDS II diffractometer using monochromated Mo$K\alpha$ radiation and frame widths of 2° in ω. The unit-cell dimensions (Table 1) were refined by least-square techniques. The data were corrected for Lorentz, polarization, absorption, and background effects. The intensity statistics indicated the space group $P\bar{1}$. During the indexing, it has been found that the crystal studied was twinned along the (001) plane. Attempts to find untwinned crystal were unsuccessful and the structure was solved and refined by means of the programs SIR-92 [9] and SHELXL-97 [10], respectively. Unfortunately, it was not possible to separate contributions from different twin components into the diffraction pattern that resulted in quite high $R1$ index of 0.081. The solution in non-centrosymmetric group $P1$ did not provide essential improvement but led to severe correlations problems. The final models included anisotropic displacement parameters for cations only. Attempts to refine B and O anisotropically resulted in physically unrealistic displacement parameters that we tend to ascribe to the severe

Table 1
Crystal data for β-$Bi_2B_8O_{15}$.

Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	4.3159(8)
b (Å)	6.4604(12)
c (Å)	22.485(4)
α (deg)	87.094(15)
β (deg)	86.538(15)
γ (deg)	74.420(14)
V (Å^3)	602.40(19)
Z	2
Range in h, k, l	$-5 \le h \le 5$, $-8 \le k \le 8$, $-28 \le l \le 26$
$\theta_{min} - \theta_{max}$	1.82 – 26.73
Total number of reflections	1803
Reflections with $I > 2\sigma(I)$	1584
R_1	0.0817
wR_2	0.1985
Goodness-of-fit	1.199
Min/max residual electron density	−2.518/3.184

Table 2
Atomic coordinates, equivalent isotropic thermal parameters U_{eq} (Å^2) and bond valence sums (*BVS*, v.u.) for β-$Bi_2B_8O_{15}$.

Atom	x/a	y/b	z/c	U_{eq}	*BVS* [14]	*BVS* [13]
Bi1	0.8733(3)	0.38024(16)	0.06739(6)	0.0307(5)	3.33	3.04
Bi2	0.4117(3)	0.89799(16)	0.43200(6)	0.0274(5)	3.23	2.98
O1	0.407(5)	0.512(3)	0.4364(10)	0.023(4)	1.97	1.98
O2	0.884(6)	−0.010(4)	0.0663(11)	0.033(5)	2.05	2.07
O3	0.440(4)	0.826(3)	0.0703(8)	0.015(4)	2.23	2.27
O4	1.354(6)	0.217(4)	0.0711(11)	0.034(5)	2.16	1.98
O5	−0.010(7)	1.349(4)	0.4378(12)	0.042(6)	1.84	1.88
O6	0.907(5)	0.733(3)	0.4273(10)	0.028(5)	2.28	2.15
O7	0.382(4)	0.859(3)	0.5265(9)	0.016(4)	2.20	1.99
O8	0.877(5)	0.372(3)	−0.0271(9)	0.021(4)	2.08	1.88
O9	0.654(5)	1.217(3)	0.3715(10)	0.027(5)	2.35	2.39
O10	0.919(6)	0.328(4)	−0.1295(10)	0.031(5)	1.74	1.74
O11	1.127(8)	0.393(5)	−0.2208(14)	0.058(8)	2.15	2.15
O12	1.097(9)	0.040(5)	−0.1961(16)	0.067(9)	1.90	1.90
O13	0.623(9)	1.543(5)	0.3176(15)	0.067(9)	1.75	1.75
O14	0.591(10)	1.894(6)	0.2862(17)	0.077(10)	1.65	1.65
O15	1.302(10)	−0.227(6)	−0.2681(17)	0.076(10)	2.60	2.60
B1	0.349(7)	0.690(4)	0.5742(13)	0.010(5)	2.89	2.89
B2	0.145(8)	0.799(5)	0.0729(16)	0.022(7)	3.19	3.19
B3	0.072(8)	1.529(5)	0.4310(16)	0.024(7)	3.20	3.20
B4	0.551(9)	1.005(5)	0.0671(17)	0.025(7)	2.82	2.82
B5	0.662(11)	1.313(7)	0.320(2)	0.038(9)	3.27	3.27
B6	1.030(12)	0.247(7)	−0.183(2)	0.043(10)	3.18	3.18
B7	1.253(17)	−0.037(11)	−0.253(3)	0.072(17)	3.02	3.02
B8	0.697(16)	1.671(10)	0.270(3)	0.062(14)	2.97	2.97
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1	0.0348(8)	0.0133(6)	0.0449(10)	−0.0028(5)	0.0054(6)	−0.0091(5)
Bi2	0.0214(6)	0.0145(6)	0.0471(10)	−0.0008(4)	−0.0039(5)	−0.0059(4)