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# Bismuth Borates: Two New Polymorphs of $BiB_3O_6$

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Two new polymorphs of $BiB_3O_6$ were identified at low temperatures using boric acid as a flux. Unlike $\alpha$-$BiB_3O_6$, which crystallizes in a noncentrosymmetric space group and, thus, shows exceptional nonlinear optical (NLO) properties, $\beta$-$BiB_3O_6$ (**I**) and $\gamma$-$BiB_3O_6$ (**II**) crystallize in the centrosymmetric space group $P2_1/n$ with the following lattice parameters: $a = 14.1664(1)$, $b = 6.7514(1)$, $c = 4.4290(1)$ Å, $\beta = 102.125(1)°$ for **I**; and $a = 8.4992(1)$, $b = 11.7093(1)$, $c = 4.2596(1)$ Å, $\beta = 121.141(1)°$ for **II**. However, from the structural point of view, the three polymorphs of $BiB_3O_6$ are closely related. The structure of $\beta$-$BiB_3O_6$ (**I**) contains a 2-dimensional borate layer, which could be considered to be an intralayered additive product of $\alpha$-$BiB_3O_6$. On the other hand, the 3-dimensional borate framework in $\gamma$-$BiB_3O_6$ (**II**) could be considered to be an interlayered additive product of $\beta$-$BiB_3O_6$ (**I**). According to the synthesis experiments and calculated density, it is proposed that compounds **I** and **II** should be the low-temperature (high-pressure) polymorphs of $BiB_3O_6$.

## Introduction

Borates have been a subject of interest for many decades, motivated by their extraordinary optical properties. Because boron may adopt not only triangular but also tetrahedral coordination with oxygen, borates often have complicated structures[1] and crystallize in noncentrosymmetric structures in many cases.[2] The nonlinear optical properties of metal borates have been extensively studied from both theoretical and experimental perspectives.[3−7] A remarkable finding recently showed that bismuth borate, $BiB_3O_6$ (hereafter $\alpha$-$BiB_3O_6$), exhibits exceptionally large nonlinear optical (NLO) coefficients.[8−11] $\alpha$-$BiB_3O_6$ crystallizes in a noncentrosymmetric space group ($C2$) and contains a 2-dimensional borate layer.[12] Theoretical calculation[10] based on first principles revealed that the NLO coefficients of $\alpha$-$BiB_3O_6$ originate mainly from the $(BiO_4)^{5-}$ group instead of borate groups, as in many other borate materials. Looking into the borate layer in $\alpha$-$BiB_3O_6$ carefully (Figure 1), one could find that the borate layer contains considerable $BO_3$ groups, which may undergo further condensation to form more condensed (or more polymerized) phases. According to the Lux−Flood acid−base concept,[13] the polymerized borates are often less stable for high-valence and small-sized cations and cannot be obtained by conventional high-temperature solid-state reactions. However, as we have demonstrated in the rare earth borate system,[14−16] the hydrated polyborates could be synthesized from boric acid flux and, then, the metastable anhydrous polyborates were obtained by using the hydrated polyborates as precursors. In the $Bi_2O_3$−$B_2O_3$ system, the compounds known so far include $\alpha$-$BiB_3O_6$,[12,17−18] $Bi_4B_2O_9$,[19]

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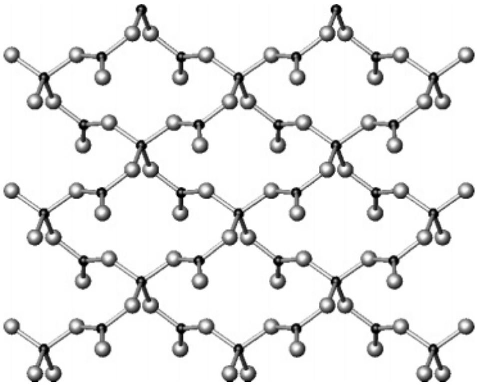

**Figure 1.** Borate layer in α-$BiB_3O_6$.

$Bi_6B_{10}O_{24}$,[20] $Bi_2B_8O_{15}$,[21,22] and $Bi_{24.5}BO_{38.25}$.[23] α-$BiB_3O_6$ was obtained by quenching from high temperature, and all of the other phases were synthesized by high-temperature reactions. Recently, we carried out a systematic study on the $Bi_2O_3-H_3BO_3$ system and identified a series of new hydrated and anhydrous bismuth borates, including $BiB_2O_4F$, $Bi_3[B_6O_{13}(OH)]$, $Bi[B_4O_6(OH)_2]OH$, $\beta$-$BiB_3O_6$, and $\gamma$-$BiB_3O_6$. In this paper, we focus only on the syntheses and structures of two new polymorphs of $BiB_3O_6$, i.e., $\beta$-$BiB_3O_6$ (**I**) and $\gamma$-$BiB_3O_6$ (**II**). The other bismuth borates will be discussed in a separate paper.[24]

## Experimental Section

**Syntheses.** The syntheses of $\beta$-$BiB_3O_6$ (**I**) and $\gamma$- $BiB_3O_6$ (**II**) were carried out in Teflon autoclaves (50 $cm^3$ volume) by using molten boric acid as a flux. **I** and **II** were formed under similar reaction conditions. Typically, 0.58 g of $Bi_2O_3$ and 3.09 g of $H_3BO_3$ were ground adequately and, then, autoclaved under autogenous pressure at 240 °C. **I** was formed in 7 days, while prolonging the reaction (14 days) led to **II**. White polycrystalline powders, which are the single-phases of **I** and **II**, were obtained by removing residual boric acid with hot distilled water. The products were dried at 80 °C for 10 h before characterizations. In many cases, the products were often mixtures containing both **I** and **II**. For example, reaction at 240 °C for 10 days yielded a product containing both $\beta$- and $\gamma$-$BiB_3O_6$. As the reaction further proceeded, the $\beta$-$BiB_3O_6$ content decreased, while the $\gamma$-$BiB_3O_6$ increased. Very often, the sample of $\beta$-$BiB_3O_6$ was not a single-phase product but contained small amounts of another unknown phase, whereas obtaining a single-phase product was much easier for $\gamma$-$BiB_3O_6$.

**Characterization.** Powder X-ray diffraction data used for structure determination were collected on a Bruker D8-Advance diffractometer with a curved germanium primary monochromator (Cu Kα1) in a transmission mode ($2\theta$ range $= 12-120°$, step $= 0.0144°$, scan speed $=$ 60 s/step, 50 kV, 40 mA) at room temperature. Chemical analysis was carried out for bismuth and boron by using the inductively coupled plasma (ICP) method. The measured Bi/B mole ratio is 1:2.94 for **I** and 1:3.08 for **II**, which confirms that both **I** and **II** are the new polymorphs of $BiB_3O_6$. IR spectra, recorded on a Nickel Magna-750 FT-IR spectrometer, indicate the presence of both $BO_3$ and $BO_4$ groups in **I** and only $BO_4$ groups in **II**. In addition, the IR study also shows no OH groups existing in these two compounds, which agrees with the thermogravimetric analysis (TGA), which shows that no weight loss occurs on heating up to 700 °C for both **I** and **II**.

**X-ray Crystallographic Studies.** The as-synthesized crystals are too small to be suitable for single-crystal structure study. Therefore, the crystal structures of these two compounds were determined by an ab initio method using powder X-ray diffraction data. The diffraction patterns of both compounds can be readily indexed to monoclinic unit cells,[25] i.e., $a = 14.1664(1)$, $b = 6.7514(1)$, $c = 4.4290(1)$ Å, and $\beta = 102.125(1)°$ for **I** and $a = 8.4992(1)$, $b = 11.7093(1)$, $c = 4.2596(1)$ Å, and $\beta = 121.141(1)°$ for **II**. Careful inspection of the reflections revealed that both compounds crystallize in the space group $P2_1/n$. Optimal estimates of the individual reflection intensities were extracted by a profile-fitting method using the EXTRA program.[26] The initial structure models were established by the direct method (Sirpow92),[27] and at this stage, all atoms in the structure were located from the E-map. The structure refinements were carried out with the Rietveld method (TOPAS).[28] The final refinement, with isotropic thermal displacement parameters, yielded $R\text{p} = 0.0520$ and $R\text{wp} = 0.0694$ for **I** and $R\text{p} = 0.0527$ and $R\text{wp} = 0.0718$ for **II**. The main reflection peaks of the unknown phase in the $\beta$-$BiB_3O_6$ sample (~5 mol % according to the reflection intensity), for example, $2\theta = 21.4°$ and 23.8°, were treated by profile refinement of individual peaks in the structure refinement. Figure 2 shows the profile fit of the diffraction patterns. Table 1 lists the crystallographic data, and Table 2 provides the selected bond lengths and angles for these two compounds.

## Results and Discussions

The formation reactions for **I** and **II** are rather similar. The only difference is the reaction time; thus, it is speculated that **I** was initially formed in the system, and as the reaction proceeded, it transformed into **II**. **I** and **II** are the two new polymorphs of $BiB_3O_6$. Regarding the known $BiB_3O_6$ as an α-polymorph, **I** and **II** are named as $\beta$-$BiB_3O_6$ and $\gamma$-$BiB_3O_6$, respectively. In fact, the products obtained from the $Bi_2O_3-H_3BO_3$ reaction system at 240 °C were often mixtures containing both **I** and **II**. The other known anhydrous bismuth borates do not appear under such conditions, but an unknown phase was often observed together with $\beta$-$BiB_3O_6$, which is characterized by several distinct reflections (for example, $2\theta = 21.4$, 23.8, 30.2, 32.6, and 46.8°). The forming conditions of this "ghost" phase were uncertain; its content in the product varied from time to time, but it was always present as a minor phase. At present, we do not know the composition and unit cell of this phase. However, its diffraction pattern is distinct from the other known

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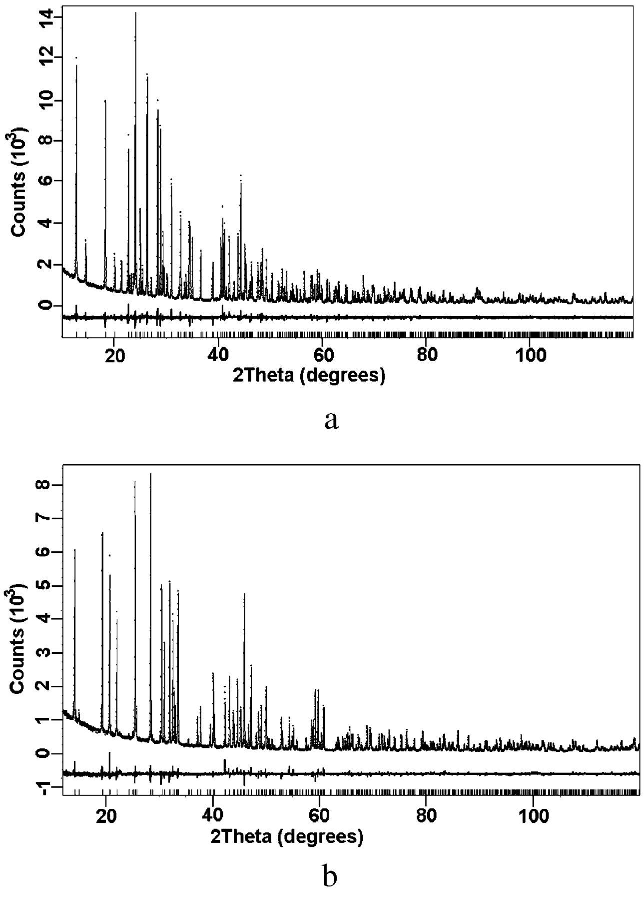


**Figure 2.** Profile fit to the powder X-ray diffraction pattern for (a) $\beta$-$BiB_3O_6$ and (b) $\gamma$-$BiB_3O_6$. A dot over a peak indicates the observed value; the solid line represents the calculated value; the difference curve is shown below the diffraction patterns; and the marks shown at the bottom of the figure are the calculated reflection positions.

**Table 1.** Crystallographic Data and Structure Refinement Parameters for $\beta$-$BiB_3O_6$ (**I**) and $\gamma$-$BiB_3O_6$ (**II**)

| structural parameter | **I** | **II** |
|---|---|---|
| empirical formula | $BiB_3O_6$ | $BiB_3O_6$ |
| formula mass | 337.41 | 337.41 |
| crystal system | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 14.1664(1) | 8.4992(1) |
| $b$ (Å) | 6.7514(1) | 11.7093(1) |
| $c$ (Å) | 4.4290(1) | 4.2596(1) |
| $\beta$ (deg) | 102.125(1) | 121.141(1) |
| $V$ (Å$^3$) | 414.151(6) | 362.830(5) |
| $Z$ | 4 | 4 |
| $\rho_{calcd}$ (g/cm$^3$) | 5.411 | 6.177 |
| diffraction technique | powder | powder |
| $R$ indices | $R$p = 0.0520<br>$R$wp = 0.0694 | $R$p = 0.0527<br>$R$wp = 0.0718 |

bismuth borates and oxides. The formation reactions of **I** and **II** in the boric acid flux can be expressed as follows:

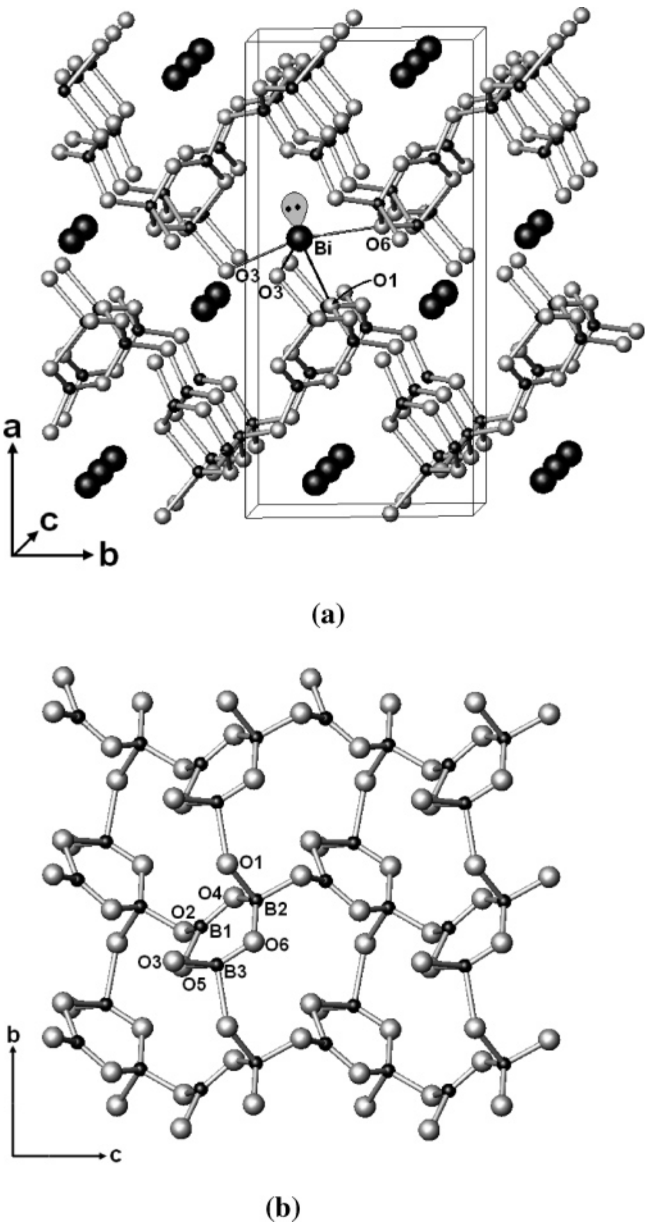
$$6H_3BO_3 + Bi_2O_3 \xrightarrow{240\ ^{o}C,\ 7\ days} 2\beta\text{-}BiB_3O_6 + 9H_2O \quad (1)$$

$$6H_3BO_3 + Bi_2O_3 \xrightarrow{240\ ^{o}C,\ 14\ days} 2\gamma\text{-}BiB_3O_6 + 9H_2O \quad (2)$$

**Structure of $\beta$-$BiB_3O_6$.** Figure 3a shows a projection of the $\beta$-$BiB_3O_6$ structure. The borate anion group in $\beta$-$BiB_3O_6$ is a buckled layer containing $BO_3$ triangles and $BO_4$ tetrahedra in the ratio of 1:2. The borate layers in the structure stack along the *a*-axis, and the bismuth cations are located between the borate layers. The fundamental building block (FBB) of the borate layer is a 3-ring unit ($2T + \Delta$, $T$ and $\Delta$ represent $BO_4$ and $BO_3$ groups, respectively) which shares four oxygen atoms forming 7-membered borate rings consisting of five $BO_4$ and two $BO_3$ groups (Figure 3b). The oxygen atoms in the borate layer could be classified into two groups. O3 is the terminal oxygen that only bonds to one boron atom (B3). The other five oxygen atoms (O1, O2, O4, O5, and O6) are bridged atoms bonding to two boron atoms. The terminal oxygen atom (O3) has strong bonding interactions with bismuth cations (Bi−O distance: 2.154, 2.425, and 2.775 Å). Similar to the cases of other bismuth compounds, the coordination polyhedron of bismuth is irregular in $\beta$-$BiB_3O_6$. In fact, the coordination polyhedron is difficult to define from the Bi−O distances, since they vary gradually from 2.15 to 2.95 Å (for CN = 9). One could, of course, include all those oxygen atoms in a coordination polyhedron.[12,21] However, a more sensible way to describe the coordination polyhedron is to include only the oxygen atoms that have strong Bi−O interactions and the lone electron pair.[10] As shown in Figure 3a, the coordination polyhedron of bismuth atoms is a trigonal bipyramid, if only

**Table 2.** Selected Distances (Å) and Angles (deg) for $\beta$-$BiB_3O_6$ (**I**) and $\gamma$-$BiB_3O_6$ (**II**)

| $\beta$-$BiB_3O_6$ (**I**) | | $\gamma$-$BiB_3O_6$ (**II**) | |
|---|---|---|---|
| Distances (Å) | | | |
| Bi−O3 | 2.154(9) | Bi−O2 | 2.159(13) |
| Bi−O1 | 2.214(9) | Bi−O6 | 2.206(9) |
| Bi−O3 | 2.425(8) | Bi−O2 | 2.338(10) |
| Bi−O6 | 2.543(8) | Bi−O3 | 2.486(9) |
| Bi−O2 | 2.736(8) | Bi−O5 | 2.504(10) |
| Bi−O5 | 2.769(9) | Bi−O4 | 2.668(8) |
| Bi−O3 | 2.775(7) | Bi−O2 | 2.976(9) |
| Bi−O2 | 2.889(10) | Bi−O4 | 2.990(10) |
| Bi−O4 | 2.950(8) | B1−O1 | 1.53(2) |
| B1−O2 | 1.394(20) | B1−O2 | 1.43(2) |
| B1−O4 | 1.375(9) | B1−O3 | 1.40(2) |
| B1−O5 | 1.384(16) | B1−O4 | 1.57(3) |
| B2−O1 | 1.419(10) | B2−O1 | 1.47(2) |
| B2−O2 | 1.571(18) | B2−O3 | 1.40(2) |
| B2−O4 | 1.470(9) | B2−O5 | 1.57(2) |
| B2−O6 | 1.385(18) | B2−O6 | 1.50(2) |
| B3−O1 | 1.514(8) | B3−O1 | 1.51(3) |
| B3−O3 | 1.527(21) | B3−O4 | 1.56(3) |
| B3−O5 | 1.398(20) | B3−O5 | 1.54(2) |
| B3−O6 | 1.434(15) | B3−O6 | 1.41(2) |
| Angles (deg) | | | |
| O2−B1−O4 | 125.2(13) | O1−B1−O2 | 104.4(11) |
| O2−B1−O5 | 116.8(3) | O1−B1−O3 | 111.3(14) |
| O4−B1−O5 | 118.0(3) | O1−B1−O4 | 106.9(15) |
| O1−B2−O2 | 106.8(3) | O2−B1−O3 | 118.7(17) |
| O1−B2−O4 | 114.0(5) | O2−B1−O4 | 108.2(12) |
| O1−B2−O6 | 112.1(5) | O3−B1−O4 | 106.6(16) |
| O2−B2−O4 | 108.5(11) | O1−B2−O3 | 117.1(17) |
| O2−B2−O6 | 101.7(5) | O1−B2−O5 | 108.7(9) |
| O4−B2−O6 | 112.8(4) | O1−B2−O6 | 103.7(9) |
| O1−B3−O3 | 111.3(11) | O3−B2−O5 | 104.1(15) |
| O1−B3−O5 | 109.8(5) | O3−B2−O6 | 112.7(15) |
| O1−B3−O6 | 109.4(5) | O5−B2−O6 | 109.8(16) |
| O3−B3−O5 | 104.3(4) | O1−B3−O4 | 105.8(12) |
| O3−B3−O6 | 108.1(11) | O1−B3−O5 | 119.2(11) |
| O5−B3−O6 | 113.5(9) | O1−B3−O6 | 110.8(14) |
| | | O4−B3−O5 | 109.9(15) |
| | | O4−B3−O6 | 104.3(13) |
| | | O5−B3−O6 | 106.0(15) |



(a)

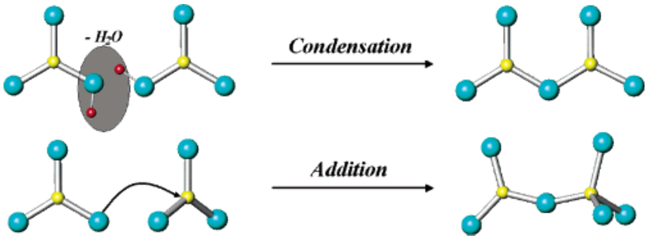
(b)

**Figure 3.** (a) Projection and (b) borate layer in the structure of $\beta$-$BiB_3O_6$.

those Bi−O bonds of less than 2.6 Å and the lone electron pair are considered.

The borate layer in $\beta$-$BiB_3O_6$ has exactly the same composition as that in $\alpha$-$BiB_3O_6$ but contains more $BO_4$ groups. The structural relationship of these two borate layers can be understood by analysis of the addition reaction on triangular borate groups. To understand the structural relationship, let us consider first a general polymerization reaction of borate groups. Starting from a triangular borate group, the polymerization may occur through condensation or addition reaction mechanisms (Scheme 1). Condensation is a dehydration process in which a water molecule was removed, resulting in a polyborate group that maintains the triangular geometry for all boron atoms. On the other hand, the triangular borate group is a Lewis acid and is susceptible to attack by oxygen. As shown in Scheme 1, the Lewis acid−base reaction converts a $BO_3$ to a $BO_4$, forming a polyborate group consisting of tetrahedral boron. This reaction is, therefore, considered to be an addition reaction on a $BO_3$ group.

**Scheme 1**



In Figure 4, we compare the borate layers in $\alpha$-$BiB_3O_6$ and $\beta$-$BiB_3O_6$. The borate layer in $\alpha$-$BiB_3O_6$ consists of triangular and tetrahedral boron atoms ($3\infty_2$: $T + 2\Delta$, $BO_4/BO_3$ ratio: 1:2). The $BO_4$ groups share four oxygen atoms with $BO_3$, and the $BO_3$ groups, on the other hand, share two oxygens with $BO_4$, forming a planar net of 8-membered borate rings. Each $BO_3$ group in $\alpha$-$BiB_3O_6$ has a terminal oxygen, which could attack the boron on the neighboring $BO_3$ group. As shown in Figure 4, the borate layer in $\beta$-$BiB_3O_6$ could be considered to be a product of an intralayered addition reaction of $\alpha$-$BiB_3O_6$, which generates a 3-membered borate ring and, at the same time, reduces the 8-membered ring to a 7-ring. The resulting borate layer consists of 3- and 7-membered borate rings with the $BO_4/BO_3$ ratio of 2:1, which is exactly the same as that in $\beta$-$BiB_3O_6$ ($3\infty_2$: $2T + \Delta$). Figure 4 represents only the structural relationship between $\alpha$-$BiB_3O_6$ and $\beta$-$BiB_3O_6$. Of course, it also implies a phase transformation from $\alpha$-$BiB_3O_6$ to $\beta$-$BiB_3O_6$ via an addition reaction (Scheme 1). However, this phase transformation might be a pressure-induced process and, thus, has not been observed experimentally in this study.

**Structure of $\gamma$-$BiB_3O_6$.** Although a number of bismuth borates, such as $\alpha$-$BiB_3O_6$,[12] $Bi_4B_2O_9$,[19] $Bi_6B_{10}O_{24}$,[20] $Bi_2B_8O_{15}$,[21,22] and $Bi_{24.5}BO_{38.25}$,[23] were identified, the borate frameworks in these compounds are all either 1- or 2-dimensional. Therefore, $\gamma$-$BiB_3O_6$ (**II**) is the only bismuth borate known so far that contains a 3-dimensional borate framework. The structure of the borate framework is rather complicated (Figure 5a), containing 3-, 4-, 6-, and 10-membered borate rings. The fundamental building block is a $B_3O_9$ unit (Figure 5b) consisting of three corner-sharing $BO_4$ groups. The oxygen atoms in $\gamma$-$BiB_3O_6$ can be classified into three groups. O2 is a terminal oxygen bonded to a boron and, in addition, has strong interactions with two bismuth atoms with the Bi−O distance of 2.159 and 2.338 Å, respectively. O1 is bonded to three tetrahedral borons (B1, B2, and B3). The other four oxygens are bridged atoms bonding to two boron atoms. The bismuth atoms are located within the 10-membered ring channels with an irregular coordination polyhedron (Figure 5a). Taking only the oxygen atoms with the Bi−O distances less than 2.6 Å into consideration, the coordination polyhedron of bismuth is a pyramid. If the lone electron pair is included, the coordination polyhedron is a distorted octahedron.

The borate framework in $\gamma$-$BiB_3O_6$ is related to the borate layers in $\beta$-$BiB_3O_6$ by an interlayered addition reaction. To

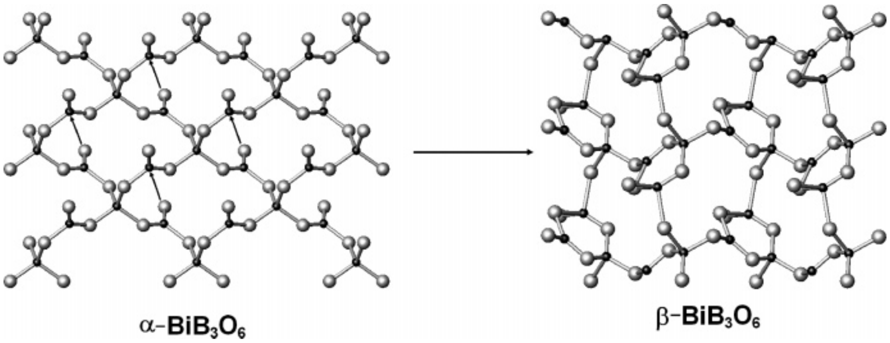
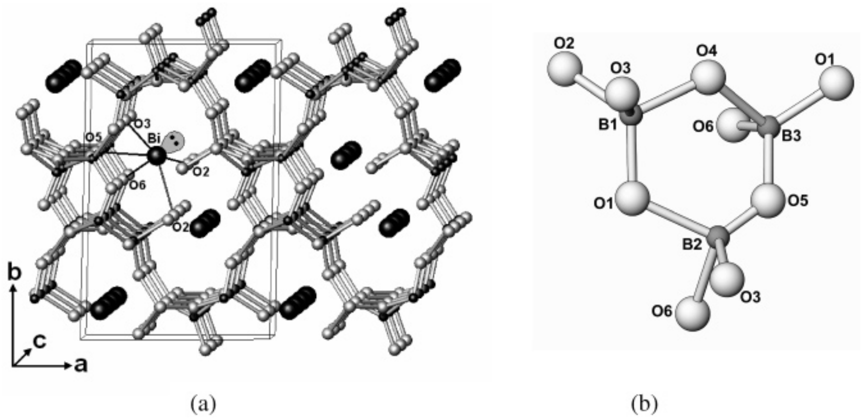


**Figure 4.** Structural relationship of the borate layers in α-$BiB_3O_6$ and $\beta$-$BiB_3O_6$. The arrows shown in the α-$BiB_3O_6$ layer indicate the hypothetical reaction process.



(a) (b)

**Figure 5.** (a) Structure and (b) fundamental building block of $\gamma$-$BiB_3O_6$.

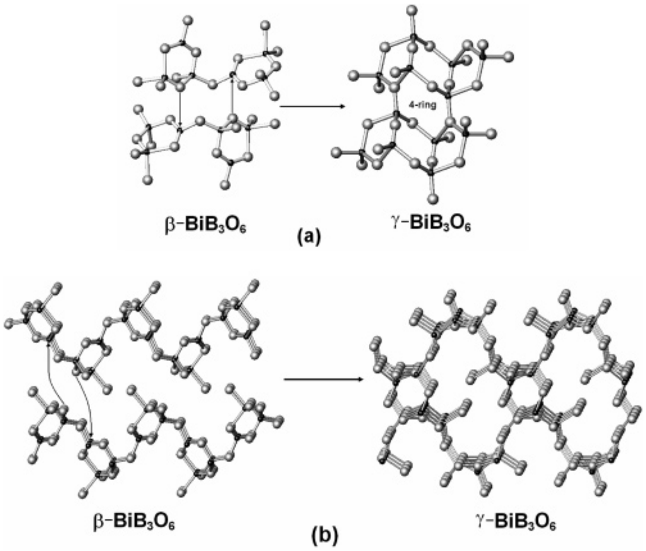


**Figure 6.** (a) Fragments in $\beta$-$BiB_3O_6$ and $\gamma$-$BiB_3O_6$ showing the interlayered addition and the formation of a 4-membered ring; (b) borates in $\beta$-$BiB_3O_6$ and $\gamma$-$BiB_3O_6$ showing the structural relationship.

emphasize the structural relationship, we show two selected fragments of the borate frameworks in $\beta$-$BiB_3O_6$ and $\gamma$-$BiB_3O_6$ (Figure 6a). The addition reaction occurs between triangular borons and bridged oxygens across the borate layers, which generates a 3-coordinated oxygen and a 4-membered ring and, at the same time, converts all triangular boron atoms to a tetrahedral geometry. The topology of the interlayered additive product of $\beta$-$BiB_3O_6$ is exactly the same as that in $\gamma$-$BiB_3O_6$, as shown in the right part of Figure 6a. In Figure 6b, we show the borate frameworks in $\beta$-$BiB_3O_6$ and $\gamma$-$BiB_3O_6$. The arrows on the left indicate the positions of the interlayered addition reactions. It can be seen that the borate framework may undergo a series of adjustments during the addition reaction but that the connection and structural topology are retained in the structure of $\gamma$-$BiB_3O_6$.

**Phase Transformation of the $BiB_3O_6$ Polymorphs.** As far as the unit cell volumes ($\bar{V}$ = 111.35, 103.54, and 90.71 Å$^3$ per formula for α-, $\beta$-, and $\gamma$-$BiB_3O_6$, respectively) and the bond enthalpy are concerned, $\gamma$-$BiB_3O_6$ should be a low-temperature and high-pressure polymorph, which would transform to the $\beta$-polymorph and then to the α-polymorph at high temperatures (or low pressures). High-temperature X-ray diffraction study indicates, however, that the $\gamma$-$BiB_3O_6$ is sustained at a temperature very close to the melting point of $BiB_3O_6$ (708 °C); therefore, the phase transitions of either $\gamma-\alpha$ or $\gamma-\beta$ were not observed during the heating treatments. On the other hand, $\beta$-$BiB_3O_6$ converts to $\gamma$-$BiB_3O_6$ at about 660 °C during the heating, and the $\gamma$-polymorph is maintained down to room temperature. Therefore, the $\beta$-polymorph could be considered to be a metastable phase under ambient pressure at low temperature. Overcoming the kinetic hindrance at 660 °C leads to the $\beta-\gamma$ transformation. Considering that α-$BiB_3O_6$ can only be obtained by a quick-quenching process, the α-polymorph might only exist in a very narrow temperature range near the melting point. In practice, α-$BiB_3O_6$ crystals can only be obtained by the top-seeded crystal growth technique,[17,18] where the α-$BiB_3O_6$

crystals formed at the melt surface are quenched quickly by pulling off the crystals. We also attempted to synthesize the α-$BiB_3O_6$ with a conventional solid-state reaction near the melting point and subsequent air quenching. The obtained product is a mixture containing both α-$BiB_3O_6$ and $\gamma$-$BiB_3O_6$. Furthermore, according to the synthesis experiments in boric acid flux at 240 °C, $\beta$-$BiB_3O_6$ was formed initially and, as the reaction proceeded, it converted to $\gamma$-$BiB_3O_6$. All of these observations support the ideas that the $\gamma$- and α-polymorphs are low- and high-temperature (or high- and low-pressure) phases for $BiB_3O_6$ and that the $\beta$-polymorph is an intermediate phase that cannot be synthesized by conventional solid-state methods.

**Conclusions.** Through synthesis reactions in boric acid flux, we identified two new polymorphs of $BiB_3O_6$. Unlike the α-$BiB_3O_6$, which is a remarkable nonlinear optical (NLO) material, both $\beta$-$BiB_3O_6$ and $\gamma$-$BiB_3O_6$ crystallize in the centrosymmetric space group $P2_1/n$. However, the structures of these polymorphs are closely related. $\beta$-$BiB_3O_6$ can be considered to be an intralayered additive product of α-$BiB_3O_6$, and $\gamma$-$BiB_3O_6$ is an interlayered additive product of $\beta$-$BiB_3O_6$. Although high-temperature X-ray diffraction cannot provide a clear picture for the phase transformation among these three polymorphs, the experiments clearly indicated that $\gamma$-$BiB_3O_6$ is a low-temperature (or high-pressure) phase that is stable near the melting point. The α-$BiB_3O_6$, on the other hand, is a high-temperature (or low-pressure) phase; thus, it can only be obtained by quick-quenching techniques. On the basis of the unit cell volumes, one may expect the phase transformation from α- to $\beta$-$BiB_3O_6$ and then to $\gamma$-$BiB_3O_6$ under high pressure. The high-pressure experiment started with α-$BiB_3O_6$ may allow one to monitor the whole phase-transformation process in situ. Additionally, the synthesis study of these two new polymorphs demonstrates once again that boric acid flux is a useful technique which may produce solid-state compounds that cannot be obtained by conventional high-temperature reactions. Finally, although these two new bismuth polyborates do not show NLO properties, knowing the structural relationship of these $BiB_3O_6$ polymorphs is useful in understanding the chemistry of bismuth borates and the procedure of crystal growth for the α-$BiB_3O_6$ material.

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**Supporting Information Available:** IR spectrum, fractional atomic coordinates, and isotropic displacement parameters of $\beta$-$BiB_3O_6$ and $\gamma$-$BiB_3O_6$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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