

# Phase transitions among four BiB<sub>3</sub>O<sub>6</sub> polymorphs: a detailed investigation†

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The stability and phase transformations of the four BiB<sub>3</sub>O<sub>6</sub> polymorphs, *i.e.*,  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -BiB<sub>3</sub>O<sub>6</sub>, were investigated under different temperatures and pressures.  $\beta$ -BiB<sub>3</sub>O<sub>6</sub> is a metastable phase which can only be obtained by boric acid flux method in a sealed system at low temperature. The other polymorphs,  $\alpha$ -,  $\gamma$ - and  $\delta$ -BiB<sub>3</sub>O<sub>6</sub>, are thermodynamic stable phases. Owing to the large kinetic effect, the phase transformations of the BiB<sub>3</sub>O<sub>6</sub> polymorphs are generally slow, thus an extensive annealing process was used in this study. The study shows that  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> is the high-temperature phase and its stable area is narrow (710–715 °C) in atmospheric conditions, while  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> is a stable phase in the intermediate temperature range (~680–710 °C). The results also confirm that  $\delta$ -BiB<sub>3</sub>O<sub>6</sub> is a high-pressure phase and all other polymorphs may transfer to  $\delta$ -phase under high pressure. However, the  $\delta$ -phase can be obtained by annealing  $\alpha$ - or  $\beta$ -BiB<sub>3</sub>O<sub>6</sub> at relatively low temperature under ambient pressure. Therefore,  $\delta$ -BiB<sub>3</sub>O<sub>6</sub> can also be regarded as the low-temperature phase in this system. Based on the experimental results, as well as the thermodynamic principles, a pressure–temperature ( $P$ – $T$ ) phase diagram for the BiB<sub>3</sub>O<sub>6</sub> system is proposed.

## Introduction

BIBO, first identified in Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> phase diagram as  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> in early 1960s,<sup>1</sup> has been demonstrated as one of the most promising nonlinear optical materials. The synthesis,<sup>2,3</sup> structure,<sup>2–5</sup> crystal growth<sup>3,6–8</sup> and physical properties of a series of compounds based on this formula have attracted considerable attention.<sup>3,9–13</sup> Up to now, four different polymorphs have been identified in BiB<sub>3</sub>O<sub>6</sub> system, *i.e.*, monoclinic  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> ( $C2$ ),<sup>1</sup>  $\beta$ -BiB<sub>3</sub>O<sub>6</sub> ( $P2_1/n$ ),  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> ( $P2_1/n$ )<sup>2</sup> and orthorhombic  $\delta$ -BiB<sub>3</sub>O<sub>6</sub> ( $Pca2_1$ ).<sup>3</sup> The structure of  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> consists of borate layers with a BO<sub>4</sub>/BO<sub>3</sub> ratio of 1/2 (Fig. 1a).<sup>4,5</sup>  $\beta$ -BiB<sub>3</sub>O<sub>6</sub> also contains a 2D borate layer, which can be depicted as an innerlayer condensation of  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub>, with a BO<sub>4</sub>/BO<sub>3</sub> ratio of 2/1 (Fig. 1b).<sup>2</sup> The borate network in  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub>, which can be expressed as interlayer condensation of the borate layers in  $\beta$ -BiB<sub>3</sub>O<sub>6</sub>, is a 3D structure that is completely constructed of BO<sub>4</sub> groups (Fig. 1c).<sup>2</sup> The fourth modification,  $\delta$ -BiB<sub>3</sub>O<sub>6</sub>, known as a high-pressure phase, also contains a 3D borate framework constructed exclusively of BO<sub>4</sub> groups (Fig. 1d).<sup>3</sup> From the structural point of view, the dimensionality of the borate framework increases from 2D in  $\alpha$ - and  $\beta$ -phases to 3D in  $\gamma$ - and  $\delta$ -phases and the BO<sub>4</sub>/BO<sub>3</sub> ratio also shows a similar increasing tendency. The effective coordination numbers (ECoN, as described by Hoppe<sup>14</sup>) of bismuth cation also increase from  $\alpha$ - to  $\delta$ -phase ( $\alpha$ : 5.1,  $\beta$ : 5.6,  $\gamma$ : 5.9 and  $\delta$ :

6.8). As a consequence, the density of these four polymorphs increases accordingly (Fig. 1).

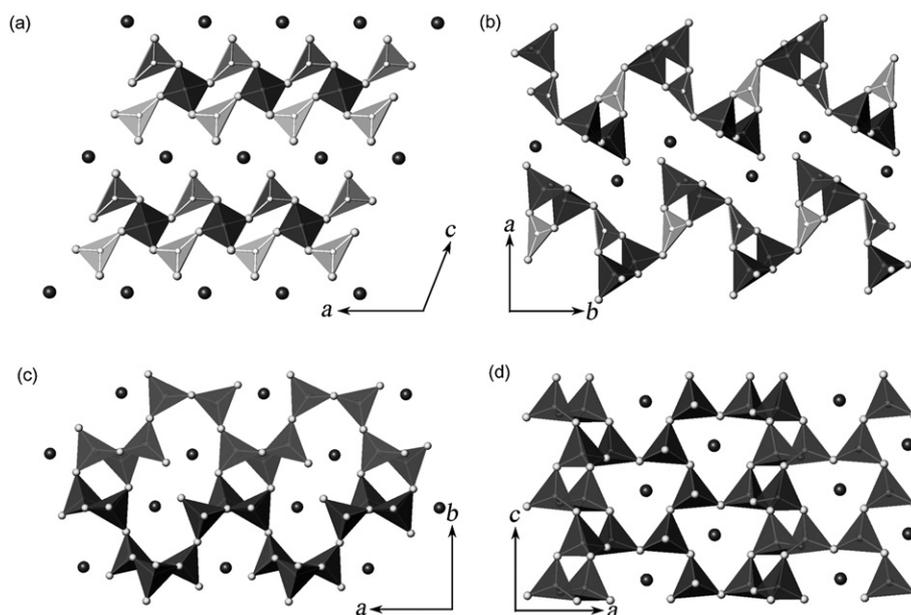
It is known that  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> crystals were grown mainly using a top-seeded method from a melt.<sup>6–8</sup> Both  $\beta$ - and  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> were identified by boric acid flux method in sealed systems,<sup>2</sup> while  $\delta$ -BiB<sub>3</sub>O<sub>6</sub> was found under high pressure.<sup>3</sup> A natural question arises for the phase relationship of the BiB<sub>3</sub>O<sub>6</sub> polymorphs, *i.e.*, whether the phase transitions may occur and under what conditions. A preliminary study in our group revealed that  $\beta$ -BiB<sub>3</sub>O<sub>6</sub> converted to  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> at about 660 °C, while the *in-situ* temperature-variable X-ray diffraction indicated that  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> sustained up to a temperature near its melting point.<sup>2</sup> The detailed study on  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> using temperature-variable neutron and X-ray diffraction techniques on powder and single-crystalline samples revealed the anisotropic thermal behavior of this phase, but did not find any evidence of structural phase transformations from  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> to any other polymorphs between 3.5 and 999 K at ambient pressure.<sup>15</sup> However, our further work indicated that the solid state reaction at about 700 °C might give out a sample in the mixture, which contained both  $\alpha$ - and  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> phases. The inconsistent results caught our attention. In the study on borates, we noticed that the kinetic effect often plays an important role in the processes of phase transition. Hysteresis is often encountered in the phase transformation process for borate systems, particularly when the formation/breakage of the B–O bonds is involved. A convincing example is YBO<sub>3</sub>, a potential luminescent material in PDP display, which has two polymorphs.<sup>16</sup> The transformation from LT-YBO<sub>3</sub> to HT-YBO<sub>3</sub> occurs at 965 °C, involving a B–O bond break from the B<sub>3</sub>O<sub>9</sub> ring to isolated BO<sub>3</sub> triangles. The reverse transition, however, occurs at far lower temperature (580 °C) on cooling.

Regarding to the technological importance of the  $\alpha$ -polymorph, it is desirable to learn the chemistry behind these polymorphs. Therefore, we carried out a systematic study on BiB<sub>3</sub>O<sub>6</sub>

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**Fig. 1** Crystal structures of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ - $\text{BiB}_3\text{O}_6$ . (a)  $\alpha$ - $\text{BiB}_3\text{O}_6$ :  $C2$ ,  $a = 7.116 \text{ \AA}$ ,  $b = 4.993 \text{ \AA}$ ,  $c = 6.508 \text{ \AA}$ ,  $\beta = 105.6^\circ$ ,  $\rho = 5.033 \text{ g cm}^{-3}$ ; (b)  $\beta$ - $\text{BiB}_3\text{O}_6$ :  $P2_1/n$ ,  $a = 14.1664 \text{ \AA}$ ,  $b = 6.7514 \text{ \AA}$ ,  $c = 4.4290 \text{ \AA}$ ,  $\beta = 102.125^\circ$ ,  $\rho = 5.411 \text{ g cm}^{-3}$ ; (c)  $\gamma$ - $\text{BiB}_3\text{O}_6$ :  $P2_1/n$ ,  $a = 8.4992 \text{ \AA}$ ,  $b = 11.7093 \text{ \AA}$ ,  $c = 4.2596 \text{ \AA}$ ,  $\beta = 121.141^\circ$ ,  $\rho = 6.177 \text{ g cm}^{-3}$ ; (d)  $\delta$ - $\text{BiB}_3\text{O}_6$ :  $Pca2_1$ ,  $a = 18.448 \text{ \AA}$ ,  $b = 4.4495 \text{ \AA}$ ,  $c = 4.2806 \text{ \AA}$ ,  $\rho = 6.378 \text{ g cm}^{-3}$ ; triangles,  $\text{BO}_3$ ; tetrahedra,  $\text{BO}_4$ ; large spheres,  $\text{Bi}^{3+}$ .

polymorphs under different temperatures and pressures. Since the phase transitions in the  $\text{BiB}_3\text{O}_6$  system also involved a considerable B–O bond breakage and formation, a long-time annealing treatment and seed-induced technique were applied in the study in order to reduce the kinetic effect. In this paper, we will present intriguing phase transition processes and propose a schematic pressure–temperature diagram to show the relationship among  $\alpha$ -,  $\gamma$ -, and  $\delta$ -phases.

## Experimental

### Synthesis

A powder sample of  $\alpha$ - $\text{BiB}_3\text{O}_6$  was prepared by conventional solid-state reactions.<sup>1,17</sup> A stoichiometric mixture of  $\text{Bi}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$  (with 1 mol% excess  $\text{H}_3\text{BO}_3$ ) was fully mixed and pre-heated at  $550^\circ\text{C}$  for 10 h (forming a mixture of  $\text{Bi}_2\text{B}_8\text{O}_{15}$  and  $\text{Bi}_3\text{B}_5\text{O}_{12}$ ). Then, the precursor was re-ground and heated to  $700^\circ\text{C}$  at a rate of  $1^\circ\text{C min}^{-1}$  and kept at this temperature for 10 h.  $\beta$ - $\text{BiB}_3\text{O}_6$  was prepared under hydrothermal conditions.<sup>2</sup> Typically, 0.5 g of  $\text{Bi}_2\text{O}_3$  and 3.32 g of  $\text{H}_3\text{BO}_3$  were ground and put into a 50 mL Teflon container, and 0.4 mL distilled water was added. The container was sealed and kept at  $240$ – $260^\circ\text{C}$  statically for 3–7 d in an oven. The solid product was washed by hot distilled water ( $80^\circ\text{C}$ ) to remove the residual boric acid and dried at  $100^\circ\text{C}$ .  $\gamma$ - $\text{BiB}_3\text{O}_6$  was prepared in a similar way but at higher temperature,  $270^\circ\text{C}$ . A specially designed PPL modified Teflon container (25 mL) was used for this high temperature synthesis. Since a small amount of  $\text{Cl}^-$  ions might be released from the PPL modified Teflon,  $\text{BiOCl}$  often appeared in the product as impurity. The high pressure phase,  $\delta$ - $\text{BiB}_3\text{O}_6$  was synthesized by treating  $\alpha$ -,  $\beta$ - or  $\gamma$ - $\text{BiB}_3\text{O}_6$  under high-pressure and high-temperature, *i.e.*, 2GPa/ $800^\circ\text{C}$  for 30 min.

### Heating treatments under ambient pressure

Polycrystalline samples of certain  $\text{BiB}_3\text{O}_6$  polymorphs were heated from room temperature to the annealing temperature at  $1^\circ\text{C min}^{-1}$  heating rate in a muffle furnace and kept at that temperature for a certain time. The temperature and its gradient distribution inside the furnace were calibrated by observation of the melting evidence of  $\alpha$ - $\text{BiB}_3\text{O}_6$ . In order to induce the reaction and increase the reaction rate, small amount (generally less than 2 wt%) crystal seeds were added into the initial samples in some batches. A few of the samples were even mixed with a considerable amount of seed crystals, as shown in the results.

### Heating treatments under high pressure

The high-pressure experiments were performed with a cubic anvil apparatus under different high pressure and heat temperature. The starting polycrystalline material ( $\sim 0.2 \text{ g}$ ) was ground into fine powder, and then pressed into a cylinder (5 mm in diameter) and encapsulated in Ag foil to prevent contamination. During the experiment, the sample was placed in the center of a pyrophyllite cube ( $25 \times 25 \times 25 \text{ mm}^3$  in size) surrounded by a pressure transmitting medium (boron nitride) to keep a constant quasihydrostatic pressure. A graphite tube and two Mo sheets attached to the top and bottom of the anvil were served as heater and contacts. The pyrophyllite cube was placed in the center cavity of the cubic anvil apparatus which could generate pressure up to 5 GPa. The pressure was increased gradually to a certain value first, then the system was heated through the Joule effect using a graphite furnace and the temperature was measured with a Ni–Cr/Ni–Si thermocouple. No correction was made for the pressure effect on the thermocouple wires. The solid–solid phase transition of a certain metal (*i.e.*, Bi, Ba) under pressure was

employed to determine the pressure inside the cell with an accuracy of  $\pm 0.05$  GPa. The reaction was terminated by temperature quenching followed by pressure releasing. The high-pressure cell was opened under ambient conditions and the product was analysed by powder X-ray diffraction.

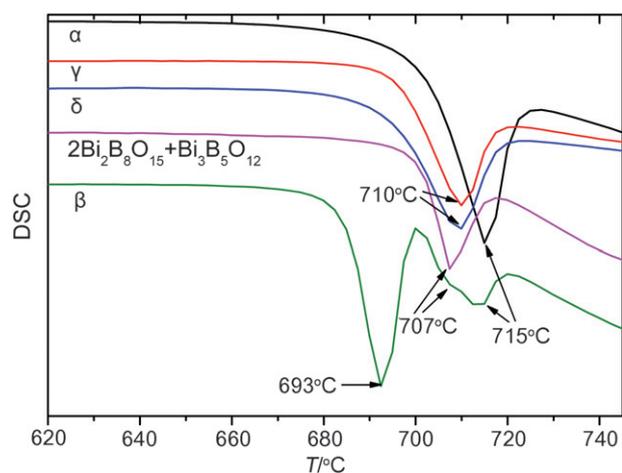
### Characterization

Powder X-ray diffraction data were collected at room temperature on a Rigaku D/Max-2000 diffractometer using a rotating anode (Cu  $K\alpha$ , 40 kV and 100 mA), a graphite monochromator and a scintillation detector. X-Ray diffraction profiles of the four  $\text{BiB}_3\text{O}_6$  polymorphs are shown in Fig. 2, where the marked peaks are used for the identification of each phase. Quantitative analysis was done by Rietveld refinements using the program TOPAS.<sup>18</sup> The DSC (differential scanning calorimetric) measurements were carried out on a NETZSCH STA449C instrument at a heating rate of 10 or 2  $^\circ\text{C min}^{-1}$  from room temperature to certain temperatures under Ar atmosphere.

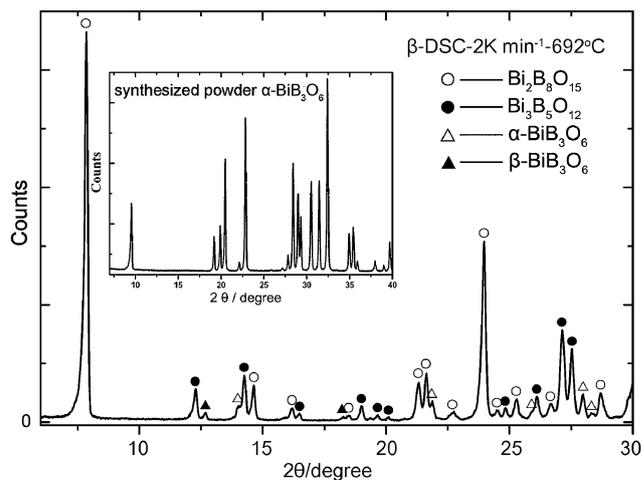
## Results

### DSC analysis

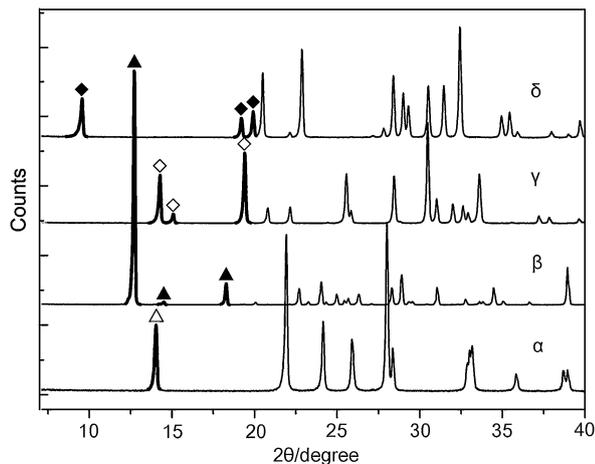
Fig. 3 shows the DSC curves of the four polymorphs. In each curve of  $\alpha$ -,  $\gamma$ - and  $\delta$ - $\text{BiB}_3\text{O}_6$ , there is only a single endothermic peak at 710  $^\circ\text{C}$  ( $\gamma$ - and  $\delta$ - $\text{BiB}_3\text{O}_6$ ) and 715  $^\circ\text{C}$  ( $\alpha$ - $\text{BiB}_3\text{O}_6$ ), while there are three peaks at about 693, 707 and 715  $^\circ\text{C}$  for  $\beta$ - $\text{BiB}_3\text{O}_6$ . The single endothermic peak in the DSC curves of  $\alpha$ -,  $\gamma$ - and  $\delta$ - $\text{BiB}_3\text{O}_6$  corresponds to the melting point of each phase. As to the three peaks for  $\beta$ - $\text{BiB}_3\text{O}_6$ , the first endothermic peak corresponds to the decomposition of the  $\beta$ -phase into  $\text{Bi}_2\text{B}_8\text{O}_{15}$  and  $\text{Bi}_3\text{B}_5\text{O}_{12}$ , which is proved by the XRD pattern of the sample heated to 692  $^\circ\text{C}$  at a rate of 2  $^\circ\text{C min}^{-1}$  and quenched quickly (Fig. 4). For comparison, the DSC curve of a mixture of  $\text{Bi}_2\text{B}_8\text{O}_{15}$  and  $\text{Bi}_3\text{B}_5\text{O}_{12}$  is also shown in Fig. 3. One can see that an eutectic melting phenomenon occurs in the mixture at about 707  $^\circ\text{C}$ , which is in accordance with the shoulder (the second peak) in the



**Fig. 3** DSC curves of  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ - $\text{BiB}_3\text{O}_6$  and the mixture of  $\text{Bi}_2\text{B}_8\text{O}_{15}$  and  $\text{Bi}_3\text{B}_5\text{O}_{12}$  (heating rate: 10  $^\circ\text{C min}^{-1}$ ).



**Fig. 4** Powder X-ray diffraction profile of the product from  $\beta$ - $\text{BiB}_3\text{O}_6$  by DSC analysis (heating rate: 2  $^\circ\text{C min}^{-1}$ ); the insert is the XRD profile of  $\alpha$ - $\text{BiB}_3\text{O}_6$  synthesized from the mixture of  $\text{Bi}_2\text{B}_8\text{O}_{15}$  and  $\text{Bi}_3\text{B}_5\text{O}_{12}$ .



**Fig. 2** The observed XRD patterns of four polymorphs of  $\text{BiB}_3\text{O}_6$  (selected peaks with different marks are used to identify the presence of the corresponding phases in the products).  $\Delta$ :  $\alpha$ -phase;  $\blacktriangle$ :  $\beta$ -phase;  $\diamond$ :  $\gamma$ -phase;  $\blacklozenge$ :  $\delta$ -phase).

DSC curve of  $\beta$ - $\text{BiB}_3\text{O}_6$ . The third peak (715  $^\circ\text{C}$ ) in the DSC curve of  $\beta$ - $\text{BiB}_3\text{O}_6$  is very close to the melting point of  $\alpha$ - $\text{BiB}_3\text{O}_6$ , one would reasonably suggest that  $\text{Bi}_2\text{B}_8\text{O}_{15}$  and  $\text{Bi}_3\text{B}_5\text{O}_{12}$  react around the eutectic melting to form  $\alpha$ -phase. In fact,  $\alpha$ - $\text{BiB}_3\text{O}_6$  was synthesized by the mixture of  $\text{Bi}_2\text{B}_8\text{O}_{15}$  and  $\text{Bi}_3\text{B}_5\text{O}_{12}$  in a furnace (see the insert of Fig. 4). The DSC results unambiguously indicate that  $\beta$ - $\text{BiB}_3\text{O}_6$  is a metastable modification, which decomposes at  $\sim 693$   $^\circ\text{C}$ , and then  $\alpha$ -phase forms by the combination of the decomposition products at higher temperature. Although the DSC analysis did not show any evidence of phase transition among  $\alpha$ -,  $\gamma$ - and  $\delta$ -phases because of the kinetic effect, it did provide useful information on the phase relations. The melting point of the  $\alpha$ -phase is the highest, which indicates that the  $\alpha$ -phase might be stable at high temperature. Furthermore, since the  $\gamma$ - and  $\delta$ -phases melt almost at the same temperature, the transition from  $\delta$ - to  $\gamma$ -phase may have occurred before the melting point but be hidden by the melting process. Since the DSC analysis was performed in a relatively

short time for a given sample, it may be difficult to get more information on the phase relationship due to kinetic hysteresis. Thus series of experiments for treating different BiB<sub>3</sub>O<sub>6</sub> polymorphs at different temperatures and pressures were performed. Long-time annealing treatment and/or crystal seeds addition were used when necessary.

### Treatment of β-BiB<sub>3</sub>O<sub>6</sub> in atmospheric conditions

β-BiB<sub>3</sub>O<sub>6</sub> underwent a series of complex changes in the temperature range 650–710 °C in atmospheric conditions, as shown in Scheme 1. β-BiB<sub>3</sub>O<sub>6</sub> decomposed to Bi<sub>2</sub>B<sub>8</sub>O<sub>15</sub> and Bi<sub>3</sub>B<sub>5</sub>O<sub>12</sub> at 680~710 °C in about 1 h, and then these two compounds reacted further, forming a mixture in which α-BiB<sub>3</sub>O<sub>6</sub> was the major phase and γ-BiB<sub>3</sub>O<sub>6</sub> and Bi<sub>3</sub>B<sub>5</sub>O<sub>12</sub> were the minor phases at the stage after 10-h treatment, which coincided with the phenomenon observed in the DSC analysis. However, further prolonging the reaction time (about 50 h) resulted in the formation of γ-BiB<sub>3</sub>O<sub>6</sub> with minor Bi<sub>3</sub>B<sub>5</sub>O<sub>12</sub>, while α-BiB<sub>3</sub>O<sub>6</sub> disappeared totally, which implied that the phase transformation from α-BiB<sub>3</sub>O<sub>6</sub> to γ-BiB<sub>3</sub>O<sub>6</sub> occurred at this temperature range. The presence of Bi<sub>3</sub>B<sub>5</sub>O<sub>12</sub> in the final product might be due to the evaporation of the boron oxide. In the batches with the addition of a small amount (<2%) of certain seed crystals, the phase transition processes were indeed influenced by different polymorph seeds, especially at the early stage of the reactions. For example, α-BiB<sub>3</sub>O<sub>6</sub> became a major phase only in *ca* 1 h by using α-BiB<sub>3</sub>O<sub>6</sub> as the seed crystals, and γ- or δ-BiB<sub>3</sub>O<sub>6</sub> phases also appeared if the corresponding seed crystals were used. However, γ-BiB<sub>3</sub>O<sub>6</sub> was always the major phase in the final products no matter what kind of seed crystals was used if the treatment time was long enough. It shows that γ-BiB<sub>3</sub>O<sub>6</sub> is the stable phase in the temperature range of 680–710 °C at ambient pressure. In the lower temperature range (650–670 °C), thermal treatment of β-BiB<sub>3</sub>O<sub>6</sub> for *ca* 100 h always results in a mixture of α-, γ-, δ-BiB<sub>3</sub>O<sub>6</sub> and Bi<sub>3</sub>B<sub>5</sub>O<sub>12</sub>. However, the ratio of these phases varied with the seed crystals and the seed-induced phase existed as the major phase. The high-pressure phase δ-BiB<sub>3</sub>O<sub>6</sub> seems to be more stable in this lower temperature range, since it appears as a major phase without seed-crystals (see the reactions under 650–670 °C in Scheme 1). It should be noted that δ-BiB<sub>3</sub>O<sub>6</sub>,

which was known as a high-pressure phase previously, can in fact be realized under ambient pressure *via* phase transformations.

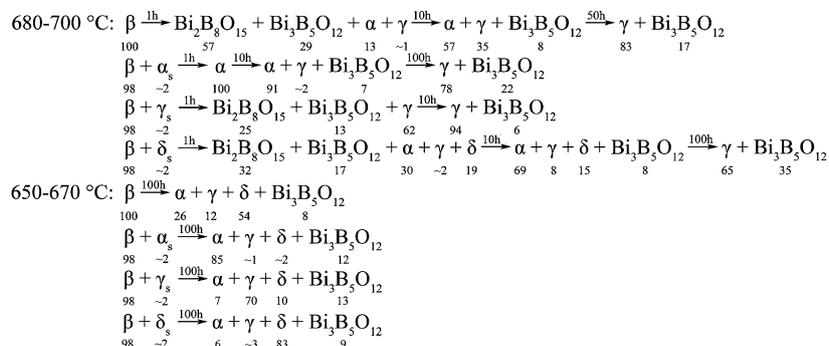
### Treatment of δ-BiB<sub>3</sub>O<sub>6</sub> in atmospheric conditions

δ-BiB<sub>3</sub>O<sub>6</sub> is a high-pressure phase and one would expect its transformation to low pressure polymorphs at ambient pressure. In the experiments, δ-BiB<sub>3</sub>O<sub>6</sub> behaved quite inertly and a pure δ-BiB<sub>3</sub>O<sub>6</sub> sample did not show any evidence of phase transition except for a small amount of decomposition to Bi<sub>3</sub>B<sub>5</sub>O<sub>12</sub> and B<sub>2</sub>O<sub>3</sub>, as listed in Table 1 (B<sub>2</sub>O<sub>3</sub> is not taken into account due to its evaporation and relatively weak scattering ability to X-ray). The inertness of δ-BiB<sub>3</sub>O<sub>6</sub> may be due to the kinetic hindrance of the break of the B–O bond. With the increase of the annealing temperature, the phase transition from δ- to γ-BiB<sub>3</sub>O<sub>6</sub> was observed above 680 °C if γ-seeds were added to the starting materials. The density difference between γ- and δ-BiB<sub>3</sub>O<sub>6</sub> is not very large (6.177 vs 6.378 g cm<sup>-3</sup>), therefore, seed crystals and high annealing temperature are necessary to induce the phase transformation. This might also be the reason that one could

**Table 1** Thermal treatment results of α- and δ-phases

Starting material <sup>a</sup>	Temperature/°C	Time/h	Product <sup>b</sup>
δ	650–700	50	δ + Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> (85/15)
δ + γ <sub>s</sub> (43/57)	650–670	50	δ + γ + Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> (32/57/11)
δ + γ <sub>s</sub> (43/57)	680–710	50	γ + δ + Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> (81/6/13)
α	650–670	50	α + Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> (86/14)
α	680–710	50	α + γ + Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> (79/12/9)
α + γ <sub>s</sub> (98/2)	650–670	50	α + γ + Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> (78/16/6)
α + γ <sub>s</sub> (98/2)	680–710	50	γ + Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> (83/17)
α + δ <sub>s</sub> (98/2)	650–670	100	α + δ + Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> (39/36/25)
α + δ <sub>s</sub> (98/2)	680–710	50	α + δ + γ + Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> (55/12/19/14)
α + δ <sub>s</sub> (98/2)	680–710	100	γ + Bi <sub>3</sub> B <sub>5</sub> O <sub>12</sub> (78/22)

<sup>a</sup> Subscript 's' means seed crystals. <sup>b</sup> The ratio in parentheses is the quantitative analytical result of each phase in the corresponding product from powder X-ray diffraction data.



**Scheme 1** The change of the β-phase treated in atmospheric conditions with temperature and time. (Subscript 's' means seed crystals, and the datum below each phase is the weight percent of the phase in the product.)

observe the growing of the  $\delta$ -phase when  $\delta$ - $\text{BiB}_3\text{O}_6$  was used as a seed during the heat treatment of  $\beta$ - $\text{BiB}_3\text{O}_6$ .

### Treatment of $\alpha$ - $\text{BiB}_3\text{O}_6$ in atmospheric conditions

In the treatment of the  $\beta$ -phase at 680~710 °C, we have observed a series of phase transitions from  $\beta$ - to  $\alpha$ -, then to  $\gamma$ - $\text{BiB}_3\text{O}_6$  with time. Further investigation of the thermal behavior of the  $\alpha$ -phase at a temperature below 710 °C (the melting point of  $\gamma$ - $\text{BiB}_3\text{O}_6$ ) revealed more information about the transformation of  $\alpha$ - $\text{BiB}_3\text{O}_6$ , as listed in Table 1. During the treatment,  $\alpha$ - $\text{BiB}_3\text{O}_6$  decomposed to  $\text{Bi}_3\text{B}_5\text{O}_{12}$  and  $\text{B}_2\text{O}_3$  slowly below 670 °C, and no evidence related to a phase transition was observed even after 50 h treatment. At higher temperatures (680~710 °C) and with prolonging the reaction time,  $\gamma$ - $\text{BiB}_3\text{O}_6$  emerged but in low yield. As expected, introducing  $\gamma$ -crystal seeds accelerated the reaction rate and promoted the formation of  $\gamma$ - $\text{BiB}_3\text{O}_6$ . If  $\delta$ - $\text{BiB}_3\text{O}_6$  was added to the initial material as seed,  $\delta$ -phase formed at 650–670 °C. In the temperature range of 680~710 °C,  $\delta$ -phase appeared at the early stages together with the  $\gamma$ -phase, and disappeared with time while the  $\gamma$ -phase became the major phase, which also revealed the phase transition process from  $\delta$ - to  $\gamma$ - $\text{BiB}_3\text{O}_6$ , as happened in the treatment of  $\beta$ - or  $\delta$ -phase.

### Heat treatments of $\gamma$ - $\text{BiB}_3\text{O}_6$ in atmospheric conditions

From the above results, it can be concluded that  $\gamma$ - $\text{BiB}_3\text{O}_6$  was the most stable phase in the temperature range of 680–710 °C. Further treatment of the  $\gamma$ -phase in the same conditions confirmed this conclusion. In the present work, it was observed that  $\gamma$ - $\text{BiB}_3\text{O}_6$  melts at 710 °C, and the cooled product was glass-like amorphous. No  $\alpha$ -phase was obtained at 710 °C even if the process was kept going for a long time.

### Treatments of $\gamma$ - $\text{BiB}_3\text{O}_6$ under high pressure

$\gamma$ - $\text{BiB}_3\text{O}_6$  is a stable phase under 680–710 °C in ambient pressure, but it should transfer to  $\delta$ -phase under high pressure due to its less density. The experimental results of the treatment of  $\gamma$ - $\text{BiB}_3\text{O}_6$  under high pressures at different temperature are summarized in Table 2. As expected, the transformation from  $\gamma$ - $\text{BiB}_3\text{O}_6$  to  $\delta$ - $\text{BiB}_3\text{O}_6$  occurred at relatively high temperature and pressure. The addition of  $\delta$ - $\text{BiB}_3\text{O}_6$  seeds induced the phase transformation and significantly reduced the reaction pressure and temperature (*i.e.* 0.6 GPa and 600 °C).

**Table 2** Products of high-temperature/high-pressure treatments on the  $\gamma$ -phase

Starting material	Pressure/GPa	Temperature/°C	Time/min	Product
$\gamma$	0.6	600–700	30	$\gamma$
$\gamma$	2	400–600	30	$\gamma$
$\gamma$	2	800	30	$\delta$
$\gamma$	5	400	30	$\gamma$
$\gamma + \delta_s$ (68/32)	0.6	600	30	$\gamma + \delta$ (59/41)

**Table 3** Products of high-temperature/high-pressure treatments on the  $\alpha$ -phase

Pressure/GPa	Temperature/°C	Time/min	Product
0.6	400	30	$\alpha$
0.6	550	30	$\alpha + \gamma + \delta$ (44/39/17)
0.6	550	60	$\alpha + \gamma + \delta$ (24/35/41)
0.6	600	30	$\gamma + \delta$ (68/32)
0.6	600	60	$\gamma + \delta$ (59/41)
2	300	30	$\alpha + \gamma + \delta$ (96/2/2)
2	400	30	$\alpha + \gamma + \delta$ (36/46/18)
2	600	30	$\gamma + \delta$ (32/68)
2	800	30	$\delta$

### Treatments of $\alpha$ - $\text{BiB}_3\text{O}_6$ under high pressure

$\alpha$ - $\text{BiB}_3\text{O}_6$  has the lowest density among the polymorphs. Using  $\alpha$ - $\text{BiB}_3\text{O}_6$  as starting material, a series of phase transformations were observed with the increase of pressure. As shown in Table 3, in most cases,  $\gamma$ - and  $\delta$ -phases exist together in the products. Considering the small density differences between  $\gamma$ - and  $\delta$ -phases, the co-formation of these two phases from  $\alpha$ - $\text{BiB}_3\text{O}_6$  under relatively mild conditions is reasonable. Under extreme conditions (2GPa, 800 °C), the final product was  $\delta$ -phase. No  $\beta$ - $\text{BiB}_3\text{O}_6$  was observed because of the metastable nature of this phase, although the density of  $\beta$ - $\text{BiB}_3\text{O}_6$  is higher than that of  $\alpha$ - $\text{BiB}_3\text{O}_6$ .

### Treatments of $\beta$ - $\text{BiB}_3\text{O}_6$ under high pressure

Different from the complex performance of  $\beta$ - $\text{BiB}_3\text{O}_6$  during the heating treatment under ambient pressure, the transformation process of  $\beta$ - $\text{BiB}_3\text{O}_6$  under high pressure is quite simple. As shown in Table 4,  $\beta$ - $\text{BiB}_3\text{O}_6$  transformed to other higher density phases ( $\gamma$ - and  $\delta$ - $\text{BiB}_3\text{O}_6$ ) directly without decomposition. At

**Table 4** The change of the  $\beta$ -phase with temperature and pressure

Pressure/GPa	Temperature/°C	Time/min	Product
0.4	600	30	$\gamma + \delta$ (34/66)
0.5	570	30	$\gamma + \delta$ (44/56)
0.55	550	30	$\beta + \gamma + \delta$ (4/68/28)
0.55	550	90	$\gamma + \delta$ (65/35)
0.6	550	30	$\beta + \gamma + \delta$ (27/55/18)
0.6	700	30	$\gamma + \delta$ (7/93)
0.75	520	20	$\beta + \gamma + \delta$ (20/10/70)
0.85	490	20	$\beta + \gamma + \delta$ (41/27/32)
1	600	30	$\gamma + \delta$ (2/98)
2	400	30	$\beta + \delta$ (97/3)
2	440	30	$\beta + \delta$ (80/20)
2	600	30	$\delta$
2	800	30	$\delta$
5	400	30	$\beta + \delta$ (74/26)
5	615	30	$\delta$
5	800	30	$\delta$

a relatively low pressure (0.4~1GPa) and low temperature (490~600 °C),  $\gamma$ - and  $\delta$ -phases always coexisted in the products after 30 min treatment. The content of the  $\delta$ -phase increased with pressure, temperature and time, and almost pure  $\delta$ -BiB<sub>3</sub>O<sub>6</sub> was obtained at 600 °C and 2 GPa after 30 min reaction.

## Discussion

From a thermodynamic view, the possible phase transition could be estimated by the Gibbs free energy  $\Delta G$ . For a given system,  $\Delta G$  depends on temperature ( $T$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ), here the latter two quantities are further affected by temperature and pressure. For a system at consistent pressure, the Gibbs free-energy change can be expressed as follows:

$$\Delta G^\circ(T) = \Delta H^\circ(T) - T\Delta S^\circ(T) \quad (1)$$

If pressure is variable, the equation becomes:<sup>19,20</sup>

$$\Delta G(P, T) = \Delta H^\circ(T) - T\Delta S^\circ(T) + \int_{p_0}^P \Delta V(P, T)dP \quad (2)$$

In a reaction with a change in volume, pressure can play an important effect on the reaction process.

It is known that  $\beta$ -BiB<sub>3</sub>O<sub>6</sub> can only be obtained by hydrothermal synthesis. The present study shows that  $\beta$ -BiB<sub>3</sub>O<sub>6</sub> is very reactive and may easily transform to the other polymorphs under appropriate conditions. In fact, there is no evidence of the inverse transformation to  $\beta$ -phase, thus,  $\beta$ -BiB<sub>3</sub>O<sub>6</sub> should be regarded as a metastable phase that cannot be expressed in the  $P$ - $T$  phase-diagram. However, the high reactivity of  $\beta$ -BiB<sub>3</sub>O<sub>6</sub> provides it as a useful precursor to get other polymorphs.

The transformations of the other three BiB<sub>3</sub>O<sub>6</sub> polymorphs can be expressed in a  $P$ - $T$  phase diagram. There are two structural parameters that may influence the phase transformation, *i.e.*, density ( $\alpha$ : 5.033 g cm<sup>-3</sup>,  $\gamma$ : 6.177 g cm<sup>-3</sup>,  $\delta$ : 6.378 g cm<sup>-3</sup>) and structure dimensionality ( $\alpha$  is 2D,  $\gamma$  and  $\delta$  are 3D). The density difference gives rise to a volume change of the reaction, which provides a driven force for the pressure-induced phase transformation. From the density of BiB<sub>3</sub>O<sub>6</sub> polymorphs, one expects phase transitions  $\alpha \rightarrow \gamma \rightarrow \delta$  with the increase of pressure. The dimensionality of the structures, on the other hand, is another factor which may influence the enthalpy and entropy change, and then influence the transformation process. In general, one expects phase transformations of  $\delta \rightarrow \gamma \rightarrow \alpha$  as the increase of temperature. The real processes are much more complicated, particularly in solid state reactions the kinetic effect often plays an important role, then higher temperature is necessary to facilitate the reaction occurrence.

$\alpha$ -BiB<sub>3</sub>O<sub>6</sub> was initially identified in the Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system.<sup>1</sup> Our experimental results show that a pure phase sample of  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> can be synthesized with a conventional solid state reaction at temperature very close to the melting point. At lower temperature (<710 °C),  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> could also be formed at the initial stage (<10 h), but it transformed to  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> if the reaction was prolonged. One of the interesting facts is that there was no report about the formation of  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> in the past many years, although studies on the synthesis, structure and crystal growth of the  $\alpha$ -phase have been carried out extensively.<sup>1,4-8</sup> Possible reasons

might be that the crystal of  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> was synthesized mostly by the top-seed crystal growth method<sup>6-8</sup> and the  $\alpha$ -polymorph is quite inert. Once it forms, it maintains. As far as the structure is concerned,  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub> exhibits the lowest density (5.033 g cm<sup>-3</sup>) and a 2D structure framework, thus one could expect that both  $\Delta H > 0$  and  $\Delta S > 0$  for the  $\gamma \rightarrow \alpha$  transition. All evidence confirms that the  $\alpha$ -polymorph is a high-temperature phase, and its stable range is very narrow, probably in a range between the melting points of the  $\gamma$ - and  $\alpha$ -phases (710–715 °C).

$\gamma$ -BiB<sub>3</sub>O<sub>6</sub> was identified first in a boric flux system at low temperature (~270 °C).<sup>2</sup> However, as indicated,  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> is a very stable phase that is encountered most frequently in our experiments; it is always the final product if the reaction time was long enough in the temperature range of 680–710 °C, no matter what polymorphs (either  $\alpha$  or  $\delta$ ) were used as the starting materials.  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> has a 3D borate framework and a lower melting point (710 °C) than that of  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub>, thus it is thermodynamically reasonable that  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> is a stable phase in this intermediate temperature range under ambient pressure. On the other hand, the phase transition  $\alpha \rightarrow \gamma$  was also observed under high pressure. In fact,  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> always appeared as one of the major phases when the  $\alpha$ -phase was used as a starting material under high pressure (Table 3). The density of  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> (6.177 g cm<sup>-3</sup>) is much higher than that of the  $\alpha$ -phase but slightly lower than that of the  $\delta$ -phase, thus it is possible that the  $\gamma$ -polymorph is an intermediate species in the high pressure phase transformation  $\alpha \rightarrow \gamma \rightarrow \delta$ . Unfortunately, we have not yet experimentally observed the phase transition from  $\gamma$ - to  $\alpha$ -phase under ambient pressure. This is understandable from the inert nature and the lower melting point of the  $\gamma$ -phase, thus the  $\gamma$ -phase may melt before phase transformation, which ends up with an amorphous glass.

The  $\delta$ -phase, first identified in the high-pressure synthetic studies, adopts a compact structure (3D borate framework) with the highest density (6.378 g cm<sup>-3</sup>) among the BiB<sub>3</sub>O<sub>6</sub> polymorphs.<sup>3</sup> This phase can be conventionally synthesized under high pressure at high temperature. In our study, we did find that the  $\beta$ -phase can easily transform to the  $\delta$ -phase in relatively mild conditions (1GP, 600 °C) (Table 4), but the transformation from  $\alpha$ - and  $\gamma$ -BiB<sub>3</sub>O<sub>6</sub> can be realized only at higher temperature (2GP, 800 °C) (Table 2, 3), which demonstrates again the inert nature of  $\alpha$ - and  $\gamma$ -phases. More interestingly, we also found that, starting from  $\beta$ -BiB<sub>3</sub>O<sub>6</sub>,  $\delta$ -BiB<sub>3</sub>O<sub>6</sub> could be formed as the major phase after 100 h annealing at 650–670 °C under ambient pressure (Scheme 1). Similarly  $\delta$ -BiB<sub>3</sub>O<sub>6</sub> also appeared in the product when  $\alpha$ -BiB<sub>3</sub>O<sub>6</sub>, together with the  $\delta$ -seeds, was used as starting material under the same conditions (Table 1). This means that, although  $\delta$ -BiB<sub>3</sub>O<sub>6</sub> is a high-pressure phase, the stability range of this phase may extend through to ambient pressure below 670 °C. At higher temperatures (680–710 °C), a reverse transition from  $\delta$ - to  $\gamma$ - phase can also be detectable under ambient pressure when a large amount of  $\gamma$ -seeds were used. Further considering the small density difference between  $\gamma$ - and  $\delta$ -phase, one could reasonably conclude that  $\delta$ -BiB<sub>3</sub>O<sub>6</sub> is a high-pressure and low-temperature phase in this system.

Based on the experimental results and thermodynamic principles, we propose a sketch  $P$ - $T$  phase-diagram for the BiB<sub>3</sub>O<sub>6</sub> system (Fig. 5). We already knew that the phase transformations  $\delta \rightarrow \gamma \rightarrow \alpha$  may occur on heating under ambient pressure. We also knew that the phase transformations  $\alpha \rightarrow \gamma \rightarrow \delta$  can be

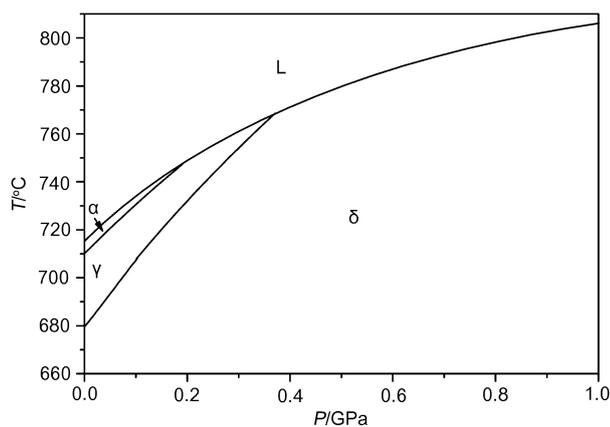


Fig. 5 Schematic drawing of the phase-diagram of  $\text{BiB}_3\text{O}_6$ .

realized along the pressure axis at an appropriate temperature. It is also well-known that melting points may increase along with pressure, so does the phase transition boundary between solid phases. Although the boundaries may not be accurately defined, this sketched  $P$ - $T$  phase diagram is very useful for understanding the chemical behavior of the polymorphs in the  $\text{BiB}_3\text{O}_6$  system. For example, regarding the narrow stable area of  $\alpha$ - $\text{BiB}_3\text{O}_6$ , the crystals can be grown from a melt by the top-seeded method, but the overcooling temperature has to be carefully controlled.<sup>6-8</sup> In addition, from the phase-diagram, it can be expected that crystals of  $\delta$ - $\text{BiB}_3\text{O}_6$  can be grown from a melt using a high pressure and high temperature apparatus.<sup>3</sup>

In fact, polymorphism is a common phenomenon in borate systems because of the  $\text{BO}_3/\text{BO}_4$  coordination modes and diverse linkages of polyborates.<sup>16,21-24</sup> Another interesting example that is comparable to  $\text{BiB}_3\text{O}_6$  is  $\text{LnB}_3\text{O}_6$ , rare earth polyborate.  $\text{LnB}_3\text{O}_6$  also has four polymorphs:  $\alpha$ - $\text{LnB}_3\text{O}_6$  ( $\text{Ln} = \text{La} - \text{Tb}$ , except  $\text{Pm}$ ) is a low-pressure form;<sup>25-30</sup> additionally, there are two high-pressure forms,  $\gamma$ - $\text{LnB}_3\text{O}_6$  ( $\text{Ln} = \text{La} - \text{Nd}$ )<sup>31,32</sup> and  $\delta$ - $\text{LnB}_3\text{O}_6$  ( $\text{Ln} = \text{La}, \text{Ce}$ ),<sup>33,34</sup> and one metastable orthorhombic variation  $\beta$ - $\text{LnB}_3\text{O}_6$  ( $\text{Ln} = \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb} - \text{Lu}$ ).<sup>35-37</sup> The structures of  $\text{LnB}_3\text{O}_6$  and  $\text{BiB}_3\text{O}_6$  are also closely related (see Fig. S1 in the ESI†). Though  $\alpha$ - $\text{LnB}_3\text{O}_6$  has a 1D borate chain structure, which is different from the layer structure in  $\alpha$ - $\text{BiB}_3\text{O}_6$ ,<sup>4,5</sup> the  $\text{BO}_3/\text{BO}_4$  ratio and their alternative connectivity are principally the same (Fig. S1a).†  $\beta$ - $\text{LnB}_3\text{O}_6$  is built up from corrugated layers by corner-shared  $\text{BO}_4$  tetrahedra, but the stacking way of the layers is similar to that in  $\beta$ - $\text{BiB}_3\text{O}_6$ . Finally,  $\gamma$ - and  $\delta$ - $\text{LnB}_3\text{O}_6$  are exactly isostructural with  $\delta$ - and  $\gamma$ - $\text{BiB}_3\text{O}_6$ ,<sup>2,3</sup> respectively. Therefore, one could expect that  $\text{LnB}_3\text{O}_6$  has a similar  $P$ - $T$  phase diagram as that of the  $\text{BiB}_3\text{O}_6$  system. Although the details of the phase relationship have not yet been established for the  $\text{LnB}_3\text{O}_6$  system, it was reported that the high-pressure forms,  $\gamma$ - and  $\delta$ - $\text{LnB}_3\text{O}_6$ , may transform to  $\alpha$ - $\text{LnB}_3\text{O}_6$  at high temperature under ambient pressure,<sup>32,33</sup> which is rather similar to the  $\text{BiB}_3\text{O}_6$  system. Owing to the higher melting points of  $\text{LnB}_3\text{O}_6$  in comparison with that of  $\text{BiB}_3\text{O}_6$ , the study of the phase relationship can proceed in a wider temperature range, which could effectively eliminate the kinetic effect of the phase transformations. Further investigating the details of a phase relationship of the phases for the  $\text{LnB}_3\text{O}_6$  system will be very interesting not only for the chemistry of the  $\text{LnB}_3\text{O}_6$  system itself

but also for providing a comprehensive understanding of the whole  $\text{MB}_3\text{O}_6$  ( $\text{M} = \text{Bi}, \text{Ln}$ )<sup>38</sup> system.

## Conclusion

The phase relationship of the four  $\text{BiB}_3\text{O}_6$  polymorphs, *i.e.*,  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ - $\text{BiB}_3\text{O}_6$ , is important for understanding the chemistry and synthetic process, particularly for the crystal growth of  $\alpha$ - $\text{BiB}_3\text{O}_6$ , a promising nonlinear optical material. However, the study of the phase transition is complicated by the kinetic effect for this borate system, thus extensive annealing and seed-inducing were used in the practical processes. Although there still are some uncertainties, the fundamental ground of the phase relationship is clearly defined. First of all,  $\beta$ - $\text{BiB}_3\text{O}_6$  is a metastable phase which can be synthesized by the boric acid flux method but cannot be expressed in the  $P$ - $T$  phase diagram.  $\alpha$ - $\text{BiB}_3\text{O}_6$  is a high-temperature phase, which is stable in a narrow temperature range (710–715 °C) under ambient pressure.  $\delta$ - $\text{BiB}_3\text{O}_6$  is a high-pressure phase, but can be present at low temperature (<670 °C) under ambient pressure.  $\gamma$ - $\text{BiB}_3\text{O}_6$ , on the other hand, is a stable phase in an intermediate temperature range (~680–710 °C). The phase stability under pressure is simply reverse, *i.e.*,  $\delta > \gamma > \alpha$ , which means that the phase transition  $\alpha \rightarrow \gamma \rightarrow \delta$  may occur as the increase of the pressure. Based on these observations, a schematic  $P$ - $T$  phase diagram has been proposed for the  $\text{BiB}_3\text{O}_6$  system, which can be used to understand the chemistry behavior of this system.

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