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Solid state phase transformation of BaB_2O_4 during the isothermal annealing process

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Solid-state phase transformation of BaB_2O_4 during the isothermal annealing process for both β to α and α to β were investigated using a platinum crucible. For the β-phase crystal at the α-phase stable temperature (> 925 °C), the β phase transforms to the α phase perfectly below the melting temperature of 1100 °C. Meanwhile, for the α-phase crystal at the β-phase stable temperature (< 925 °C), the α phase transforms to the β phase perfectly above 800 °C. There is some difference in phase transformation behaviour between bulk-shape crystals and the powder, caused by thermal stress.

1. Introduction

The low-temperature β phase of BaB_2O_4 (BBO) is important for non-linear optical devices. Single crystals of the β phase are usually grown from high-temperature solutions (flux growth) [1–3], but recently they have been grown by the Czochralski method from nominally pure and supercooled melt [4–6]. The difficulties encountered in the Czochralski growth of the β-BBO are of seeding problems, because the β phase single-crystal seed transforms to the high-temperature α phase before seeding. Meanwhile, the α-phase seed crystal also transforms to the β phase before seeding. Furthermore, single crystals of the β or α phase having many cracks are sometimes grown from the melt, because the β- or α-phase crystal grown transforms to the α or β phase during a cooling process after the growth. It is thus necessary to study the phase transformation behaviour of BBO in order to obtain single crystals of β-BBO or α-BBO after the cooling to room temperature. For the solid-state phase transformation on the BBO, the dependence on the synthesis method of the starting material was mainly studied [7]. In addition, the study was only for the β to α phase transformation [7, 8].

In this work, we report the effects of annealing as an isothermal process for the phase transformation from room temperature, and on the kinetics of annealing, for both the β to α phase transformation using the β-phase samples in the α-phase stable temperature range, and the α to β phase transformation using the α-phase samples in the β-phase stable temperature range, using differently shaped (bulk and powder) samples in order to study a thermal stress effect.

2. Experimental procedure

BaB_2O_4 source material was reacted as a melt in an air atmosphere for 5 h at 1150 °C ($T_{mp} = 1100$ °C) using powders of $BaCO_3$ and B_2O_3 (99.99%) in a platinum crucible, and was cooled slowly to room temperature in the furnace. The phase after the reaction was β phase. The α-phase sample was obtained by rapid cooling, i.e. removing the sample from the furnace, after a 5 h annealing of the β-phase sample at 1070 °C. Bulk samples were obtained by breaking apart the solidified BBO ingot. Powder samples were obtained by grinding some of these bulk samples. The average particle diameter was 2 mm for the bulk and 0.04 mm for the powder. The bulk sample consisted of many fine grains. A difference of 50 times the particle diameter is sufficient to study the thermal stress effect.

Table I shows the impurities of the BBO measured by inductively coupled plasma (ICP) mass spectroscopy. Platinum was a major impurity because a platinum crucible was used for the synthesis. The impurity level is believed to be low enough not to affect the phase transformation very much. No endothermic peak corresponding to a eutectic reaction was observed by differential thermal analysis (DTA) [7].

Samples weighing 10 mg were used to study the solid-state phase transformation behaviour in a platinum crucible and in a graphite crucible for reference. The β-phase samples were heated in a furnace for DTA, which had a molybdenum heater, from room temperature to 950, 975, 1000, 1025 and 1050 °C, at a heating rate of 15 $°C\,min^{-1}$, and then rapidly cooled after 0, 5, 10, 15, 30 and 60 min annealing by turning off the power of the furnace. Meanwhile, the α-phase samples were heated from room temperature to 500, 550, 600, 650, 700, 750 and 800 °C, and were annealed in the same manner. The present cooling rate was about 100 $°C\,min^{-1}$. The phases formed were verified by powder X-ray diffraction (XRD). The symmetry of the α phase is $R\bar{3}c$ [9] and that of the β phase is $R3c$ [10, 11]. The mass per cent of each phase present in the sample was obtained by a peak intensity relationship between the $(1\,0\,\underline{1}\,0)$ of the α phase and the (1 1 3) of the β phase. The experiment was carried out two or three times, and the values were averaged. The total absolute error in determining the mass per cent of

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TABLE I Impurities of BaB_2O_4 measured by the ICP mass spectroscopy (p.p.m.). Other elements are less than 5 p.p.m.

Mn	Y	Zr	Hf	Ta	Pt
2	2	0.1	19	10	30

each phase was estimated to be ± 10% including a temperature error of ± 5 °C and an XRD error of ± 5%. The relative error of each experiment was below ± 5%.

3. Results and discussion

3.1. β–α phase transformation

Fig. 1 shows a typical example of the time–annealing temperature dependence on the solid-state β to α phase transformation for the bulk and the powder. The β phase transformed to the α phase above 975 °C for the bulk, and transformed perfectly at 1050 °C. The phase transformation did not occur below 950 °C. Meanwhile, for the powder, the β phase transformed above 1050 °C, and did not transform below 1000 °C. The difference in the bulk and the powder is presumed to be caused by a thermal stress. The thermal expansion coefficient and the thermal conductivity along the *c*-axis of the β-phase crystal are ten times larger than those along the *a*-axis [12, 13]. As shown in Fig. 1a by an arrow, the cooling rate necessary to prevent the β-phase crystal growth as a metastable state from the phase transformation to the α phase in the α-phase stable temperature range, is found to be larger than 5 °C min^{-1} as a constant cooling rate. Here the starting temperature of the cooling is assumed to be 1020 °C, which is a temperature at which the β-phase crystal can be grown from the melt as a metastable state. Similar results were obtained in rapid heating and cooling experiments in a graphite crucible [8]. No endothermic peak corresponding to the phase transformation was observed by the DTA.

Table II shows the phase obtained during the cooling process from a melt of 1250 °C with different cooling rates. The β-phase crystal was obtained at a cooling rate above 5 °C min^{-1}. Meanwhile, at 1 °C min^{-1}, the β + α mixture phase crystal was obtained. This result is in agreement with the results of the annealing experiment, as shown in Fig. 1a.

Fig. 2 shows the α/β phase ratio transformed from the β phase depending on the annealing time, obtained

TABLE II Phases obtained during the cooling process from a melt of 1250 °C at different cooling rates.

	Cooling rate (°C min^{-1})			
	100	10	5	1
Phase	β	β	β	β + α

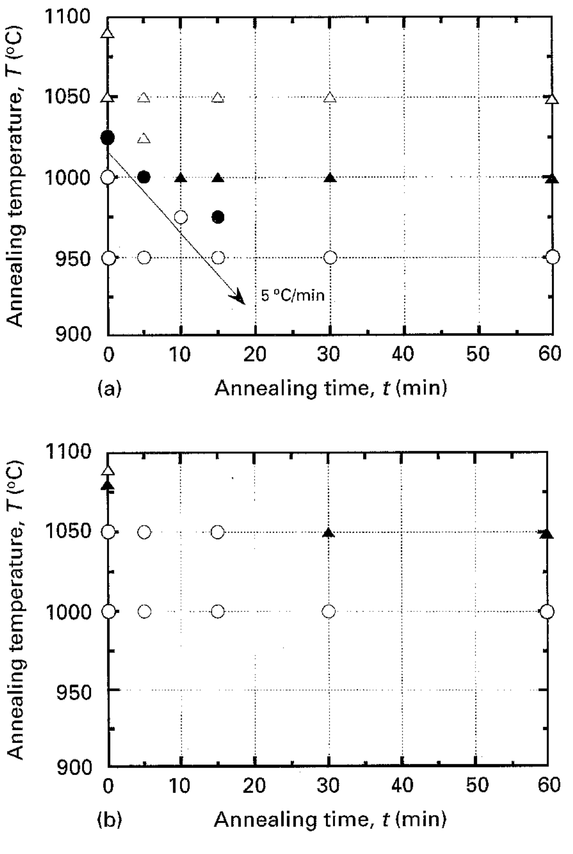


Figure 1 Time–annealing temperature dependence of the β to α phase transformation at several different annealing temperatures for (a) bulk, and (b) powder. Arrows indicate the cooling process at 5 °C min^{-1} from 1020 °C, for example. (○) β, (●) mixture (β-rich), (▲) mixture (α-rich), (△) α.

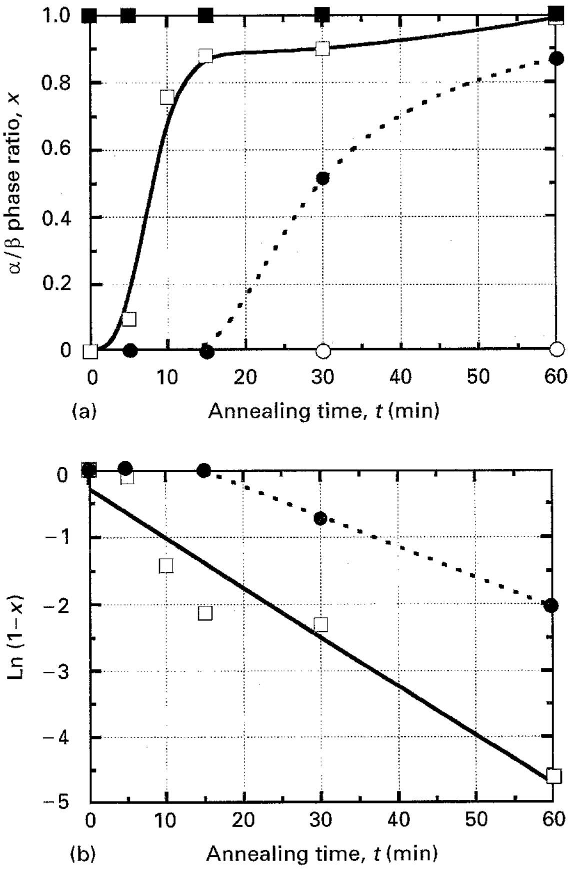


Figure 2 Time dependence of α/β phase ratio, *x*, transformed, obtained from the XRD peak intensity: (a) normal plot, and (b) logarithmic plot, heated at (○, □) 1000 and (●, ■) 1050 °C for (□, ■) bulk and (○, ●) powder.

by XRD peak intensity, heated at 1000 and 1050 °C for both the bulk and the powder. An induction period was observed for the powder. Fig. 2b shows the logarithmic relationship for Fig. 2a. This transformation follows a nucleation model given by Toschev *et al.* as denoted by [14, 15]

$$x = 1 - \exp[-I_0(t - t_0)] \qquad (1)$$

where x is the α/β phase ratio transformed, I_0 is the nucleation rate of the α phase, t is the time, t_0 is the induction period.

The following numerical relationships are obtained. Here t is the time (min)

$$x = 1 - \exp[-7.4 \times 10^{-2}(t + 3.8)] \quad (1000\,^{\circ}\mathrm{C}, \text{bulk}) \qquad (2)$$

$$x = 1 - \exp[-4.5 \times 10^{-2}(t - 15)] \quad (1050\,^{\circ}\mathrm{C}, \text{powder}) \qquad (3)$$

The phase transformation of the bulk was faster than that of the powder in the early part, but changed to be slower during the final part, i.e. I_0 of the bulk was large. The reason why the nucleation model can be applied is that the sample consists of many fine grains.

Fig. 3 shows the heating-rate dependence of the β to α phase transformation from 5–20 °C min^{-1} heated from room temperature to 1000 °C for the bulk and to 1050 °C for the powder with constant heating rate in whole temperature range, along with the dependence on heating from room temperature to 900 °C at 200 °C min^{-1} and then heating to each temperature with various heating rates [8]. The α-phase ratio was increased exponentially with increasing heating rate depending on the sample shape. The linear lines for the bulk and the powder were almost parallel to each other. The phase transformation in Fig. 3 was affected by thermal stress, σ_s, denoted by Equation 4 assuming a parabolic thermal distribution [16]

$$\sigma_s = \left(\frac{E_\alpha}{1 - \mu}\,\frac{1}{\lambda/\rho C_p}\right) F_g \phi r_m^2 \qquad (4),$$

where E is the Young's modulus, a is the linear expansion coefficient, μ is the Poisson's ratio, λ is the thermal conductivity, ρ is the density, C_p is the heat capacity, F_g is a geometric factor, ϕ is the heating rate, and r_m is the half thickness of the crystal. A large effect of thermal history is observed in Fig. 3, such as the heating-rate dependence of the β to α phase transformation, i.e. slow and rapid heating rates from room temperature to 900 °C.

According to the phase formation from the melt, the phase formed in a graphite crucible was different from that in a platinum crucible [8], i.e. graphite affected the phase formation. In this solid-state phase transformation, the phase-transformation behaviour was similar in both the graphite and platinum crucibles, and the dependence on the crucible material was small. The phase transformation in the platinum crucible was somewhat faster than that in the graphite crucible [8].

The BBO crystal transforms from the β to α phase before melting using both the bulk and the powder in the present experimental conditions.

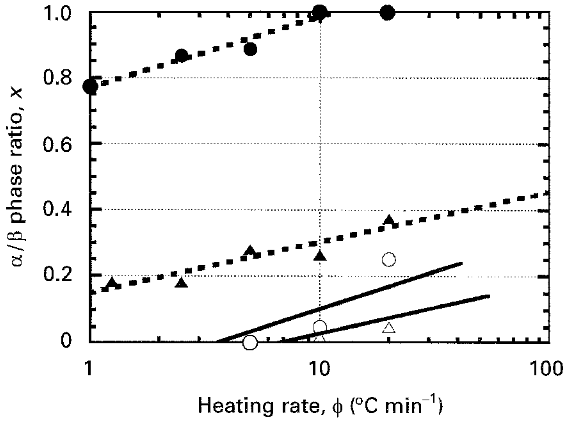


Figure 3 Heating-rate dependence of the β to α phase transformation from 5–20 °C min^{-1}, heated from room temperature to (●, ○) 1000 °C for the bulk and to (▲, △) 1050 °C for the powder with (△, ○) constant heating rate (slow) over whole temperature range, along with (▲,●) the dependence on heating from room temperature to 900 °C at 200 °C min^{-1} and then heating to each temperature at various heating rates (rapid) [8].

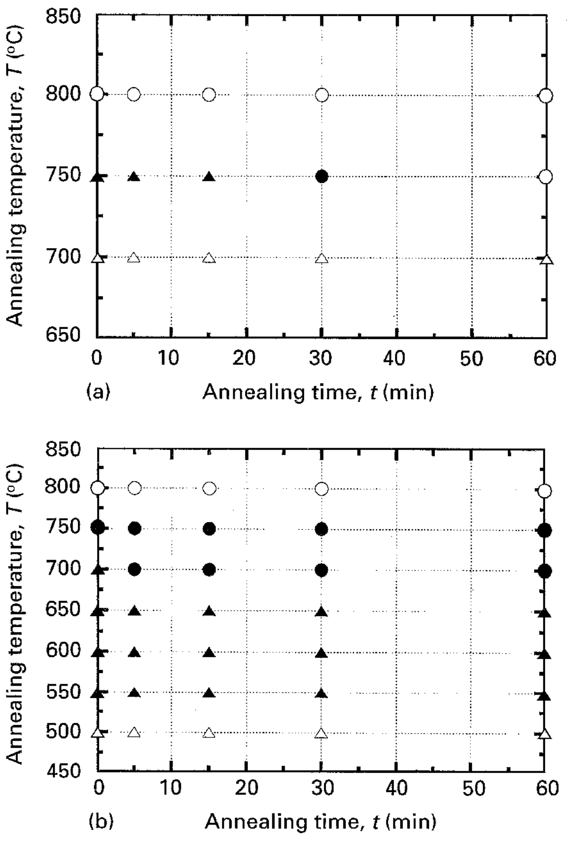


Figure 4 Time–annealing temperature dependence of α to β phase transformation at several different annealing temperatures for (a) bulk, and (b) powder. (△) α, (▲) mixture (α-rich), (●) mixture (β-rich), (○) β.

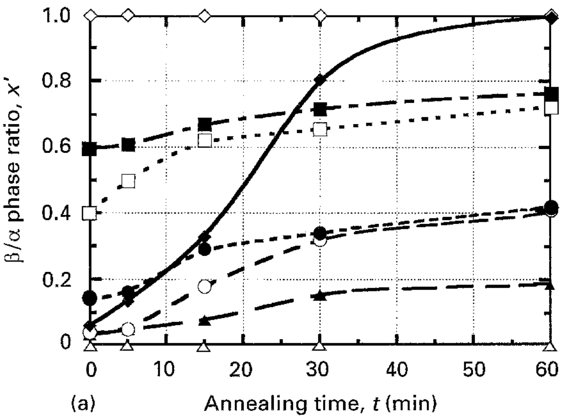
3.2. α–β phase transformation

Fig. 4 shows a typical example of the time–annealing temperature dependence on the solid state α to β phase transformation for the bulk and the powder. The α phase transformed to the β phase perfectly at 800 °C for both the bulk and the powder with the present heating and cooling rates. The phase transformation for the powder began at a lower temperature than that for the bulk. The difference in the phase transformation behaviour lies in the heating process (elevated temperature process). An exothermic peak corresponding to the phase transformation was not observed in DTA. From the results in Fig. 4, it appears difficult to obtain the α-phase crystal on cooling down to room temperature.

Table III shows the phase obtained during the cooling process from the α-phase crystal from 1070 °C with different cooling rates. Compared with the results in Fig. 4, the α-phase crystal was found to be obtained at a cooling rate of above 2 °C min^{-1}, and the α + β mixture phase crystal was obtained with many cracks at 1 °C min^{-1}. Comparing these results with those of the annealing experiments, the effects of the thermal stress during the heating process before annealing are believed to be large, for the α to β phase transformation. It is difficult to use single crystals of α-BBO as seed crystals.

TABLE III Phases obtained during cooling from the α-phase crystal at 1070 °C at different cooling rates.

	Cooling rate (°C min^{-1})				
	100	10	5	2	1
Phase	α	α	α	α	α + β



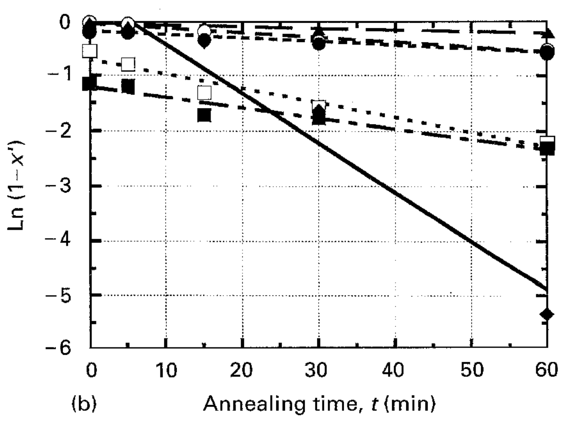


Figure 5 Time dependence of β/α phase ratio, x', transformed, obtained from the XRD peak intensity: (a) normal plot, and (b) logarithmic plot, (◆) heated at 750 °C for the bulk and 500–800 °C for the powder (no mark). (△) 500 °C, (▲) 550 °C, (○) 600 °C, (●) 650 °C, (□) 700 °C, (■) 750 °C, (◇) 800 °C.

Fig. 5 shows the β/α phase ratio transformed from the α phase depending on the annealing time, obtained by XRD peak intensity, heated at 750 °C for the bulk and 500–800 °C for the powder. Fig. 5b shows the logarithmic relationship for Fig. 5a. The following numerical relationships are obtained. Here x' is the β/α phase ratio and t is the time (min). The nucleation model can be applied.

$$x' = 1 - \exp[-8.9 \times 10^{-2}(t - 5.1)] \quad (750\,^{\circ}\mathrm{C, bulk}) \qquad (5)$$

$$x' = 1 - \exp[-0.30 \times 10^{-2}(t + 14)] \quad (550\,^{\circ}\mathrm{C, powder}) \qquad (6)$$

$$x' = 1 - \exp[-0.86 \times 10^{-2}(t + 6.0)] \quad (600\,^{\circ}\mathrm{C, powder}) \qquad (7)$$

$$x' = 1 - \exp[-0.66 \times 10^{-2}(t + 28)] \quad (650\,^{\circ}\mathrm{C, powder}) \qquad (8)$$

$$x' = 1 - \exp[-2.6 \times 10^{-2}(t + 27)] \quad (700\,^{\circ}\mathrm{C, powder}) \qquad (9)$$

$$x' = 1 - \exp[-1.9 \times 10^{-2}(t + 65)] \quad (750\,^{\circ}\mathrm{C, powder}) \qquad (10)$$

For the bulk, it may be difficult to keep homogeneous thermal conditions, so that the error may be large compared with the results for the powder. The phase transformation of the powder began sooner than that of the bulk, before an annealing time of 30 min owing to the phase transformation during the heating process before annealing. The nucleation rate, I_0, in Equation 1 was increased with increasing temperature for the powder, so that the α to β phase transformation occurred as a thermal activation process. The increase of the absolute value of t_0 was greater with increasing temperature. This was also caused by the phase transformation during the heating process before annealing. The behaviour also depends on the thermal properties. The thermal properties have not yet been measured on α-BBO, so that further discussion is difficult. This α to β phase transformation of the crystal is one reason why a single crystal with many

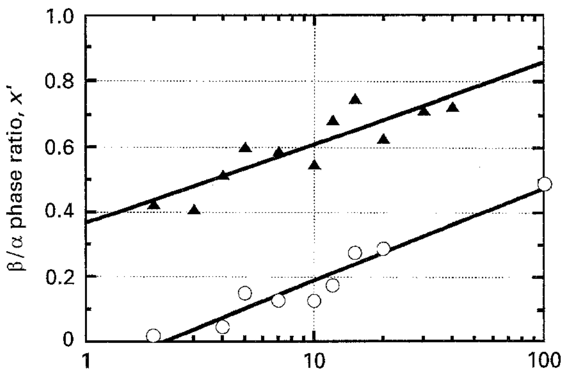


Figure 6 Heating-rate dependence of α to β phase transformation on heating from room temperature to 750 °C for (○) bulk and (▲) powder at a constant heating rate.

cracks is obtained, as shown in Table III, during the cooling process after growth.

Fig. 6 shows the heating-rate dependence of the α to β phase transformation from 2–100 °C min^{-1} heated up to 750 °C with constant heating rate from room temperature. The faster the heating rate was, the faster was the phase transformed, depending on the sample shape following the thermal activation process. The difference in the results for the bulk and powder depends on the homogeneous thermal conditions.

4. Conclusion

Solid-state phase transformation of BaB_2O_4 for both the β to α and the α to β were investigated using a platinum crucible. For the β-phase sample at the α-phase stable temperature (> 925 °C), the β phase transformed to the α phase perfectly below a melting temperature of 1100 °C. The cooling rate required to obtain the β phase as a metastable phase from the melt, to suppress the β to α phase transformation, needed to be larger than 5 °C min^{-1} in the α-phase stable temperature range. For the α-phase sample at the β-phase stable temperature (< 925 °C), the α phase transformed perfectly to the β phase above 800 °C. A difference in the phase transformation behaviour, caused by thermal stress, was observed for the bulk and the powder shape samples on both the β to α and the α to β phase transformations.

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