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B. -G. WANG[1,2], Z. -P. LU[2], A. VOIGT[1]

[1]The research center caesar, Germany
[2]Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

On the Iso-Diameter Growth of b-BaB_2O_4 (BBO) Crystals by Flux Pulling Method

The iso-diameter growth of β-BaB_2O_4(BBO) crystals by the flux pulling method have been studied based on the phase equilibrium diagram in the BaB_2O_4-Na_2O pseudo-binary system and from the interface stability. The mathematical expressions for the cooling rate in the growth of the crystals with constant diameter under stable growth conditions are derived, the experimental phenomena such as diameter contraction and difficulty to grow a lengthy crystal by the flux pulling method are explained, the prerequisite for iso-diameter BBO crystal growth from the flux is suggested; a new continuous charging flux pulling method is introduced to grow large-sized high quality crystals with a relative high growth rate.

Keywords: β-BaB_2O_4(BBO), crystal growth, flux pulling method, diameter control, phase equilibria, interface stability

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1. Introduction

β-BaB_2O_4 (BBO) crystals, as an excellent nonlinear optical material (CHEN C.-T et al.), have been widely applied in the second harmonic generation (SHG), optical parametric amplification (OPA) and optical parametric oscillation (OPO) of high pulse power lasers. The crystal growth from high temperature solutions with or without pulling (for example, JIANG et al.; FEIGELSON et al., 1989; BORDUI et al.; TANG et al.) have been widely carried out in the past decade; but to grow larger high quality BBO crystals still is a problem and requires further investigations (CHEN T.-P et al.; WANG et al.; TSVETKOV et al.). Particularly, the diameter of the grown crystals usually contracts with increasing crystal length when the flux pulling method is applied. This results in bowl-shaped crystals and will greatly affect the crystal processing for NLO devices. On the other hand, techniques for automatic diameter control (HURLE, 1977) which have been utilised in the Czochralski growth with either optical imaging of the crystal or direct measurement of the crystal weight used to determine the instantanous radius seem difficult to be transferred into the BBO crystal growth since the growth rate is very slow. In this paper, we will analyse the iso-diameter conditions of β-BaB_2O_4 (BBO) crystal growth by the flux pulling method based on the phase equilibrium diagram in the BaB_2O_4-Na_2O pseudo-binary system and the interface thermodynamics. The mathematical expressions for the cooling rate in the growth process of the iso-diameter crystals of β-BaB_2O_4 will be derived, some experimental phenomena will be explained, and a continuous charging flux pulling method will be introduced.

2. BaB_2O_4-Na_2O phase equilibrium diagram and BBO crystal growth

2. 1 The fit of the liquidus curve of BBO crystal growth in the BaB_2O_4-Na_2O phase diagram

Many fluxes such as oxides (Na_2O, K_2O), fluorides (KF, NaF, BaF_2), and sodium metaborate ($Na_2B_2O_4$) were used for BBO crystal growth. Here we choose the typical BBO-Na_2O growth system to show the application of the BaB_2O_4-Na_2O phase diagram to the growth of BBO crystals by flux pulling method. The phase equilibrium of BaB_2O_4-Na_2O pseudo-binary system is shown in Fig.1 (HUANG et al.;), in which the growth region is shown in Fig. 2 for clarity.

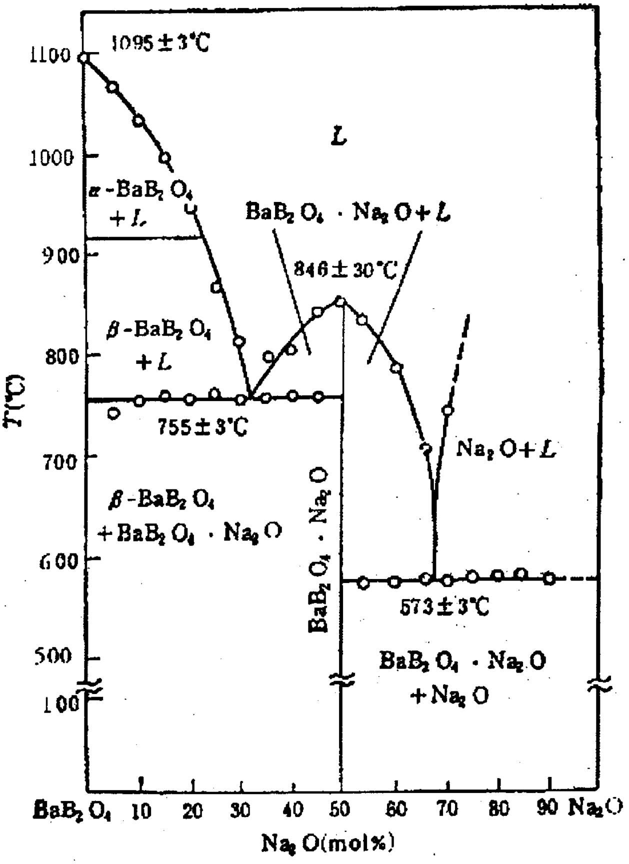


Fig. 1: Phase equilibrium diagram of BaB_2O_4-Na_2O pseudobinary system (After LIANG)

It is found that the concentration of the melt will decrease downward the CE curve in Fig. 2 with progress of the crystal growth, the slope of a point on the CE line is

$$m = \Delta T / \Delta x \qquad (1)$$

Where Δ T is the cooling rate in one day (°C/*d*), Δx is the concentration change of the melt in one day (mol%/d). Since x is related to the amount of the material to be grown, the slope of the liquidus curve m is very important to the crystal growth from flux by the temperature lowering method. So it is necessary for us to fit and obtain the functional expression of the liquidus curve. For simplicity, suppose a three-order equation for it, which can produce a satisfactorily fitted result

$$T = ax^3 + bx^2 + cx + d \tag{2}$$

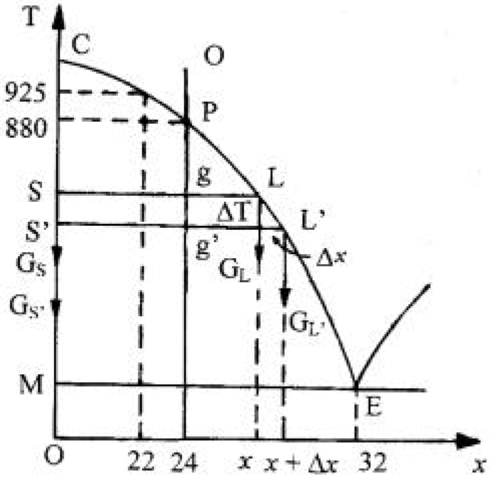


Fig. 2: The schematic drawing of the region of the temperature lowering during BBO crystal growth

Four points (0, 1100), (12, 1020), (24, 880), (30, 760) were taken from the CE curve (see Table 1) and put into (2), the coefficients *a, b, c*, and *d* were obtained as follows: $a = -11/1296 \cong 0.0085$, $b = 7/72 \cong 0.097$, $c = -119/18 \cong 6.6$, $d = 1100$. Therefore, the mathematical expression of the CE curve is

$$T = -0.0085x^3 + 0.097x^2 - 6.6x + 1100 \tag{3}$$

The Na_2O concentrations, crystallization temperatures are calculated based on (3) and listed in Table 1. It is found that the results by fit are satisfactory. Compared with the value from HUANG and LIANG, the maximum deviation is only about 0.5%. The slopes of the liquidus curve can be obtained by deriving (3) and are also listed in Table 1:

$$m = dT/dx = -0.0255x^2 + 0.194x - 6.6 \tag{4}$$

x mol% Na_2O	12.0	18.0	20.0	21.8	22.4	24.0	26.2	27.4	28.0	30.0
T (H. & L.)	1020	960	940	920	900	880	840	820	800	760
T (calculation)	1020	963	939	914	915	880	841	817	804	760
m (calculation)	7.94	11.37	12.92	14.49	15.04	16.63	19.02	20.43	21.16	23.73

Table 1: The Na_2O concentrations, crystallization temperatures and slopes of the liquidus curve for BBO crystal growth

According to Fig.1, the melting point of α-BaB_2O_4 is 1095°C, whereas the temperature of the phase transformation to the β-type is about 920°C. Furthermore, β-BaB_2O_4 can form the eutectic system with Na_2O at the temperature 755°C. Therefore, the crystal growth of the low temperature phase β-BaB_2O_4 (BBO) should be carried out from flux at the range 920 ~

755°C, and the concentration of Na_2O should be within 20 ~ 32mol% (It is suggested that the concentration of Na_2O should not be less than 22% in order to avoid the formation of α-BBO which have no NLO efficiency). In our experiments, BBO crystals were grown from the flux of BaB_2O_4-Na_2O with pulling.

2.2 The determination of the cooling rate

In order to assure a suitable supersaturation of the solution it is necessary to reasonably lower the temperature during the whole process of crystal growth. Suppose P is the start point for the crystal growth, and O is the growing temperature in Fig.2. When the temperature of the solution decreases from O point to P point, β-BBO begins to crystallize and the concentration of the mother phase will decrease from P point along CE curve, the seed will gradually get larger shoulder; when the temperature of the solution is decreased to *g* point, the shouldering is stopped, and the crystal is initially pulled. In Fig. 2, S is solid phase and L is liquid phase, on the SL line BBO keeps coexistence of two phase and satisfys the lever principle with Na_2O concentration in the melt x (LIANG): $G_S \cdot \overline{Sg} = G_L \cdot \overline{gL}$, the ratio of the solid and liquid at *g* point is

$$G_S / G_L = \overline{gL} / \overline{Sg} \tag{5}$$

where G_s is the crystallized amount at the end of crystal growth, G_L is the amount of the remained in melt, the total amount of the melt (BBO + Na_2O) is $G = G_s + G_L$. Then (5) becomes

$$\overline{gL} = \overline{Sg} \cdot G_S /(G - G_S) = 24G_S /(G - G_S) = x - 24 \tag{6}$$

Suppose that the cooling rate in one day from *g* point is ΔT(°C/day) and the pulling rate is v (cm/day), then (7) is held when the temperature of the melt is down from *g* to *g′* in one day based on the lever principle

$$\overline{g'L'} = 24G'_S/(G - G'_S) = \Delta x + x - 24 \tag{7}$$

and the crystallized BBO amount every day is

$$\Delta G_S = G'_S - G_S = p\, R_S^2 u\, r\, /\, m \tag{8}$$

where R_s is the radius of the crystal (cm), r the density (3.83g/cm^3), μ molar weight (223g/mol). From (6) and (7), G_s and G'_s are obtained

$$G_s = G\,(x\text{-}24)/x \tag{9}$$

$$G'_s = G(\Delta x + x\text{-}24)/(\Delta x + x) \tag{10}$$

Therefore, (8) becomes

$$\Delta x = \Delta G_s x^2 \,/\, (24G\text{-}G_s x) \tag{11}$$

Here x is within 24~32 mol. Since ΔG_s is much smaller than G (in gerneral, $\Delta G_s/G < 0.5\%$, i.e. $\Delta G_s \ll 24G$) and can be neglected, (11) is simplified as

$$\Delta x = \Delta G_s x^2/24G \tag{12}$$

From (8), (12) and (1) the cooling rate in one day is obtained

$$\Delta T = \Delta G_S mx^2/24G = p R_S^2 u r mx^2/24\mathrm{m}G = 0.00225u R_S^2 mx^2/G \tag{13}$$

3. Discussions

3. 1. The cooling and pulling rates determined by stable growth of the crystals with constant diameter

The (13) formula clearly indicates that the crystal diameter is correlated with the concentration of the solution, the slope of the liquidus curve and the growth parameters (pulling and cooling rates). We can apply the formula (14) to describe the relations of the crystal diameter with these factors:

$$R_S^2 \sim \frac{\Delta T \cdot G}{u \cdot mx^2} \tag{14}$$

This provides the guidelines for choice of the growth conditions of the crystals by flux pulling method. When the pulling rate is increased or even it is constant, the cooling rate should correspond to be increased; if ΔT still is kept constant, the grown crystal must become a bowl-shaped boule; at worst, the crystal will be pulled out from the solution. Therefore, when the lengthy crystals should be grown, the pulling rate at the later stage should be decreased (this leads to a long growth period). On the other hand, if the pulling rate is fixed, and we suppose that the growth rate is the same as the pulling rate, then in order to keep a constant diameter of the crystal, from (14) we have the relation between ΔT and the time t: $\Delta T \sim mx^2$, and thus have $\Delta T \sim t^3$, which shows the same law as SCHEEL and ELWELL obtained. However, it is noted that if the cooling rate is too large, this could lead to larger supercooling of the solution and result in the formation of inclusion and polycrystalline as well as cellular growth. In a word, in order to keep the crystal with iso-diameter, it is necessary to increase ΔT and mx^2 with the same step. The supersaturation of the solution resulted from the increase of the cooling rate should be regulated by the pulling rates (ΔT should be controlled within the range of 2~3°C in one day corresponding to the pulling rate 0.1~0.15 cm/day).

The Fig.2 and Table 1 show that x and m will gradually increase from 24 mol% and 16.6°C/mol respectively at the beginning with progress of crystal growth. If the ΔT and v are kept constant during growth, and suppose that the radius of the crystal before pulling is R_{so} and the radius of the growing crystal at interface is R_s, and if BaB_2O_4 concentration variation due to shouldering the seed is neglected, then the Na_2O concentration of the melt at this point (begin to pull the crystal) is x_o = 24 mol%, while m_o = 16.6°C/mol%. So $\sqrt{m_0}\, x_o \cdot R_{so}$= 97.78$R_{so}$, then $R_s/R_{so} = \sqrt{m_0}\, x_o/\sqrt{m}\, x$=97.78/√($m$)$x$. Since x and m gradually increase from x_o and m_o with the crystal growth, $\sqrt{m}\, x$ will be larger than $\sqrt{m_0}\, x_o$. Thus, the ratio of 97.78/$\sqrt{m}\, x$ is smaller than 1. This can explain the experimental phenomenon why the crystal diameter usually gradually contracts with pulling.

Now take an example. Suppose that the radial temperature distribution at the growth interface is not taken into account, and the radius of the growing crystal R_{so}=2.5 cm, the pulling rate v=0.1 cm/day, the crystal starts to grow from the point P (see Fig.2) where the concentration of Na$_2$O x_o = 24mol%, the slope of the liquidus curve m_o = 16.6°C/mol%. The amount of BBO melt in crucible is 4 mol, then the weight of the melt G = 4/76% = 5.26 mol, in which the concentration of Na$_2$O is 5×24% = 1.26 mol. Therefore, according to (13) the cooling rate in one day is ΔT = 2.6°C. Suppose that the crystal length is 1.5 cm, the growth period is 15 days. If the cooling rate is constant, then the total amount of the temperature lowered is about 40°C. From Fig.2 and Table 1, it is found that the Na$_2$O concentration at the end of crystal growth x = 26.2 mol%, the slope of the liquidus curve at this point m = 19.0°C/mol%, then the diameter of the grown crystal at the end can be obtained from (15): R_s=97.78$R_{so}/\sqrt{m}\, x$=2.1 cm. This calculation agrees well with the experimental result. In a practical growth experiment with the above parameters, the diameter of the crystal contracts from ϕ 50mm at the top to ϕ40mm at the bottom. In order to obtain an iso-diameter crystal, the cooling rate should increase from 2.6°C/day at the beginning to 3.5°C/day at the end.

3. 2. Effect of the height of the growing crystals on the constant diameter

To achieve the condition of the steady growth with constant diameter requires that the net heat flow through the interface exactly balances the rate of evolution of latent heat due to the crystallization process (HURLE). Assuming for the moment a planar interface, for the flux pulling method this condition can be expressed as

$$K_s\left(\frac{\partial T}{\partial z}\right)_S = Kv+K_l\left(\frac{\partial T}{\partial z}\right)_l \tag{15}$$

or as

$$KvA=Q_s\text{-}Q_l \tag{16}$$

where $Q_s=K_s\left(\frac{\partial T}{\partial z}\right)_s\cdot A$ is the heat loss at the interface by the crystal, $Q_l=K_l\left(\frac{\partial T}{\partial z}\right)_l\cdot A$ is the heat flow at the interface from the melt, $K_{s,l}$ are the thermal conductivities of the crystal and melt, K is an coefficient determined by the latent heat of crystallisation, the solution concentration and the molecular diffusivity, A the area of the growth interface, $\left(\frac{\partial T}{\partial z}\right)_{s,l}$ are the axial temperature gradients in the crystal and melt at the interface, v the growth rate.

From (16), it is found that the crystal diameter can be controlled by changing the pulling rate (suppose that the pulling rate is equal to the growth rate) if the temperature gradients are invariant. However, the axial temperature gradients in the crystal and melt at the interface are changed with the height of the growing crystal. If the change of the temperature gradient in the melt due to the decrease of the solid-liquid interface during the crystal growth is neglected, then the main problem in BBO crystal growth is the change of the temperature gradient in the crystal. Since oxide crystals are optically semi-transparent (MÜLLER, OSTROGORSKY), the growing crystal has a large absorption over the radiadtion from the melt. According to the heat transport equation (CAO)

$$\frac{\partial^2 T}{\partial^2 r}+\frac{1}{r}\cdot\frac{\partial T}{\partial r}+\frac{\partial^2 T}{\partial^2 z}=-\frac{Q_0\, l\, e^{-lz}}{k} \tag{17}$$

where k is the thermal conductivity, Q_o is the heat flow from the melt to the crystal per unit area. Assuming the heat losses only from the top of the crystal, then $\frac{\partial T}{\partial r}$=0, $\frac{\partial^2 T}{\partial^2 r}$=0, the following formulas are held

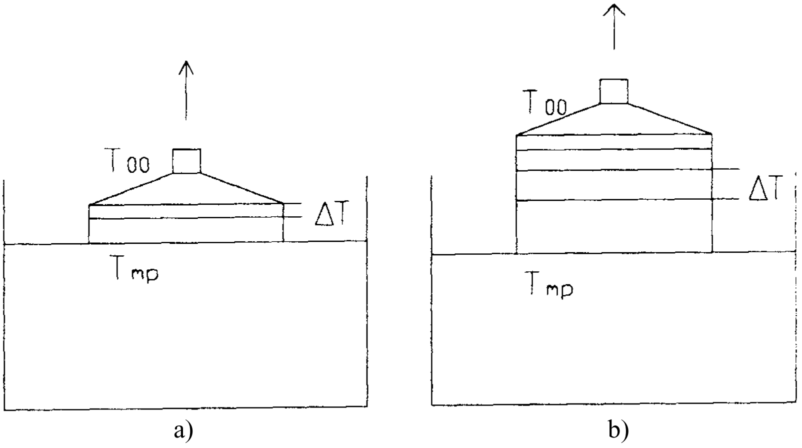
$$\frac{\partial^2 T}{\partial^2 z} = -\frac{Q_0 l e^{-lz}}{k} \tag{18}$$

$$Q_s = Q_0 e^{-lz} \tag{19}$$

Therefore, the axial temperature gradient in the growing crystal is not uniform. Moreover, the released latent heat is further accumulated at the growth interface with the progress of crystal growth. So the temperature gradient near the interface gets smaller when the lengthy crystal is grown. We can use the Fig.3 to show this problem. In Fig.3(a) the crystal is just pulled after shouldering, since there is a large temperature gradient in the crystal, the growth rate is large; after the period when the crystal becomes large, the temperature gradient in the crystal becomes small due to absorption of the crystal over the heat from the melt, as seen in Fig.3(b), thus the growth of the crystal becomes slow. If the stable growth interface is kept, the maximal growth rate (ELWELL, SCHEEL) is

$$v_{\max} = \frac{D \Delta H C_s}{r R T^2} \cdot \left(\frac{\partial T}{\partial z} \right) \tag{20}$$

where D is the diffusion coefficient, ΔH the enthalpy, C_s the equilibrium concentration of the solute. So this formula also shows that the pulling rate should become smaller with the progress of crystal growth. Otherwise, the cooling rate should get larger with the time. Therefore, here we can explain the interface instability during BBO crystal growth: (1) if the cooling and pulling rates are constant, the crystal is easily pulled out from the melt; (2) when the pulling rate is fixed, the cooling rate becomes large with the time according to the requirments of the phase equilibrium and the heat transport equation, but a lot of inclusions or cellular structure may be readily formed at the bottom of the crystal due to supercooling (normally the perfect crystal less than 2.0 cm). So it's not easy to balance the cooling and pulling rates in the practical crsytal growth, a great skill is required to control the growth of high quality crystals with large-size.



a) b)

Fig. 3: The axial temperature distribution in the growing crystal due to release of the latent heat and the absorption over the radiation. (a) The axial temperature gradient in a short crystal is large; (b) The axial temperature gradient in a lengthy crystal is small. T_{00} is the temperature of the crystal surface, T_{mp} the crystallisation temperature at growth interface, ΔT temperature difference between isothermal lines. Note that the temperature changes at the crystal surface and at the interface during growth are neglected in both cases.

3. 3. A continuous charging flux pulling method

Therefore, the normal flux pulling method is difficult to grow high quality BBO crystals with large-size. In order to improve the growth process, some growth techniques should be developed. A continuous charging flux pulling method was designed by us. As shown by Fig.4, the solute BBO is added into the solution at a proper interval, the concentration x of Na_2O keeps constant, and the crystals were grown at the certain point m_o of the liquidus curve, and thus to avoid the variations of m_o and x which are one reason to cause the variation of the crystal diameter. On the other hand, the growing crystal is cooled by pulling rod. Since the axial temperature gradient in the crystal is large in this technique, the growth rate is relatively high. Besides, since the growth parameters are seldom changed in the whole process, the growth will be stable and thus the high quality crystals can be obtained. In fact, this technique called "Continuous Charging Czochralki method, CC-CZ technology" has been also used for the growth of other crystals (KITAMURA et al.).

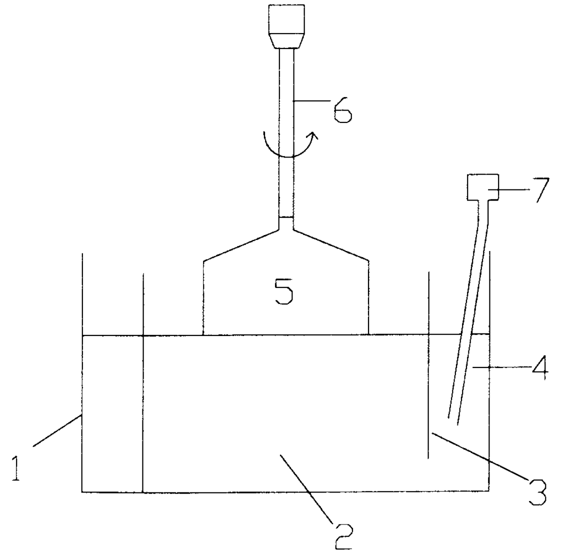


Fig. 4: Schematic drawing of the furnace for BBO crystal growth by the continuous charging flux pulling technique. (1) Pt crucible (2) melt (3) Pt partition (4) Pt tube (5) crystal (6) the rod with cooling system (7) polycrystalline BBO

In addition, since $R_s \sim 1/\sqrt{m}\,x$ (see (14)), the diameter of the grown crystal contracts with the increase of the concentration (x) Na_2O in the solution and the decrease of the slope of liquidus curve if the pulling rate is fixed. When BBO crystals were grown from Na_2BO_4 flux, however, the contraction of the crystal diameter gets smaller compared with that from Na_2O flux due to the less variation of the slope of the liquidus curve (HUANG, LIANG) and thus the crystal growth from Na_2BO_4 will be easier than from Na_2O in view of the diameter control. Here it's worthwhile to note that even though the crystal diameter tends to be contracted when the flux pulling method is employed, due to the higher quality of the grown crystals this method still is preferred compared with the flux mthod without pulling. Of course, the method of the crystal growth from the metastable phase (ITOH et al.; FEIGELSON et al., 1995) could be also an efficient way to solve the problems in the growth of BBO crystals by flux methods, but the crystals grown from the metastable phase seem not to be commercializd until now. Therefore, the flux pulling method still is a main method in the growth of BBO crystals, but this method can be improved by the continuous charging technique as above and thus leads to improvement of the crystal quality and shortens the growth period.

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Contact information:

Dr. Bu-Guo WANG
The research center caesar
Postfach 7025
53070 Bonn
Germany

e-mail: wang@caesar.de