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# Effect of the Temperature Fluctuation of the Melt on β-$BaB_2O_4$ (BBO) Crystal Growth

In this paper the effect of the growth temperature fluctuation, for instance, the transient furnace temperature variation due to a short-term electric power supply interruption on BBO crystal growth was investigated based on the theory of temperature wave transmitting in melt and the boundary layer theory of melt. It was found that the critical width of the temperature pulse to avoid the temperature wave penetrating through the boundary layer and reaching to the growth interface at a constant rotation speed (9~4 *r/min*) is 69~150 *s* and the corresponding amplitude of the temperature pulse is high more than 60 °C due to the large thickness of the velocity boundary layer of the melt. This result indicates that a small transient temperature fluctuation has no significant effect on the crystal quality, and therefore implies that not only transport processes but interface growth kinetics, a two-dimensional nucleation growth mode at the interface may also dominate the crystal growth.

Keywords: β-$BaB_2O_4$ (BBO), flux pulling method, interface stability, temperature wave theory, boundary layer theory

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## 1. Introduction

The growth of β-$BaB_2O_4$ (BBO) crystals, an excellent nonlinear optical material, from high temperature solutions with or without pulling have widely been carried out for more than one decade. However, the crystals used as the frequency conversion devices, which should have no macro inclusions and scattering particles, still cannot meet commercial demands. Particularly, the growth of those larger-sized crystals with high quality still encounter a lot of difficulties, because the crystal perfection may be influenced by various inherent or external factors. One of the factors is that every growth circle takes a long period (one month or even longer if using the ordinary flux pulling technique) (WANG, LU, VOIGT), the transient temperature fluctuations of the furnace during growth may inevitably happen due to the temperature-control system instability, and thus influence the crystal quality. In this paper, we aim to investigate the effect of the growth temperature fluctuations, as a special case, the sudden drop of furnace temperature due to a deliberate short-term electric power supply failure on BBO crystal growth. Based on the theory of temperature wave transmitting in melt and the velocity boundary layer theory of melt, the relationships between the temperature pulse width, frequency, wave length and the penetration depth of the temperature wave in the BBO melt are studied. The critical width of the temperature pulse to avoid the temperature wave penetrating through the boundary layer and reaching to the growth interface at a constant rotation speed is found. Since crystal growth is a dynamic process which is composed of heat and mass transport and interface kinetics, the crystal growth is also

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discussed by interface kinetic effects in order to reasonably reveal the formation of inclusions.

## 2. The temperature wave in the melt

### 2.1 The furnace configuration

In order to get a large growth rate (1 ~ 1.5 *mm/day)* without supercooling of the melt, a large temperature gradient of the furnace is required (WANG, LU, VOIGT). Therefore, the crucible was put on the top of the heater in our furnace. Here, we suppose that the heater is completely located under the bottom of the crucible. Since the system is axisymmetrical, we suppose that the central point O at the bottom of the crucible is the heat source of the melt, and that the temperature variations of the melt result from the heat perturbation from O, as seen in Fig. 1.

The geometry parameters in our system are: the melt height is about 70 *mm*, the crystal diameter is about 45 ~ 75*mm*, and the crucible diameter is about 90 ~ 140*mm*. The temperature at O point was measured to drop about 20 ~ 40°C after 60 seconds when the normal growth is stopped by a sudden power interruption in the system.

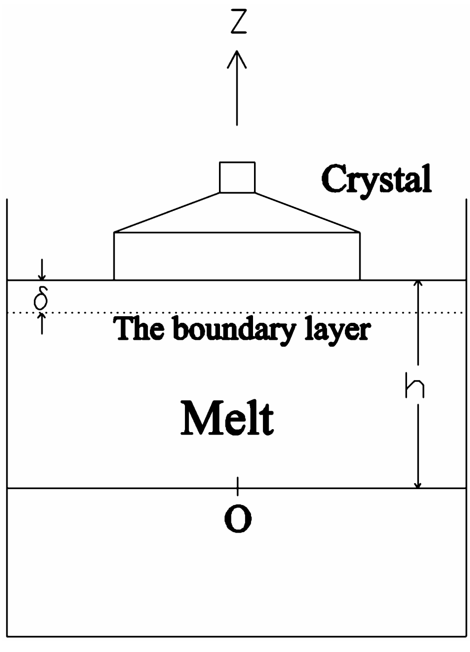


Fig. 1: Temperature waves transmitting from O point to the growth interface

### 2.2 The wave equation expression of the temperature pulses

Suppose that the temperature fluctuation of the melt in the crucible due to a short-term electric power supply interruption is taken as a singular-perturbation's variation, then the temperature pulse $\Delta T(t)$ from the point O in Fig.1 can be divided into the sum of a series of sinusoidal waves with different wavelength, amplitude and pulse time:

$$\Delta T(t) = \sum_{n=1}^{\infty} \frac{4A_0}{np} \sin nwt \qquad (1)$$

where $n = 1,3,5$ ..., $w=p/t=2pf$, $f=1/(2t)$. $w$ is the angular frequency of the fundmental wave, $f$ is the frequency of the fundmental wave, $t$ is the duration of electric power supply interruption, i.e. the width of the temperature pulse, and $A_0$ is the drop amplitude of the furnace temperature after the electric power supply interruption, which is also the amplitude of the temperature pulse.

As the temperature pulses are the sum of odd sinusoidal waves by angular frequency $w$ and the amplitude $4A_0$, when $n = 1$, the frequency of the fundamental wave is the lowest meanwhile the amplitude is the largest, and thus has the biggest effect on the crystal growth; when $n > 3$, the effects of the harmonic waves can be neglected since the frequencies are large and the amplitudes are small in this case. Therefore, when the duration of electric power supply interruption is 60 seconds, the temperature drop $A_0$ of the crucible is about 20~40°C, the amplitude of the fundamental wave is $4A_0/p$ » $27$~$54$°C, the angular frequency of the fundamental wave $w$ » 0.05 *rad/s*, the frequency of the fundamental wave $f$ » *0.5 min*.

According to the boundary layer theory (SCHLICHTING), there exists a boundary layer around the growth interface. The temperature waves, decaying from the perturbation source O at the bottom of the crucible through the melt layer $h$ to the growth interface, firstly penetrate in the melt outside the boundary layer, then through the boundary layer reaching the growth interface. If the temperature decay outside the boundary layer is neglected (see below), then under this condition, whether the temperature waves have effects on the crystal growth or not is depending on whether the temperature fundamental waves can penetrate from the bottom of the boundary layer through $\delta_v$ to the growth interface. Therefore, according to the theory of temperature wave transmitting in melt, if the temperature wave $l=2pa$, then the amplitude of the temperature waves will attenuate in $e^{-az}$ along $z$ direction in the melt, then the temperature perturbation is

$$\Delta T = \frac{4A_0}{p}\exp(-ad_v)\ . \qquad (2)$$

The attenuation coefficient $a$ is

$$a = \frac{1}{2k}\left[-v_z + \sqrt{\frac{1}{2}\left(v_z^2 + \sqrt{v_z^4 + 16w^2k^2}\right)}\right] \qquad (3)$$

where $k$ is the thermal diffusivity of the melt, $v_z$ the axial velocity of the wave.

## 3. Discussion

### 3.1 The boundary layer's thickness

It has been noted that Cz crystal growth can be taken as a rotating disc (HURLE); the rotation of the seed or crucible only changes thickness of the boundary layer around the growth interface. Beyond the boundary layer, the axial flow $v_z$ of the fluid is large, and the tangential and azimuthal velocities $v_j$ , $v_r$ are small; on the contrary, within the boundary layer, $v_z$ is small, and $v_j$ , $v_r$ are large. The flow in the boundary layer is taken as a laminar flow. Therefore, for heat or solute transports the convection is dominant beyond the boundary layer, whereas the diffusion is dominant within the boundary layer. In our experiments, it was found that the growth interface is planar when the rotation rate was kept within 9~4 *r/min*. So the thickness of the velocity boundary layer is

$$d_v = 3.6\sqrt{u/\Omega} \tag{4}$$

where $u$ is the kinematic viscosity ($cm^2/s$) of the melt, Ω is the angular velocity of rotation of the crystal $W = 2pn_s$ and $n_s$ the rotation rate of the crystal (*r/s*). The thickness of the thermal and solute boundary layers is obtained by

$$d_T = 1.61\left(\frac{u}{\Omega}\right)^{\frac{1}{2}} \Pr^{-\frac{1}{3}} = 1.61 k^{\frac{1}{3}} u^{\frac{1}{6}} \Omega^{-\frac{1}{2}} \tag{5}$$

$$d_c = 1.61\left(\frac{u}{\Omega}\right)^{\frac{1}{2}} Sc^{-\frac{1}{3}} = 1.61 D^{\frac{1}{3}} u^{\frac{1}{6}} \Omega^{-\frac{1}{2}} \tag{6}$$

respectively, where $k$ is the thermal diffusivity, $D$ the mass diffusivity, $Pr$ the Prandtl number and $Sc$ the Schmidt number. According to (4)~(6), the thickness of the velocity, thermal and concentration boundary layers were calculated. The results are listed in Table 1, along with the paramters we used.

Table 1: The physical parameters and the boundary layer's thickness

| Names | Symbol | Values | Units | Comments |
|---|---|---|---|---|
| The rotation rate of the crystal | $n_s$ | 9 ~ 4 | *r/min* | Experiments |
| Kinematic viscosity of the melt | $u$ | 0.52 | $cm^2/s$ | Estimated from [LU] |
| Thermal diffusivity of the melt | $k$ | 0.0042 | $cm^2/s$ | Estimated from [LU] |
| Solute diffusivity | $D$ | $10^{-5}$ | $cm^2/s$ | Estimated from [JIN] |
| The boundary layer's thickness | $d_v$ | 2.7 ~ 4.0 | *cm* | From Eqn (4) |
| | $d_T$ | 0.24 ~ 0.36 | *cm* | From Eqn (5) |
| | $d_c$ | 0.032 ~ 0.048 | *cm* | From Eqn (6) |

### 3.2 Effect of the temperature fluctuations on the growth interface of BBO crystals

Now let us see whether the temperature waves due to the transient temperature fluctuation caused by a short-term electric power supply interruption can penetrate through the velocity boundary layer and have an effect on the growth interface. When $z = l$ ($l$ is one unit of wavelength), $e^{-a z} = e^{-a l} = e^{-2p} = 0.002$, it means that the temperature waves can not penetrate through the layer with the thickness of one unit wavelength. Therefore, the penetrating thickness of the temperature waves can be defined as

$$l = \lambda = 2\pi/\alpha \tag{7}$$

Since far away from the boundary layer, the convection is dominant for heat transport. The convection velocity at $z$ direction (TILLER) $v_z = 0.886\sqrt{u\Omega}$ » 0.62 ~ 0.42 *cm/s*. So when the duration of electric power supply interruption is larger than 0.3 *s* (i.e. $t >> 0.3$ *s*), $16\omega^2 k^2$ in (3) can be neglected ($16\omega^2 k^2 << v_z^4$), then *a»0*. This means that the temperature wave nearly has no attenuation from O to the boundary layer, the remaining question is whether the temperature wave can penetrate through the boundary layer and reach to the growth interface and finally affect the crystal growth.

On the other hand, within the velocity boundary layer the diffusion plays a dominant role. At this moment, $v_z$ *» 0*, so (3) can be simplified as

$$a = \sqrt{w/2k} \; . \qquad (8)$$

Therefore, the penetration thickness in relation to the duration of the power supply interruption (i.e. the wavelength of the temperature wave) is obtained from (7) and (8)

$$l = l = \sqrt{8pkt} \; . \qquad (9)$$

So when the width of the temperature pulse gets larger, or say the duration of power supply interruption is longer, the penetration thickness of the temperature waves will also get larger. The critical width of the temperature pulse to avoid the temperature wave penetrating through the boundary layer and reaching to the growth interface should be

$$l \,£ d_v . \qquad (10)$$

When the penetration thickness *l* of the temperature wave is larger than the velocity boundary layer $d_v$, the solid-liquid interface temperature will be varied and thus affect the crystal growth. The temperature pulse width, frequency, wave length and the penetration depth of the temperature wave of BBO melt are calculated and listed in Table 2. Here, we suppose that the crystal still keeps a constant rotation rate when the transient temperature variations take place. It was found that when the rotation rate is 9~4 *r/min* ($d_v$ = 2.7~4 *cm*), the duration is 60 *s* and the temperature drop is 35 °C, the interface temperature variation is only between 0.05°C and 0.002°C. The critical width of the temperature pulse to avoid the temperature wave penetrating through the boundary layer and reaching to the growth interface is found to be 69 *s* at the rotation rate 9 *r/min* and 150 *s* at 4 *r/min*.

Table 2: The temperature fluctuation amplitude of the furnace due to electric power supply interruption 1~5 *min* and the corresponding interface temperature variations

| *t (s)* | $A_o$ *(°C,exp.)* | *f (Hz)* | *w (rad/s)* | *a* (cm$^{-1}$) | *l (cm)* | *D T (°C)* | |
|---|---|---|---|---|---|---|---|
| | | | | | | $d_v$ *2.7 cm* | $d_v$ *4.0 cm* |
| 60 | 35 | 0.0083 | 0.052 | 2.49 | 2.52 | 0.05 | 0.002 |
| 120 | 59 | 0.0042 | 0.026 | 1.76 | 3.57 | 0.7 | 0.07 |
| 180 | 77 | 0.0028 | 0.018 | 1.46 | 4.30 | 2.0 | 0.3 |
| 240 | 91 | 0.0021 | 0.013 | 1.24 | 5.06 | 4.0 | 0.8 |
| 300 | 103 | 0.0017 | 0.011 | 1.14 | 5.51 | 6.0 | 1.3 |

From (8) one can find when *w* gets smaller and *k* larger, the propagation attenuation of the temperature wave along *z* direction becomes smaller, in other words, the small-frequency waves easily penetrate through the boundary layer with high value of *k* to the growth interface, and thus lead to the temperature fluctuation of the interface. Fortunately, *k* value of BBO-$Na_2O$ is small comparing with other oxide materials such as $KNbO_3$ (KN) and $LiNbO_3$ (LN)($4.2 \cdot 10^{-3}$ $cm^2/s$ for BBO, $1.4 \cdot 10^{-2}$ $cm^2/s$ for KN (JIN) and $8.4 \cdot 10^{-3}$ $cm^2/s$ for LN (LU), respectively). Therefore, the temperature wave does not easily penetrate through the BBO melt boundary layer. This characteristic is actually beneficial to the temperature control of the crystal growth. On the other hand, it is noted that the temperature fluctuation techniques can be used to produce the induced striations in some garnet crystals and investigate the growth mechanism (GÖRNERT). In molten oxides, which have very low *k*, $d_v$ may extend ten times as far into the fluid as $d_T$; furthermore, even in molten oxides, there is a characteristic difference between heat transfer in borates and other oxides due to the different viscosities, as seen from the Fig. 2. The dynamic viscosity of the BBO-$Na_2O$ melt at the growth temperature (for example, at 880 °C) is estimated at about 2 *Poise* and *Pr* is larger than 120, so the thickness of the velocity boundary layer $d_v$ of BBO crystal growth is larger than that of other oxide materials. In short, the velocity boundary layer of the melt with the high Prandtl Number (*Pr*) is larger than those with smaller *Pr*, while for the thermal boundary layer, the situation is vice verse (ROSENBERGER). The temperature fluctuation's range to be permitted is determined by $d_v$ and *k*.

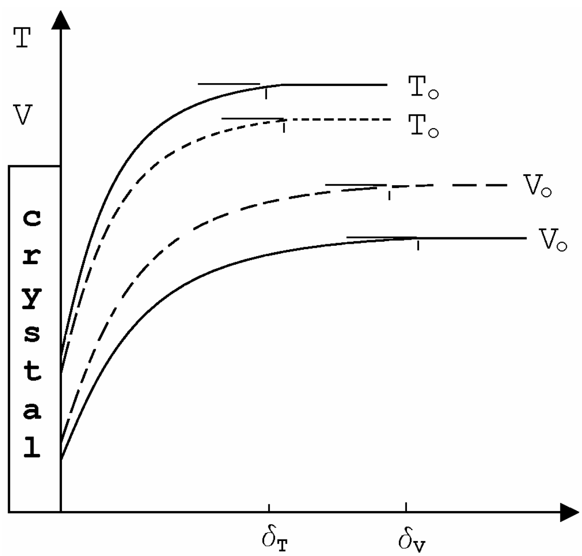


Fig. 2: Comparison between velocity and temperature distribution at solid-liquid interfaces for different fluid group with $Pr \geq 1$. The full line represents the melt has a *Pr* number larger than the dashed one, and thus has a larger velocity boundary layer. $T_o$, $V_o$ denote the temperature and velocity far away from the boundary layer

### 3.3 The inclusion's formation and the interface growth kinetics

According to calculation above, the duration of electric power supply failure is allowed high up to 1~ 2.5 *min* in our growth system. In practice, experimental results also comfirmed that there are no obvious detrimental effects on BBO crystal growth when the power interruption is less than 1 *min*. When the duration of electric power supply failure is 3 *min* or longer, however, the grown crystals almost become imperfect polycrystalline or contain much more mother liquid or tend to crack due to larger composition supercooling. From these experimental phenomena and theoretical analysis, we can obtain that occasionly small short-term transient temperature fluctuations have no significant effects on the crystal quality during BBO crystal growth. Of course, a stable temperature control, particularly a uninterrupted power supply during the entire growth process is best for growth of the high quality crystals.

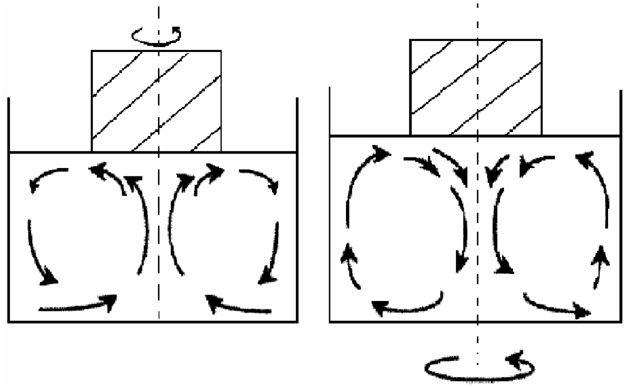

Fig. 3: Two typical kinds of flux flow patterns found in the stable Czochralski oxides crystal growth

Fig. 4: A typical crystal grown by the flux pulling technique, here the inclusions that are three-fold axisymmetrically distributed in the central part can be seen

The small transient temperature fluctuation doesn't greatly affect the interface stability, the flow patterns' variation in the melt may also have no great influence on the crystal growth. Although there are several kinds of heat and mass transfer processes appeared in the BBO flux pulling growth, two typical kinds of flux flow patterns have been classified in the stable Czochralski oxide crystal growth (MUELLER), as shown in Fig. 3, which are determined by the rotation modes. Both kinds of flow patterns can explain the inclusions' distribution in the crystals which are mainly located in the central part, as seen in Fig. 4, because there is a large supersaturation just below the center of the growing crystal caused by the convective flow frontier in both patterns. However, irrespective of the state of convection in the melt, the inclusions are mostly 3-fold symmetrically distributed in the crystals. Moreover, TSURU and OGAWA also observed numerous narrow and tiny light scatters locate on the rhombohedral planes of both the Czochralski and flux-grown crystals. It can be inferred that 3-fold symmetrically distributed inclusions in the crystals are only related to the crystal structure (space group *R3c*) and the crystal growth mechanism. In fact, it has been found the crystal structure, seeding orientation, raw materials systhesis as well as supersaturation all affect the crystal quality (WANG et al., 1998; TSVETKOV, et al.).

We have investigated the growth kinetics of (0001) and ($10\bar{1}0$) faces of BBO crystals in BBO-$Na_2O$ melts (TANG). It was found that the growth rate of (0001) has an exponential relation with the solution supersaturation under low supersaturation conditions, which indicates that there is a two-dimensional nucleation growth mode on the growth interface, when we use a [0001] seed. This is a smooth face growth, the growth rate is very slow and depends on the solution supersaturation and the growth unit's size (nucleation's barrier). Therefore, it can be concluded that the growth of BBO crystals from $Na_2O$ solutions by flux pulling method may not be only dominated by heat and mass transfer processes but also by interface attachment kinetics (TILLER). Since the thickness of the solutal boundary layer is very small (see Table 1), the composition at the growth interface will be easily changed by even a small fluctuation from fluid flow instability, therefore, the formation of the growth units and incorporation into the crystal is easily disrupted by supersaturation at the growing interface. The crystal growth process is actually characterized by complicated, nonlinear interactions between fluid dynamics, heat flow and mass transport as well as interface kinetics, therefore, when we try to simulate the BBO crystal growth process by computer it is very necessary to simulate the heat and mass transfer processes in combination with the interface kinetic effects (KWON and DERBY).

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