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CRYSTAL GROWTH OF $\text{Li}^{10}\text{B}_3\text{O}_5$

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Crystal Growth of $\text{Li}^{10}\text{B}_3\text{O}_5$

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The growth of boron 10 isotope enriched L^{10}BO ($\text{Li}^{10}\text{B}_3\text{O}_5$) optical crystal has been developed from Top-Seeded-Solution-Growth using a resistance furnace. In the preparation for growth materials, we have made further improvement on a charge loading technique to a crucible and succeeded in forming suitable high temperature flux for producing crystals. Adequate temperature gradient of 1K/cm inside the crucible was achieved from searching for a combination of setting temperatures in the vertical three-zone furnace and installing a ceramic ring under the crucible. We have also optimized seed holder configuration and established growth conditions by several attempts. As a result, two good quality L^{10}BO crystals were produced with sizes of 14 x 25 x 22 mm and 13 x 10 x 12 mm from <001> oriented seed crystals. Although these sizes were limited by the size of the crucible used, appropriate oriented samples were extracted for detailed studies in optical measurements.

Keywords: Non-linear Laser Crystal, TSSG, Crystal Growth, Isotope Material, LBO

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Li¹⁰B₃O₅ 光学結晶の育成

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高濃度ボロン同位体¹⁰Bを含むL¹⁰BO光学結晶の育成を抵抗加熱型炉を用いたトップシード融液成長法により行った。結晶原料の調整において、我々は原料のるつぼ装荷方法を改良し、結晶成長に適する高温のフラックスを作成することができた。縦方向に3分割されたヒーターを有する育成炉の設定温度をそれぞれ最適化することと共に、るつぼ下部にセラミクス製の円環を配置することにより、1K/cmの温度勾配をるつぼ内のフラックスに付けることが可能となった。また繰り返し行った試験結果をもとに、シードホルダー形状の最適化を行い、適切な結晶育成条件を決めた。その結果、結晶サイズ14x25x22 mm 及び 13x10x12 mmの2つの良質なL¹⁰BO結晶を<001>方位の種結晶から育成した。使用したるつぼの大きさに依存して小さなサイズの結晶しか育成することが出来なかったが、今後の詳細な光学実験に使用するための特定の方位を有するサンプルを抽出することができた。

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1. Introduction

LBO (LiB_3O_5) is one of the most versatile non-linear optical crystal having excellent properties for applications in the laser frequency conversions such as SHG, THG, and OPO. The crystal was discovered by Chen et al. in 1989 in China as a nonlinear laser crystal¹. It belongs to the orthorhombic system with the space group $Pna2_1$, $a=8.446(2)$, $b=7.380(2)$, $c=5.147(2)$ Å, $Z=4$. LBO is primarily composed of non-planar $(\text{B}_3\text{O}_7)^{5-}$ borate ring which has a tetrahedrally coordinated boron atom and two sets of a planar three-fold coordinated boron atom. The ring structure tends to have a large nonlinear susceptibility because of the delocalisation of π -electrons along the ring. Specifically, LBO shows shorter absorption edge in UV region on account of the non-planar part of $(\text{B}_3\text{O}_7)^{5-}$ rings where π -electrons break delocalisation². Furthermore, LBO has high optical damage threshold over 10 GW/cm². From these specific optical characteristics, LBO has been recognized for one of suitable nonlinear laser crystals in the wavelength conversion for high power lasers.

LBO is composed of oxygen, lithium and boron which have natural abundances of $^{16}\text{O} : ^{17}\text{O} : ^{18}\text{O} = 99.76\% : 0.04\% : 0.2\%$, $^6\text{Li} : ^7\text{Li} = 7.5\% : 92.5\%$ and $^{10}\text{B} : ^{11}\text{B} = 18.7\% : 81.3\%$, respectively. If they are replaced with single isotopes of low natural abundances, the crystals might be expected to exhibit some novel optical characteristics by the shift of lattice vibrational frequencies based on the mass effect which appears typically in small atomic number elements. To compare several optical characteristics with normal LBO, we have grown an isotope enriched L^{10}BO ($\text{Li}^{10}\text{B}_3\text{O}_5$) crystal by using a boron oxide compound, $^{10}\text{B}_2\text{O}_3$, which can directly give any differences in the borate ring due to the change of lattice vibrational frequency.

2. Selection of raw materials for LBO crystal

In LBO crystal growth, the binary system of $\text{Li}_2\text{O} - \text{B}_2\text{O}_3$ improved by Sastry³ has been employed in different combinations of compounds such as Li_2CO_3 , Li_2O , LiOH , $\text{Li}_2\text{B}_4\text{O}_7$, LiBO_2 , B_2O_3 , H_3BO_3 ⁴⁻⁷. The phase diagram of $\text{Li}_2\text{O} - \text{B}_2\text{O}_3$ system shown in Fig. 1, indicates that LBO melts incongruently in the range of over 90 wt% of B_2O_3 . As a typical composition used for the growth of LBO crystal contains 80.5 ~ 80 mol% of B_2O_3 (90.6 ~ 90.3 wt% of B_2O_3), the flux generally associates with high viscosity of about 60 poise at 1073 K⁷. Addition of small amount of NaCl or NaF can lower the flux viscosity⁸. However, we didn't use these additives in our attempts to measure the optical characteristics of the isotope enriched L^{10}BO crystal with a moderate size, since we had to prevent from any possible deteriorate effects in the measurement by the additives. If the high viscosity causes fatal problem in our crystal growth, we will change the composition such as 19.4 mol% of Li_2O and 77.6 mol% of B_2O_3 , and 3 mol% of NaCl, (9.4 wt% of Li_2O , 87.8 wt% of B_2O_3 , and 2.8 wt% of NaCl) based on the Qi's paper⁹.

In the selection of raw materials for LBO crystal growth, the most desirable combination of compounds are $\text{Li}_2\text{B}_4\text{O}_7$ and B_2O_3 as they don't thermally produce secondary inconvenient chemicals, for examples, CO_2 or H_2 gas which make the crystal growth difficult. On the other hand, commercially available enriched isotopic oxide for lithium and boron are only Li_2CO_3 and B_2O_3 . Therefore, the development of initial heating procedure for these compounds is essentially required whenever we grow the isotope enriched L^{10}BO .

3. HFT (Hot Filling Technique)

This section describes our HFT which is essential procedure for the initial preparation of Li_2CO_3 and $^{10}\text{B}_2\text{O}_3$ powder in TSSG (Top Seeded Solution Growth) method for L^{10}BO crystal growth.

In the first trial for the preparation, we made a heat treatment for premixed (30 min shaken by hand) powder of Li_2CO_3 and B_2O_3 . The mixed powder, 18 g of Li_2CO_3 and 70 g of B_2O_3 , was put into a platinum crucible of 60 mm diameter and 60 mm height. Then, it was installed in a single zone heat resistance furnace. Temperature was raised from the room temperature by a rate of 20 K/h. As a result, the powder expanded and the volume exceeded the capacity of crucible at 823 K. Lower rate of 10 K/h in the second trial also showed the same result. The expansion was caused by CO_2 gas evolved from Li_2CO_3 of which melting point is about 200 K higher than that of B_2O_3 . Li_2CO_3 powder surrounded by melting B_2O_3 started decomposing into CO_2 and Li_2O at around 773 K, and successive heat treatment accelerated the swelling of the partially melted specimen.

In the next trial, we made an individual heat treatment of Li_2CO_3 and B_2O_3 . We assumed that pre-melting procedure of Li_2CO_3 can reduce the amount of CO_2 gas in a following heat treatment where we add B_2O_3 powder. To pull out CO_2 effectively, we tried three different heat treatments of Li_2CO_3 ; 5 hours at 1273 K (case A), 5 hours at 1373 K (case B) and 20 hours at 1373 K (case C). The amount of CO_2 was 6.4 w% in case A and 12.2 w% in case B, respectively. In longer heat treatment of case C, we had expected further evolution rate of CO_2 . However, in this case, Li_2CO_3 volatilized nearly 90 wt% and coloured dark green as shown in Fig. 2 (a). Hence, we couldn't use it for the optical material and we couldn't find any good results in the procedure of

individual heat treatment.

Concerning the heat treatment of premixed compounds of Li_2CO_3 and B_2O_3 , Markgraf proposed HFT⁶; after an empty platinum crucible is heated to 1173 K in a furnace, a small amount of premixed powder is successively added to the hot crucible, and the process is repeated until the proper amount of powder is charged in the crucible. In the next stage, we used this technique and made further improvement focused on the concretion of pre-mixed powders into pellets. This procedure makes its handling easier than the Markgraf's HFT and can reduce the filling loss which has usually happened in case of using powder specimens. The process of our HFT for the platinum crucible of 60 mm diameter and 60 mm height is as follows;

- a. Preheating of the Pt crucible at 1173 K for 3 hours
- b. Mixing the powder of Li_2CO_3 : 28.2 g and B_2O_3 : 110 g, then shaking it for 30 min by hand
- c. Pressing the mixed powder to 4000 lbf/in² with a hand press machine
- d. Breaking of the lump into pellets of about 8 cubic mm
- e. Dropping the pellets into the hot crucible one after another
- f. Repeating twice of the process b.~ e. until the total filling amount reaches 414.6 g
- g. Heat treatment of the specimen at 1173 K for 2 days to expel CO_2 completely

Figure 2 (b) shows the melted mixture of Li_2CO_3 and B_2O_3 . This clear and glassy flux is suitable for the LBO crystal growth.

4. Furnace temperature survey for seeding process

This section describes for finding the suitable temperatures for seeding process in case of using single zone and three-zone furnaces.

Generally, when the temperature of flux reaches slightly under its melting point which varies according to the composition, self-nucleation occurs and polycrystalline crystals appear in the lowest temperature part inside the crucible. To suppress the random nucleation in the crystallization process, a small seed crystal is introduced into the flux surface. In this case, supersaturated substances tend to coagulate along the facets of the seed, where the single crystal grows continuously. From our several observations at different temperatures of the single zone furnace, starting temperature of random nucleation with the seed was about 10 K lower than that without the seed crystal. It seems that heat conduction of the flux might be much more dominant than heat convection on account of the high viscosity flux. Rotational mixing by the seed not only reduces thermal gradient around the flux surface but also generates small vibrational waves which can prevent from forming the self-nucleation on the surface. If the flux had moderate viscosity, the temperature difference of 10 K would be smaller.

Figure 3 shows the magnified phase diagram of $\text{Li}_2\text{O} - \text{B}_2\text{O}_3$ system measured by Sastry³. The melting point of the seed is 1107 ± 4 K (834 ± 4 °C) and is 3 K higher than the melting point of the flux composed of 9.4 wt% Li_2O and 90.6 wt% B_2O_3 . Assuming the starting temperature of self-nucleation on the surface without the seed crystal is 1104 K (IT (Indicated Temperature): 905 ± 3 °C), we may use the furnace in the range of 1104 ~ 1094 K (IT: 905 ± 3 ~ 895 ± 3 °C) for TSSG without self-nucleation. Considering a cooling rate of 0.5 K/day and growth period for 14 days, allowable temperature width for the seeding process is about 3 K, 1104 K ~ 1101 K in our single zone furnace. To ensure the crystal growth perfectly, we have to drop the temperature

below 1104 K, and the optimum temperature was found at around 1102 K (IT: 903 °C) for the initial temperature to start cooling.

In a following stage, we measured temperatures inside the platinum crucible installed in a three-zone furnace. Compared to previous single zone furnace, the three-zone furnace has several merits such as one order higher accuracy of temperature control, independent temperature controls and addition of a rotational bottom stage which can be used for ACRT (Accelerated Crucible Rotation Technique) to enhance the transport of ions in the high viscosity flux.

Figure 4 shows the temperature gradient inside the heat furnace at each setting temperature. In the three-zone furnace, we also used a ceramic ring under the crucible to keep higher temperature at the bottom than the flux surface to suppress the spontaneous nucleation at the bottom by taking into account of the results in the single zone furnace. As can be seen from the data given in Fig. 4, independent control of the three-zone furnace temperature could raise the bottom temperature of about 4 K against the surface and keep the suitable temperature gradient at 1 K/cm for LBO crystal growth inside the crucible.

Since temperatures were measured in the absence of a seed crystal, a series of data may deviate from real temperature under the crystal growth. However, these data are essential to find the desirable growth temperature of LBO.

5. Optimization of the seed holder configuration

This section shows several attempts to improve the seed holder configuration which can suppress the formation of poly-crystals inside the grown crystal.

From our previous results, it was possible to grow LBO crystal with TSSG method as shown in Fig. 5. However, we couldn't be satisfied with the results as they were found to be composed of both single crystal and poly-crystals. It is clear that poly-crystals are easily created under fast crystal growth rate. The growth rate strongly depends on the heat dissipation from the seed crystal as well as the cooling rate of the furnace.

To establish the efficient crystallization, the seed is wound by platinum wire at an edge of the seed holder made by ceramic tube which makes effective heat transfer from the seed. However, if the heat dissipation through the holder exceeds a certain extent, it also induces generation of the random nucleation as a result of decreasing temperature around the surface in contact with seed. The degree of heat dissipation extremely depended on the wiring connection of the seed.

In our initial seed holder configuration shown in Fig. 6 (a), the seed crystal was easily melted as the configuration had less heat dissipation. To prevent from melting, higher heat flow was required at seed connection with the holder. Then, we used a platinum tube of 4.5 cm length after the platinum wire to enhance heat flow from the seed between the ceramic tube and the seed crystal as shown in Fig. 6 (b). We also added a platinum foil, covering the top of seed for protection of chemical attack by the flux vapor. With a set of modifications, we could grow a LBO crystal as shown in Fig. 5.

In the next stage, we tried the growth in the condition without the platinum foil cover with a short platinum tube of 1.5 cm length as shown in Fig. 6 (c). This attempt didn't affect to decrease the growth rate significantly. Finally, we returned

again to the first simple configuration of the seed holder, shown in Fig. 6 (d). The final configuration which is slightly different from that in Fig. 6 (a) employed four twisted platinum wires for the seed connection. In spite of the small change, this configuration could reduce the heat flow down to about 1/3 in the configuration of Fig. 6 (c). With this improvement, we tried to grow LBO crystals in the three-zone furnace.

6. Crystal growth

6.1. Crystal growth of LBO

This section describes the LBO crystal growth with $\text{Li}_2\text{B}_4\text{O}_7$ and B_2O_3 by using the three-zone furnace. From previous works, we settled the temperature gradient inside the platinum crucible by adjusting three vertically independent temperatures of the furnace and improved the seed holder configuration to realize the suitable condition for LBO crystal growth.

The premixed powder was composed of $\text{Li}_2\text{B}_4\text{O}_7$: 177 g and B_2O_3 : 146 g, which was equivalent to Li_2O : 9.7 wt% and B_2O_3 : 90.3 wt% in the binary system by Sastry³. The purity of both powder (Johnson Matthey Company) was over 99.9%. In this experiment, we didn't use HFT for the flux preparation since the powder doesn't generate inconvenient gases by heating. After shaking by hand for 15 min, the premixed powder was heated by the following process.

- a. Increasing the furnace temperature up to 1233 K (indicated temperature at the middle part of the furnace), about 45 K higher than the melting point of $\text{Li}_2\text{B}_4\text{O}_7$, and keeping it for 5 hours
- b. Decreasing the furnace temperature to 1137 K
- c. Mixing the flux for 24 hours using a platinum paddle at 1137 K

- d. Keeping the flux for another 24 hours at 1137 K after the paddle was fully extracted from the flux.

After finishing the flux preparation, we made pre-heating of the seed. In the seeding process, we also have to take caution about thermal fracture of the seed by heat shock as well as thermal expansion of the holder due to the large expansion coefficient of 1% at temperature difference of 1000 K. Ignoring the thermal expansion resulted in lowering of the seed contacting position from the initial setting point and in quick melting the seed. Therefore, the seed holder with a seed of 4 x 5 x 7 mm selected from our previously grown crystals was rotated at 15 rpm for 1 hour at the edge of upper part of the furnace. Then, the furnace temperature was suddenly dropped from 1137 K to 1107 K (melting point of the composition) at a rate of 1.5 K/min, maximum speed in this furnace. The holder was translated downwards to the top of crucible simultaneously with the temperature decrease according to the procedure shown in Fig. 7. After the furnace temperature reached at 1107 K, the seed was dipped for 1.8 mm into the flux surface, and kept for 1.5 hours at the same temperature to get a clean surface by dissolving the outer layer of the seed. The elimination of some imperfections developed in the outer layer is essential for the single crystal growth. Then, the furnace temperature was quickly dropped by 3 K to secure to prevent from melting the seed. At the furnace temperature where the flux is slightly supersaturated before occurring the nucleation, the seed was kept for 24 hours to reach thermo-equilibrium in the growth area on the surface. In the operation of three-zone furnace, we also used ACRT to enhance the heat convection for mixing the flux during the crystal growth.

Figure 8 shows the heat schedule of this trial. When we observed inside the crucible after 24 hours from the starting point of cooling, several self-nucleated crystals

were floating on the surface. It means the temperature at the growing part was too low the single crystal to grow. Therefore, we heated the furnace temperature again by each 1 K step until the floating crystals disappeared. They were extinguished at 1110 K, 3 K higher than the melting point of its composition. It seems that the surface temperature was lowered by the heat dissipation through the holder after the seed was dipped. We kept the furnace temperature at 1110 K for 1.5 hours, then dropped to 1108 K and kept for 24 hours. After reaching the thermo-equilibrium once again, we resumed the crystal growth by cooling the furnace of 0.007 K/h that was calculated from the real elapsed time and temperature drop in case of using the minimum controllable rate of 0.01 K/h. After the growth period for 10 days, the crystal was fully extracted from the flux and cooled down to room temperature during 44 hours.

Figure 9 shows a grown crystal of LBO. The weight of the crystal was 2.8 g. In this trial, we didn't pull up the crystal during the growth period, therefore the crystal was grown inside the flux. From the crystal size, we estimated the growth rate of the crystal; 0.03 mm/h along the seed direction, 0.09 mm/h and 0.05 mm/h in radial directions, respectively. As the fastest growth axis shows the direction of $\langle 001 \rangle$, we supposed the seed orientation was $\langle 110 \rangle$. Furthermore, the seed orientation was also confirmed by crystal habit shown in Markgraf's paper⁶.

6.2. Crystal growth of Li^{10}BO

This section describes the L^{10}BO crystal growth using $^{10}\text{B}_2\text{O}_3$ and Li_2CO_3 in three-zone furnace. The growth materials were prepared in $\text{Li}_2\text{O} : 9.7 \text{ wt}\%$ and $^{10}\text{B}_2\text{O}_3 : 90.3 \text{ wt}\%$ by mixing with $\text{Li}_2\text{CO}_3 : 51.72 \text{ g}$ and $^{10}\text{B}_2\text{O}_3 : 194.93 \text{ g}$. The purity of Li_2CO_3 (Aran Isles Chemical Inc.) and of $^{10}\text{B}_2\text{O}_3$ (ISOTEC Inc.) were over 99.99% and over 99.98%, respectively. The enrichment of the ^{10}B was 99.61 atm% in $^{10}\text{B}_2\text{O}_3$. After preparing the flux by HFT, the crucible was charged by 70% of its capacity. The melted flux was stirred by a platinum paddle to get rid of CO_2 gas for 100 hours at 1173 K. Successively, the flux was kept for 24 hours at the same temperature after the paddle was extracted.

We made 4 trials of L^{10}BO crystal growth with this flux. Unfortunately, successive second and third trials were failed as the melting point of the flux had been lowered by a small change of the composition after first grown crystal was extracted. From the difference of seed contacting temperatures at the first and fourth trials in Table 1, it is assumed that the composition was shifted to the boron oxide rich direction of $\text{Li}_2\text{O} : ^{10}\text{B}_2\text{O}_3 = 9.34 \text{ wt}\% : 90.66 \text{ wt}\%$, which lowered the melting point of 4 K in the phase diagram, shown in Fig. 1.

Growth conditions and the heat schedules in the first and fourth trials were summarised in Table 2 and Fig. 10 (a), (b), respectively. In the first trial, the reset of furnace temperature shown in Fig. 10 (a) was caused from the random self-nucleation on the surface after 8 days elapsed from the start cooling. To reduce the co-produced crystals, the furnace temperature was raised again and the crystal growth was resumed with the same cooling rate although the grown crystal from the seed might be attacked by melt back. The result in Fig. 11 (a) shows that the heat treatment wasn't appropriate

procedure to suppress the formation of the self-nucleated crystals. The grown crystal had two parts, clear and opaque parts composed of single crystal and poly-crystals. The polycrystalline part might be appeared after resuming the growth. Therefore, we didn't change the furnace temperature even if the self-nucleation was also happened in the fourth trial. After the growth period in both trials, the crystals were fully extracted from the solution and cooled down to room temperature for 50 hours using three different cooling rates to avoid cracks inside the crystal by thermal stress.

The grown crystal in the fourth trial is shown in Figure 11 (b). Size and weight of the crystal were 13 x 13 x 8 mm and 3.6 g. Compared with the first trial, the weight in fourth trial was 5 times lighter on account of shorter growth period. Although transparent part was wider than previous result in Figure 11 (a), center part of the crystal had opaque and included poly-crystals. The polycrystalline part introduced cracks inside the crystal as the heat expansion between poly-crystal and single one is quite different. To get high quality crystal, we may have to use better flux with no evolution of CO₂. In the next trial, longer heat treatment period or heating procedure under atmospheric pressure will be required for the preparation of the suitable flux for L¹⁰BO crystal.

7. Summary

We made several attempts to achieve the $L^{10}BO$ crystal growth. Before the crystal growth, first of all, we improved on the previous HFT by focusing on the concretion of pre-mixed materials into pellets. Our HFT was a promising procedure for the flux to grow $L^{10}BO$. Secondary, we searched to settle the adequate thermal gradient inside the crucible by using ceramic ring and finding the appropriate vertical temperature combination in the three-zone heat furnace. As the result, we could raise the bottom temperature of about 4 K against the surface and adjust the temperature gradient of 1 K/cm inside the crucible.

The seeding process was the most difficult in the crystal growth. We tried the process over forty times with single and three-zone furnaces to get the best condition for the suitable heat dissipation by modifying the seed holder configuration in different furnace temperatures. The best configuration of the holder is shown in Fig. 6 (d).

The grown $L^{10}BO$ crystals had cracks caused by thermal stress which depends on two different phases of polycrystalline and single crystals. To grow higher quality $L^{10}BO$, another treatment in the flux preparation will be required, for example, a heating procedure under atmospheric pressure. Furthermore, we will also adjust the rotational rate of the seed crystal to reduce the random nucleation on the flux surface.

References

- 1 C. Chen, Y. Wu, A. Jiang, B. Wu, G. You, R. Li, and S. Lin, "New nonlinear-optical crystal: LiB_3O_5 ," *J. Opt. Soc. Am. B*, vol.6, No.4, 616 (1989)
- 2 P. Thomas, "Inorganic nonlinear materials," *Physics World*, March, 34 (1990)
- 3 B. S. R. Sastry, and F. A. Hummel, "Studies in lithium oxide systems: V, $\text{Li}_2\text{O} \cdot \text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$," *J. Amer. Ceramic Soc.*, vol.42, No.5, 216 (1959)
- 4 Z. Shuqing, H. Chaoen, and Z. Hongwu, "Crystal growth and properties of lithium triborate," *J. Crystal Growth*, 99, 805 (1990)
- 5 X. B. Hu, S. S. Jiang, X. R. Huang, W. Zeng, W. J. Liu, C. T. Chen, Q. I. Zhao, J. H. Jiang, Z. G. Wang, Y. L. Tian, and Y. Han, "The formation mechanisms of dislocations and negative crystals in LiB_3O_5 single crystals," *J. Crystal Growth*, 163, 266 (1996)
- 6 S. A. Markgraf, Y. Furukawa, and M. Sato, "Top-seeded solution growth of LiB_3O_5 ," *J. Crystal Growth*, 140, 343 (1994)
- 7 H. Hong, W. Zhong, Z. Lu, T. Zhao, and S. Hua, "Growth and habit of lithium triborate crystal by flux pulling method," *SPIE*, vol. 1863, 184 (1993)
- 8 R. Kruh and K. H. Stern, *J. Am. Chem. Soc.*, 78, 278 (1956)
- 9 X. Qi, "Growth and optical characterization of novel crystals for applications in laser and non-linear optics," Ph. Doctoral Thesis, University of Strathclyde (1996)

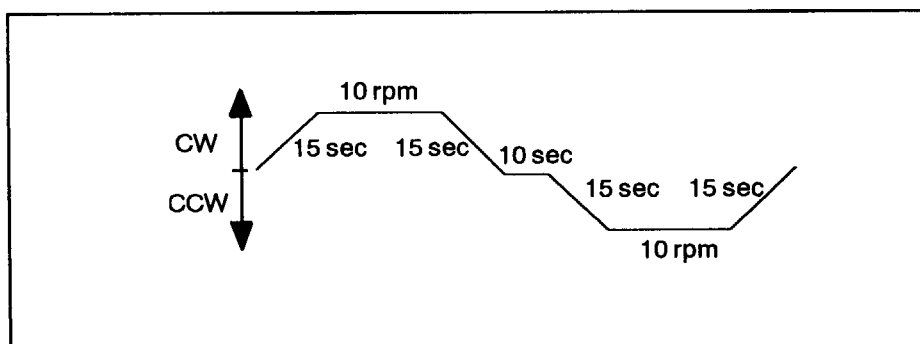
Table 1 Furnace temperature conditions for the seeding process in L¹⁰BO growth.

Trial	Dipped (K)	Start cooling (K)	Results
1st	1110	1106	grown
2nd	1108	1106	seed was melted
3rd	1107	1104	seed was melted
4th	1106	1102	grown

Table 2 $L^{10}BO$ growth conditions for the first and fourth trials (see text).

Parameters	Conditions	
Composition	$Li_2O : B_2O_3 = 9.7w\% : 90.3w\%$ ($Li_2CO_3 : ^{10}B_2O_3 = 51.72 g : 194.93 g$)	
Seed crystal size	1st: 4 x 4 x 6 mm	4th: 3 x 3 x 8 mm
Seed crystal orientation	<001>	
Seed crystal rotation	15 rpm	
Pulling rate	1st: 0.75 mm / day	---
ACRT*	10 rpm Period: 99 / Duration: 80 AMP: 3.5 / Slope:Max.	
Platinum crucible	60mm ϕ x 60 mmH / 436.7 g	
Seed contact	1st: 1110 K (Indicated temp.: 833°C)	4th: 1106 K (Indicated temp.: 829°C)
Start cooling	1st: 1106 K (Indicated temp.: 829°C)	4th: 1102 K (Indicated temp.: 825°C)
Cooling rate	0.007 K/h (pre-setting rate: 0.01 K/h)	
Growth period	1st: 30 days	4th: 7 days
Crystal weight	1st: 16.5g	4th: 3.6g
Crystal size	1st: 14x 25 x 22 mm	4th: 13 x 10 x 12 mm

ACRT* motion



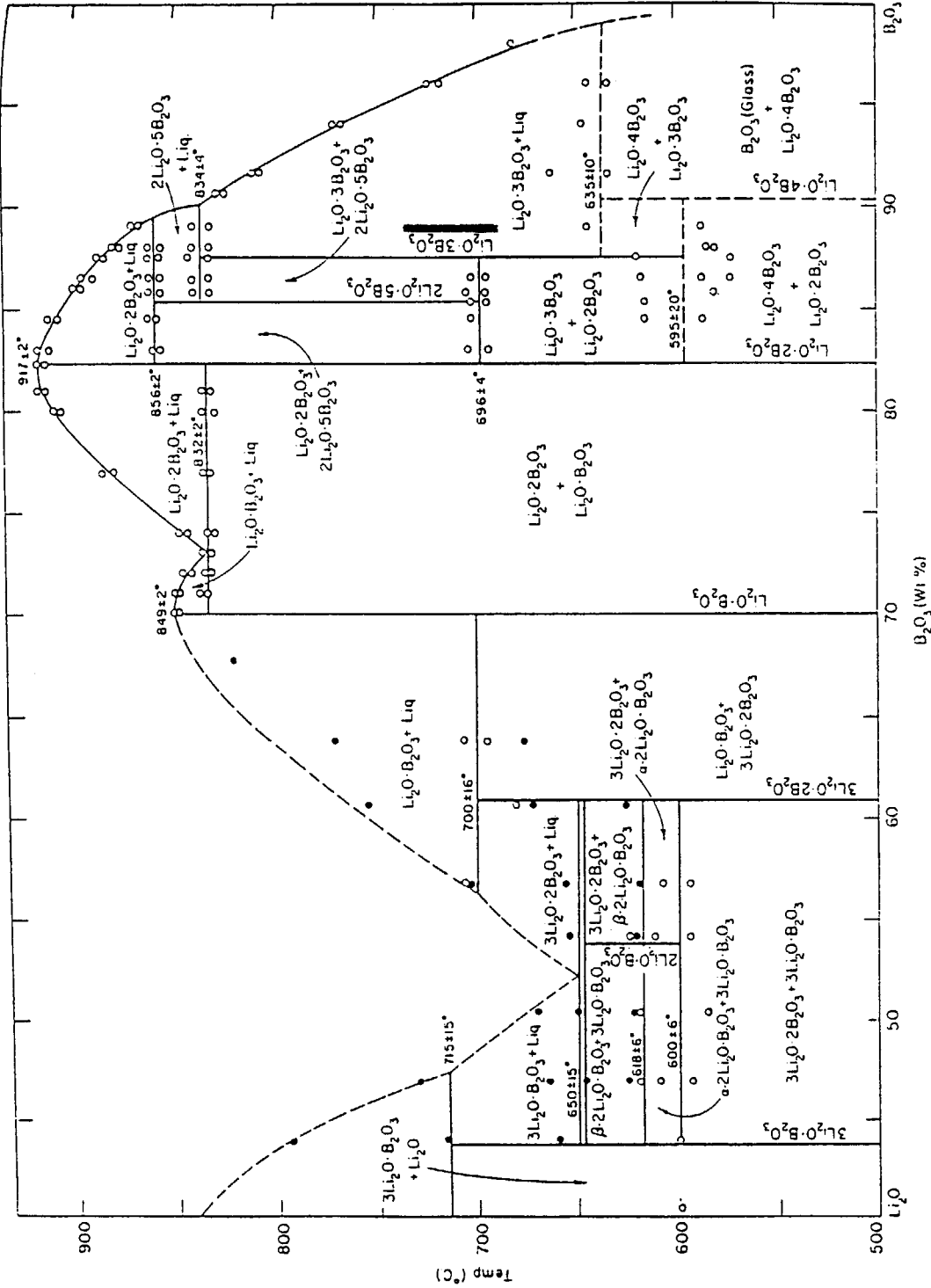
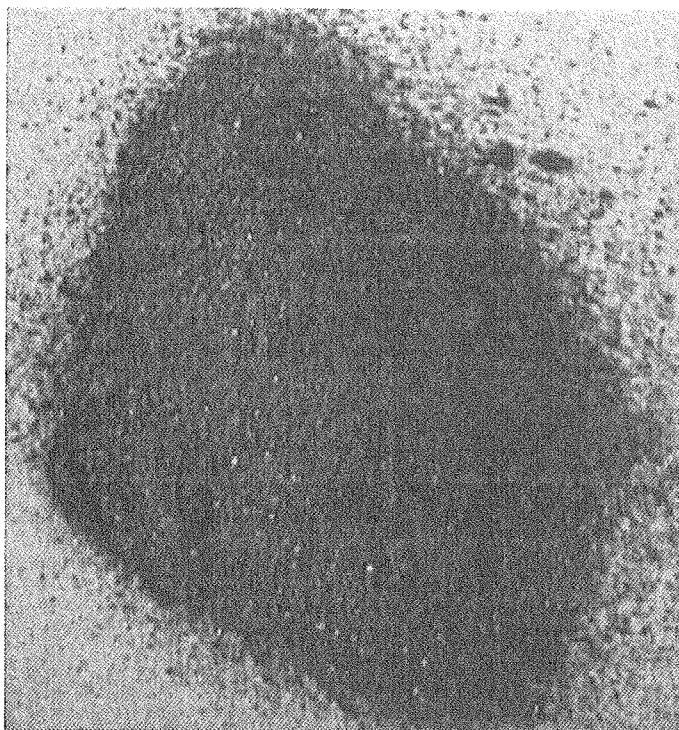
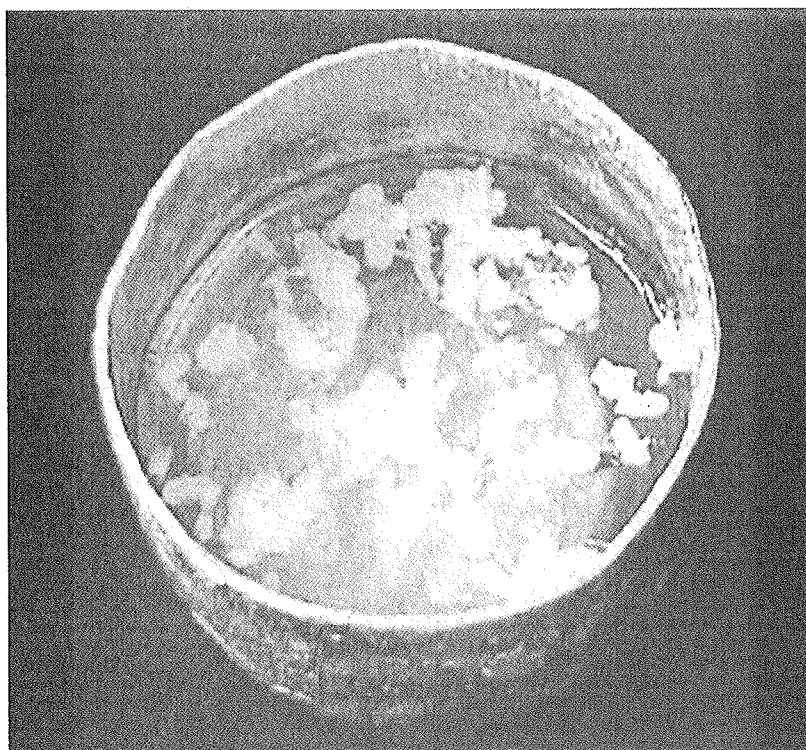


Figure 1 Phase diagram of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system.

Under lined $\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ means LBO.



(a)



(b)

Figure 2 Results of the heat treatment of raw materials.

(a); individual heat treatment of Li_2CO_3 in case C (see text).

(b); the flux by using HFT.

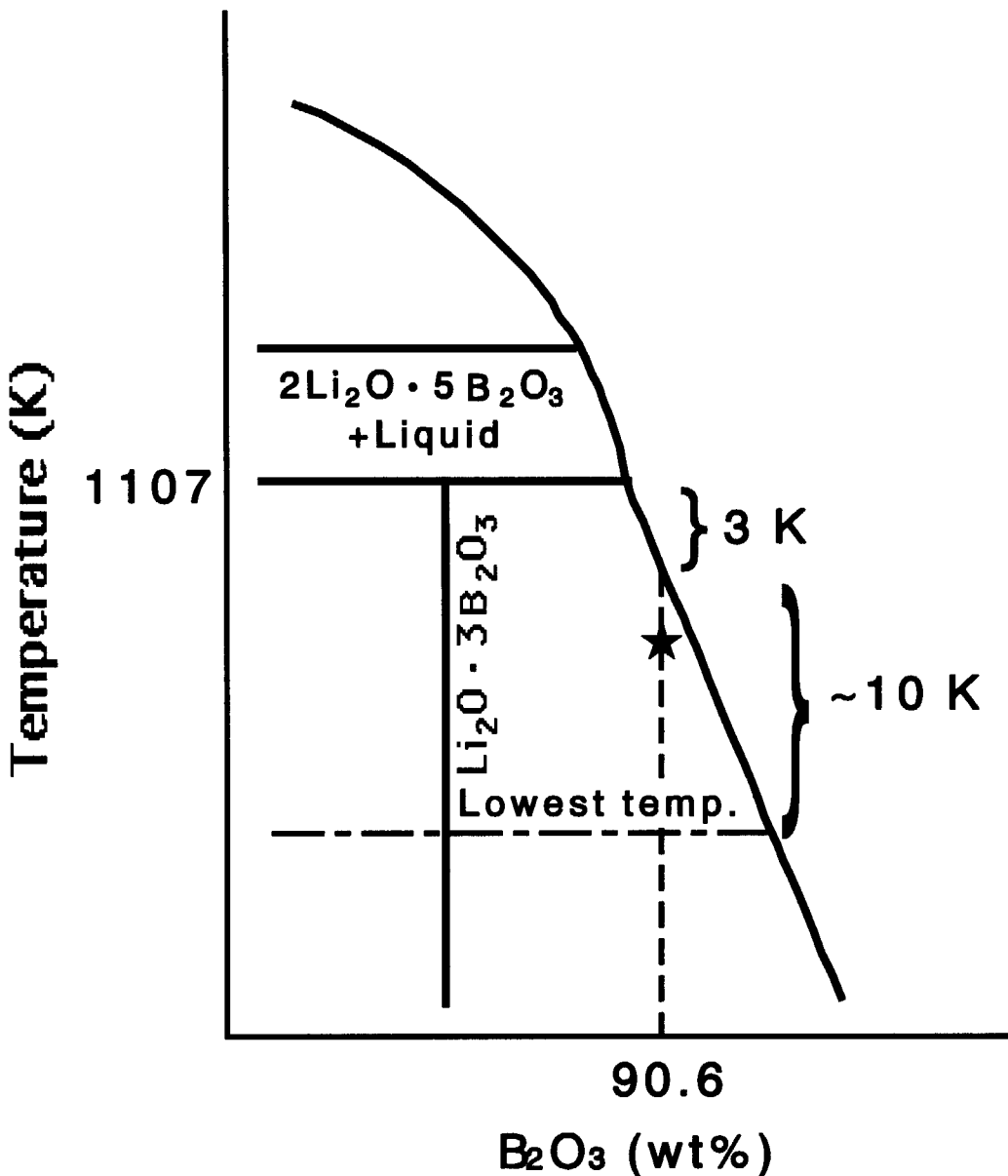
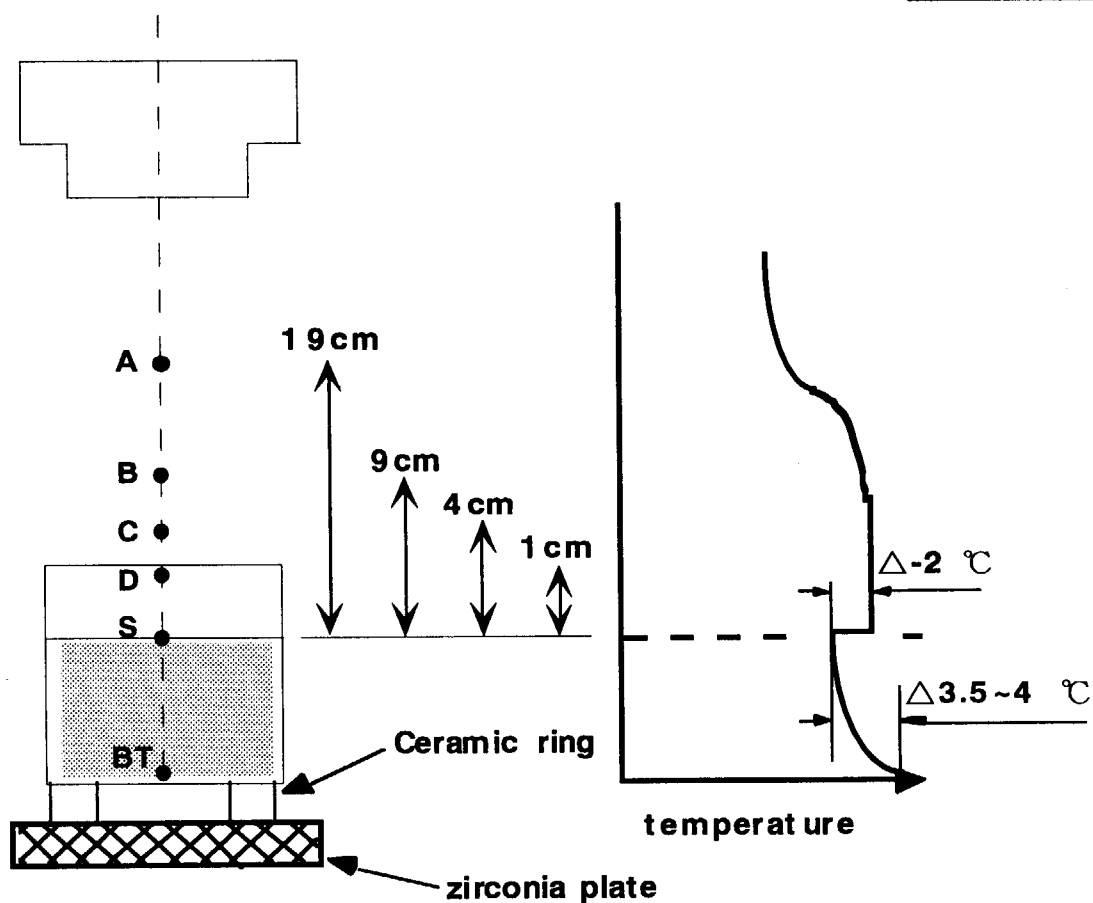


Figure 3 Magnified phase diagram for LBO crystal growth.
 Asterisk shows admirable furnace temperature for the seeding process.

3-zone furnace



Measured Points	Indicated temperatures (1)/(2)/(3) °C			
	835.5/859.8/895.3	805.5/830.0/865.7	801.2/826.0/861.7	795.6/820.1/855.8
A	826.5	796.0	792.5	785.0
B	862.0	830.0	826.0	820.0
C	868.0	836.5	833.0	825.5
D	868.0	836.5	833.0	825.5
S	866.0	834.0	830.5	824.5
BT	870.0	838.0	836	831

Figure 4 Temperature gradient in the three-zone furnace.

(1)/(2)/(3) of indicated temperatures show upper, middle and lower part of the temperature controllers composed of vertical three-zone furnace. Accuracy of measured temperature was $\pm 2^{\circ}\text{C}$.

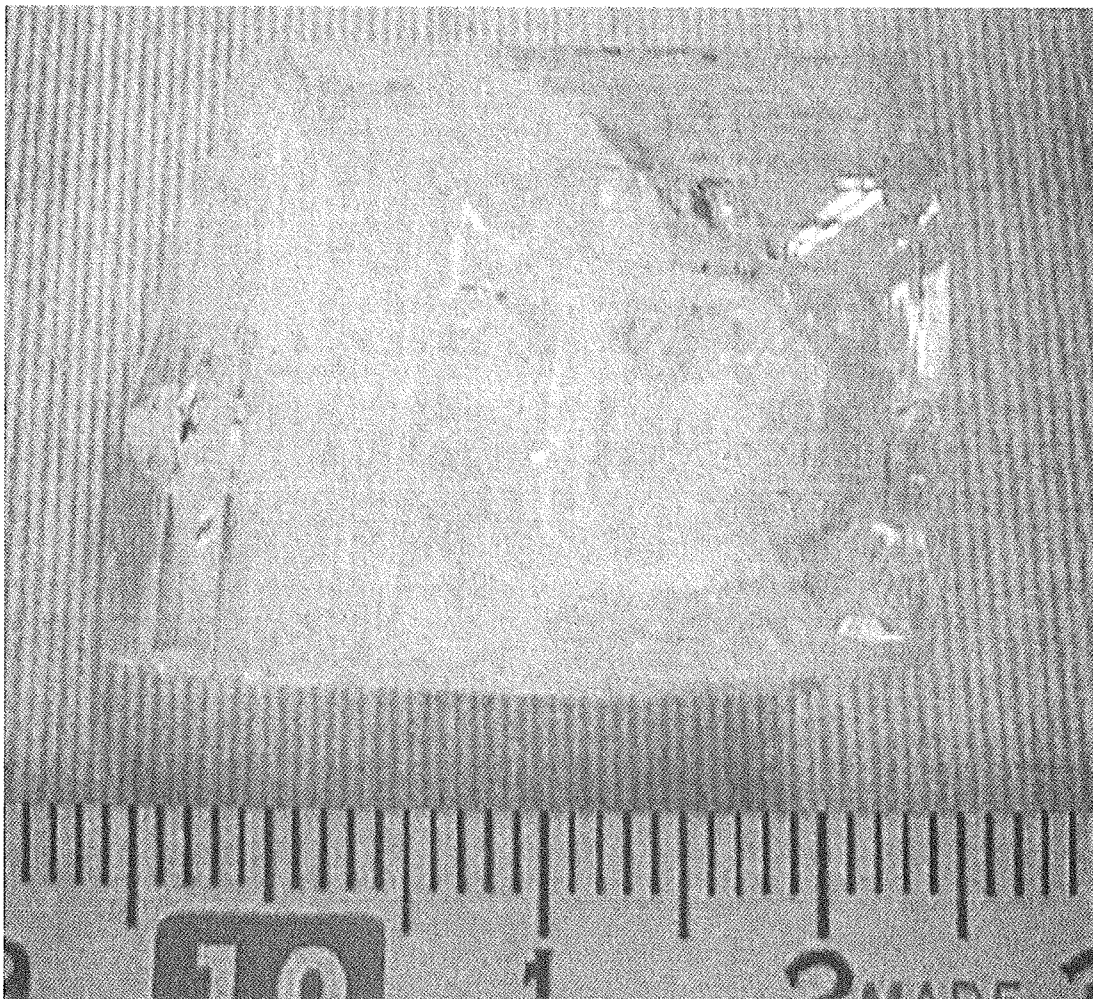


Figure 5 Photo of grown LBO in the early trial.

From the typical morphology of parallelogram shape, it is supposed that this crystal was grown from the seed with $\langle 001 \rangle$ orientation.

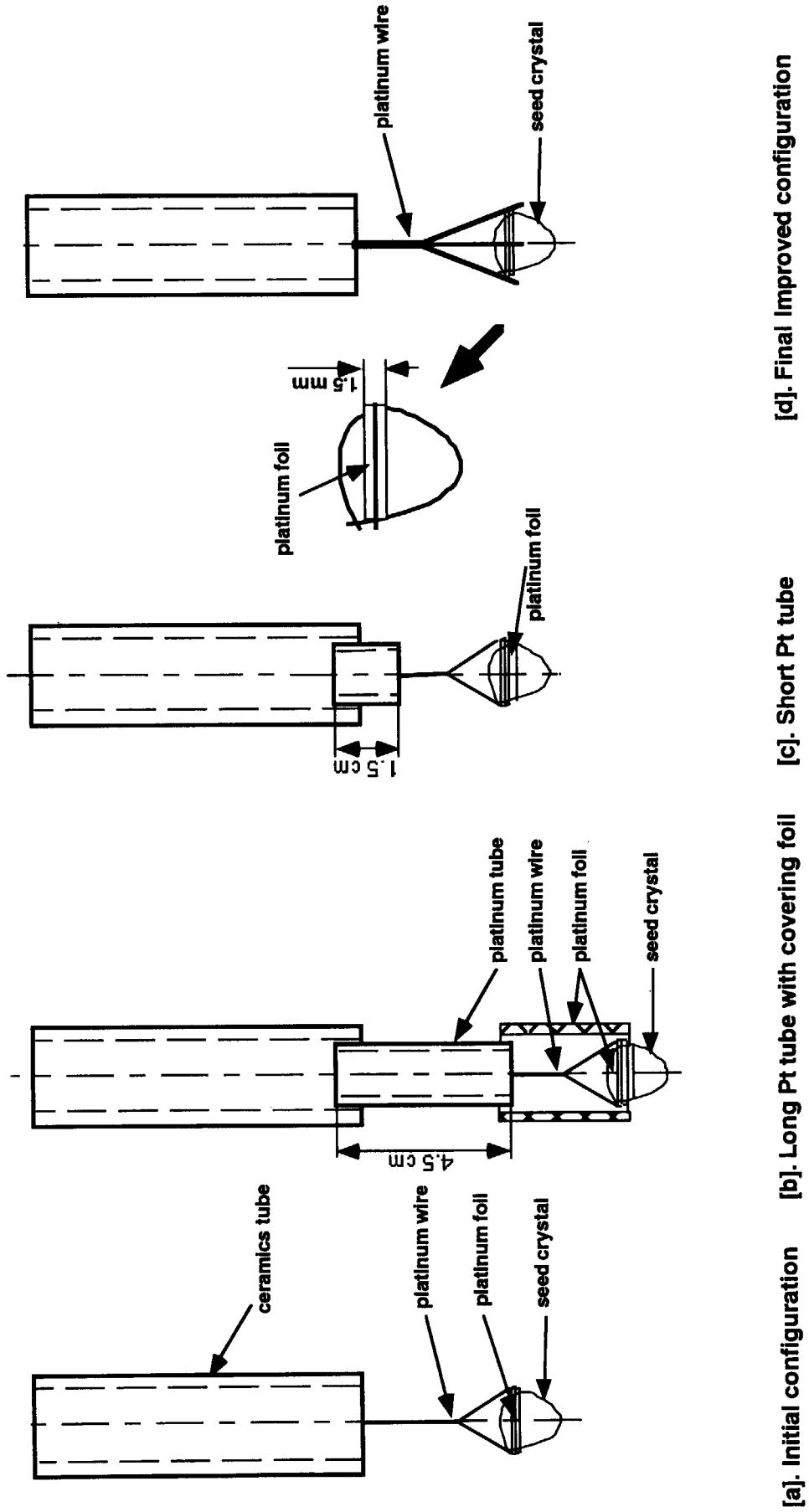
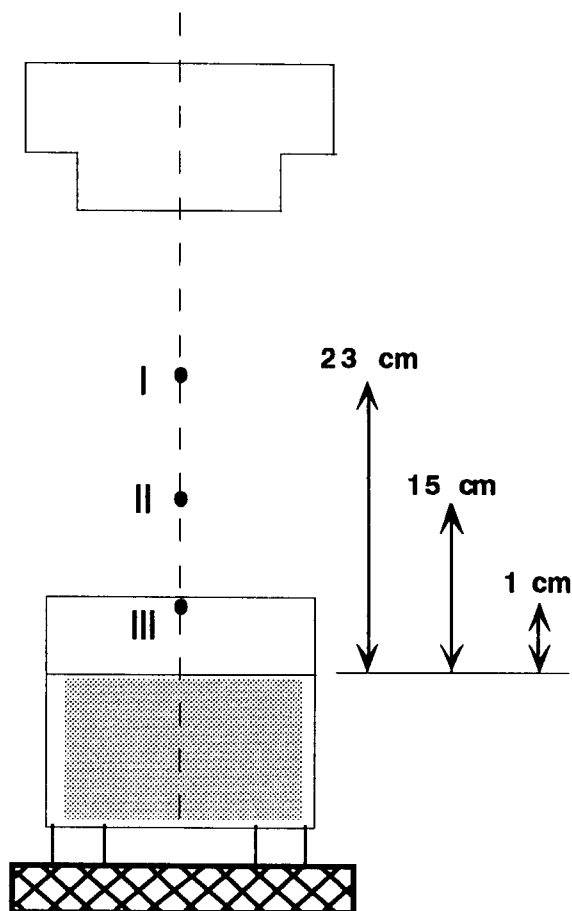


Figure 6 Optimization for the seed holder configuration.

3-zone furnace

Positions	Indicated temp. of No.(2) (°C)	Expected temp. at each position (K)	Holding time (min)
I	860	---	10
II	840	1097	4
III	835	1114	4

Figure 7 Procedure of pre-heat treatment for the seed crystal.

The seed was located downwards to the crucible at each point with different holding times.

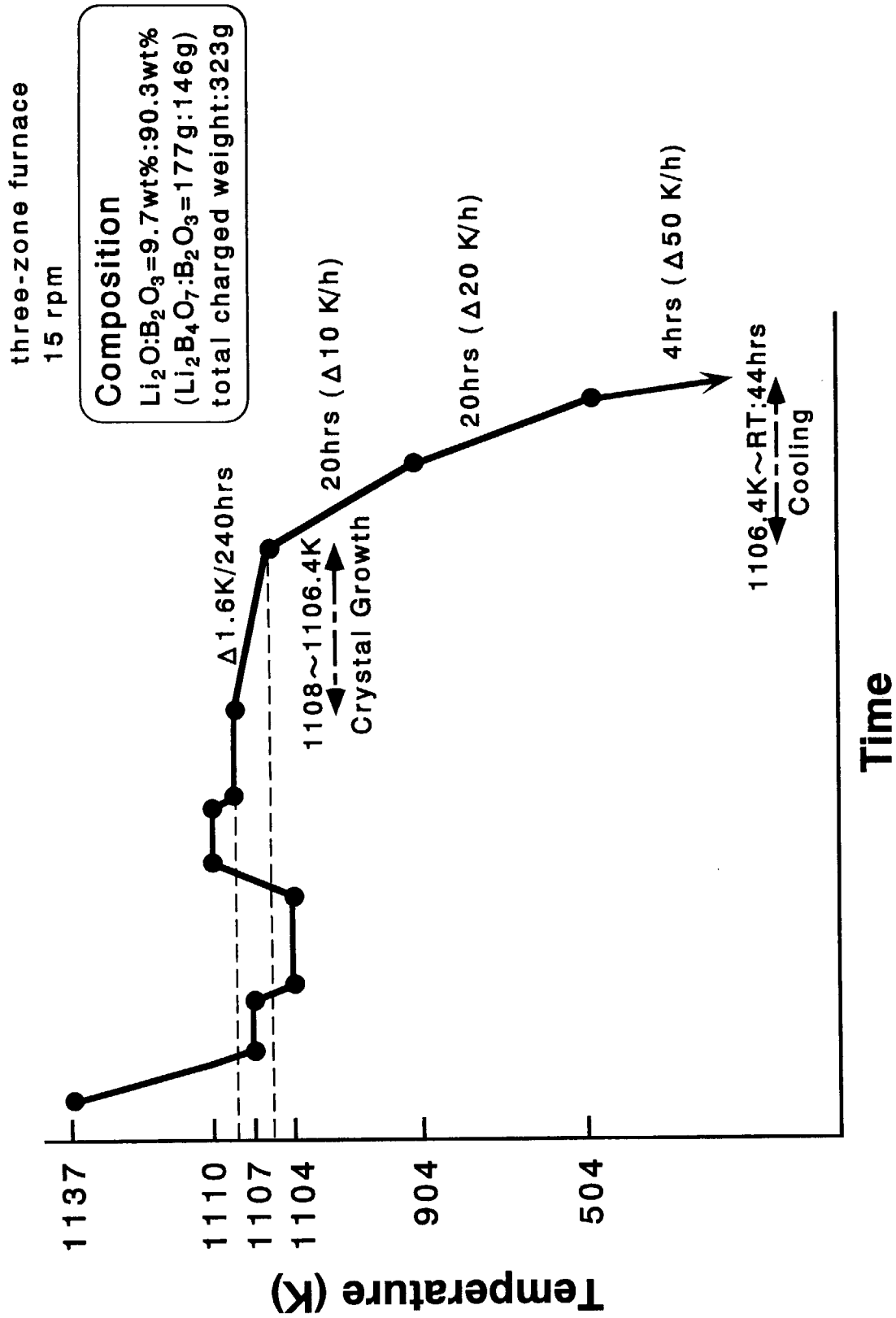


Figure 8 Heat schedule of LBO crystal growth with $\text{Li}_2\text{B}_4\text{O}_7$ and B_2O_3 powder.

Vertical axis shows the estimated surface temperatures of the flux deduced from data in Fig. 4.

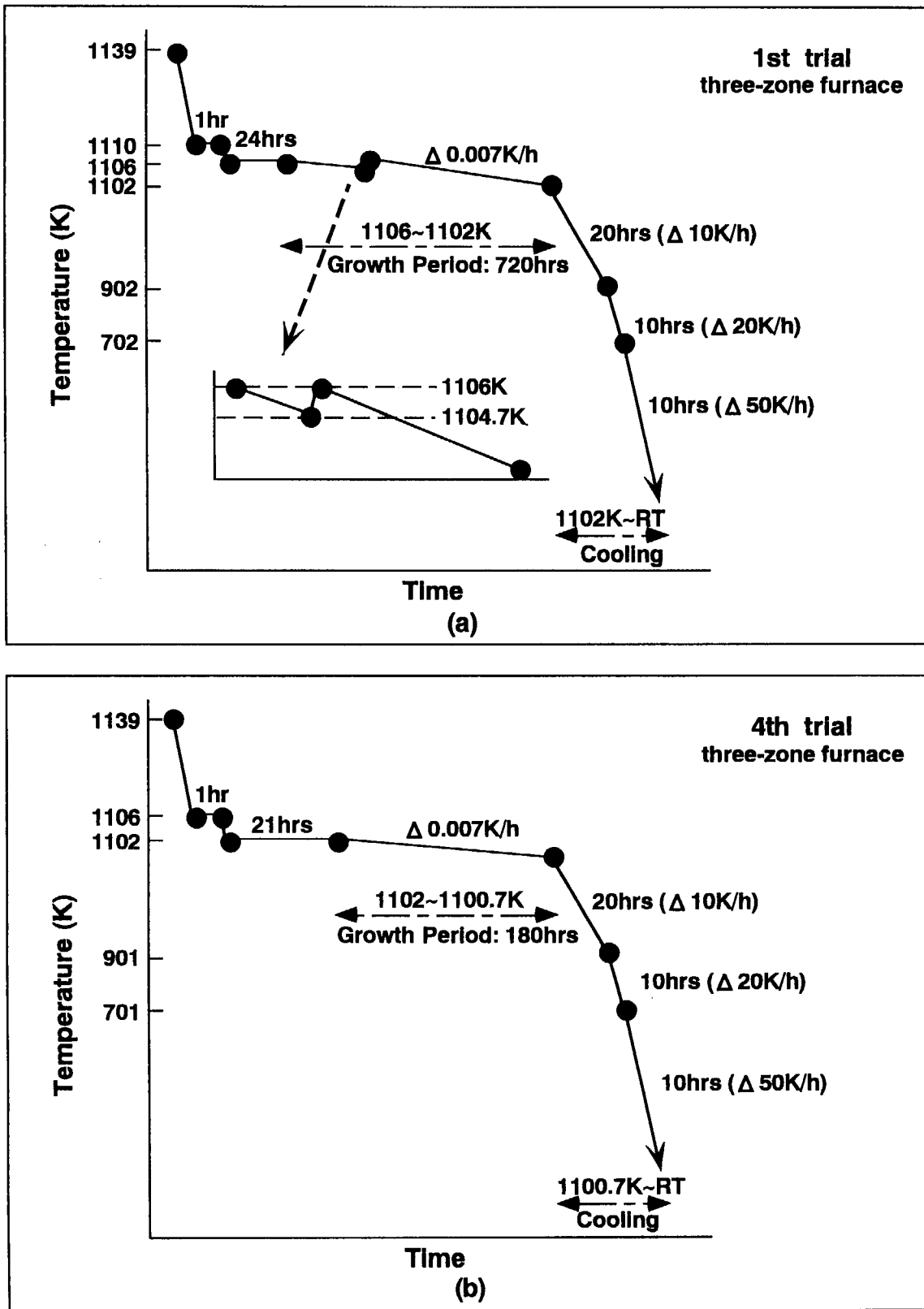


Figure 10 Heat schedule of $L^{10}\text{BO}$ crystal growth with boron10 enriched oxide.

(a) and (b) show first and fourth trials, respectively.

Vertical temperatures deduced from data in Fig. 4 shows the estimated flux surface temperatures.

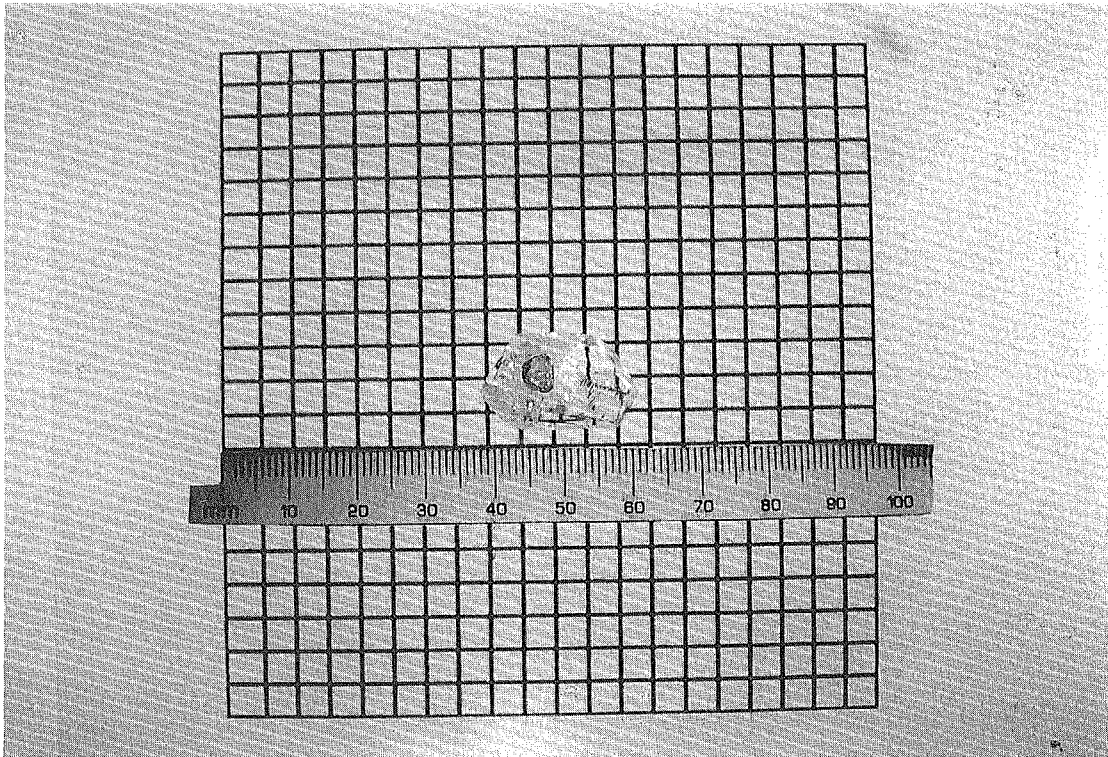
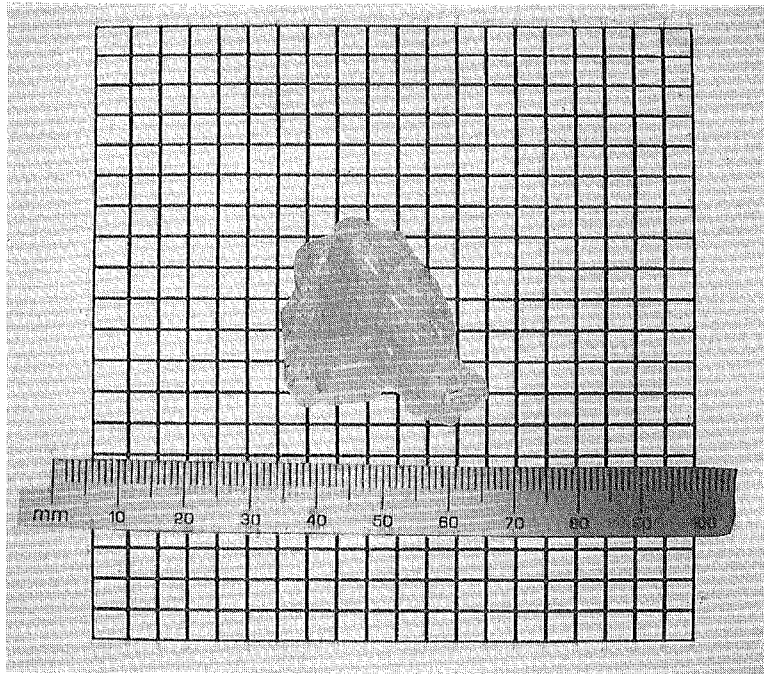
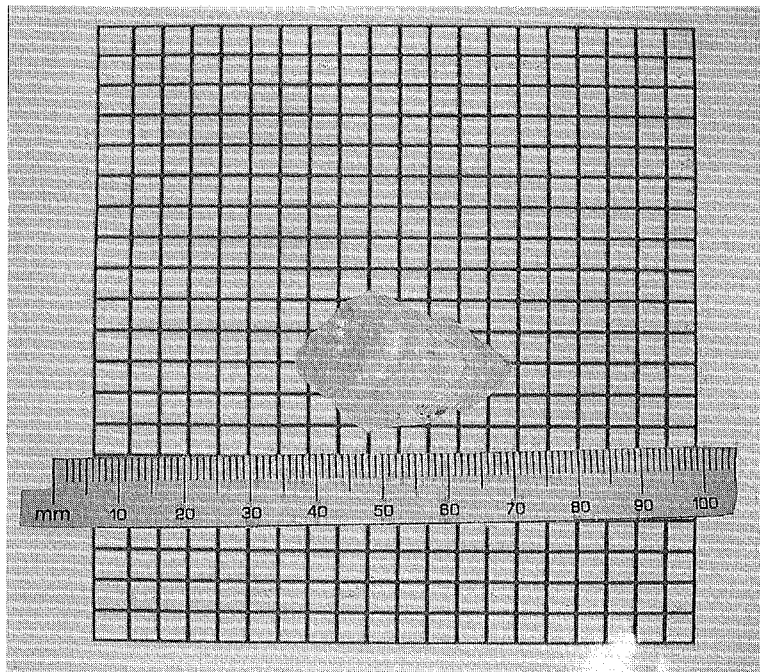


Figure 9 Photo of grown LBO using tetraborate and normal boron oxide powder. Parallel direction to the ruler shows $\langle 001 \rangle$ orientation which is the fastest growth axis. The crystal had flat bottom face.



(a)



(b)

Figure 11 Photo of grown $L^{10}BO$.

(a); first trial and (b); fourth trial, respectively (see text).

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国際単位系 (SI) と換算表

表1 SI基本単位および補助単位

量	名称	記号
長さ	メートル	m
質量	キログラム	kg
時間	秒	s
電流	アンペア	A
熱力学温度	ケルビン	K
物質量	モル	mol
光度	カンデラ	cd
平面角	ラジアン	rad
立体角	ステラジアン	sr

表3 固有の名称をもつSI組立単位

量	名称	記号	他のSI単位による表現
周波数	ヘルツ	Hz	s ⁻¹
力	ニュートン	N	m·kg/s ²
圧力, 応力	パスカル	Pa	N/m ²
エネルギー, 仕事, 熱量	ジュール	J	N·m
工率, 放射束	ワット	W	J/s
電気量, 電荷	クーロン	C	A·s
電位, 電圧, 起電力	ボルト	V	W/A
静電容量	ファラド	F	C/V
電気抵抗	オーム	Ω	V/A
コンダクタンス	ジーメンス	S	A/V
磁束	ウェーバ	Wb	V·s
磁束密度	テスラ	T	Wb/m ²
インダクタンス	ヘンリー	H	Wb/A
セルシウス温度	セルシウス度	°C	
光束度	ルーメン	lm	cd·sr
照射度	ルクス	lx	lm/m ²
放射能	ベクレル	Bq	s ⁻¹
吸収線量	グレイ	Gy	J/kg
線量当量	シーベルト	Sv	J/kg

表2 SIと併用される単位

名称	記号
分, 時, 日	min, h, d
度, 分, 秒	°, ', "
リットル	l, L
トン	t
電子ボルト	eV
原子質量単位	u

1 eV = 1.60218 × 10⁻¹⁹ J
1 u = 1.66054 × 10⁻²⁷ kg

表4 SIと共に暫定的に維持される単位

名称	記号
オングストローム	Å
バ	b
バール	bar
ガリ	Gal
キュリー	Ci
レントゲン	R
ラド	rad
レム	rem

1 Å = 0.1 nm = 10⁻¹⁰ m
1 b = 100 fm² = 10⁻²⁸ m²
1 bar = 0.1 MPa = 10⁵ Pa
1 Gal = 1 cm/s² = 10⁻² m/s²
1 Ci = 3.7 × 10¹⁰ Bq
1 R = 2.58 × 10⁻⁴ C/kg
1 rad = 1 cGy = 10⁻² Gy
1 rem = 1 cSv = 10⁻² Sv

表5 SI接頭語

倍数	接頭語	記号
10 ¹⁸	エクサ	E
10 ¹⁵	ペタ	P
10 ¹²	テラ	T
10 ⁹	ギガ	G
10 ⁶	メガ	M
10 ³	キロ	k
10 ²	ヘクト	h
10 ¹	デカ	da
10 ⁻¹	デシ	d
10 ⁻²	センチ	c
10 ⁻³	ミリ	m
10 ⁻⁶	マイクロ	μ
10 ⁻⁹	ナノ	n
10 ⁻¹²	ピコ	p
10 ⁻¹⁵	フェムト	f
10 ⁻¹⁸	アト	a

(注)

- 表1-5は「国際単位系」第5版、国際度量衡局1985年刊行による。ただし、1 eV および 1 u の値は CODATA の1986年推奨値によった。
- 表4には海里、ノット、アール、ヘクタールも含まれているが日常の単位なのでここでは省略した。
- bar は、JISでは流体の圧力を表わず場合に限り表2のカテゴリーに分類されている。
- EC閣僚理事会指令では bar, barn および「血圧の単位」mmHg を表2のカテゴリーに入れている。

換算表

力	N (=10 ⁵ dyn)	kgf	lbf
	1	0.101972	0.224809
	9.80665	1	2.20462
	4.44822	0.453592	1

粘度 1 Pa·s (N·s/m²) = 10 P (ポアズ) (g/(cm·s))

動粘度 1 m²/s = 10⁴ St (ストークス) (cm²/s)

圧	MPa (=10 bar)	kgf/cm ²	atm	mmHg (Torr)	lbf/in ² (psi)
	1	10.1972	9.86923	7.50062 × 10 ³	145.038
力	0.0980665	1	0.967841	735.559	14.2233
	0.101325	1.03323	1	760	14.6959
	1.33322 × 10 ⁻⁴	1.35951 × 10 ⁻³	1.31579 × 10 ⁻³	1	1.93368 × 10 ⁻²
	6.89476 × 10 ⁻³	7.03070 × 10 ⁻²	6.80460 × 10 ⁻²	51.7149	1

エネルギー・仕事・熱量	J (=10 ⁷ erg)	kgf·m	kW·h	cal (計量法)	Btu	ft·lbf	eV
	1	0.101972	2.77778 × 10 ⁻⁷	0.238889	9.47813 × 10 ⁻⁴	0.737562	6.24150 × 10 ¹⁸
	9.80665	1	2.72407 × 10 ⁻⁶	2.34270	9.29487 × 10 ⁻³	7.23301	6.12082 × 10 ¹⁹
	3.6 × 10 ⁶	3.67098 × 10 ⁵	1	8.59999 × 10 ⁵	3412.13	2.65522 × 10 ⁶	2.24694 × 10 ²⁵
	4.18605	0.426858	1.16279 × 10 ⁻⁶	1	3.96759 × 10 ⁻³	3.08747	2.61272 × 10 ¹⁹
	1055.06	107.586	2.93072 × 10 ⁻⁴	252.042	1	778.172	6.58515 × 10 ²¹
	1.35582	0.138255	3.76616 × 10 ⁻⁷	0.323890	1.28506 × 10 ⁻³	1	8.46233 × 10 ¹⁸
	1.60218 × 10 ⁻¹⁹	1.63377 × 10 ⁻²⁰	4.45050 × 10 ⁻²⁶	3.82743 × 10 ⁻²⁰	1.51857 × 10 ⁻²²	1.18171 × 10 ⁻¹⁹	1

1 cal = 4.18605 J (計量法)
= 4.184 J (熱化学)
= 4.1855 J (15 °C)
= 4.1868 J (国際蒸気表)
仕事率 1 PS (仏馬力)
= 75 kgf·m/s
= 735.499 W

放射能	Bq	Ci
	1	2.70270 × 10 ⁻¹¹
	3.7 × 10 ¹⁰	1

吸収線量	Gy	rad
	1	100
	0.01	1

照射線量	C/kg	R
	1	3876
	2.58 × 10 ⁻⁴	1

線量当量	Sv	rem
	1	100
	0.01	1

