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# Growth and optical properties of $MgO:Li_2B_4O_7$ single crystals from the melt including MgO

Yusuke Shiro, Ryuichi Komatsu, Ko Ikeda and Shigeru Fujino*
Graduate School of Science and Engineering, Yamaguchi University
2-16-1 Tokiwadai, Ube, Yamaguchi, 755-8611, Japan
(Fax: 81-0836-85-9601, e-mail: c036fg@yamaguchi-u.ac.jp)
*Interdisciplinary Graduate School of Science and Engineering, Kyusyu University
Fax: 092-583-7529, e-mail: fujino@asem.kyushu-u.ac.jp

There has been currently much interest in borate crystal for the development of all solid-state ultra violet (UV) laser systems. $Li_2B_4O_7$ crystal is one of promising nonlinear optical crystals in UV region. Recently, it has been reported that effective nonlinear coefficient of $Li_2B_4O_7$ crystal including MgO (1mol%) is larger than that of pure $Li_2B_4O_7$ crystal. In this paper, we describe growth and characterization of $Li_2B_4O_7$ crystals from the melt including MgO. In addition, effect of dry air flow during growth is also investigated to grow scatters-free $Li_2B_4O_7$ crystals.
Key words: $Li_2B_4O_7$, CZ method, MgO dope, scatters, dry air gas

## 1. Introduction

There have been strong and continuing demands for a low-cost, high-power ultraviolet (UV) light source for various applications such as semiconductor lithography, micromachining and medical. Excimer laser has been exclusively used as UV light source. But with expanding the market scale, solid-state UV laser has also been attracted much attention because of their low cost, high reliability, easier maintenance and small size. This laser consists of nonlinear optical crystals and infrared solid-state laser such as Nd:YAG [1]. Thus, suitable nonlinear optical crystals are indispensable in developing such solid-state UV lasers.

Various borate crystals, as $Li_2B_4O_7$ (LB4) [2], $\beta$-$BaB_2O_4$ (BBO) [3] and $CsLiB_6O_{10}$ (CLBO) [4] have been studied as promising nonlinear crystals for wavelength conversion in the UV region. However, those crystals are not sufficient for industrial high-power and high repetition UV solid-state laser because of the degradation of crystal due to the absorption of UV radiation. Scatters in borate crystal have been reported [5]. Scatters consists of void with less than 1 $\mu$m in size, and scatters are too small compared with resolution of X-ray topography and refraction index measurement. These scatters result dispersion of light, transmission loss in UV region, and variation of damage threshold. Thus, it is important to grow scatters-free high quality borate crystals.

$Li_2B_4O_7$ crystals show superior transmission and highest damage threshold in other nonlinear borate crystals. But its nonlinear coefficient is smaller than that of them. Thus, this small coefficient is the subject to improve for the development of UV solid-state laser using this crystal.

On the other hand, Kwon et al. (1997) reported that effective nonlinear coefficient of $Li_2B_4O_7$ crystal including MgO (1mol%) was larger than that of pure $Li_2B_4O_7$ crystal [6]. However, detailed research has not been done yet. In this paper, we grew $MgO:Li_2B_4O_7$ single crystal from the melt including MgO, and investigated optical properties of the grown crystals.

## 2. Experimental procedure

4N $Li_2B_4O_7$ poly crystalline and powder 3N MgO were used as starting materials. $MgO:Li_2B_4O_7$ single crystals were grown by CZ method using a resistance heating furnace, as shown in Fig.1 [7].

$Li_2B_4O_7$ poly crystalline contain MgO (2, 5, 15 mol%) were kept at 950℃ for 12h and the melt was poured into a Pt crucible for growth. Growth conditions were as follows: pulling velocity, 0.3 - 0.5 mm/hr; rotation rate, 3-15rpm; cooling rate, 4-6 ℃/day and dry air gas flowed, 200 ml/min. <110> crystal bar was used as seed crystal. The Pt crucible for the growth was 50mm $\phi$ $\times$ 50mm/h. The growth conditions are shown Table. 1.

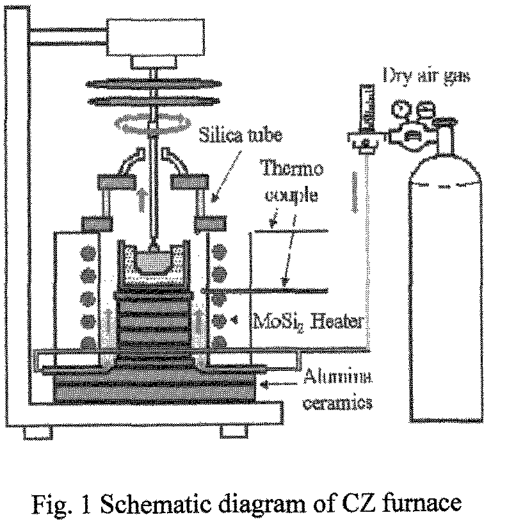


Fig. 1 Schematic diagram of CZ furnace

Table.1 Growth conditions for $Li_2B_4O_7$ single crystal growth

| | |
|---|---|
| pulling rate | 0.3-0.5 mm/hr |
| rotation rate | 3-15 rpm |
| dry air gas ($N_2$+$O_2$) flow | 200 ml/min |
| cooling rate | 4-6 ℃/day |
| Pulling direction | <110> |

Grown crystals were investigated by X-ray diffraction (XRD) using a RINT2000 with Cu $K\alpha_1$ radiation, polarized microscope, analyzed by [EPMA]. In addition, generation of fourth harmonics of Nd:YAG laser and transmittance measurement in UV region. Schematic diagram to observe scatters in a crystal is shown in Fig.2. In a dark room, LD light (532nm, 1mW) was irradiated into polished side plane for 30 seconds, and scattering light due to scatters was detected from upper side by mean of stereoscopic microscope with CCD camera.

3. Result and discussion

$MgO:Li_2B_4O_7$ crystal grown from the melt with 2mol% MgO is shown in Fig.3. This crystal is transparent and colorless. XRD result indicates that the grown crystal did not contain other phases. While $MgO:Li_2B_4O_7$ crystal from the melt with MgO 15mol% is shown Fig.4. The grown crystal is opaque and polycrystalline. XRD result indicates $Li_2B_4O_7$ intergrowth with $Mg_2B_2O_5$.

In order to avoid $Mg_2B_2O_5$ growth and control stoichiometric composition of melt $MgO:Li_2B_4O_7$, crystal was grown from the melt with 5mol% $MgB_4O_7$. The grown crystal is shown in Fig.5. XRD result indicates $Li_2B_4O_7$ and partly $Mg_2B_2O_5$ exist.

From the observation of polished thin plate for $MgO:Li_2B_4O_7$ crystal from the melt with 5mol% $MgB_4O_7$ by mean of the polarization microscope. $Mg_2B_2O_5$ observed in this plate. Almost $MgB_4O_7$ crystals were observed in the opaque part, whereas $Mg_2B_2O_5$ was not observed in the transparent part. Thus opaque is due to $Li_2B_4O_7$ and $Mg_2B_2O_5$ intergrowth. This result is shown in Fig.6.

XRD results are shown in Fig.7. It may be considered that MgO in the melt was less than 2mol% to grow transparent crystal.

MgO content were analyzed by means of EPMA. MgO content is less than 0.1mol% in all the grown crystals. Phase matching angle for generation of fourth-harmonics of Nd:YAG and efficiently do not change compared with pure $Li_2B_4O_7$. Therefore, it may be difficult to grow $MgO:Li_2B_4O_7$ single crystal containing MgO with 0.1mol% and above. Although growth method to make $MgO:Li_2B_4O_7$ single crystal is the same of Kwon's reported. Our results were different considerably from it.

Scatters in Li2B4O7 crystals grown in air or in dry air flow are shown in shown Fig.8.

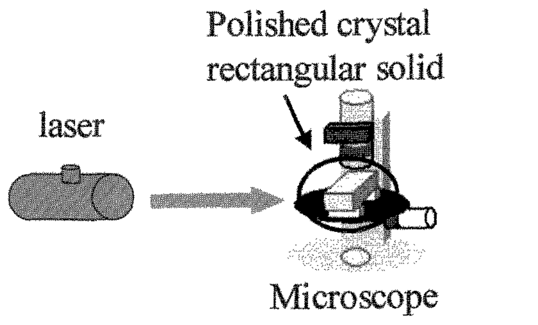


Fig.2 Schematic diagram to observe scatters in crystal

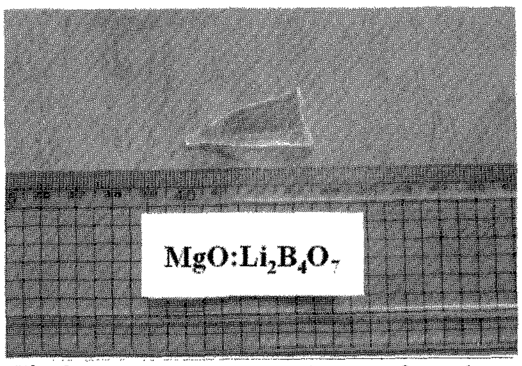


Fig.3 $MgO:Li_2B_4O_7$ crystal grown from the melt with 2mol% MgO

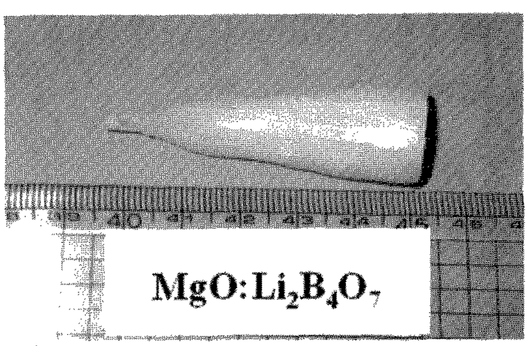


Fig.4 $MgO:Li_2B_4O_7$ crystal grown from the melt with 15mol% MgO

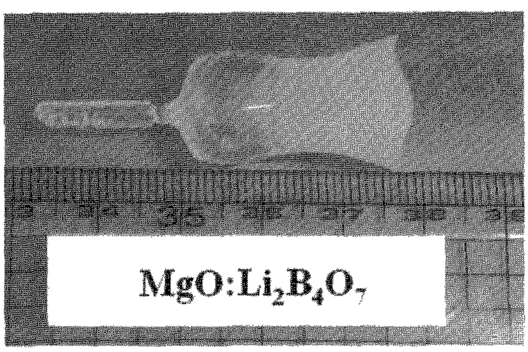


Fig.5 $MgO:Li_2B_4O_7$ crystal grown from the melt with 5mol% $MgB_4O_7$

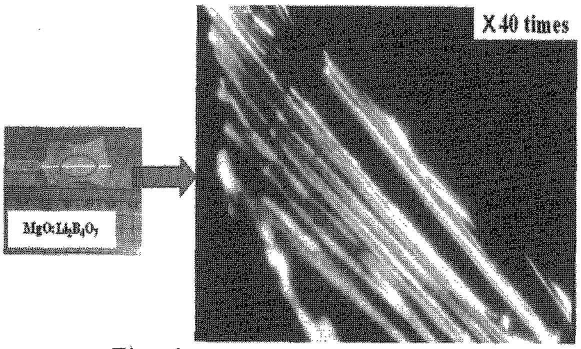


Fig. 6 $Mg_2B_2O_5$ in grown crystal

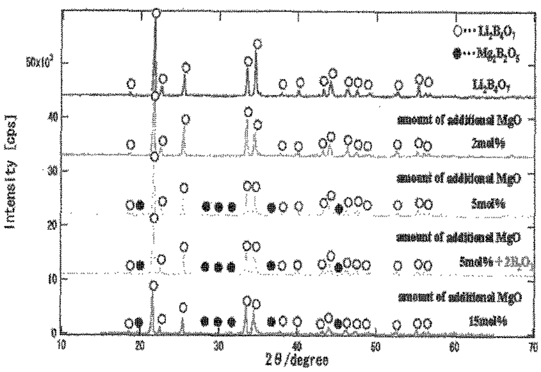


Fig. 7 Result of XRD

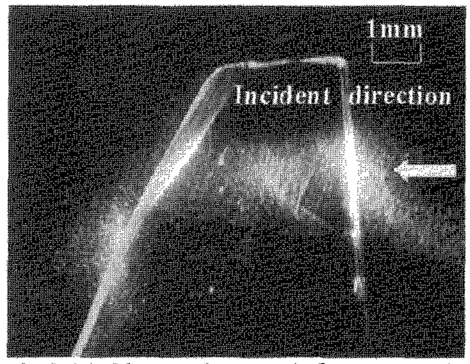


Fig.8 (a) Observation result for scatters in $Li_2B_4O_7$ grown in air

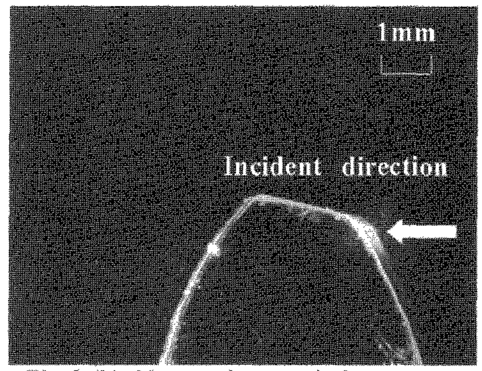


Fig.8 (b) Observation result for scatters in $MgO:Li_2B_4O_7$ grown in dry air flow

These were many scatters in $Li_2B_4O_7$ grown in air as shown in Fig.8(a), while scatters were not observed in $MgO:Li_2B_4O_7$ grown from the melt with 2mol% MgO in dry air gas flow of 200ml/min as shown in Fig.8 (b).

Transmittance curve using polished plates with 1mm and 2mm thickness, fabricated for crystal grown from the melt with 2mol% MgO are shown in Fig.9. Transmission does not depend on plate thickness. Thus, it is revealed that there is no absorption in the grown crystal.

On the other hand, transmittance curve of grown crystal in dry air flow is compared with that of crystal grown in air are shown in Fig.10. Transmission in $Li_2B_4O_7$ in air is smaller than in grown crystal flow dry air. From the Fig.8, scatters are observed in $Li_2B_4O_7$ in air. Wherever, scatters are not observed in grown crystal in dry air flow.

Thereby, it is concluded that scatters cause the decrease of transmittance in VUV region and can be eliminated by dry air flow during growth.

## 4. Conclusion

$MgO:Li_2B_4O_7$ crystal were grown from the melt including MgO by CZ method. MgO content in grown crystals, however, is less than 0.1mol% because of $Li_2B_4O_7$ intergrowth with $Mg_2B_2O_5$. Nonlinear coefficient in grown crystals dose not differ from that in pure $Li_2B_4O_7$.

It was also reveled that scatters in the crystal can be eliminated by dry air flow during growth. Transmission curve of grown $Li_2B_4O_7$ crystal in

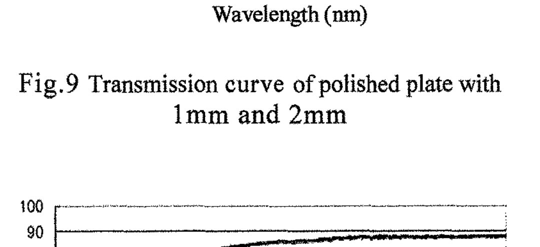


Fig.9 Transmission curve of polished plate with 1mm and 2mm

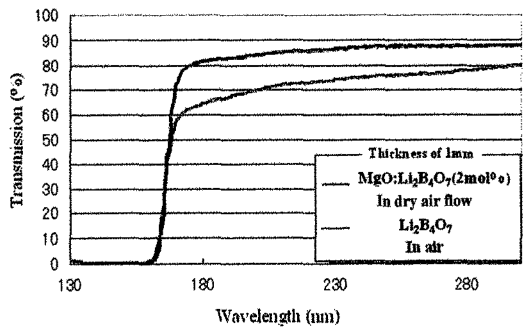


Fig.10 Transmission curve of grown crystals in dry air flow and in air

dry air flow in VUV region is superior compared with that of grown $Li_2B_4O_7$ crystal in air and grown crystal in air contain many scatters. Thus, it is considered that growth of Li2B4O7 crystal in dry air flow is promising technique to grow high quality Li2B4O7 crystal improving variation of damage threshold and degradation of crystal.

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