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Influence of scattering centers on UV transmittance in $Li_2B_4O_7$ single crystals and its origin

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Nonlinear optical borate crystal has been attracted much attention as wavelength conversion device with development of ultra violet (UV) all solid-state laser systems. $Li_2B_4O_7$ crystal is one of promising nonlinear optical crystals in UV region as well as piezoelectric substrate for SAW and BAW devices. In this paper, we have examined scatter center with submicron size, which is most effective defects, leading to the degradation of nonlinear optical devices in UV region. The scatter center is a void and the size distribution of scatter centers is revealed by the transparency measurement in UV region. From these experimental results, scatter free $Li_2B_4O_7$ single crystals showing high transparency in UV region have been successfully grown by Czochralski (CZ) method with dry air flow.
Key words: $Li_2B_4O_7$, scattering center, transmittance in UV region, dry air flow, Czochralski (CZ) method

1. Introduction

With the rapid development of ultraviolet (UV) light, continuing and strong demands for a low-cost, high-power and compact UV light for various applications such as micromachining, semiconductor lithography, and medical, has been coming out. To satisfy these demands all solid-state UV laser systems have been attracted much attention because of their low cost, long-lived and safety. This laser system consists of nonlinear optical crystals and infrared solid-state lasers such as Nd:YAG laser [1]. Thus, suitable nonlinear crystals are indispensable in developing such solid-state UV lasers.

Various borate crystals, as $Li_2B_4O_7$ (LB4) [2] and $CsLiB_6O_{10}$ (CLBO) [3], β-BaB_2O_4 (BBO) [4] have been studied as promising nonlinear crystals for wavelength conversion in the UV region. $Li_2B_4O_7$ single crystals have been one of superior transmission and highest damage threshold compared with other nonlinear borate crystals. $Li_2B_4O_7$ single crystals have grown by CZ method. Moreover, $Li_2B_4O_7$ single crystals have remarkably been easy to cut and polish for device making. But these borate crystals have several problems to solve. In particular, it has been required to improve crystal quality to bear high-power and high repetition UV light for industrial use. Most serious problem, affecting crystal properties in UV region, is scattering center in these borate crystals. These scattering centers are less than 1 μm, and are too small to detect by X-ray topography and refraction index measurement. Scattering centers in borate single crystals are voids originating from water in melt [5], and result in the transmittance loss in UV region and the fluctuation of damage threshold. Thus, we have been examined to develop the growth technique for scatters-free high quality borate crystals. Since the cause of the scattering center is water in melt, it may be required the decrease of water content in melt to grow scattering centers free borate crystal. We examined to decrease water in melt with the decrease of vapor pressure of water above the melt by carrying away dry air and by extracting water from the melt.

In this paper, scattering centers free $Li_2B_4O_7$ single crystals have been successfully grown in dry air. We also investigated the transmittance in UV and visible region of grown crystals in various air flow rate and influence of scattering center on the transmittance, resulting in degradation of grown crystals.

2. Experimental procedure

4N $Li_2B_4O_7$ poly crystalline was used as starting materials. $Li_2B_4O_7$ single crystals were grown by CZ method using a resistance heating furnace, as shown in Fig.1.

$Li_2B_4O_7$ poly crystalline was kept at 950℃ for 12 hr and melt was poured into a Pt crucible for the growth. Growth conditions were as follows: pulling velocity, 0.3 - 0.5 mm/hr; rotation rate, 3-15rpm; cooling rate, 40-60 ℃/day and dry air flow of 0-200ml/min. <110> crystal bars were used as seed crystals. The Pt crucible for the growth was 50mmφ×50mm/h. The growth conditions is shown Table. 1.

Grown crystals were measured transmittance in UV and visible region, investigated etch pit by microscope and observed scatters. Scatters diagram to observe scatters in a crystal shown in Fig.2. In a dark room, LD light (532nm, 1mW) were irradiated into polished side place, and scattering light due to scatters in a crystal were observed from upper side by mean of stereo microscope with CCD camera.

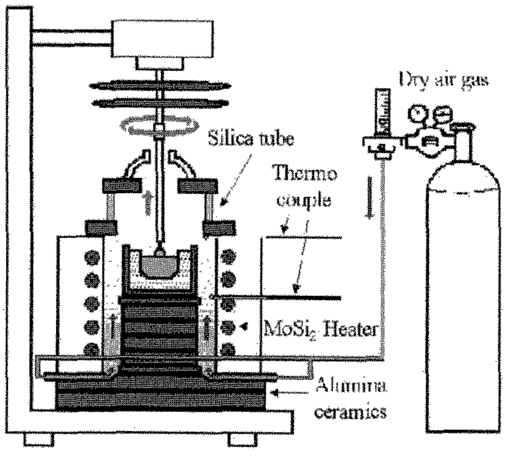

Fig. 1 Schematic diagram of CZ furnace

Table.1 Growth conditions.

pulling rate	0.3-0.5 mm/hr
rotation rate	3-15 rpm
dry air gas (N_2+O_2) flows	0-200 ml/min
cooling rate	40-60 ℃/day

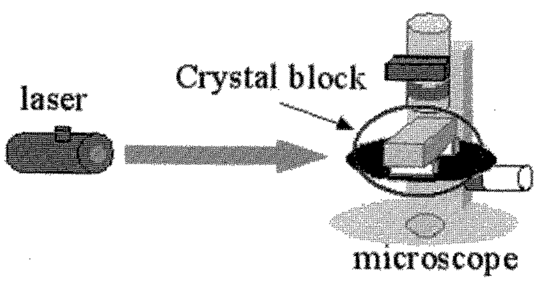

Fig.2 Microscopic instruments to observe scatters in crystal.

3. Results and discussion

Grown crystal with dry air flow of 200ml/min and 100 ml/min. is shown in Fig.3 and Fig.4, respectively. Grown crystal in airs is also shown in Fig.5. These grown crystals were transparent and colorless.

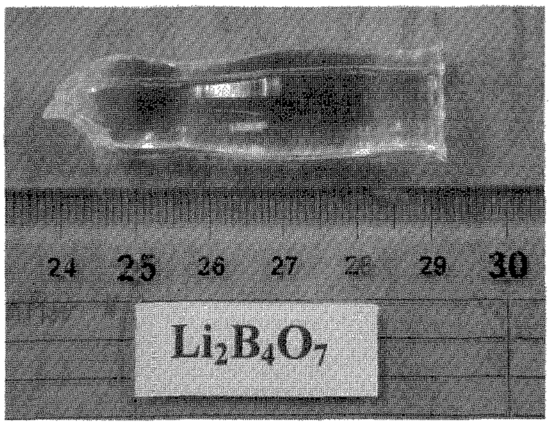

Fig.3 Grown crystal with dry air flow of 200 ml/min.

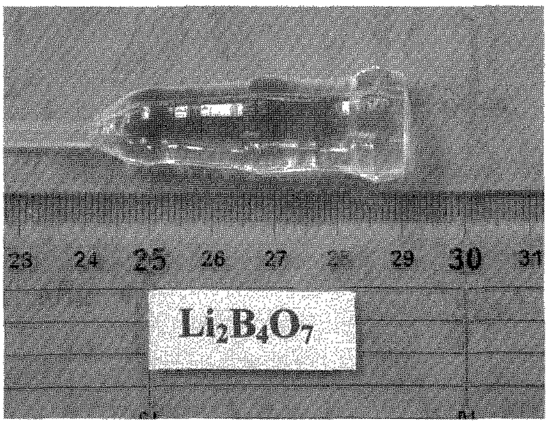

Fig.4 Grown crystal with dry air flow of 100 ml/min.

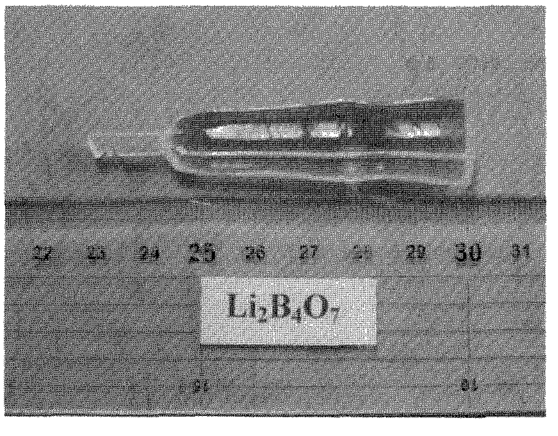

Fig.5 Grown crystal in air.

Grown crystal was cut off in the rectangular solid respectively and polished each plane. Photo images showing scattering centers observation result are shown in Fig.6. Scattering light was not detected in the crystal grown in dry air of 200 ml/min., whereas scattering light due to scattering centers were detected in the crystal grown in air.

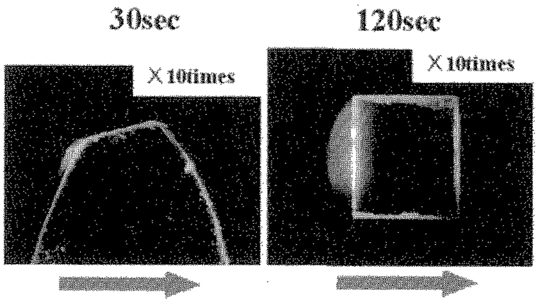

Fig. 6(a) Observed scattering centers in grown crystal with dry air flow of 200ml/min

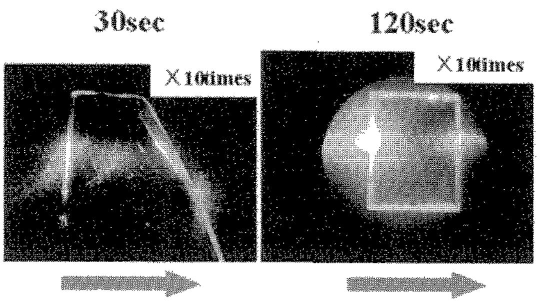

Fig. 6 (b) Observed scattering centers in grown crystal in air

It is obviously concluded that dry air flow during growth is useful to avoid the formation of scatter center in a grown crystal. Scatter center is a void. Laser diode of 532nm as irradiation light was used to observe scatter center in crystal, and thus void less than 532 nm in size can not be observed exactly by using 532 nm LD.

In order to evaluate the precise size distribution of scattering centers, transparency in DUV region were measured. Transmittance curve in each polished crystal plate is shown in Fig.7. Although the difference of transparency between these crystals does not clear in visible and infra-red region, scattering centers obviously influence transparency in DUV region. This result shows that scattering centers with 500nm or less in size widely distributes in crystal and that these scattering centers influence the transparency in DUV region. Transmission curve from 130 to 330 nm using polished crystal plates with 1mm and 2mm thicknesses are shown in Fig.8. These crystal plates was fabricated from scattering centers free crystal, grown in dry air flow of 200 mi/min. Transmittance curve in DUV region does not change with plate thickness. This indicates that scattering centers free $Li_2B_4O_7$ single crystal can be successfully grown by dry air flow during growth, and that higher effective conversion can be obtained if this scattering centera free borate crystal is used as nonlinear optical devices in UV region. Although the origin of sub-micron void leading to scattering light is not clear, it may be considered that the origin of scatter centers is similar to that of cops, which is formed by the accumulation of vacancy or interstitial during cooling in Si crystal.

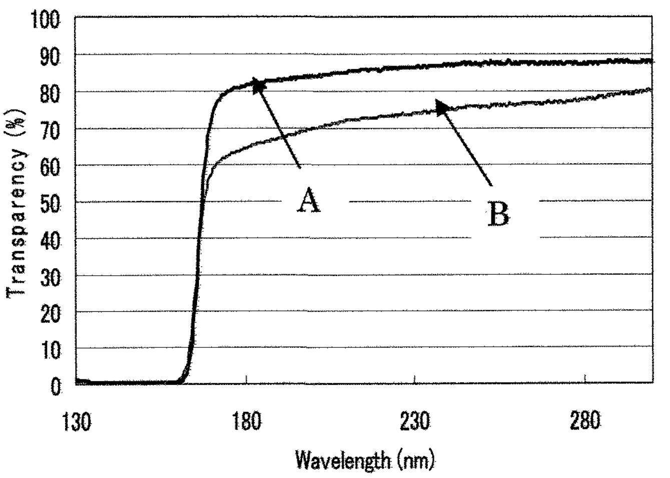

Fig.7 Transmittance curve of polished crystal plates: A showing scattering centers free crystal and B showing crystal including scattering centers.

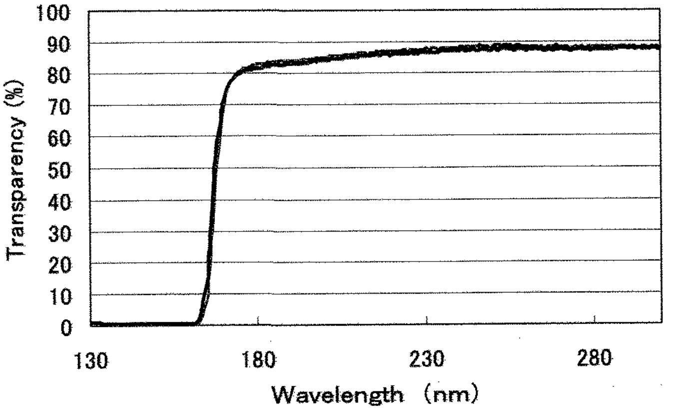

Fig.8 Transmittance curve of polished crystal plates with 1mm and 2 mm thickness.

4. Conclusions

We grew $Li_2B_4O_7$ single crystals in various dry air flow rate of 0-200ml/min by CZ method. These grown crystals were transparent and colorless. However, scattering centers were detected in grown crystal in air and the size of these scattering centers was estimated to be almost less than 532 nm. In contrast, scattering centers free crystal have been successfully grown with dry air flows rate of 200ml/min during growth. It was revealed that grown scattering centers free crystal had higher transmittance more than that of crystal including scattering centers

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