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Growth and Characterization of Transparent High Quality $LiKB_4O_7$ Single Crystal by Czochralski Method

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With the rapid expansion of market in micromachining, all-solid-state Ultra Violet(UV) laser has been required. Many efforts have been performed to look for new nonlinear borate crystal in order to use it as stable UV wavelength converter in solid-state UV laser. In this paper, we describe growth and transparent properties of a new nonlinear optical crystal: $LiKB_4O_7$(LKB4) single crystals by Czchralski(CZ) method. Transparent crack-free LKB4 single crystals have been successfully grown for the first time. In addition, effect of dry air flow during growth has been investigated to grow scatters free crystals, leading to superior transmittance in UV region.

Key words: $LiKB_4O_7$, scatters, dry air, UV solid-state laser, CZ method

1. Introduction

There have been strong and continuing demands for a low-cost, high-power UV light source for various applications. Under such circumstances, in addition to excimer laser, solid-state UV laser which consists of wavelength-conversion crystals and infra-red solid-state laser such as Nd:YAG laser, has been attracted much attention because of it's low-cost, high-reliability and easier maintenances [1]. Thus, qualified nonlinear optical crystals are indispensable in developing such a solid-state UV laser.

Various borate crystals, β-BaB_2O_4 (BBO) [2], $CsLiB_6O_{10}$ (CLBO) [3] and $Li_2B_4O_7$ (LB4) [4] have been already studied as promising nonlinear crystals for wavelength conversion in UV region. However, those crystals have some problems to improve in order to develop solid-state UV laser, and so it's very important to develop new nonlinear UV crystal since properties of this solid-state UV laser depend heavily on wavelength converter using borate crystal.

On the other hand, it was reported that there're many scatters in borate crystals and these scatters could be detected by light scattering method. Scatterer consist of void with less than 1 μm in size and can not be observed by means of X-ray tomography method and refractive-index measurement. Those sacatterer in crystal cause variation of damage threshold, leading to the degradation of nonlinear crystals [5]. Thus it is important to grow scatters-free borate crystal.

$LiKB_4O_7$ (LKB4) is a new nonlinear optical (NLO) crystal [6],and belongs to the space group of $P2_12_12_1$ with lattice parameters a=8.4915 Å, b=11.1415 Å and c=12.6558 Å. Framework structure of $LiKB_4O_7$ contains two kinds of anionic groups, $(B_3O_8)^{7-}$ and $(B_5O_{10})^{5-}$, in the unit cell. The $(B_3O_8)^{7-}$ anionic group is a six-membered ring consisting of one BO_3^{3-} and two BO_4^{5-} group, while the $(B_5O_{10})^{5-}$ group is composed from two six-membered ring joined by sharing a tetrahedrally coordinated boron atom [6]. It is well known that both $(B_3O_8)^{7-}$ and $(B_5O_{10})^{5-}$ groups have large microscopic nonlinear optical (NLO) susceptibilities [6].

$LiKB_4O_7$ is a congruent compound and can be grow by CZ method. However, grown LKB4 crystals by CZ method almost cracked during cooling after growth as shown Fig.1.

In this study, we examined growth conditions to grow transparent crack-free LKB4 crystals, and then growth of scatters-free LKB4 crystals was also investigated associated dry air flow during growth by CZ method.

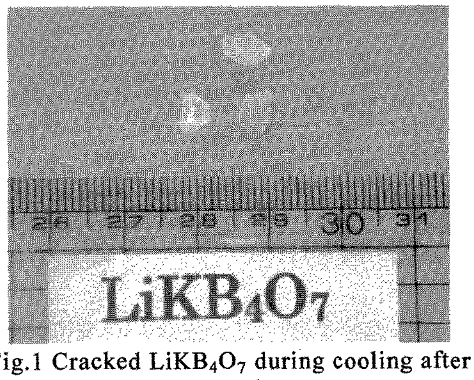


Fig.1 Cracked $LiKB_4O_7$ during cooling after growth

2. Experimental procedure

$LiKB_4O_7$ single crystals ware grown by the CZ technique. 3N Li_2CO_3, K_2CO_3 and B_2O_3 powders were used as raw materials. Two starting materials were prepared. One (I) was polycrystalline powder with the stoichiometric composition through a solid-solid reaction at 705 ℃ for 10h after calcinations to degrease water content in each raw material. The other(II) was glass with the stoichiometric composition, made from the melt of a mixture of raw materials to reduce water content in melt. The melt which kept at 900℃ for 1h was poured into a Pt crucible(50mmϕ ×50mm/h), and then cooled Pt crucible was kept in a dry oven to avoid water absorption. The CZ furnace used is shown in Fig.2. The pulling rate was from 0.1 to 0.3 mm/h, the rotation rate was from 10 to 25 rpm and the thermal gradient above the melt was from 90 to 110 ℃/cm. LKB4 crystals were grown in dry air gas flow ranging from 0 to 0.25 l/min.

As-grown crystals were cut and polished carefully, and examined by X-ray diffraction (XRD), polarization microscope. Scatters in grown crystal were checked by light scattering method. Rectangular solids were fabricated from grown crystals and each plane was polished. Scatter observation was done by using these solid in a dark room. LD light(660nm,1mW) were irradiated into polished side plane for 3 minutes, and scattering light due to scatters were detected from upper side by mean of stereoscopic microscope with CCD camera. The transparency at wavelength 120 to 300nm, 200 to 1100nm and 1282 to 4000nm was measured using polished crystals with thicknesses of 1mm and 2mm.

3. Results and discussion

As-grown $LiKB_4O_7$ crystal is shown in Fig.3. XRD results are shown in Fig.4. X-ray result of grown crystal corresponds with that of starting materials(I). It is revealed that grown crystal is $LiKB_4O_7$. The growth condition is shown in Table.1. Although the grown crystal was translucent, it did not crack after growth. Thus crack-free crystal can be grown in consistent with previous works. It may be considered that growth condition and starting materials(I) are proper compared with previous one. Grown crystals were cut parallel and normal to the growth direction, and polished. Periodical cloud in grown crystal were observed as shown in Fig.5(a), and cloud consist of many voids as shown in Fig.5(b). Voids were formed by the supersaturation of H_2O in the melt near the solid-liquid interface, and the incorporation of voids into the crystal took place by the sudden increase of the growth rate due to the cellular growth [5,7]. Thus, it was important to decrease H_2O content in melt and prevent the cellular growth in order to grow transparent crystals. The condition to avoid the cellular growth is derived as follows:

$$G/v > (mC_L/D)(1-k_0)/k_0 \qquad (1)$$

where G is the thermal gradient, v the growth

Table.1 Growth conditions for crack-free crystal

pulling rate	0.3 mm/h
rotation rate	10 rpm
thermal gradient above the melt	90 ℃/cm
starting materials	(I)
dry air flow	150 ml/min
growth direction	<110>

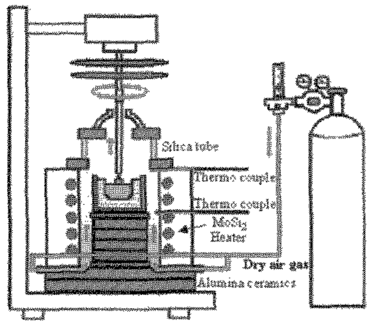


Fig.2 Schematic diagram of CZ furnace

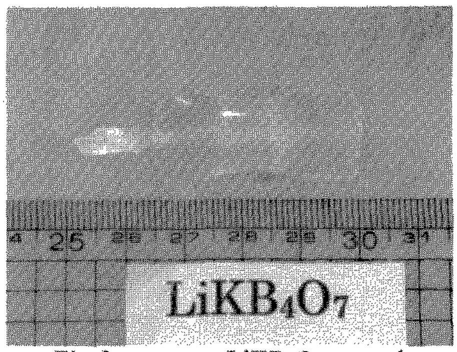


Fig.3 as-grown $LiKB_4O_7$ crystal

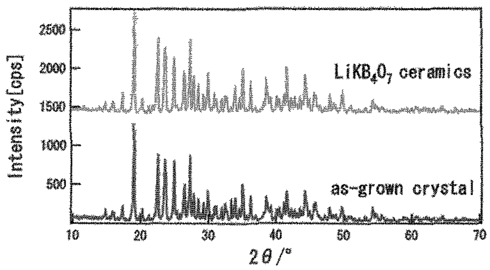


Fig.4 X-ray diffraction patterns of $LiKB_4O_7$

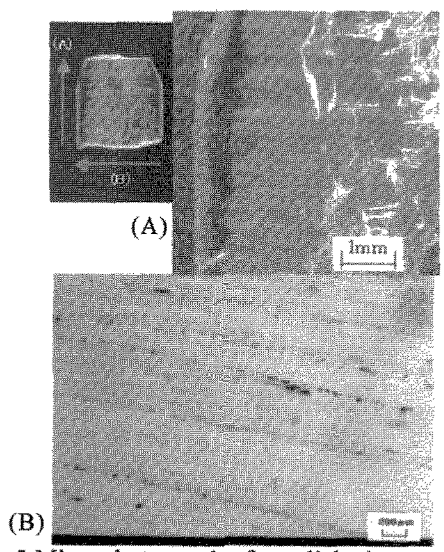


Fig.5 Microphotograph of a polished crystal plate
A: Parallel to growth direction
B: Normal to growth direction

speed(pulling rate), m the gradient which carried out straight line approximation of the liquidus, C_L the impurity concentration , D the diffusion constant in melt of impurities and k_0 the equilibrium distribution coefficient [8]. From this condition, it was required to increase the thermal gradient, decrease impurities in the melt and the pulling rate.

According to growth conditions in Table.2, grown $LiKB_4O_7$ single crystal is shown in Fig.6. Dry air flow was increased from 150 to 250 ml/min to decrease water content in melt, and transparent and crack-free crystals have been successfully grown.

Table.2 Growth condition for high-quality LKB4 single crystal

pulling rate	0.1 mm/h
rotation rate	25 rpm
thermal gradient above the melt	110 ℃/cm
starting materials	(Ⅱ)
dry air flow	250 mℓ/min
growth direction	<010>

Fig.6 high-quality as-grown $LiKB_4O_7$ crystal

Polished plate from grown crystal was prepared. As the result of microscopic observation, this plate does not contain inclusion such as voids or other phase. Photoimage showing scatters observation result is shown in Fig.7. Scattered light was not detected, and thus it was conduced that scatterer larger than 660 nm in size were not contain in a grown crystal.

Transmission curve from 130 to 4000nm using polished plates with 1mm and 2mm thickness are shown in Fig.8. Grown $LiKB_4O_7$ crystal has a wide transparency from 180nm to 3500nm and shows superior transparent compared with isomorphous $LiRbB_4O_7$ crystal. Transmittance curve in Vacuum Ultraviolet (VUV) region does not change with plate thickness as shown in Fig.8(a). This shows that grown crystal contain no scatterer less than 660 nm in diameter, which was not detected by using 660nm LD.

Sugawara et al. reported that scatters in crystal were eliminated by dry air flow during growth [5]. In the growth of $LiKB_4O_7$ single crystal, it's considered that dry air flow is useful to avoid scatters incorporation in a grown LKB4 crystal, consistent with LB4. Further, He-Ne laser(633nm) and LD laser(660nm) laser are used to detect scatters in LB4 and LKB4 respectively. But in this detection method, scatters in diameter less than these wavelengths were not detected. In our study, it may be considered that scatters in diameter less than laser wavelength can be evaluated by

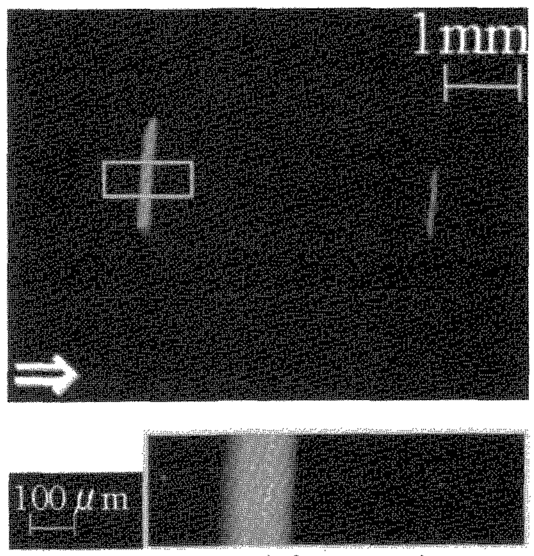
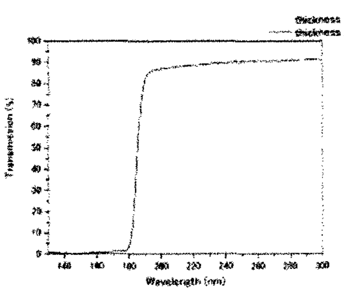
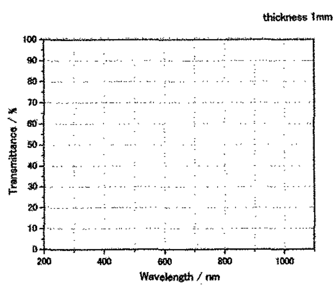


Fig.7 Observation result for scatters in grown LKB4 single crystal

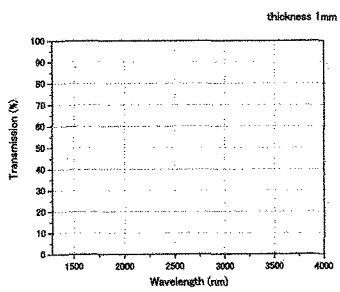
An arrow indicates the direction of radiation.



(a) Ultraviolet wavelength 120 to 300nm



(b) Visible wavelength 200 to 1100nm



(c) Infrared wavelength 1282 to 4000nm

Fig.8 Transparency of $LiKB_4O_7$ single crystal transmittance measurement using crystal plate with different thickness in VUV region.

As for formation mechanism of voids resulting scattering, it may be similar to that of COPs (crystal originated pits) in Si crystals because COPs is a void with similar size to one in borate crystals.

4. Conclusions

A newly developed nonlinear optical crystal $LiKB_4O_7$ has been successfully grown by CZ method. Growth conditions were also investigated to grow transparent and scatter-free LKB4 single crystals. Starting materials with few amounts of water and dry air flow during growth are very effective factor to grow transparent and scatters-free LKB4 single crystal. In addition, superior transmittance curve in VUV region was obtained in grown scatters-free crystal. This indicates that degradation of crystal due to harmonic generator in VUV region can be improved.

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