Growth and morphology of large LiB₃O₅ single crystals

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**ABSTRACT**

LiB₃O₅ (LBO) is one of the most widely used nonlinear optical crystals, therefore the growth of large high quality boules is of major significance to the photonics industry. In the past, LBO single crystals were limited in both size and quality, the latter of which was primarily due to the presence of bubbles, flux inclusions and striations. Furthermore, commercially available material exhibited variable optical absorption.

In this research we have perfected the Top-Seeded Solution Growth (TSSG) technique for the growth of LBO single crystals from MoO₃-based fluxes. This particular growth process was developed through a thorough study of melt dynamics. Based on the results observed in our modeling experiments, the major growth parameters were optimized. The crystal morphology was modified in order to increase the material yield and eliminate inclusions. As a result we have achieved LBO single crystals of both size and quality, which we believe to be market leading.

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1. Introduction

After initially being discovered by Chen et al. [1], LBO has become one of the most commonly used nonlinear optical materials. In the laser industry, LBO is widely utilized for the generation of the second and third harmonics of 1064 nm radiation. Industrial strides aimed towards the scaling up of laser power have resulted in paramount importance being placed on high optical quality and low optical absorption at the wavelengths of interest, as well as the utilization of larger nonlinear optical elements.

LBO melts incongruently at ~834 °C [2], thus a flux method must be used for its production. The use of B₂O₃ as a flux was first suggested in [1] and had remained the solvent of choice to industrially produce LBO single crystals for over a decade. Most of the difficulties encountered with this particular growth process were related to the high viscosity of the flux, which has been reported to increase during crystallization, in the range of ~2000–20,000 cP [3]. It was shown that inclusion and crack-free crystals could be grown only from a relatively narrow range in the LBO-B₂O₃ system, namely 72–82 wt% LBO, with a corresponding viscosity of 2000–4000 cP. As a result, the as-grown crystals were limited in size, typically less than 200 g, and exhibited variable optical quality.

Significant progress in the growth of larger LBO crystals was achieved as a result of the development of lithium molybdate (LM) fluxes [4], which demonstrate a wide crystallization range combined with a high solubility for LBO. Theoretically, crystallization of ~40% of the crucible charge by weight is possible as compared to fewer than 30% obtainable from B₂O₃. As it will be shown below, these fluxes are much less viscous compared with the self fluxes. LM fluxes allowed for a significant overall improvement in both size and quality of commercially available LBO material. The achievable boule size in the industry increased to ~300 g [4] with some record demonstrations of up to 1.3 kg [5]; however, growth inclusions and striations were still present in some sectors of the as-grown crystals [5,6]. Based on our data, the absolute values of optical absorption of the LBO material available in the market have been within the range of 3–500 ppm/cm at 1064 nm and 1–400 ppm/cm at 532 nm (with the majority of the material clustered at the low end of the range).

The research presented below has been aimed towards the development of an efficient technology for the growth of large LBO crystals with high optical quality, record low absorption and a complete absence of inclusions/striations.

2. Experimental

We started our research by investigating the LBO crystallization field from an LM flux [4] in the vicinity of the pure LBO composition in detail and determined that it is difficult to obtain the LBO phase if the LBO concentration in the LM flux exceeded 80 mol%.

When determining an optimal starting point for an LBO growth run, one should take into consideration the corresponding
viscosity values. The viscosities of LBO-LM fluxes have been directly measured by the disk oscillation damping technique, as well as modeled for various compositions. The dependence of a typical dynamic viscosity at a corresponding saturation temperature \( (T_s) \) on the LBO concentration in the LM flux is shown in Fig. 1. The indicated saturation temperatures were determined by observation of dissolution/growth of an LBO seed with an accuracy of \( \pm 1 \) °C.

As one can see, the flux viscosity decreases rapidly as the LBO material is extracted from the solution. This behavior is rather unusual for borates as typically the flux viscosity increases while the crystal is growing. Such a viscosity trend is mostly driven by the temperature decrease down the liquidus line. Yet in the LBO-LM case the temperature trend is overpowered by a relatively fast increase in the LM concentration, which makes the flux thinner. As shown in Fig. 1, this concentration trend prevails over a wide range of compositions; an increase in viscosity due to temperature effects should occur only below \( \approx 50 \) mol% LBO. It should be noted that even concentrated LBO-LM fluxes are not as viscous as self-fluxes, which is beneficial because growth from a system with viscosities of 300–800 cP is only moderately difficult in the crystal growth practice. In addition, the LBO-LM system offers a wide range of compositions with viscosity even lower than 200 cP. All of the above should be considered in the selection of an adequate starting composition and temperature, as it necessitates a trade-off between the higher amounts of LBO potentially dissolved in the flux and the potentially lower viscosity of the flux. The particular LM flux compositions (\( Li_2Mo_4O_{13} \), \( Li_2Mo_4O_{15} \), or other \( Li_2O/MoO_3 \) mixtures within the phase field of LBO) are rather close to each other with respect to \( Li_2O \) to \( MoO_3 \) ratios [4]. In the LBO-LM phase field shown in [4], we specifically studied the range of 40–65 mol % LBO. The corresponding starting temperatures are in the range of 720–745 °C and the viscosity is below 200 cP.

After the viscosity values were determined, an experimental set up replicating our system was built. A transparent glass vessel of the same size as our growth crucible (\( \approx 150 \) mm in diameter) has been utilized with various fill factors. Glycerol–water solutions were used to simulate the particular flux viscosity. The flow has been visualized with fine particles dispersed in the solution. In order to study the characteristic flow patterns, models of LBO crystals with different sizes and shapes, representing the actual geometry of the boule at different stages of growth, were rotated in the solution. Typical flow patterns have been simulated for various boule shapes, sizes, temperature gradients, rotation rates and flux viscosity values. Growth parameters were optimized in order to ensure that a steady laminar flow across major LBO crystal facets is maintained throughout the entire growth cycle. For example, we have modeled our typical melt flow patterns near the run completion. At that stage, the viscosity of the melt approaches a value of 50 cP, as the flux becomes depleted in LBO and the temperature gradients diminish due to the combined effects of the boule rotation and the low viscosity of the melt. The boule model employed was 13 cm in the \( \langle 100 \rangle \) direction, which is typical for the last phase of growth. Under such conditions, it was determined that the rotation rate reaches a critical value at about 15 rpm, where the flow becomes turbulent, thereby setting the upper limit for this parameter. The above modeling was instrumental in optimizing rotation rates in the actual growth runs.

The particular fluxes were prepared in platinum crucibles by mixing high purity \( Li_2CO_3 \), \( B_2O_3 \) and \( MoO_3 \) with the appropriate ratios. Different flux compositions were investigated. Seeds were oriented along the \( \langle 001 \rangle \) direction. LBO crystals were grown by the TSSG technique without pulling. Custom-made vertical, resistive, multi-zone furnaces have been used. The temperature was maintained by Eurotherm controllers with an accuracy of better than 0.1 °C. The rotation rates were varied based on the modeling results, so that the convection in the crucible was not inverted and the flow next to crystal facets remained laminar.

Taking all phase diagram peculiarities into consideration, the cooling rates were varied throughout the process to maintain supersaturation levels resulting in a steady growth rate of about 1 mm/day. The growth rate in the radial direction was monitored at the melt surface through an observation port. After a process was completed, the crystal was slowly pulled out of the melt and the furnace was cooled to room temperature at a rate of \( \approx 10^{-4} \) °C/h to prevent the boule from cracking.

3. Results and discussion

A typical as-grown boule is shown in Figs. 2 and 3. This particular LBO crystal has a weight of exactly 2.0 kg, which is the market leading size to the best of our knowledge. The process is repeatable and reproducible. On average, one out of every ten runs needs to be aborted early due to formation of secondary nucleation.

There are some very peculiar aspects of the as-grown boule morphology differentiating our crystals from what has been previously grown. Historically, LBO boule morphologies were quite similar whether grown from \( B_2O_3 \) or LM fluxes [1,4]. Typical LBO boules described in the literature are predominantly shaped by primary \( \langle 110 \rangle \), \( \{011\} \), \( \{201\} \) and secondary \( \{111\} \) and

![Fig. 1. Typical dynamic viscosity of LBO-LM solution as a function of LBO concentration at saturation temperature (T_s). The values for T_s are shown next to the experimental points.](Image)

![Fig. 2. LBO boule grown by TSSG technique from LM flux with a weight of 2.0 kg.](Image)
(1 2 2) facets, the former of which are responsible for creating a near pyramidal shape. The presence of a small (1 0 0) facet is rather uncommon and has been reported only for LBO grown from a self-flux [7]. This particular crystal habit is a limitation for the effective extraction of LBO material from a typical crucible. The pyramidal corners are first to reach the crucible wall (terminating the growth run) while there is still a substantial amount of LBO dissolved in the flux. Another unfavorable aspect related to traditional LBO morphology is the presence of (1 2 2) facets, the former of which are responsible for creating a veil/striation formation and flux entrapment. In either self-flux or LM fluxes these facets are prone to facets. In either self-flux or LM fluxes these facets are prone to veil/striation formation and flux entrapment.

Throughout the course of the current work, it has been determined that the morphology of the LBO boule is affected by the degree of supersaturation, an observation which is consistent with an earlier report for LBO boules crystallized from B₂O₃ fluxes [8]. As it was mentioned above, our goal was to develop an effective production process for relatively large LBO boules with no flux entrappings. To this end, adequate control of the suppression, temperature gradient and boule rotation was required in order to achieve the desired morphology. As a result, a suppression of the growth rate in the (1 1 0) and (1 0 0) directions was attained, generating large corresponding facets. Inversely, the growth rate in the (1 1 1) and most importantly in the (1 2 2) directions was promoted, such that the (1 1 1) facets were minimized and the (1 2 2) facets were absent altogether. As a result, the as-grown LBO boule shown in Figs. 2 and 3 exhibits a desirable morphology. It is significantly elongated in the crystallographic (0 0 1) direction compared to the (1 0 0) and (0 1 0) directions. Large (1 1 0) facets are well developed and uncommon (1 0 0) facets are present as well (Fig. 3). Prone to flux entrapment, (1 2 2) facets are completely eliminated; hence the boule has no inclusions. Altogether the boule starts to resemble a parallelepiped rather than a pyramid. In addition, the boule has the same aspect ratio as our typical crucible. When such a boule grows, it efficiently fills the crucible volume allowing for an effective extraction of LBO material from a reasonably small crucible.

The boule shown in Figs. 2 and 3 is free of any defects, inclusions and striations with the exception of a small veil in the capping region near the seed. The as-grown material has been examined using specially prepared polished samples, including entire boule cross-sections. For bulk quality inspections we utilized optical microscopes with magnification up to 500 x and for better illumination of internal defects we used focused green laser beams. No defects, sectorial boundaries or striations similar to those reported in [6] were detected. We attribute the absence of striations to high melt purity and good process control, resulting in a steady crystal growth rate. The optical homogeneity of the as-grown material is high (Δn < 10⁻⁶/cm) as determined by a Zygo-interferometer.

Samples of the as-grown material have been studied by combined UV/VIS/NIR and FTIR spectrometries. The results of these analyses indicate no detectable absorption, nor any abnormal absorption bands throughout the transmission range of LBO. The optical absorption at the critical wavelengths of 1064 and 532 nm has been measured by the photo-thermal common path interferometer technique (PCI) [9]. Typical absolute absorption values were consistently within the range of 3–10 ppm/cm at 1064 nm and 1–2 ppm/cm at 532 nm. The absolute absorption at 355 nm was about 40 ppm/cm as measured by a laser calorimeter. We deem these low absorption levels to be market leading.

4. Conclusions

We have demonstrated an industrial TSSG process for LBO single crystals utilizing a MoO₃-based flux. Optimization of the LBO crystal morphology allowed us to make this process cost efficient and to completely eliminate inclusions and striations. The as-grown crystals are market leading with respect to their size, and most importantly, with respect to their optical quality.

References