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Abstract. Borate-based materials are of high interest to generate an UV laser light from a crystal. Fiber-shaped crystals combining the advantages of fiber lasers and crystalline lasers, we have investigated the growing conditions required to obtain usable fibers of Bi\textsubscript{2}ZnB\textsubscript{2}O\textsubscript{7} (BZBO) and LaBGeO\textsubscript{5} (LBGO). For BZBO, the major drawback was the pronounced color of the fibers and for LBGO, it was the high viscosity of its melt leading to use a flux. This paper presents our state of the art to obtain good quality BZBO and LBGO crystal fibers.

1. Introduction
To generate an ultraviolet laser light from a crystal, the only efficient way is currently by frequency conversion of a visible of near-infrared source. For that purpose, several crystals can be used on condition that they possess high non-linear properties, wide window of transparency and high optical damage threshold. A lot of crystals of the borate family possess more or less these characteristics. Borates are considered as essential materials for the achievement of lasers able to replace excimer lasers and more generally for solid state lasers in the blue-UV range. Among crystals of the borate family, one can cite \(\beta\)-BaB\textsubscript{2}O\textsubscript{4} (BBO), LiB\textsubscript{3}O\textsubscript{5} (LBO), CsB\textsubscript{2}O\textsubscript{5} (CBO), CsLiB\textsubscript{6}O\textsubscript{10} (CLBO), Ca\textsubscript{5}(BO\textsubscript{3})\textsubscript{3}F (CBF), and YCa\textsubscript{3}O(BO\textsubscript{3})\textsubscript{3} (YCOB) widely used for efficient second harmonic generation (SHG) of Nd:YAG lasers. [1–5]. Despite recent significant progress in growth and characterization, these crystals also possess some drawbacks such as difficult crystal growth or hygroscopicity.

The Czochralski technique is generally the technique used for growing borate crystals. This method does not allow both quickly growing the samples and enhancing their crystal quality and optical properties. By else, it is however time consuming. On the contrary, the production of crystal fibers by specific growing method can present a solution to the drawbacks of the Czochralski technique. The most common methods used to grow crystalline fibers are laser heated pedestal growth (LHPG) and micro-pulling down (\(\mu\)-PD) techniques [6–8]. They have shown to be versatile methods for the growth of high quality crystals of a large variety of materials. By else, in addition to their unique set of properties allowing various uses in optoelectronic devices, the final shape of crystal fibers is suitable for physical and optical testing, reducing time and cost of preparation. In addition, this specific shape of crystal fibers is directly usable for laser applications with an interlacing length/thickness ratio allowing to combine the advantages of fiber lasers and crystalline lasers, in particular the large heat exchange surface.
The goal of our research was to investigate fiber-shaped borate crystals for solid-state lasers and optical applications. We have investigated the growth of two new materials belonging to the borate family: Bi$_2$ZnB$_2$O$_7$, noted BZBO and LaBGeO$_4$, noted LBGO. Only few publications, from a few research groups, deal with these materials in literature: for BZBO [9-13] and for LBGO [14-18]. These choices are driven by applications. BZBO is considered as an interesting alternative of the well-known KDP (KH$_2$PO$_4$) because its doubling efficiency would be three or four times higher [9] and LBGO crystals are phase-matchable for Nd-laser and its SHG, while LaBGeO$_4$-Nd are promising materials for self frequency doubling laser applications.

In this paper, we report the recent progress achieved in the growth of BZBO and LBGO fiber crystals by the micro-pulling down method (μ-PD). Indeed, the viscosity being very high, it appeared to be a serious drawback for pulling LBGO by the μ-PD technique. In particular, we discuss here the contributions to the quality of the fibers obtained by the use of different fluxes that we have selected to overcome it.

2. Experimental

BZBO was synthesized from the starting materials Bi$_2$O$_3$ (Aldrich 99.9%), ZnO (Aldrich 99.99%) and H$_3$BO$_3$ (Acros 99.99%). In a first method [19] the samples were introduced in a furnace at 665°C during two weeks before reducing the temperature to 550°C with a cooling rate of 5°C.h$^{-1}$ temperature at which the sample was maintained for 1 h before cooling down to room temperature by increasing the rate up to 20°C.h$^{-1}$. It exists a second method [11] much simpler in which the samples were placed in the furnace and then, the following temperature program was applied: up to 630°C with a heating rate of 6°C.h$^{-1}$, keeping at 630°C for 48 h and cooling down to room temperature with the same rate.

LBGO was prepared using a conventional solid-state reaction method. A mixture of 25% La$_2$O$_3$ (99.99% from Materion), 25%H$_3$BO$_3$ (99.99% from Acros) and 50% GeO$_2$ (99.999% from Neyco) was prepared and grinded in an agate mortar. Then, it was pressed into pellets, heated to 1050°C at 12°C.h$^{-1}$, annealed in air for 82 h, then cooled down to room temperature at 24°C.h$^{-1}$. The LBGO powders were checked by X-ray diffraction and DTA analysis.

In the μ-PD method, as used with the device installed in our laboratory, the material to be grown is molten in a small platinum crucible fitted with a pipe-shaped capillary at its bottom. The crucible is resistively heated but RF furnace is also used when melting temperatures above 1500 1C are required. When complete melting is obtained, a seed is placed into contact with the droplet of liquid at the end of the capillary. The fiber is obtained by pulling the seed in the downward direction. An after-heater allows controlling axial temperature gradients.

The pulled fibers were characterized by differential thermal analysis (DTA), scanning electron microscopy (SEM), EDX microprobe and Raman microspectroscopy.

3. Results

3.1. BZBO

BZBO has a non-centrosymmetric orthorhombic structure, belonging to the Pba2 space group. It possesses large nonlinear optical coefficients ($d_{ij} = 0.91$ pm.V$^{-1}$ [13]), a pretty large birefringence (0.085–0.106 [12]) and is transparent from 350 nm to more than 2500 nm [11]. Its growth is less complicated that the standard BBO because it has a congruent melting with no undesirable solid phase transition. It is non-hygroscopic and resistant to deliquescence [12].

Several fibers were easily pulled in air atmosphere with a platinum wire as seed and pulling rates ranging from 4.5 to 12 mm.h$^{-1}$. With a quasi-circular cross-section, their diameter was regular and between 300 and 550 μm (according to the pulling speed) for a fiber length up to 100 mm (figure 1). As-grown fibers were transparent and free of cracks and bubbles, but were uniformly colored from yellow to orange-red whichever was growth atmosphere (figures 1 and 2). X-ray diffraction showed that the pulled fibers were c-axis oriented with the lattice parameters: $a = 10.8233(4)$ Å, $b = 11.0203(6)$ Å and $c = 4.8864(2)$ Å. These values are in very good agreement with those given in the literature [19].
In all cases, SEM revealed that all along the fibers, small clear parts of different shapes were dispersed in a darker matrix and elongated in the growth direction (figure 3). EDX microprobe showed that oxygen was very slightly less concentrated in the clear parts than in the dark ones (less bright color in the clear zones). On the contrary, bismuth seemed slightly more concentrated in the clear zones because its color was brighter. However, the differences were too small to be quantitatively measured. That microstructure and the color of fibers were initially ascribed to a reaction between BZBO melt and platinum crucible. The growth of other fibers by LHPG, a crucibleless growth technique, invalidated this hypothesis because the obtained fibers were always colored and presented the same microstructure.

![Figure 1. Bi₂ZnB₂O₇ fibers grown in air atmosphere](image1)

![Figure 2. Examples of Bi₂ZnB₂O₇ fibers grown in oxygen and nitrogen](image2)

![Figure 3. SEM images of different parts of the microstructure of a BZBO fiber grown in air](image3)

The elemental analysis of several crushed fibers was performed by inductively coupled plasma (ICP-AES) after complete mineralization. It revealed, during the growth process, a non-negligible loss of 13.5% boron oxide (molar composition) compared to the starting composition, probably evaporated mainly from the melt.

Correlated to DTA measurements, high temperature X-ray powder diffraction experiments performed on crushed fibers between 590 and 680°C (just before melting) showed that phase transformations occurred due to a composition shift in the Bi₂O₃-B₂O₃-ZnO system corresponding to the loss of boron oxide. All these observations suggested an incongruent behavior of the BZBO melting, possibly, of peritectic type. Then, low pulling rates are required to allow the completion of
the invariant reaction and to obtain pure BZBO crystals. To validate that interpretation, a pulling rate of 0.15 mm h\(^{-1}\) was used to grow a small transparent and colorless crystal with a 3 mm length. The very low pulling rate did not allow to obtain longer fibers. Thoroughly studied by Raman spectroscopy, the quality of the crystal was confirmed (figure 4). However, a deeper investigation of the composition is necessary on a longer fiber to assess the true stoichiometry of the crystal.

![Figure 4. Typical Raman spectra of a BZBO crystal pulled at 0.15 mm h\(^{-1}\)](image)

3.2. LBGO

LBGO structure is similar to that of stillwellite belonging to the \(C3\)\(^2\) space group. The trigonal unit-cell parameters are \(a=7.020(5)\) Å, \(c=6.879(4)\) Å and \(Z = 3\). The differential thermal analysis of LBGO showed that this crystal is congruently melting [15, 16]. By else, due to the high viscosity of the melt and violent evaporation of \(B2O3\), at the melting temperature (\(T = 1150–1200^\circ\)C), during pulling, the growth procedure is complicated.

The growth of LBGO crystal fibers directly from the melt was impossible due to its high viscosity which entailed the separation of the seed from growth interface after less than 1 mm of pulling of an opaque, white crystal. The, the use of a flux was necessary to reduce the viscosity and allow the growth of good quality crystals with usable sizes. Fluoride ions being known to break extended –O-B-O- chains and then reduce viscosity, LiF was considered as a possible flux after determination of the phase diagram LBGO-LiF (figure 5) because of the wide crystallization range of LBGO between 1200 and 760°C.

![Figure 5. Phase diagram of the LBGO-LiF system](image)

Numerous attempts to grow LBGO single crystal fibers using LiF flux were made. From the LBGO-30%LiF and LBGO-50%LiF mixtures, pulling was not successful. The melt was still very viscous combined with a strong LiF evaporation. In order to check the evaporated LiF amount, a growth test was made from a LBGO-80%LiF mixture. With a 3 mm h\(^{-1}\) pulling rate, we obtained an
opaque and white polycrystalline fiber (Fig. 6(a)). The length of the as-grown fiber is limited due to the high volatility of LiF and an important migration of the melt on the crucible walls.

The fiber was analyzed by Raman spectroscopy and compared to the Raman spectrum of LBGO powder of literature [20]. Fig. 6(b) shows that it corresponds well to that of LBGO. This shows that a strong evaporation of LiF occurred since with the LiF starting amount used, the crystallizable compound is not LBGO according to the phase diagram (Fig. 5). It can be concluded that more than 70% of the initial LiF amount evaporated, mainly during the first times of the growth experiment where temperature can vary rather quickly during the adjustment period required to attain the steady state leading to regular fibers.

Figure 6. LBGO crystal (a) and Raman spectra of powder and crystal (b)

To limit LiF evaporation during the growth, B$_2$O$_3$ was added to the starting LBGO-LiF mixture as reported earlier [21]. Several ratios LiF/B$_2$O$_3$ were investigated to find the optimal mixture to grow good quality LBGO fiber crystals. Growth attempts from LBGO-30 mol% LiF-10 mol% B$_2$O$_3$ and LBGO-40 mol% LiF-10 mol% B$_2$O$_3$ were unsuccessful, the liquid still being too viscous. From LBGO-40 mol% LiF-20 mol% B$_2$O$_3$, the pulling was difficult and we obtained a small polycrystalline white fiber. From LBGO-50 mol% LiF-10 mol% B$_2$O$_3$ and LBGO-50 mol% LiF-7 mol% B$_2$O$_3$ mixtures, with a 3 mm.h$^{-1}$ pulling rate, we obtained a 3 cm in length opaque white fiber. Its Raman spectrum confirmed that the fiber contained LBGO, but supplementary bands could be seen, attributed to a still unknown compound.

Fig. 7 shows the microstructure of a LBGO crystal fiber pulled from the 50mol% LiF-7 mol% B$_2$O$_3$, observed by SEM.

Figure 7. Microstructure of a fiber pulled from LiF-B$_2$O$_3$ flux

Three different areas can be seen, generally oriented parallel to the growth axis (Figure 7(a)) or more or less disoriented (Figure 7(b)). The darkest zones were found empty of matter except some amounts of silica due to polishing products and identified by EDX microprobe. The deficiency of
matter was already found in our study of the growth of Ca$_5$(BO$_3$)$_3$F crystal fibers by μ-PD [22]. The clearest zones were also shown to be more concentrated in lanthanum and boron than the grey ones, but poorer in germanium.

Typical Raman spectra of these two areas are given in Fig. 8. They show that they do not correspond to LBGO phase but to unknown compounds. The Raman spectrum of the clearest zone was reported earlier by Stone et al. [23] and attributed to a La-rich and B-depleted phase, in comparison to the LBGO phase. This confirms our observations.

![Figure 8. Raman spectra of clear and dark zones of a LBGO fiber pulled from a LiF-B$_2$O$_3$ flux](image)

The observed microstructure can be interpreted taking the viscosity of the melt into account. Indeed, in a standard resistively heated micro-pulling down crucible, the melt and the meniscus are strongly stirred by thermo-capillary convection (Marangoni effect) whereas the flow through the capillary is a steady Poiseuille flow [24]. Then, one can assume that, in our experiments, the viscosity of the melt is still too high and strongly disturbs the thermo-capillary convection leading to chemical homogeneities in the melt which impact the flow through the capillary and lead to crystallization of different species inside the fiber. To solve this problem, the flux needs to be improved.

4. Conclusion
In this work, first of all, we have studied the conditions necessary to grow transparent and colorless BZBO crystal fibers. Due to the evaporation of some boron oxide from the melt, its composition is displaced into the ternary system B$_2$O$_3$-Bi$_2$O$_3$-ZnO undergoing an incongruent melting and crystallization behavior. Then, the growth of crystals needs very slow pulling rates. Using them, we succeeded in growing transparent and colorless BZBO fibers.

Concerning LBGO, the high viscosity of its melt requires the use of a flux to grow usable fibers. The phase diagram LBGO-LiF showed that LiF would be convenient. However, its evaporation combined by an insufficient decrease of viscosity led to combine boron oxide and lithium fluoride in the flux to obtain fibers with suitable length. The use of such a flux led to multiphase fibers containing unknown compounds and the flux needs to be improved. This work is in progress.

References