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# Towards good quality $Bi_2ZnB_2O_7$ fibers grown by the micro-pulling down technique

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ABSTRACT

$Bi_2ZnB_2O_7$ (BZBO) fibers grown by the micro-pulling down technique (μ-PD) usually present a more or less pronounced color ranging from yellow to red and a microstructure showing glassy clear parts (more concentrated in bismuth) dispersed in a darker matrix. In a previous paper, we assumed a reaction between the platinum crucible and the melt to explain both their color and microstructure. To confirm or invalidate this hypothesis, BZBO fibers were pulled under different conditions by the μ-PD or laser heated pedestal growth (LHPG) techniques. Various physical characterizations methods such as: SEM, EDS microprobe, Raman micro-spectroscopy, DTA and X-ray diffraction were performed to evaluate their crystal quality. Finally, it appears that the origin of the observed features of the fibers grown lies in the evaporation of a substantial amount of boron oxide from the melt. This leads to a shift of its composition in the $ZnO$-$B_2O_3$-$Bi_2O_3$ ternary system and an incongruent melting behavior. Therefore, the obtainment of colorless and transparent fibers requires very low pulling rates.



## 1. Introduction

Compounds with the formula $X_2YZ_2O_7$ belonging to the melilite structural family offer considerable cation substitution possibilities. Thus, they are expected to be interesting hosts for various dopants useful for luminescent devices and other applications operating in new wavelength ranges. While the luminescent properties of rare earth ions in several silicate, aluminate or gallate melilites have been reported [1–3], little research has concerned the borate melilite $Bi_2ZnB_2O_7$ (BZBO) [4,5]. Discovered by Barbier et al. [6], its structure was found to be a noncentrosymmetric orthorhombic structure, belonging to the Pba2 space group. According to the literature, it has large nonlinear optical coefficients ($d_{31}$=0.91 pm $V^{-1}$ [7]), a relatively large birefringence (0.085–0.106 [8]) and is transparent from 350 nm (UV cut-off wavelength) to more than 2500 nm [9]. It is also non-hygroscopic and considered to be a potential competitor for KDP ($KH_2PO_4$) because its doubling efficiency would be three or four times higher [6,8].

The goal of our research was to investigate fiber-shaped BZBO crystals for solid state lasers and optical applications. In a previous paper, we reported on the growth and characterization of BZBO crystal fibers by the micro-pulling down technique (μ-PD) [10]. The fibers obtained had a uniform color from yellow to orange–red and a microstructure which was attributed to the presence of disordered or glassy parts. The origin of the disordered parts was considered to be connected to the presence of a still unidentified Bi-rich phase produced by the reaction of the melt with the platinum crucible. The high viscosity of the melt would impede its total dispersion and dilution resulting in the formation of the colored amorphous zones [10]. The principal objective of this paper was to confirm or disprove these hypotheses and to define the growth conditions allowing the preparation of colorless BZBO single crystal fibers. To this end, BZBO fibers were grown by two techniques: the micro-pulling down method (μ-PD) and the laser heated pedestal growth technique (LHPG).

## 2. Experimental

Powders of stoichiometric BZBO were prepared by solid state reaction of the starting materials: $Bi_2O_3$ (Aldrich 99.99%), ZnO (Aldrich 99.99%) and $H_3BO_3$ (Acros 99.999%). The detailed procedure is described elsewhere [10].

For the growth of BZBO fibers, the micro-pulling down device installed in our laboratory was used. The growth apparatus and the experimental conditions were described in our previous article [10]. Briefly, in the μ-PD method, the material to be grown is molten in a small platinum crucible fitted with a pipe-shaped capillary at its bottom. The fiber is obtained by pulling the seed in the downward direction. Several fibers were also pulled by the

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crucibleless laser heated pedestal growth technique (LHPG) [11,12]. In this technique, a $CO_2$ laser beam (10.6 μm) is focused onto the end of a ceramic source rod of the material to be grown. When melting is obtained, a seed (single crystal or sintered rod) of smaller diameter than the source rod is dipped into the molten zone, maintained in equilibrium by interfacial tension forces. The fiber crystal is then withdrawn from the molten zone. The source rod is moved into the laser beam in order to feed the molten zone and keep constant its volume. The ratio of pulling and feeding rates fixes the diameter of the fiber.

The fibers obtained were characterized by differential thermal analysis (DTA), using a Mettler Toledo TGA/SDTA 851$^e$ thermal analyzer working with an air gas flow of 20 $cm^3\ min^{-1}$ and with a heating and cooling rate of 10 °C $min^{-1}$. The samples were wrapped in a thin platinum sheet before being placed in the platinum crucible used to avoid evaporation of volatile components. The measurement accuracy was within 10 °C.

Raman spectroscopy was also used to characterize the crystallinity of BZBO fibers using a micro-spectrometer Horiba-Jobin-Yvon Aramis operating in backscattering geometry with a 785 nm laser excitation wavelength (spot diameter: 1 mm and spectral resolution: 1 $cm^{-1}$). Raman spectroscopy is a useful tool to study the crystallinity of a material because the peak width depends on it: the more the peaks broaden, the more the disorder increases and the crystallinity decreases.

SEM investigations were performed with an environmental microscope Fei Quanta Feg 200 (pressure: 150 Pa, acceleration voltage: 15 kV) fitted with an energy dispersive spectrometer Edax Genesis XM 4i (acceleration voltage: 6 kV, emergence angle: 36°). The analyses were performed without standards.

High temperature X-ray powder diffraction experiments were carried out with a Philips X'Pert Pro diffractometer equipped with an Anton Parr HTK 1200N furnace accessory. The diffractograms were recorded with Cu-Kα radiation, between 10 and 75° in 2-theta and in the temperature range 580 and 670 °C. The heating rate was 5 °C $min^{-1}$ and the temperature was continuously raised with no time out for recording spectra.

## 3. Results and discussion

### 3.1. μ-PD growth with oxygen or nitrogen flow

To verify whether the growth atmosphere did or did not influence the color of the fibers, several growth attempts were made using flowing oxygen and nitrogen. Fig. 1 shows typical fibers obtained with a pulling rate of 4.2 mm $h^{-1}$. It can be seen that

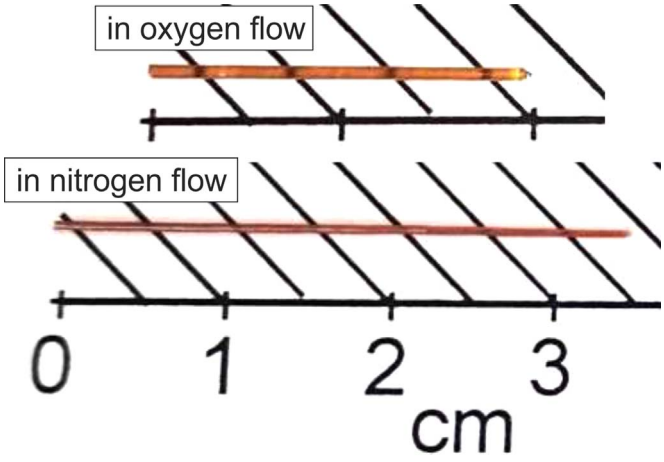


**Fig. 1.** BZBO fibers grown by μ-PD (a) in oxygen flowing, (b) in nitrogen flowing.

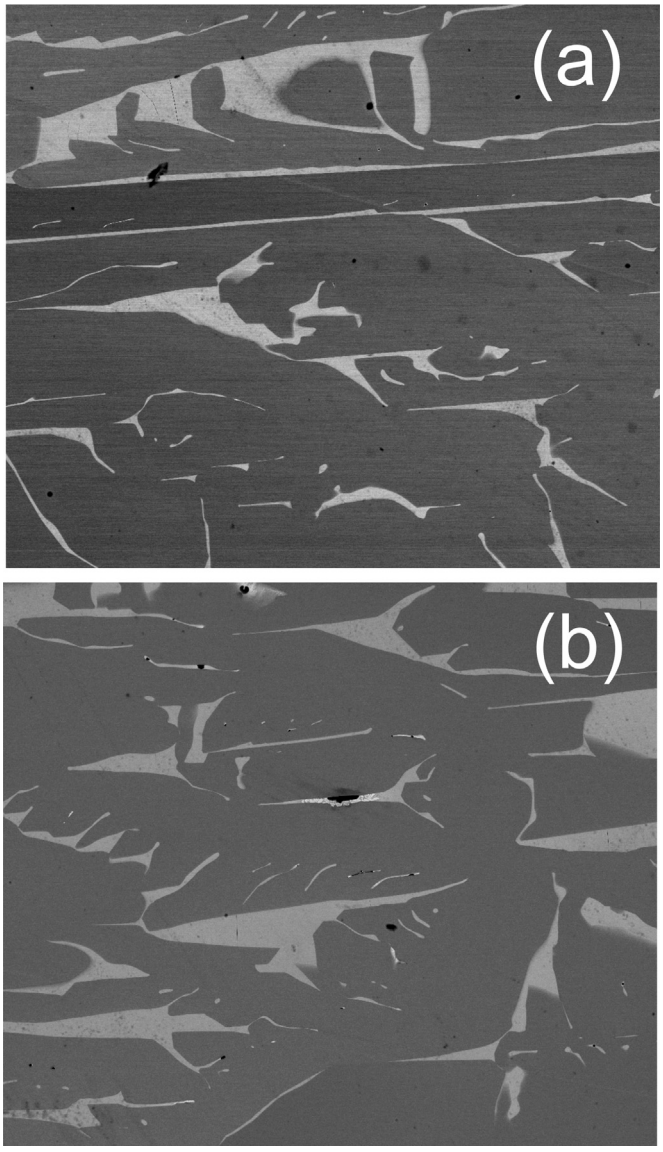


**Fig. 2.** SEM images of BZBO fibers grown by μ-PD (a) in oxygen flowing, (b) in nitrogen flowing. The clear zones correspond to a disordered structure according to Ref. [10].

whichever was used atmosphere, the crystals were always colored and had the same microstructure as fibers previously obtained in an air atmosphere [10]. It was found that the clearest zones were more concentrated in bismuth than boron compared with the darker ones, as shown by EDS microprobe (Fig. 2).

### 3.2. LHPG experiments

To confirm or invalidate the existence of a reaction between BZBO melt and platinum crucible, fiber growth was attempted by LHPG. The first trials were performed with a pulling speed of 60 and 120 mm $h^{-1}$ and a feeding speed of 45 mm $h^{-1}$ or higher. A multiphase seed grown by μ-PD with a diameter of about 600 μm was used. The ceramic feed rods were cut from a sintered pellet of BZBO powder and had a square section with a side between 500 μm and 1.2 mm. In all cases, the crystals rapidly separated from the feed rod due to the fact that the required shape stability condition was not satisfied [12]. Only little boules of about three millimeters long could be obtained. However, they were transparent and colorless (Fig. 3(a)). The Raman spectrum in the