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ON THE FEASIBILITY OF GROWING $\text{Ca}_5(\text{BO}_3)_3\text{F}$ FIBER CRYSTALS BY THE MICRO-PULLING DOWN TECHNIQUE USING A LiF-BASED FLUX

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INTRODUCTION

Compact all solid-state lasers emitting in the ultraviolet range are more and more required for numerous applications such as materials processing, micromachining, photolithography, sensors for the detection of gaseous pollutants, or in biology and medicine. In this frame, single crystals allowing the generation of a UV radiation by frequency conversion of an infrared one are promising materials. Crystals of the borate family and especially fluoroborates are good candidates as the new compound $\text{Ca}_5(\text{BO}_3)_3\text{F}$ (CBF) which is chemically stable and not hygroscopic. Bulk single crystals were very recently grown for the first time by a flux method from the CBF-LiF system [1, 2]. The growth of good quality single-crystal fibers could be very advantageous for the miniaturization of devices. In this paper, we shall report on the first growth and characterization of such crystal fibers using the micro-pulling down technique (μ -PD).

EXPERIMENTAL

The CBF phase was prepared by reacting high purity H_3BO_3 , CaF_2 and CaCO_3 according to

the procedure described by Chen et al. [2]. The second annealing step (1000 °C during 48 h) was repeated six times to complete the reaction. The crystal fibers were pulled with our resistivity μ -PD equipment in air atmosphere with growing rates in the range 0.05-0.15 mm.min⁻¹. For these first attempts, 10x5x3 mm³ Pt crucibles with a 1.5-2 mm in length and 0.7 mm of internal diameter capillary nozzle were used. The obtained crystals were characterized by optical microscopy (Leica DM 4000 M), Raman spectroscopy (Labram Aramis Jobin-Yvon) and SEM microscopy (FEI Quanta FEG 200 fitted with EDAX Genesis XM 4i).

RESULTS

Several fibers between 10 and 40 mm were pulled with a c-axis oriented CBF seed from a flux of composition: 70% CBF, 22.5% LiF and 7.5% B_2O_3 . B_2O_3 was used to slow down LiF volatilization. Fig. 1 gives an example of a pulled fiber. As the pulling rate increased, we observed that the fiber diameter strongly diminished and became irregular. Fibers with a practically constant diameter were only

obtained for pulling rates lower than $0.075 \text{ mm}\cdot\text{min}^{-1}$.

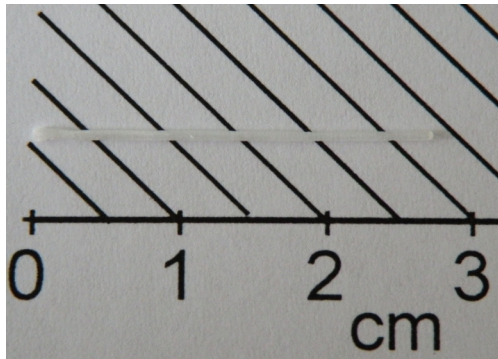


Fig. 1 – Typical CBF crystal fiber

After embedding in epoxy resin and polishing, the fibers revealed, under the optical microscope, a strong translucency caused by the presence of empty spaces: holes and channels mainly parallel to the growth axis as shown by Fig. 2:

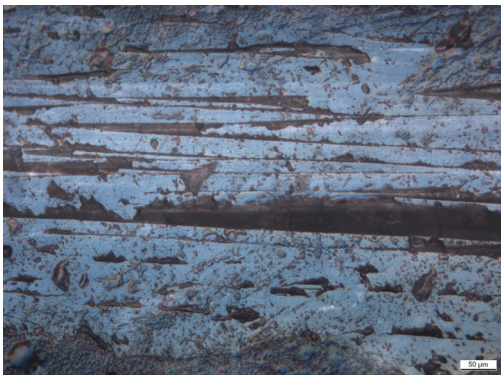


Fig. 2 – CBF fiber internal microstructure

These channels weakened the crystal during polishing causing cracks:

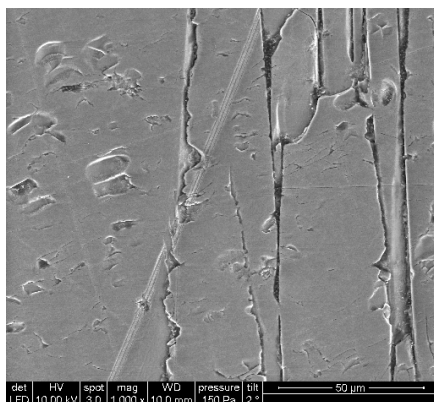


Fig. 3 – Internal morphology of a CBF fiber observed by SEM

However, the fibers appeared to be compositionally homogeneous as shown by EPMA :

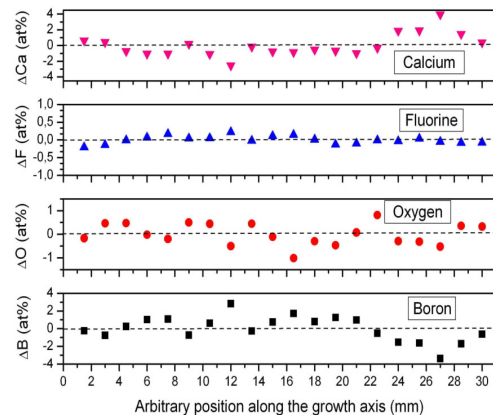


Fig. 4 – Chemical analysis of CBF fibers

It is known that borate melts are very viscous and it can be assumed that the internal microstructure as well as diameter reduction and irregularities observed at the higher pulling rates are due to a bad flow of the melt into the capillary. To ascertain this hypothesis, a growth with a larger hole (1.3 mm) was attempted and led to a small and much more transparent CBF crystal.

CONCLUSION

For the first time, CBF crystal fibers have been pulled by μ -PD. They were shown to be regular and compositionally homogeneous but not transparent. This drawback could be overcome by using a larger hole in the bottom of crucibles.

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