GROWTH AND CHARACTERIZATION OF LiYF₄: Er⁺³ FIBERS

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Abstract. The growth of single crystal fibers of LiYF₄ (YLF) doped with Er⁺³ was studied through the resistive micro-pulling-down (µ-PD) technique. The growth chamber was modified to achieve vacuum of approximately 10⁻⁷ torr. Single crystal fibers of YLF: Er (1, 10 and 20 mol %), with 0.7 mm of diameter and up to 120 mm of length were grown. The use of a static atmosphere was found to be inappropriate for elimination of spurious contamination from growth environment for this experimental setup.

1. Introduction

Laser systems are attractive tools for many applications, as for example environmental monitoring, medicine, industry and basic research. Hence, laser action in solid state systems has been investigated using a wide variety of materials in different conditions and new laser systems are under continuous development as a consequence of the demand created by new applications. The need of compact laser sources led, for example, to the investigation of laser crystals in the fiber geometry. The light-guiding properties of fibers can be combined with the conversion properties of bulk single-crystals as active laser media [1]. Moreover, the fiber geometry improves the output power on these systems because it removes heat efficiently due to the short distance between the pumping region and environment [2].

Yttrium lithium fluoride crystals (LiYF₄ or YLF) doped with rare earth elements present laser emission in a wide wavelength range. This fluoride material is a well-known laser host in the shape of bulk crystals. Nevertheless, there are not many reports about its growth as fibers, particularly when doped with Er⁺³. Undoped and Nd⁺³ doped YLF fibers were grown by Santo et al. [1, 3] from a composition slightly enriched with LiF. A peritectic transient preceding the growth of the crystalline YLF: Nd was reported.

In this work we report the preparation and characterization of YLF-doped Er⁺³ fibers grown by the micro-pulling down technique [2]. YLF:Er fibers were obtained without the formation of an initial peritectic transient.

2. Experimental procedure

Starting compounds (YF₃, ErF₃) were obtained through hydrofluorination of commercial oxides [4]. The LiF compound was pre-purified through the zone melting process. Pure YLF single crystals also obtained through zone melting were used as starting material. The Er-doped YLF was prepared

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through melting of the components under protective reactive atmosphere (HF). Five mol percent of LiF excess was used in the initial charge, since previous works have shown that the best results to the growth of YLF fibers, in a micro-pulling down system, were achieved when such LiF excess was introduced [1].

Previously to the growth process, the quartz growth chamber was first heated under vacuum of $10^{-3}$ torr and back-filled with ultra-pure argon. Subsequently, the chamber was evacuated up to a pressure of $10^{-7}$ torr, which was sustained for at least 24 hours and was back-filled with a mixed atmosphere of CF$_4$ plus Ar for the fiber growth. The growth experiments were performed under a static atmosphere of this mixture in a modified commercial micro-pulling down system, in resistive mode. Platinum handmade crucibles were used; the method to fabricate the crucible was adapted in order to achieve reproducibility [5].

The fibers were analyzed through an Infinity video-microscope of inspection; model InfiniVar CFM-2TM, for evaluation of macroscopic defects and segregation. Micro-X-ray Fluorescence Spectrometry (micro-EDX) was carried out by Shimadzu spectrometer, model micro-EDX-1300, using a Si(Li) detector operated at 50kV and 50µA. The measurements were performed with a scan rate of 100s per point (live time) using an incident beam diameter of 50µm, to determine the dopant distribution. In the micro-EDX technique the Li and F quantities are not measurable; therefore the values of these ions were fixed according to the stoichiometric parameters.

Diffraction patterns were obtained, by pulverizing the single crystals fibers. The measurements were performed on a powder X-ray diffractometer Bruker-AXS, model-D8, at room temperature, in a 2$\theta$ interval ranging from 20 to 80 degrees in steps of 0.05 degree. An Scanning Electron Microscope (SEM) with incorporated Energy Dispersive X-ray (EDS), OXFORD model LEO 440, was used to determine the formation of defects and to investigate the chemical composition of the fibers. The visible and the infrared absorption spectra were collected in a Cary 17D-Olis modified spectrometer and in a Thermo-Nicholet – 6750 FTIR spectrometer, respectively, to verify the incorporation of Er$^{3+}$ and the eventual occurrence of water contamination.

3. Results and discussion

The single crystal fibers were grown with lengths of up to 120mm, and with large transparent regions of constant diameters ($\sim0.7$mm). Erbium doped YLF: fibers with 1, 10 and 20 mol% concentration are presented in figure 1.

An uniform YLF phase was directly crystallized at the seeding process, differently from previous works where a peritetic transient preceding the growth of pure and doped crystalline YLF was reported [1, 3]. In the previous works the fibers were grown under gas flux and on the present one the growth was done under a static atmosphere after a high vacuum treatment.

![Figure 1. Optical characterization LiYF$_4$: Er$^{3+}$ fibers with concentrations of 1, 10 and 20 mol%.

Pastor et al. [6] reported that YLF crystals present congruent melting behavior in highly pure atmosphere conditions. The above results indicate that the high vacuum treatment preceding the growth was probably more effective than the gas flux treatment to eliminate spurious impurities and consequently the initial peritetic transient.
A single phase identified as YLF: Er was observed in the X-ray power diffractogram showed on figure 2. The micrographs obtained through SEM substantiated the existence of only one phase (figure 3). Nonetheless, micro-inclusions (P1) were observed within some of the fibers, as well as an external thin superficial layer (P3).

![Figure 2. X-ray powder diffractogram of LiYF$_4$: Er$^{3+}$ 10mol% fiber.](image)

It is important to mention that by reason of a mechanical problem in the pulling system used, which resulted in significant diameter variations in a few of the fibers, adjustments of some of the growth conditions were occasionally required, such as temperature gradient and pulling rate. In a few cases the apparatus misalignment problem resulted also in oxygen contamination because of bellows connections detachment. Although oxygen presence was detected though SEM/EDS, it was not possible to determine the exact concentrations of this impurity. The radial Erbium incorporation was found to be almost constant (Table 1).

![Figure 3. Micrographs of LiYF$_4$ Er$^{3+}$ 10mol% and the measure points of EDS](image)
Table 1. Concentrations of Er$^{3+}$ in the following points of interest: P1 (micro-inclusion), P2 (center of the fiber), P3 (superficial layer) determined by EDS on SEM measurements.

| Element | P1 (inclusion) | P2 (center) | P3 (surface) |
|---------|----------------|-------------|--------------|
| Er      | 13.5 % molar   | 13.5 % molar| 12.9 % molar |
| O       | detected       | not detected| detected     |

Erbium incorporation along the fibers was determined through micro-EDX to be approximately constant (figure 4). Measured concentrations were close to the nominal values of the starting materials with 1 and 20 mol% of Er. Nonetheless, a higher concentration (11 mol% of Er$^{3+}$) was found in the sample corresponding to the nominal concentration of 10 mol%.

The dopant fluctuation observed in these micro-EDX measurements can be attributed to experimental error or to small diameter variations at some stage in the pulling process. Small mechanical instabilities during fibers pulling may result in unstable solid-liquid interfaces. The growth process of the 20mol% Er fiber was particularly mechanically disturbed, and consequently resulted in the sharpest oscillations. The growth process may be further disturbed by crucible imperfections, which may have also contributed to the dopant fluctuation observed. Nevertheless, only 5mm samples are necessary for the laser action tests and spectroscopic characterization, therefore uniform dopant samples could be selected from the grown fibers.

Figure 4. Distribution of Er$^{3+}$ in LiYF$_4$ fibers measured by micro-EDX technique.
The characteristic absorption bands of Er\(^{3+}\) were observed in the measured visible absorption spectrum (figure 3a and 3b). A broad absorption band in 3000-3600cm\(^{-1}\) region was observed (figure 3c) in the IR, which can be associated to OH\(^-\) incorporation resulting from moisture and oxygen contamination during the growth process [7].

![Figure 5](image)

**Figure 5.** Visible and infrared absorption spectra of LiYF\(_4\): Er\(^{3+}\) 10mol%

### 4. Conclusion
The micro-pulling down method was determined to be suitable to grow transparent LiYF\(_4\): Er\(^{3+}\) fibers. The high vacuum treatment preceding the growth process was able to eliminate the peritectic transient, though the static atmosphere did not prevent oxygen contamination caused by mechanical problems. Additional studies are underway to eliminate mechanical instabilities observed in our system which resulted in fluctuations of the dopant concentration along the fibers.

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