



## Growth of $\text{LiYF}_4$ single-crystalline fibres by micro-pulling-down technique

A.M.E. Santo<sup>a</sup>, I.M. Ranieri<sup>a</sup>, G.E.S. Brito<sup>b</sup>, B.M. Epelbaum<sup>c</sup>, S.P. Morato<sup>d</sup>,  
N.D. Vieira Jr.<sup>a</sup>, S.L. Baldochi<sup>a,\*</sup>

<sup>a</sup>*Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP (CLA), Av. Prof. Lineu Prestes 2242, CEP 05508-900, São Paulo, SP, Brazil*

<sup>b</sup>*Instituto de Física, USP, CP 66318, 05315-970 São Paulo, SP, Brazil*

<sup>c</sup>*Department of Materials Science, University of Erlangen-Nurnberg, D-91058 Erlangen, Germany*

<sup>d</sup>*LaserTools Tecnologia Ltda., 05379-130 São Paulo, SP, Brazil*

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### Abstract

Pure yttrium–lithium tetrafluoride (YLF) fibres have been successfully grown by the micro-pulling-down ( $\mu$ -PD) technique in resistive mode. The influence of the growth atmosphere and starting melt composition on growth process were studied. YLF fibres grown from Li-rich melt (5 mol%) contain more than 70% of colourless, transparent and single-phase material. After a short length of the peritectic transient ( $\approx 10$  mm), the fibres were uniform in diameter (800  $\mu\text{m}$ ) and quite long ( $\approx 60$  mm). This work reports a suitable and reproducible growth process for high-quality YLF single-crystalline fibres.

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### 1. Introduction

Since the 1960s, research and development efforts on optical fibres have driven the commercialization of a variety of optical devices due to

their well-adapted as-grown shape. Over the last years, there has been an increasing interest on single-crystal fibres. This kind of material shows special properties such as impact and thermal shock resistance and high yield strength, for the production of low-cost and low-loss optical and electronic devices. For laser applications, the light-guiding properties of fibres can be combined with

\*Corresponding author. Fax: +55 11 38169315.

E-mail addresses: [amesanto@ipen.br](mailto:amesanto@ipen.br) (A.M.E. Santo), [baldochi@ipen.br](mailto:baldochi@ipen.br) (S.L. Baldochi).

the conversion properties of bulk single-crystals as active laser media [1]. Moreover, the fibre geometry improves the output power because it removes heat efficiently and is very interesting to the development of compact laser systems. For instance, to observe laser action in a neodymium doped fibre of yttrium lithium tetrafluoride (YLF), it needs dimensions of about 5 mm in length and 300  $\mu\text{m}$  in diameter, depending of the dopant concentration and cross-section.

The two most common methods for single-crystal fibre growth from the melt are: laser heated pedestal growth (LHPG) [2] and the micro-pulling-down ( $\mu$ -PD) [3] techniques. Due to the absence of a crucible and the use of a  $\text{CO}_2$  laser for melting, the LHPG method is especially useful for high melting point materials having a good absorption at 10.6  $\mu\text{m}$ . Otherwise, stable growth regimes over long lengths, ensuing constant diameter fibres, can be obtained more easily by the  $\mu$ -PD method. This fibre growth method is favoured by the stability of the meniscus, which helps in maintaining a stable growth condition and leads to uniform composition distribution and constant diameters from 10  $\mu\text{m}$  to several millimeters [4] along the fibre.

Both methods have been used for the growth of several materials, such as eutectics, semiconductors and oxide single crystals. However, the growth of complex fluoride fibres has not received much attention. Using the LHPG technique, Shaw and Chang [5] found problems related to feed material purity in the rod and to difficulties controlling the growth atmosphere. Recently, the growth of fluoride-based single crystal fibres by the  $\mu$ -PD technique was reported [6,7]. To the authors knowledge there have been no previous studies related to the growth of complex fluoride fibres by the  $\mu$ -PD method. In the current paper, the growth and characterization of uniform diameter YLF single-crystalline fibres by the  $\mu$ -PD method is reported.

## 2. Material preparation

The base fluoride  $\text{YF}_3$  was prepared by hydro-fluorination of commercial  $\text{Y}_2\text{O}_3$  (Aldrich

99.99%), and the LiF powder (Aldrich 99.9%) was previously purified by zone-refining technique under a reactive atmosphere [8]. The YLF compound was prepared from a mixture of  $\text{YF}_3$  and LiF in a non-stoichiometric composition, melted in platinum crucibles under mixed a gas flow composed of HF and argon. Subsequently, the synthesized material was placed in graphite crucibles and purified by the zone-refining technique in a single-pass, also under the same reactive mixed flow [9]. The purified and stoichiometric single-phase part of the YLF ingot was chosen as starting material for the fibre growth by the  $\mu$ -PD method.

The modification of a commercial system to the preparation of fluoride single-crystalline fibres was accomplished during the previous study of lithium fluoride fibres growth [6]. The material was placed in a directly heated platinum crucible, known as resistive mode  $\mu$ -PD method. The crucibles were hand-made in our laboratory in an appropriate shape and dimensions. A quartz chamber encloses the heating part allowing operation under inert gas flow, but this unique operation is not effective enough to avoid typical fluoride moisture contamination. Therefore, a vacuum system was specially connected to the pulling system in order to evacuate the chamber prior to introducing the gas flow, keeping the heating part and the mechanical pulling system during the growth tightly closed. In earliest experiments, a strong deviation from the initial melt composition was observed due to the evaporation of lithium fluoride, since it has a higher vapour pressure than  $\text{YF}_3$  at the melting temperature. The large exposed surface area of the liquid in the crucible also enhances this effect.

Before growth, the quartz chamber was first heated to 80  $^\circ\text{C}$  under a vacuum of  $10^{-3}$  Torr for approximately 12 h and then back-filled with ultra-pure argon previously dried in molecular sieve traps. Afterwards, the chamber was evacuated for 30 min and back-filled again with the gas. This last step, the chamber cleaning, was repeated at least three times before the growth.

### 3. Results and discussion

#### 3.1. Influence of the growth atmosphere

During the first experiments to pull YLF fibres using only a pre-purified argon atmosphere, we observed melt migration to the crucible borders and a change in melt from transparent to opaque liquid. Actually, the first phenomenon is observed at the beginning of the melting process. The melt goes down through the capillary covering both capillary and crucible outer walls. This effect made the seeding process and meniscus anchoring very difficult, conditions that are essential for a stable fibre growth regime [10]. The second phenomenon occurs more slowly, after the material is completely melted. A hydrolysis reaction due to moisture contamination in the growth atmosphere can be pointed out as a possible cause [11].

In order to reduce wetting effects, the balance of the interfacial tensions must be considered. There are actually only two possibilities: to change the ambient gas or the crucible material. Since platinum is the only readily available material for our purposes, we have investigated the influence of gas composition on wetting effects.

Instead of pure argon, the experiments were performed under a mixed gas flow of argon and carbon tetrafluoride ( $\text{CF}_4$ ). This composition led to a slight reduction of the capillarity and wetting effects, which proved to be sufficient to allow the meniscus anchoring and made the seeding possible. Furthermore, a considerable reduction of oxifluoride formation by hydrolysis was observed. The melt kept under this atmosphere was completely colourless and transparent. The  $\text{CF}_4$  gas acts as an efficient fluorinating agent to eliminate moisture contamination in the growth chamber. Previous studies of the melting process in the  $\text{YF}_3$ –LiF system showed that congruent melting occurs when oxygen and water vapour are rigorously excluded from the preparative environment [12,13].

#### 3.2. Influence of composition

Small pieces of LiF crystals were added to the stoichiometric YLF crystals in order to control the

starting composition. Previous work had shown that the initial composition for YLF growth from the melt could be close to the stoichiometric composition if moisture contaminants are eliminated. It has been found that it is possible to grow YLF crystals by the Czochralski technique from an initial molar composition of 50.5% LiF:49.5%  $\text{YF}_3$  [14]. Usually, the composition of 52mol% LiF:48mol%  $\text{YF}_3$  [15] is used because of slight incongruency resulting from residual moisture contamination. We have tested two compositions: one initial LiF: $\text{YF}_3$  mixture of 52.4 mol%:47.6 mol%, corresponding to a YLF melt with 10 mol% of excess of LiF and another initial LiF: $\text{YF}_3$  mixture of 51.2 mol%:48.8 mol%, corresponding to an excess of LiF of 5 mol% in the YLF melt.

The mixture was placed in platinum crucibles and melted under argon plus  $\text{CF}_4$  mixed flow of  $0.21 \text{ min}^{-1}$ . The fibres were pulled down at a constant rate of  $0.75 \text{ mm min}^{-1}$  from a platinum capillary with inner diameter of 0.8 mm. The first seeding was done by touching a platinum wire of 1 mm diameter to the liquid in the capillary. Afterwards, an oriented piece of the grown fibre was used as a seed for further growth experiments. Using this procedure, the starting YLF melt with 10 mol% excess of LiF resulted in a fibre with variable composition. Fig. 1 shows a sequence of photomicrographs of different regions along the grown YLF fibre. Initially, a translucent region was crystallized (Fig. 1(a)). In sequence, a transient region is observed, followed by the transparent stoichiometric phase YLF (Fig. 1(b)). This region is attributed to the peritectic reaction. The total length of the initial transient region was approximately 30 mm. The stoichiometric phase, 25 mm in length, was homogeneous and regular in diameter. The existence of longitudinal growth ridges along this region must be pointed out (Fig. 1(c)). These lines, in general, are observed in perfectly oriented YLF single-crystals grown by the Czochralski technique. At the end of the pulling process, the fibre was opaque (Fig. 1(d)). From this point, the solidified fibre corresponded to the eutectic mixture.

In order to identify the different phases along the fibre, X-ray powder diffractometry (XRD) and

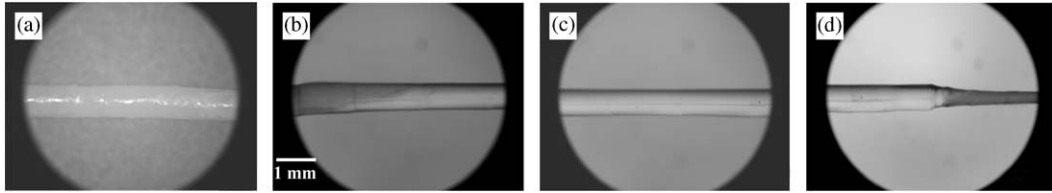


Fig. 1. Optical micrographs of different regions along the YLF fibre grown from a melt with 10 mol% of LiF excess.

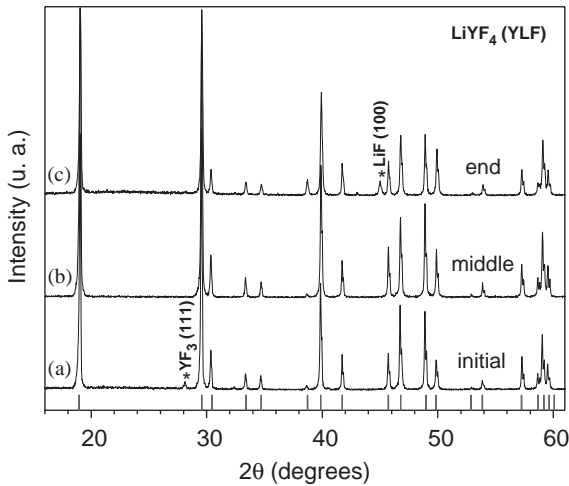


Fig. 2. X-ray powder diffractograms of the YLF fibre.

scanning electron microscopy (SEM) were carried out on the samples in the initial, middle and final regions, corresponding to diffractograms (a), (b) and (c) of Fig. 2, respectively. For SEM characterization, the samples were sectioned along the fibre and embedded in resin. The cross-section surfaces of the samples were polished flat and parallel using  $\text{Al}_2\text{O}_3$  suspension in ethanol, followed by graphite film deposition in order to assure electrical conductivity.

Comparing the diffractograms obtained, the main phase, YLF, was found in all samples. In the diffractogram of the initial region, Fig. 2(a), only one additional peak is observed, identified as the strongest line of the  $\text{YF}_3$  phase. This phase can be seen in the corresponding SEM micrograph (Fig. 3(a)), as white plates corresponding to yttrium-based precipitates in the YLF

matrix. This region corresponds to the peritectic transient.

All the peaks observed in the diffractogram of the stoichiometric phase (Fig. 2(b)), belong to the YLF compound, also evidenced by the large homogeneous region in the micrograph shown in Fig. 3(b). This region corresponds to the single-phase YLF. As the fibre pulling process evolves, the melt composition becomes enriched in LiF, following the well-known phase diagram of the  $\text{LiF}-\text{YF}_3$  system [16]. The presence of the additional LiF phase, identified in the diffractogram shown in Fig. 2(c) (final region), is expected since the LiF was added in excess. This is confirmed by the observation of the microstructure in this region (Fig. 3(c)). At the end of the solidification, regular eutectic microstructures, composed of LiF (dark region) and YLF (light grey region), are embedded in the major YLF primary phase.

The starting YLF melt with 5 mol% excess of LiF, resulted in a fibre with relatively short peritectic transient (10 mm) and long stoichiometric single-phase YLF (60 mm). The fibre is shown in Fig. 4. Once again, the growth ridges can be clearly observed as well as the smoothly square morphological shape of the grown fibre. The crystal quality and the growth direction were verified by a Laue diagram. The Laue diagram was made using Mo radiation (20 mA, 40 kV) in the backscattering mode and recorded on an image plate (100 mm  $\times$  86 mm) with imaging distance of 30 mm from the crystal. The exposure time was 30 min. The picture was taken with the cleavage plane perpendicular to the incident beam and it is shown in Fig. 5(a). The image was treated using OrientExpress 3.3 software [17]. The simulation shows that the cleavage plan is the (013), as displayed in the inset of Fig. 5(b), and the

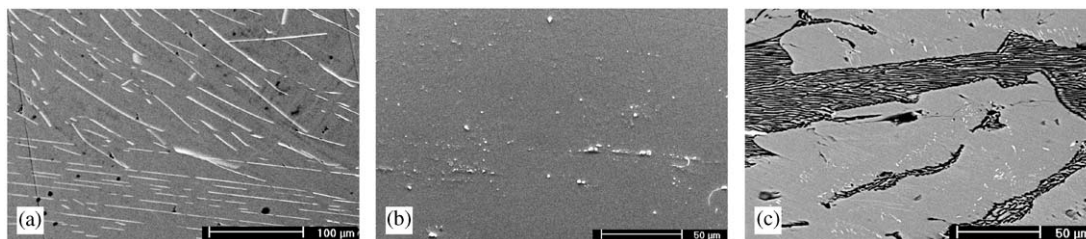


Fig. 3. Scanning electron micrographs of the YLF fibre. The scale bars are: (a) 100 µm, (b) 50 µm and (c) 50 µm.

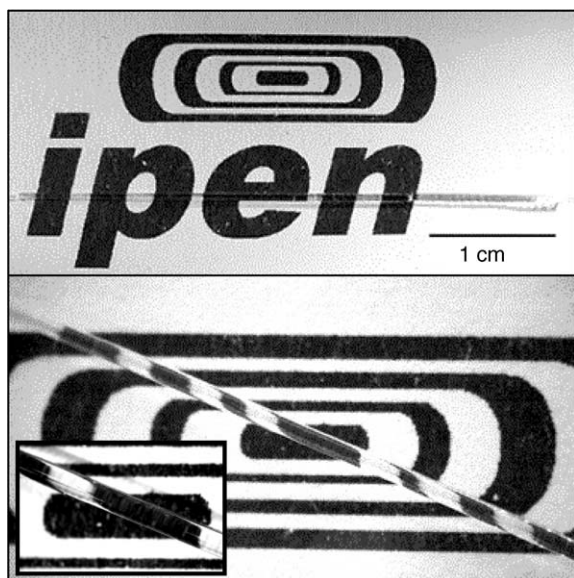


Fig. 4. Photograph of the YLF fibre grown from a melt with 5 mol% of LiF excess.

measured angle between cleavage plane and the growth direction is  $35^\circ$ , according to the angle formed between (0 1 3) plane and [0 0 1] direction.

#### 4. Conclusions

Homogeneous, transparent, colourless and constant diameter  $\text{LiYF}_4$  single-crystalline fibres were obtained by the resistive micro-pulling-down technique. These fibres are between 0.7 and 0.8 mm in diameter and up to 60 mm in total length showing good quality.

It was found that the growth chamber must be carefully treated before the growth process. The growth atmosphere plays an important role in the chemical stability and melting behaviour of the material. The use of a mixed flow of  $\text{CF}_4$  and argon did not completely suppress the melt migration to the capillary and crucible outer walls. However, this atmosphere changed the balance of the interfacial surface tension so that it made the seeding process and meniscus anchoring on the capillary tip possible. Moreover, the use of  $\text{CF}_4$  as active gaseous atmosphere for fluorinating YLF melt was proven effective to reduce moisture contamination by hydrolysis.

The best results were observed for the starting YLF melt with 5 mol% excess of LiF, resulting in a fibre with relatively short peritectic transient (10 mm) and long stoichiometric phase YLF (60 mm). The starting composition determines the phase distribution along the fibre, as well as the yield of the pulled YLF phase. The fibre exhibits good crystal quality and the fibre was grown towards the  $c$ -axis, as shown in the Laue picture.

Comparing the present technique with the Czochralski technique, in which the pulling rate is much lower than that usually used for the  $\mu$ -PD technique, the obtained results are very promising. The crystal growth by the  $\mu$ -PD method is faster and cheaper, and it is shown here to be appropriate for the preparation of fluoride single-crystalline fibres for optical applications. The growth process is stable and highly reproducible. Preliminary experiments show that the methodology developed here to pull undoped YLF fibres can be reproduced for the growth of rare-earth doped YLF single-crystalline fibres.

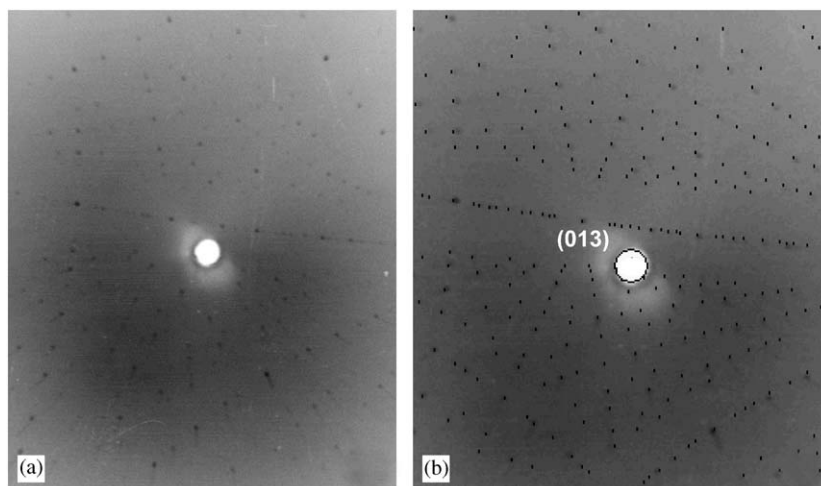


Fig. 5. Back-reflexion Laue diffractograph of the YLF fibre taken on the cleavage surface of the fibre: (a) Laue picture and (b) simulation and orientation.

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