Journal of Crystal Growth 317 (2011) 4–7

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Synthesis and growth of materials for solid state lasers: Nd:YLF and Nd:LLW single crystal fibers ☆

S.L. Baldochi [a,*], F.R. Silva [a], J.R. de Moraes [a], J. Jakutis [a], N.U. Wetter [a], A.M.E. Santo [b]

[a] Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Av.Prof. Lineu Prestes, 2242, CEP 05508-000, São Paulo, SP, Brazil
[b] Vale do Paraíba University, UNIVAP, Av. Shishima Hifumi, 2911, CEP 12244-000 São José dos Campos, SP, Brazil

ARTICLE INFO

Presented at the Romanian Conference on Advanced Materials—ROCAM 2009, August 25–28, 2009, Brasov, Romania
Available online 18 November 2010

Keywords:
A2. Micro pulling-down fiber growth
B1. Fluorides
B1. Tungstates
B3. Solid state lasers

ABSTRACT

Despite new developments for compact laser devices, the neodymium ion (Nd^{3+}), continues to be the most widely used active laser ion. In this article, the growth of Nd:$LiYF_4$ (Nd:YLF) and Nd:$LiLa(WO_4)_2$ (Nd:LLW) single crystal fibers growth is reported considering their use as laser media. Homogeneous and good optical quality single crystals fibers of both materials were obtained. Additionally, structural and optical characterizations were performed on Nd:LLW single fibers. The dependence of the atmosphere on Nd:YLF fibers growth were also studied. Dopant distribution was measured along the fibers. Loss and gain tests were performed on the fluoride single crystal fiber to prove that laser action is achievable.

1. Introduction

Since the discovery of the laser, there has been a concerted effort to develop solid-state media. Classical laser materials consist of an active medium, a glass or a bulk crystalline host, to which a dopant is added. Although high perfection bulk crystals are still important for lasers and other applications, in addition to studies to improve their quality, research on single crystal fibers is developing continuously in view of the increasing demand of compact devices [1]. Laser devices benefit by using laser fibers first in reason of their faster and lower cost preparation (compared to bulk crystal growth techniques). In addition to, single crystal fiber lasers hold the premise of combining the advantages of bulk crystals (high emission cross sections and good thermal conductivity [2]) and fiber lasers (capability of maintaining high pump intensities over relatively long distances, good beam quality and good thermal management).

Several works on single crystal fiber growth were done for oxide crystals in recent years, improving considerably their optical and structure quality for laser applications. Recent works showed efficient laser action with Nd:YAG [3,4] single crystal fibers. However, fluorides and double tungstates single crystal laser fibers have not often been investigated when compared to other compounds.

The $Li(RE)(WO_4)_2$ compounds are among the recently studied crystals from the rare earth (Re) double tungstate family materials. Klevtsov and Kozeeva [5] and Klevtsova et al. [6] reported the preparation and structural studies of rare earth and yttrium lithium tungstate crystals. The $LiLa(WO_4)_2$ (LLW) crystals have a relatively low melting point (1065 °C), melt congruently and Nd-doped LLW bulk crystals can be grown by the Czochralski (CZ) method. A study of the crystals' spectroscopic characteristics showed them to be potential solid-state laser crystals [7,8]. To our knowledge there is only one report about the single crystal fiber growth of rare earth double tungstate crystals. Terada et al. [9] reported the preparation of pure and Nd-doped $NaGd(WO_4)_2$ (Nd:NGW) single fibers by the micro-pulling down (μ-PD) technique, but not Nd:LLW.

The crystal quality of Nd^{3+}-doped $LiYF_4$ (Nd:YLF) has been improved reasonably over the last 40 years, and this laser host of high quality is commercially available, as laser rods or bulk crystals. For optical applications, rare earth doped-YLF is usually grown by the CZ method [10,11]. A small excess of LiF is frequently used in CZ crystal growth to compensate the evaporation of this component during the process and to overcome any variation of composition due to some residual moisture contamination.

Growth by the μ-PD method of pure YLF and Nd and Er-doped YLF single crystal fibers was first reported by our group [12,13]. It was noted that the growth atmosphere plays an important role in the chemical stability and melting behavior of YLF single fibers. Additionally, the growth atmosphere considerably influences the capillarity and wetting effects in YLF single crystal fibers growth. A mixed CF_4 and Ar flow was essential for the reduction of oxifluoride formation and for obtaining an appropriate meniscus anchoring for controlled seeding. In these fiber growth experiments, melts with different starting compositions were tested. Moisture contamination and some other complications were avoided by careful cleaning the growth chamber under vacuum (10^{-3} Torr), and replenishing with the inert gas. For YLF single

☆ Presented at the Romanian Conference on Advanced Materials – *ROCAM 2009*, August 25–28, 2009, Brasov, Romania.

* Corresponding author. Tel.:+55 11 3133 9355; fax: +55 11 3133 9374.
E-mail address: baldochi@ipen.br (S.L. Baldochi).

0022-0248/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2010.11.026

fibers growth, LiF in excess was needed. The same methodology was applied to pull Nd:YLF single-crystalline fibers with nominal concentrations of 1.7 mol% [14] with similar results.

In this work, we studied the synthesis and growth process of two crystal fibers for use as laser media: Nd:YLF and Nd:LLW. These materials were chosen because of their good laser properties, already demonstrated in bulk crystals and for their low melting point and possibility of doping with several rare earth ions, for studies at different wavelengths.

2. Experimental description

2.1. Fiber growth

YF_3 and NdF_3 were obtained through hydrofluorination of commercial oxides [15]. The LiF compound was pre-purified through a zone melting process [16]. The Nd-doped YLF was prepared by melting the three components under a reactive atmosphere (HF) and used as a starting material for the growth of the fibers. Five mol percent LiF in excess was used at start in the growth charge. The nominal Nd concentrations in two experiments were 0.5 and 1.5 mol%.

The starting materials for the Nd:LLW fiber growth experiments were synthesized through solid state reactions under an air atmosphere. The initial analytical grade chemicals, La_2O_3, Nd_2O_3, WO_3 and Li_2CO_3, were mixed in the appropriate molar ratios to obtain a $LiLa_{0.99}Nd_{0.01}(WO_4)_2$ compound. The nominal Nd concentration was 1.0 mol%.

The Nd:YLF fiber growth experiments were performed in a modified commercial resistive μ-PD system with atmosphere control. Before the Nd:YLF growth process, the growth chamber was first heated under a vacuum of 10^{-3} Torr and back-filled with ultra-pure argon, following a procedure already described in previous works [12–14]. To improve the purity of the atmosphere, the growth chamber was kept under 10^{-7} Torr vacuum, for 24 h. Instead of using a flow of gas during the growth process, the chamber was back-filled with a mixed atmosphere of CF_4 plus Ar and kept at constant pressure (0.1 Kgf/cm^2). All fluoride growth experiments were performed under a static atmosphere of this mixture. The Nd:LLW experiments were performed in the same system but under an air atmosphere. Platinum (for YLF) or Platinum/Gold (for LLW) handmade crucibles were used; the fibers were pulled down with rates ranging from 0.06 to 0.2 mm min^{-1} from a capillary with an inner diameter of 0.8 mm. The visual control of all experiments was performed with a stereo microscope.

2.2. Materials characterization

The fibers were analyzed and photographed through a video-microscope to evaluate macroscopic defects and segregation. X-ray powder diffraction (XRD) analyses of the materials were carried out with a Rigaku RINT 2000/PC diffractometer. The data were collected at room temperature in the range of 15–80° with a step scan of 0.02°/5 s. All measurements were performed from powders. Micro-X-ray Fluorescence Spectrometry (micro-EDX) was carried out on a Shimadzu spectrometer, model micro-EDX-1300, using a Si(Li) detector operated at 50 kV and 50 μA. Measurements were performed using an incident beam diameter of 50 μm to determine the dopant distribution. Optical absorption spectra were obtained with a Newport spectrometer, model OSM400 VIS-NIR.

Loss and gain tests were performed with a Nd:YLF fiber sample. The two end faces were lightly polished to avoid light scattering; the sample fiber was placed between two plane substrates, and glycerin droplets (index matching fluid) were deposited on the faces, where the fiber touched the substrates. An optical setup was mounted to focus a TEM_{00} laser beam from a Nd:YLF laser (1053 nm) into the fiber. The laser beam was focused into the fiber through a 30 cm focal length lens, which provides a focus with the Raleigh range equal to half the fiber length and guarantees a collimated beam of approximately constant diameter inside the fiber.

3. Results and discussion

3.1. Nd:LLW fiber growth

Homogeneous 1 mol% doped single-crystalline fibers of Nd:LLW (Fig. 1), of 30 mm length and 0.7–0.8 mm diameters were grown. Transparent and good optical quality fibers (without scattering) were obtained with a pulling rate of 0.06 mm/min. Higher pulling rates induced internal defects resulting in opaque fibers. It is interesting to note that this pulling rate is six times higher than the bulk LLW crystal growth by CZ method, quoted in the literature [7].

Careful control of the power supply was required to keep the fiber diameter constant. The occurrence of liquid overheating increased the meniscus height, and consequently, the fiber diameter decreased. This behavior is typical in materials that do not wet the crucible. An analysis of the XRD data of the grown fibers reveals that fiber crystallization occurs in the scheelite-like tetragonal system, as already reported about the bulk crystals [7].

The non-polarized absorption spectrum of a Nd:LLW single crystal fiber in the wavelength range of 400–1000 nm was measured. Fig. 2 shows the 750–850 nm region in detail. As already reported for CZ crystals, the absorption lines occur at wavelengths near 530, 588, 750, 804 and 872 nm, which are due to the *4fn–4fn* transitions of the Nd^{3+} ion. According to the literature data [7,8], a very weak polarization

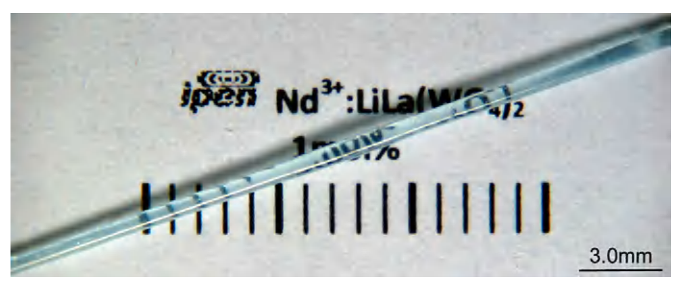

Fig. 1. . As-grown Nd^{3+}:LLW single-crystalline fiber doped with 1 mol%.

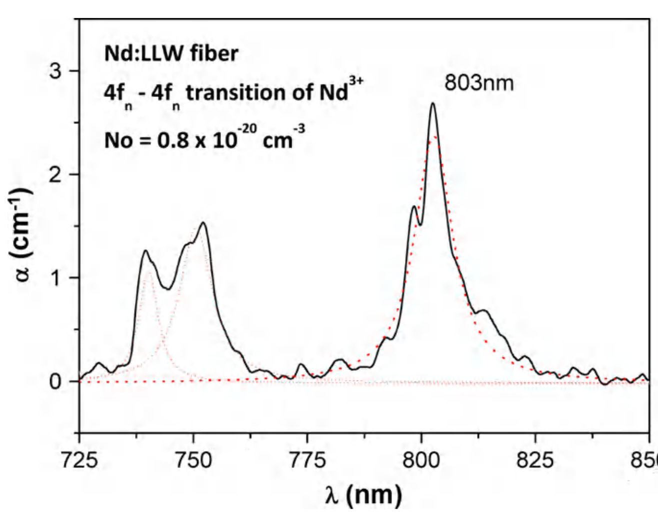

Fig. 2. Non-polarized absorption spectra of Nd:LLW single crystal fiber.

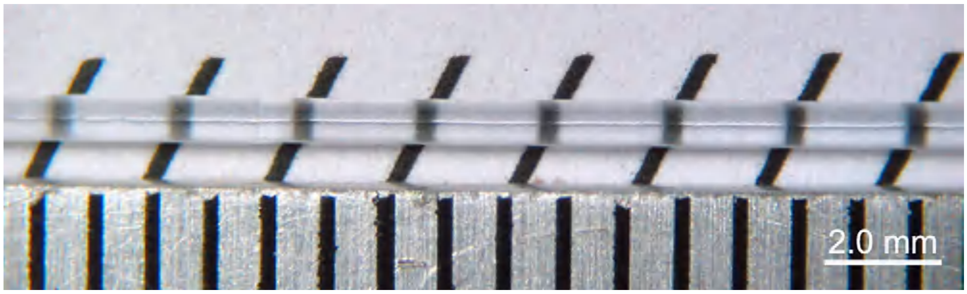

Fig. 3. As-grown single crystal fiber of YLF doped with 1.5 mol% Nd^{3+}.

was observed at the 803 nm wavelength, that is, the absorption band at 803 nm is similar for π- and σ-polarizations. Considering the absorption cross section of 2.9×10^{-20} cm^2 [8], the number density of absorption centers (due to Nd) in the grown fibers was estimated to be 0.8×10^{-20} cm^{-3}. It is important to mention that such a broad absorption band is suitable for the pumping of an AlGaAs diode-laser that emits an output of 808 nm and is not restricted to the temperature stability of the output wavelength of a diode laser.

3.2. Nd:YLF fiber growth

Nd:YLF single crystalline fibers of ~80 mm length and diameters 0.7–0.8 mm (Fig. 3) were grown using the experimental conditions described above. The YLF phase was directly crystallized on the fiber seeding without the formation of the peritetic transient stage, reported in previous works of our group [12,14]. Such diverse behavior may be attributed to modifications in the methodology of Nd:YLF single fiber growth: the additional high vacuum treatment (10^{-7} Torr pressure inside the growth chamber) carried out before the fiber pulling and the use of a static atmosphere instead of a continuous gas flow on the growth process.

As already known [17], moisture and oxygen contaminants can degrade the optical quality of Nd:YLF crystals and affect the melting behavior of this compound, from congruent to non-congruent. Thus, improving the atmosphere purity will ensure a higher reduction of spurious moisture contamination, resulting in a uniform and congruent crystallization of the YLF phase on the fiber-seed. The gas flow introduces temperature oscillations, affecting the species transport in the melt and consequently, the peritectic formation with specific complications. Additional studies of flowing, or static atmosphere influence during the seeding process are needed.

The dopant distributions of Y and Nd along the two Nd:YLF fibers were measured by micro-EDX, while Li and F content in YLF was estimated from stoichiometry. The Nd distributions in fibers of 0.5 mol% concentration in the melt (80 mm long) and two samples of 1.5 mol% concentration in the melt (80 and 30 mm long) are presented on Fig. 4.

The Nd distribution of the doped single crystal fiber was quite uniform, with the segregation coefficient k~0.33, for 0.5 mol% (nominal concentration in the melt). However, at the end of the pulling process (~65 mm), a small increase in the concentration was noticed, showing the segregation of Nd dopant have $k<1$ in the YLF lattice host [18].

Dopant distribution along the 80 mm fiber (fiber #2 in Fig. 4) had a somewhat larger dispersion and the mean value of ~0.65 mol% Nd concentration in fiber (versus 1.5 mol% in the melt) and the segregation coefficient k~0.43.

During the unidirectional growth of a crystal, convection in the liquid phase can be driven by several forces. Buoyancy driven convection is very weak in μ-PD fiber growth due to the small

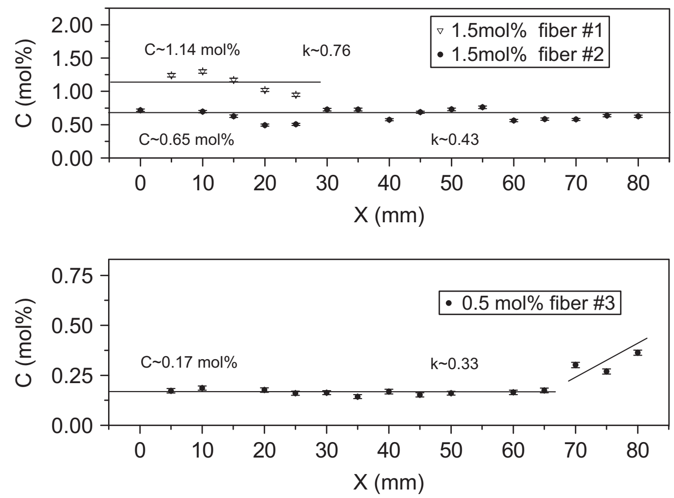

Fig. 4. Nd distribution on different YLF fibers with: (a) 1.5 mol% and (b) 0.5 mol% concentration.

physical dimensions of the system. However, some influence of the thermocapillary, or the Marangoni convection might have an important role [19]. A theoretical analysis (numerical simulation) would be necessary for better understanding this feature, but this is beyond the scope of the present work. Additional studies on this subject are underway.

3.3. Nd:YLF loss and gain tests

A fiber sample with dimensions of 10 mm in length and 0.7 mm in diameter, with an average Nd concentration of 1.0 mol%, was selected from a single crystal fiber grown with a nominal concentration of 1.5 mol% in the melt.

The loss and gain measurements were performed through the setup shown in Fig. 5 [20]. A fiber loss of 1.90% was obtained, and the loss coefficient was calculated to 0.0192 cm^{-1}. To obtain the gain of the fiber, a 40 W diode laser bar (Coherent) and beam shaper optics were used for pumping. The diode laser was thermally tuned to operate at 805 nm. A Nd:YLF laser beam was injected into the fiber through the 30 cm focal length lens, generating a focus of radius 47 μm. At an average power of 8 mW before the fiber, the calculated intensity was 1.6 kW/cm^2.

The saturated gain (g) was calculated by the Beer–Lambert law: $P=P_0\exp(gL)$, where P and P_0 are the output powers measured at the detector position, with and without pumping, respectively, g is the gain coefficient and L is the fiber length. The tested Nd:YLF fiber sample presented a gain coefficient of 0.104 cm^{-1} (gain minus loss) and a gain per pass of 11%. These values also include the intrinsic losses of the fiber. The calculated non-saturated gain was estimated

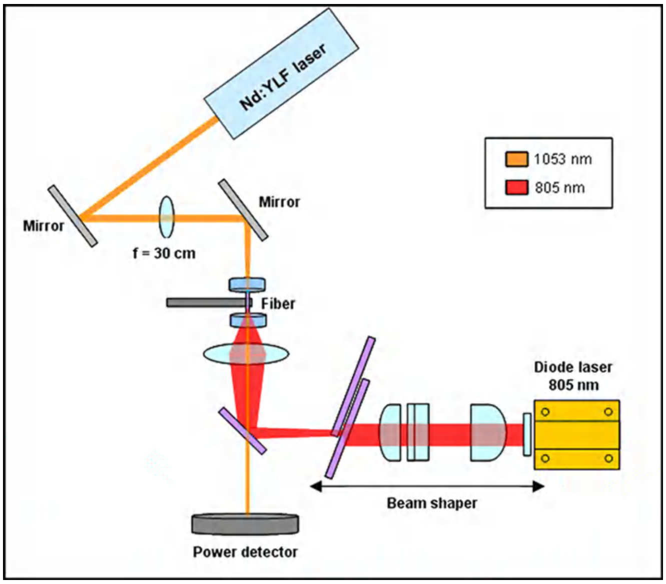

Fig. 5. Longitudinal pump setup [20].

to be 20.9%. This value is much higher than the measured losses of 1.9%, and therefore, laser action was shown to be possible.

The Nd:YLF fiber was butt coupled to the cavity mirrors by index matching fluid and pumped by a beam shaped diode bar emitting at 806 nm. A detailed report on this first Nd:YLF fiber laser was recently published by our group [21].

4. Conclusions

Homogeneous and transparent single crystal fibers of Nd:LLW up to 30 mm long were prepared with appropriate structural and optical quality for laser tests. This media, prepared for the first time in the single crystal fiber shape, may be a good choice for the construction of an efficient and compact laser device, with diode pumping at 808 nm, and emission at 1.06 μm.

In the Nd:YLF single crystal fibers growth experiments, we observed the direct crystallization of the doped-YLF phase on the seeding process, analogous to that which was reported on the CZ growth of this fluoride [18]. This effect mainly related to the atmosphere and a higher melt purity, was obtained with the enhanced vacuum treatment.

Quite uniform Nd dopant distributions were obtained in carefully elaborated samples, of nominal concentrations 0.5 and 1.5 mol% in the melt. Reproducible dopant distributions of Nd, particularly for melt concentration of 1.5 mol%, have not been achieved. The fiber diameter control in the micro-pulling-down system and the influence of other parameters (pulling rates and the melt convection in the molten zone) has to be further considered. However, the distribution coefficient of Nd, found to be around 0.43 (Fig. 4) was clearly less than one and in fair agreement with some other literature data [18].

Loss and gain laser tests were performed for fiber samples and it was found that the gain value is much higher than the measured losses. Thus, the laser action of Nd:YLF single crystal grown fibers was proven to be useful for applications.

Acknowledgments

This work was supported by CNPq (project no 573916/2008-0, *INCT de Fotônica*), CNPq (no 142510/2008-4) and FAPESP (no 2008/10721-9) fellowships. We also acknowledge Prof. Horia Alexandru for discussion and suggestions to this work.

This paper was presented as an invited paper, in the International Conference ROCAM 2009, held under the auspices of the Academy of Romanian Scientists.

References

[1] V.I. Chani, Micro-pulling down and related growth methods, in: T. Fukuda, V.I. Chani (Eds.), Shaped Crystals—Growth by Micro-pulling Down Technique, Springer, 2007, p. 22.
[2] A.W. Al-Alimi, M.H. Al-Mansoori, A.F. Abas, M.A. Mahdi, M. Ajiya, Optimization of tunable wavelength erbium-doped fiber laser, Laser Phys. Lett. 6 (2009) 727.
[3] D. Sangla, I. Martial, N. Aubry, J. Didierjean, D. Perrodin, F. Balembois, K. Lebbou, A. Brenier, P. Georges, O. Tillement, J. Fourmigue, Appl. Phys. B—Lasers Opt. 97 (2009) 263–273.
[4] J. Didierjean, M. Castaing, F. Balembois, P. Georges, D. Perrodin, J. Fourmigue, K. Lebbou, A. Brenier, O. Tillement., High-power laser with Nd:YAG single-crystal fiber grown by the micro-pulling-down technique, Opt. Lett. 31 (2006) 3468–3470.
[5] P.V. Klevtsov, L.P. Kozeeva, Preparation and polymorphism of crystals or rare earth and yttrium lithium tungstates, Sov. Phys. Crystallogr. 15 (1970) 44–47.
[6] R.F. Klevtsova, L.Yu. Kharchenko, S.V. Borisov, V.A. Efremov, P.V. Klevtsov, Triclinic modification of lithium-rare earth tungstates $LiLn(WO_4)_2$ where Ln is La-Sm, Sov. Phys. Crystallogr. 24 (1979) 258–263.
[7] X. Huang, Z. Lin, Z. Hu, L. Zhang, J. Huang, G. Wang., Growth, structure and spectroscopic characterizations of Nd^{3+}-doped $LiLa(WO_4)_2$ crystal, J. Cryst. Growth 269 (2004) 401–407.
[8] X. Huang, Q. Fang, Q. Yu, X. Lü, L. Zhang, Z. Lin, G. Wang, Thermal and polarized spectroscopic characteristics of Nd^{3+}:$LiLa(WO_4)_2$ crystal, J. Alloys Compds. 468 (1–2)(2009) 321–326.
[9] Y. Terada, K. Shimamura, T. Fukuda., Growth and optical properties of RE doped bulk and fiber single crystals by Czochralski and micro pulling down methods, J. Alloys Compds. 275–277 (1998) 697–701.
[10] B. Cockayne, J.G. Plant, R.A. Clay., The Czochraslki growth and laser characteristics of Li(Y,Er,Tm,Ho)F_4 and Li(Lu, Er, Tm, Ho)F_4 scheelite single crystals, J. Cryst. Growth 54 (1981) 407–413.
[11] S.L. Baldochi, K. Shimamura, K. Nakano, N. Namujilatu, T. Fukuda., Ce-doped $LiYF_4$ growth under CF_4 atmosphere, J. Cryst. Growth 205 (1999) 537–542.
[12] A.M.E. Santo, I.M. Ranieri, G.E.S. Brito, B.M. Epelbaum, S.P. Morato, N.D. Vieira Jr., S.L. Baldochi, Growth of $LiYF_4$ single-crystalline fibres by micro-pulling-down technique, J. Cryst. Growth 275 (2005) 528–533.
[13] A.M.E. Santo. PhD Thesis, IPEN, University of São Paulo, USP, 2005. 〈http://www.teses.usp.br/teses/disponiveis/85/85134/tde-13032006-112231/〉.
[14] A.M.E. Santo, A.F.H. Librantz, L. Gomes, P.S. Pizani, I.M. Ranieri, N.D. Vieira Jr., S.L. Baldochi., Growth and characterization of $LiYF_4$:Nd single crystal fibres for optical applications, J. Cryst. Growth 292 (2006) 149–154.
[15] I.M. Ranieri, S.L. Baldochi, A.M.E. Santo, L. Gomes, L.C. Courrol, L.V.G. Tarelho, W. de Rossi, J.R. Berretta, F.E. Costa, G.E.C. Nogueira, N.U. Wetter, D.M. Zezell, N.D. Vieira Jr., S.P. Morato, Growth of LiYF4 crystals doped with holmium, erbium and thulium, J. Cryst. Growth 166 (1996) 423–428.
[16] S.P. Morato, L.C. Courrol, L. Gomes, V. Kalinov, A. Shadarevich., Me^{2+}–OH^- complex control in LiF, Phys. Status Solidi (b) 163 (1991) K61.
[17] R.C. Pastor, M. Robinson, W.M. Akutagawa, Congruent melting and crystal growth of LiRF4, Mater. Res. Bull. 10 (1975) 501–510.
[18] I.M. Ranieri, N.M. Moraes, H.M. Shihomatsu, S.P. Morato, XII National Meeting on Condensed Matter Physics, XII ENFMC, Sao Lourenco, MG, Brazil, 1999, p. 247.
[19] B.M. Epelbaum, G. Schierning, A. Winnacker, Modification of the micro-pulling-down method for high temperature solution growth of miniature bulk crystals, J. Cryst. Growth 275 (2005) e867–870.
[20] J. Jakutis Neto, Master in Science Thesis, IPEN-University of São Paulo, (2008) 〈http://www.teses.usp.br/teses/disponiveis/85/85134/tde-04092009-161816/〉.
[21] J. Jakutis Neto, T.S. Moura, F.R. Silva, S.L. Baldochi, N.U. Wetter, Lasing of a single Nd^{3+} fluoride fiber, Opt. Commun. 283 (2010) 3487–3491.