

GROWTH OF YB³⁺ DOPED LiNbO₃ CRYSTALS USING LASER HEATED PEDESTAL GROWTH METHOD

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ABSTRACT

The growth of LN single crystals free from defects greatly doped with rare earth elements (RE³⁺) and having a high optical quality is still an unresolved problem. Always, crystals of the niobate lithium contain a deficiency in lithium causing the appearance of intrinsic defects and thus a doping is required for the homogeneity. Our work was aimed to study the growth of Lithium niobate and their structural characterization, it focusses on congruent to stoichiometric Yb: LiNbO₃ (LN) crystals. These crystals were synthesized with different doping concentrations of Yb³⁺ (1.0, 2.0, 3.0, 4.0, 5.0 mol%) by the LHPG method which is faster, less expensive and clean, Three analysis techniques were used: Structural characterization made up 5.0 mol% by X-ray diffraction, Optical Microscopy and micro-Raman spectroscopy showed that the obtained material is single crystal, good optical quality and homogeneous. As we know, the results obtained with doping up to 5% are encouraging. Our approach provides excellent spectroscopic properties of crystals, low self-quenching property and can be used to applications such as solid-state laser.

Keywords: Niobates Dielectric Materials, Laser Materials, Chemical Synthesis, Crystal Growth From Melts Method

1. INTRODUCTION

Since the early work of Verneuil and Czochralski on crystal growth (Wang *et al.*, 2009; Doiphode and Psingh, 2012), scientific researchers have been mainly concentrated on the improvement of growth techniques in order to obtain crystals of high performance. The growth techniques of single crystals are limited to few methods, because of the complexity of the systems and their costs. The cutting of a single crystal made by Czochralski technique is complex and the finishing of the cut products is also very difficult because of the hardness and fragility of the single crystals. The modern engineering requiring high quality crystals of sizes and orientation well-defined, the development of fibers single crystals and of compositions well controlled are the basis of a new generation of crystals (Li *et al.*, 2010).

Lithium niobate requires a special interest since it's the final non-linear crystal. This is the reason why this

material has been studied extensively and thus well known properties, first as a solid material and lately as a thin layer or waveguide. It continues to attract considerable interest for integrated optics (Chen *et al.*, 2009; Boudrioua, 2006).

Lithium Curie temperature is comparatively high ($T_c = 1210^\circ\text{C}$), below T_c , the crystal becomes ferroelectric and belongs to the trigonal system (space group C3v) and above T_c , it becomes in its para electric stage and consequently it allows the utilization of numerous techniques for the waveguide development of lithium niobate (Kumar *et al.*, 2010; Svecova *et al.*, 2010a; 2010b; Mackova *et al.*, 2010; Bhatt *et al.*, 2011; Nekvindova *et al.*, 2012; Malinsky *et al.*, 2012; Vacik *et al.*, 2012).

The problem is that the niobate crystallizes in a non stoichiometric (ALRahman *et al.*, 2013), it has always a deficit in lithium causing the formation of intrinsic defects (vacancies, anti-sites,...) and so a doping is needed to make it homogeneous. Recently it was shown that the

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addition of magnesium oxide may drastically change some physicochemical properties of LiNbO_3 (Rattanachan *et al.*, 2013; Tao *et al.*, 2013), for example reduce the variation of the medium index, also experiments of micro Raman spectroscopy and X-rays diffraction were performed on LiNbO_3 fibers doped Mg^{2+} (1 to 5%) to study the homogeneity. The pure compound is spatially inhomogeneous in contrast to the compound doped with 5 % in which the substitution of antisites by dopants reduces greatly the number of lithium vacancies and thus restores the homogeneity. Although structural problems have been solved with the incorporation of Nd^{3+} and it has been possible to generate the second harmonic in LN doped with Nd^{3+} YAG laser (1064 nm). The presence of many absorption lines of Nd^{3+} in the visible remains a major disadvantage for the development of sources self IR frequency doublers. Therefore, we must look for the incorporation of other rare earth ions or other transition elements in the LN that do not absorb neither laser Infrared (IR) Radiation nor the radiation of the laser frequency doubling in the entire visible spectrum

This study aims the elaboration of fibers LN single crystal doped with rare earth ions (Yb^{3+}), in order to obtain structurally modified materials which may be used for example in telecommunications as auto frequency doublers of laser sources in the solid state.

The paper is organized as follow: In the first section, we investigate research techniques of elaboration in the field of materials. Review importance of LiNbO_3 used in most optical systems to review the crystal structure and review the current understanding of non-stoichiometric problem of material and solution. In the next section we explain the preparation and production of fibers by LHPG method (ALRahman *et al.*, 2013). In section 3, we present the characterization and confirmation of the homogeneity of fiber, with some results and discussion. In section 4, we give a finally conclusion.

2. EXPERIMENTAL APPROACH LN

LHPG (Laser Heated Pedestal Growth) method allows to grow crystal fibers LN. In this approach, a CO_2 laser beam (10.6 μm , Adron source) is concentrated on the top of a source rod of appropriated chemical composition, by using mirrors. The laser has a power able to melt the source rod's tip creating a little molten area in which a crystal seed is dipped. When the interfacial tension forces are in equilibrium between the molten area and the seed, it becomes possible to remove a new crystal fiber. The biggest contribution LHPG approach is that no crucible is used and contamination does not exist.

In this study congruent Yb: LiNbO_3 compounds were prepared from blends of Li_2CO_3 by reaction in the solid-state, Nb_2O_5 , powders (99.99% purity), cold pressed under 1 kgf cm^{-2} into discs with a diameter of 15 mm. The pellets were sintered at 800°C for 10 hours (h) and at 1000° C for 20 h in air atmosphere. The formation of the LN phase was verified by x-ray powder diffraction analysis at room temperature. After cooling, the pellets were ground and mixed with the required amount of dopant (Yb_2O_3) and 0,5% mass of a briquetting agent (Chemplex Spectroblend) followed by a cold pressing under 1 kgf cm^{-2} into 30×5×5 mm³ pellets. The pellets were then heat processed in two phases: The first one at 600°C during 4 h and the second one at 1100°C for 10 h; after cooling, they were sliced into 30×1×1 mm³ source rods. The seed used was a b-axis-grown undoped LN crystal fiber, previously produced by the LHPG approach and directed by X-ray Laue diffractometry. The choice of a b-axis-grown fiber as seed is due to earlier studies (ALRahman *et al.*, 2013; Laidoune *et al.*, 2013), showing that such type of material can double a laser material. The seed is 30 mm long and 0,8 mm diameter. After growth, the crystal fiber was annealed at 800°C for 10 h. The various fibers we had grown were ground and blended with silicon powder in order to get their X-ray diffraction spectra. We polished both sides of fibers along the b-axis until all superficial striations are vanished for doing micro-Raman and optical analysis. The nominal composition of Li, Nb and Yb was obtained by plasma emission spectroscopy. Quantitative analyses for Li, Yb and Nb were made by EPMA along the pulled fibers.

3. RESULTS

For our studies we produced several LN sample sets of six different compositions. The compositions were 0, 1, 2, 3, 4 and 5 mol% Yb^{3+} ; the samples have been analyzed by optical microscopy; some relevant results are presented in **Fig. 1 and 2**.

3.1. Characterization by Emission Plasma

The concentration of Li, Nb and Yb in the sample is measured by (ICP) technique and it's presented in **Table 1**.

3.2. Characterization by Raman Spectroscopy

In order to confirm the homogeneity of the samples, we polished fibers. Subsequently, we obtained the micro-Raman (dylor XY) spectra as depicted in **Fig. 3 and 4**.

Table 1. Plasma emission spectroscopy analysis of undoped and Yb³⁺ doped LN

Composition	Elements		
	Li	Nb	Yb
LiNbO3	0.982	0.953	0.000
Li _{0,99} Yb _{0,01} NbO3	0.953	0.990	0.009
Li _{0,98} Yb _{0,02} NbO3	0.954	0.992	0.019
Li _{0,97} Yb _{0,03} NbO3	0.968	0.882	0.029
Li _{0,96} Yb _{0,04} NbO3	0.940	0.980	0.038
Li _{0,95} Yb _{0,05} NbO3	0.948	0.852	0.049



Fig. 1. Crystal fiber after polishing crystal growth without striations crystal fiber

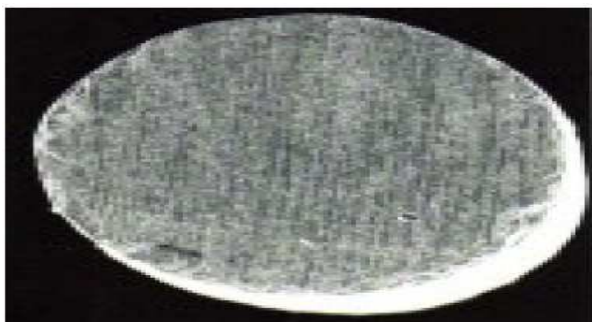


Fig. 2. Cross-section of a b-axis oriented LN: Yb³⁺ crystal fiber.

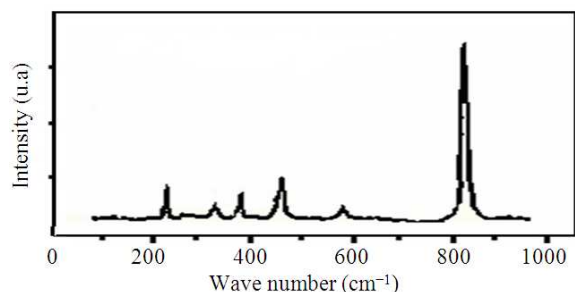


Fig. 3. Raman micro spectroscopy of crystal fiber: 2 mol% Yb³⁺ doped stoichiometric lithium niobate

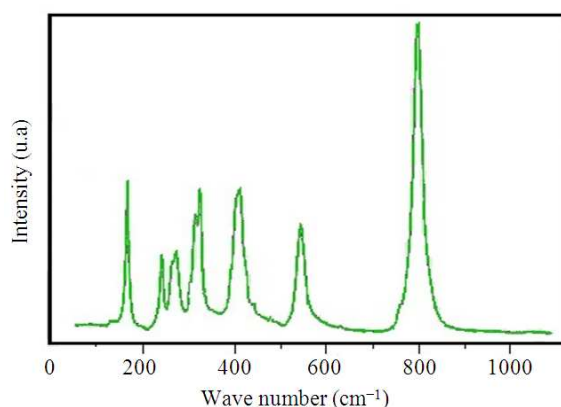


Fig. 4. Raman microspectroscopy of crystal fiber: 3 mol % Yb³⁺ doped lithium niobate congruent

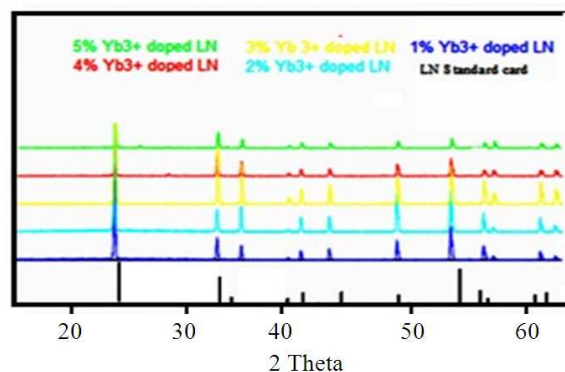


Fig. 5. Evolution of powders X-ray diffraction at room temperature as a function of Yb³⁺ substitution comparing with JCPDS card

3.3. Characterization by X-ray Diffraction

Finally, in **Fig. 5**, we present the X-ray diffraction patterns of Yb (1 mol-5mL %): LiNbO₃ crystals.

4. DISCUSSION

The optical microscopy analysis showed the transparency of fiber, a diameter was constant In **Fig. 1**, both sides of the fiber are darker because they are off the polishing axis. The cross-section of an oriented b-axis fiber after polishing is presented in **Fig. 2** the fiber is almost circular, with growth ridges and no growth faults, such as micro-twins or cracks, can be observed, isn't present inside the crystal and were compared with (Tao *et al.*, 2013), The quantitative chemical analysis was done by plasma emission spectroscopy (ICP).

Although this analysis technique is very precise, it does not allow to conclude on local variations in composition during the draw. It was therefore necessary to complete our analysis with a local measure of the composition. The dosage of lithium material is extremely difficult because of the lightness of this element which makes it very difficult to measure by direct methods or microprobe for a homogeneous crystal congruent, which is impossible for a single crystal. So we need to make indirect measurements of the composition to obtain sufficient accuracy and conclude on the actual composition of our crystals (**Table 1**). Therefore, we undertook a further analysis by micro Raman check for defects.

The effective segregation coefficient k_{eff} for each sample can be calculated using the following Equation (1):

$$k_{\text{eff}} = \frac{c_s}{c_i} \quad (1)$$

where, C_s is the doping ion concentration in the crystal and C_i is that in the melt segregation coefficient of Yb^{3+} in Yb-doped LN is about 1.2, which is the same as that measured by (Montoya *et al.*, 1999). Nevertheless the value is slightly less than unity as reported in (Bodziony *et al.*, 2008) and it can be noticed that all the samples neither have an accuracy of $\pm 1,5$ at % in their element contents and that loss of neither Li nor of other elements is observed. Furthermore, EPMA performed on undoped and doped Yb^{3+} Crystal fiber.

The obtained congruent spectrum shows the appearance of a doublet at 380 cm^{-1} and a peak at 550 cm^{-1} more intense relatively to the stoichiometric measures, moreover sliding peaks is observed. These results are in good agreement with the results encountered in literature.

The results showed that all spectra were almost the same, irrespective of the side or point, confirming the homogeneity of the structure. In these figures only the results for the 2, 3 mol% Yb^{3+} doped LN crystal fibers are presented because the spectra are almost the same for the entire set.

Compared with the standard card of lithium niobate and (Tao *et al.*, 2013), the high crystallinity of these materials could be deduced from the XRD results, no additional peaks appeared, which confirmed that the obtained crystals are a single phase of LiNbO_3 and the rare-earth the impurity ions occupied the Li^+ or Nb^{5+} sites instead of the interstitial sites. The slightly changed intensities of X-ray peaks indicate that lattice constant deviations are due to the different ionic radii. When the concentration of Yb^{3+}

varies, some peaks changed in the XRD spectra, which might be attributed to the impurities of LiNbO_3 crystals resulting from the doping ions of Yb^{3+} .

5. CONCLUSION

In this study, congruent to stoichiometric Yb: LiNbO_3 (LN) crystals were synthesized by LHPG method with different doping concentrations of Yb^{3+} (1.0, 2.0, 3.0, 4.0, 5.0 mol%). Their characterization by X-ray diffraction shows that the obtained crystal is a single phase of LiNbO_3 , Optical Microscopy analysis showed that the fibers produced are of good crystalline quality and micro-Raman spectroscopy showed their homogeneous composition all along the growth axis. The evolution of the lattice vibration spectra as a function of composition was related to the increase of the structural disorder when the amount of Li_2O decreases. This technique is to be very promising to obtain fibers of lithium niobate stoichiometric composition.

However it seems difficult to obtain the material stoichiometric composition because this is the limit of a eutectic which causes the precipitation of a secondary phase heating resulting in fluctuations in temperature of the molten zone and thus the Li_2O content at the interface of crystallization. These difficulties are mainly due to insufficient control of CO_2 laser power. Indeed a doping percentage too high can lead to constraints on the structure that prevents single crystal growth by the formation of defect as 5% is sufficient to remove the anti-site niobium without deforming the structure.

This work allowed us to conclude that as-grown crystals of Yb: LiNbO_3 are good candidates. So there is a need to focus our attention on the effect of (5.0 mol%) rare earth composition on the material optical properties, in order to develop a micro ship laser under 980 excitation to obtain the highest emission efficiency at $1.54 \mu\text{m}$. We decided to continue our investigations in this direction

6. REFERENCES

- ALRahman, L.A., R.I. Raja and R.A. Rahman, 2013. Experimental study on natural fibres for gree acoustic absorption materials. *Am. J. Applied Sci.*, 10: 13071314. DOI: 10.3844/ajassp.2013.1307.1314
- Bhatt, R., S. Ganesamoorthy, I. Bhaumik, A.K. Karnal and G. Bhagavannarayana *et al.*, 2011. Effect of annealing in Li-rich ambient on the optical absorption and crystallinity of Er doped LiNbO_3 crystals. *J. Optoelectron. Adv. Materials*, 13: 245-250.

- Bodziony, T., S.M. Kaczmarek and C. Rudowicz, 2008. EPR and optical study of magnetically coupled Yb³⁺ ion pairs in weakly doped LiNbO₃: Yb single crystal. *Phys. B*, 403: 207-218. DOI: 10.1016/j.physb.2007..08.224
- Boudrioua, A., 2006. *Integrated Optics Theory and Application*. 1st Edn., Lavoisier, ISBN-10: 2746214458, pp: 348.
- Chen, F., Y. Tan and D. Jaque, 2009. Ion-implanted optical channel waveguides in neodymium-doped yttrium aluminum garnet transparent ceramics for integrated laser generation. *Opt. Lett.*, 34: 28-30. DOI: 10.1364/OL.34.000028
- Doiphode, P.G. and V.P. Singh, 2012. Different approaches to crystallization of membrane proteins. *Online J. Biol. Sci.*, 12: 118-122. DOI: 10.3844/ojbsci.2012.118.122
- Kumar, P., S.M. Babu, S. Perero, R.L. Sai and I.S. Bhaumik *et al.*, 2010. X-ray photoelectron spectroscopy, high-resolution X-ray diffraction and refractive index analyses of Ti-doped lithium niobate (Ti: LiNbO₃) nonlinear optical single crystal. *Pramana J. Phys.*, 75: 1035-1040. DOI: 10.1007/s12043-010-0159-8
- Li, M., X. Liang, X. Xu, S. Solanki and T. Chong, 2010. Study on Ag doping in congruent lithium niobate crystal. *J. Crystal Growth*, 312: 3020-3024. DOI: 10.1016/j.jcrysgro.2010.07.003
- Laidoune, A., K. Lebbou and D. Bahloul, 2013. Growth Microstructure of theytria doped Al₂O₃-ZrO₂ Eutectic fibers grown by the Laser Heated Pedestal Growth (LHPG) method. *J. Crystal Growth*, 380: 224-227. DOI: 10-1016/j.jcrysgro2013.06.26
- Mackova, A., P. Malinsky, B. Svecova, P. Nekvindova and R. Grotzsche, 2010. Study of Er³⁺ ion-implanted lithium niobate structure after an annealing procedure by RBS and RBS/channelling. *Nucl. Instruments Meth. Phys. Res.*, 268: 2042-2045. DOI: 10.1016/j.nimb.2010.02.021
- Malinsky, P., A. Mackova, V. Hnatowicz, R.I. Khaibullin and V.F. Valeev *et al.*, 2012. Properties of polyimide, polyetheretherketone and polyethyleneterephthalate implanted by Ni ions to high fluences. *Nucl. Instruments Meth. Phys. Res.*, 272: 396-399. DOI: 10.1016/j.nimb. 2011.01.109
- Montoya, E., A. Lorenzo and L.E. Bausa, 1999. Optical characterization of LiNbO₃:Yb³⁺ crystals. *J. Phys. Condens. Matter*, 11: 311-320. DOI:10.1088/0953-8984/11/1/026
- Nekvindova, P., B. Svecova, J. Cajzl, A. Mackova and P. Malinsky *et al.*, 2012. Erbium ion implantation into different crystallographic cuts of lithium niobate. *Opt. Mater.*, 34: 652-659. DOI: 10.1016/j.optmat.2011.09.011
- Svecova, B., P. Nekvindova, A. Mackova, P. Malinsky and A. Kolitsch *et al.*, 2010a. Study of Cu⁺, Ag⁺ and Au⁺ ion implantation into silicate glasses. *J. Non-Crystalline Solids*, 356: 2468-2472. DOI: 10.1016/j.jnoncrysol.2010.03.031
- Svecova, B., J. Spirkova, P. Nekvindova, M. Mika and L. Svecova. 2010b. Ion exchange as a new tool to evaluate and quantify glass homogeneity. *J. Non-Crystalline Soli.*, 356: 1509-1513. DOI : 10.1016/j.jnoncrysol.2010.03.014
- Vacik, J., V. Lavrentiev, P. Horak and R. Fajgar, 2012. Structural variation of transition metal-fullerene thin films modified by thermal annealing and ion or laser beam bombardment. *Adv. Mater. Res.*, 463: 1387-1391. DOI: 10.4028/www.scientific.net/AMR.463-464.1387
- Wang, J., Y. Zhang, H. Xia and J. Sheng, 2009. Growth of Nd³⁺ doped LiNbO₃ crystals using bridgman method and its spectral properties. *Bull. Mater. Sci.*, 32: 183-186. DOI: 10.1007/s12034-009-0028-6
- Rattanachan. S., T.P. Krongarrom and T. Fangsuwannarak, 2013. Influence of annealing temperature on characteristics of bismuth doped zinc oxide films. *Am. J. Applied Sci.*, 10: 1427-1438. DOI:10.3844/ajassp.2013.1427.1438
- Tao Y., Y. Yonggui, G. Yongjie, S. Yuanhua and X. Min *et al.*, 2013. Growth, structural optical and thermal properties of Yb doped and Yb-Mg codoped LiNbO₃ single crystals. *J. Alloys Compounds*, 564: 1-7. DOI: 10.1016/j.jallcom.2013.01.177