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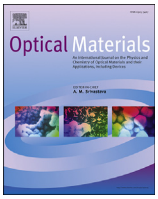

Effect of Zn doping on the photoluminescence properties of $LiNbO_3$ single crystals

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ABSTRACT

An extraordinary violet luminescence at 418 nm together with the intrinsic blue band at 440 nm with excitation in the UV region (380 nm) was observed in a series of $LiNbO_3$ single crystals doped with Zn. Structural and photoluminescence properties were studied by Raman, UV reflectance, and fluorospectrometry, respectively. The emission peaks in PL spectra varied in amplitude according to the level of concentration of Zn in $LiNbO_3$ crystals. It was found, from Raman spectroscopy studies, a connection between the appearance of the new emission band centered at 418 nm and a diminishing in the Li concentration in crystals, which suggest the displacement of the Li ions from their regular sites by the Zn ions. The maximum peak intensity of each one of the three PL emission components found from a deconvolution process shows a linear dependence on the Zn concentration present in the crystals studied.

1. Introduction

Lithium niobate ($LiNbO_3$; LN) is a photorefractive material with excellent pyroelectric, piezoelectric, and strong non-linear optical properties with high potential in advanced photonic applications including the store and process of information [1,2]. This ferroelectric material, at room temperature has a characteristic rhombohedral structure rather than the perovskite structure. In general, LN crystal is grown from a congruent melting composition (Li/Nb = 48.6:51.4) by the Czochralski method with a great compositional stability during growth [3]. Although usually a compositional variation along the growth axis occurs in the crystal and affects several of its physical properties. Congruent crystals generally have good optical quality and uniformity. However, they have a non-stoichiometric composition, and Nb anti-site defects occupying Li-ion sites and cation vacancies are always present [4]. Nevertheless, fortunately, stoichiometric or quasi-stoichiometric crystals have a perfect lattice which is expected to show improved performance in some applications [5]. Several physical properties, like the phase transition temperature and those related to optics (birefringence and UV band edge) strongly depend on the [Li/Nb] ratio, for this reason is very important to determine its deviation from the unity.

In the optical properties context, LN doped with low concentrations of Zinc (2 mol%) shows an enhancement on the speed of holographic recording which is comparable to that obtained for low-doped LN:Fe [6]. In addition, the holographic recording in LN:Zn is not accompanied by the photoinduced light scattering, which is characteristic of $LiNbO_3$:Fe that hampers its holographic applications [6]. Zn doping similarly to In doping makes LN suitable for ultraviolet recording grating applications [7]. This because both dopants modify efficiently the photo-refraction efficiency and hence improve the data storage capabilities [6,7]. Instead, Zn doping with high concentrations above 6 mol % in nominal melt in LN crystals significantly improves the optical damage resistance [8]. This makes LN:Zn crystal a perspective material for the non-linear optical applications [8–10]. Zn-doped LN crystals have additional interest due to the possibility of fabrication of planar waveguides by Zn diffusion from ZnO source in congruent LN [11]. In fact, LN crystals doped with ZnO concentrations in the melt between 5 and 10 mol % are promising for the frequency doubling of 1064 nm

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radiation exhibiting conversion efficiencies higher than highly-doped LN:Mg [8,10].

On the other hand, recently, S. K. Kushwaha et al. made a comparison of structural and vibrational properties between pure and Zn-doped at 1 mol% LN single crystals [12]. They found that the distribution of dopant ions in the lattice matrix of a host single crystal depends on the concentration, size and ionic state of dopant. In fact, this one is incorporated homogeneously in the lattice only up to certain concentration value [13]. At higher concentrations of Zn, high strain is developed in the lattice. As a consequence of this process, defects take place which leading to agglomeration of point defects and dislocations [14].

In view of the importance of LN single crystals doped with Zn in photonic applications, the main aim of the present work is to study the photoluminescence properties of LN single crystals highly doped with Zn. This because, high concentration of Zn doping in LN crystals improves its non-linear optical properties making it a promising material in integrated optics applications [9,15]. In fact, it has been reported in the literature, simultaneous generation of red, green, and blue continuous-wave laser radiation in Nd^{3+} doped LN. This due to the multisite character of Nd^{3+} doped LN which gives the possibility of lasing different centers in different channels due to the inhomogeneous broadening character of fluorescent emissions [15]. Hence, it is important to research the photoluminescence properties of LN doped with Zn, especially because Zn doping could enhances the photoluminescence capabilities of LN in the UV–Vis portion of the electromagnetic spectrum.

This work also reports the spectroscopy analysis of Zn-doping in a range between 5.0 mol% and 9.0 mol% in LN single crystals growth by the Czochralski (CZ) technique. In this work were performed Raman spectra studies to reveal the effect of Zn dopant on the modes of vibration. On the other hand, absorption spectra were obtained from measurement of optical transmission and optical reflectance in the UV–Vis–NIR ranges to evaluate the direct band gap. The stoichiometry (Li/Nb) was evaluated by Raman and UV–Vis spectroscopy. Finally, photoluminescence studies performed with an excitation in the UV region (380 nm) have revealed an extraordinary violet luminescence centered at 418 nm and a blue emission centered at 488 nm in addition to the well-known blue band centered at 440 nm usually present in LN crystals.

2. Experimental details

A set of six $LiNbO_3$ single crystals with different ZnO concentrations in melt, 5, 5.5,6.5,7,7.5 and 9 mol% were acquired from a commercial supplier (Impex High-Tech, Germany). These samples were grown by the Czochralski method in air. A Li/Nb ratio equal to 0.945 was selected to get a growing process of congruent phase, and the polar axis for each sample was parallel to the pulling direction. The samples were subsequently cut along the crystallographic axes to obtain rectangular shapes with dimensions $a \times b \times c = (8 \times 1 \times 10)\ mm^3$ for all crystals.

Raman spectroscopy was performed using a Micro RAMAN Labram HR VIS-633 Horiba model, equipped with an Olympus microscope with a 10× objective, a laser spot diameter ~15 μm and a CCD detector. The spectra were scanned between 180 and 1000 cm^{-1} with five accumulations using a He–Ne laser at a wavelength of 632.8 nm with a power of 14 mW.

By using UV–Vis–NIR spectroscopy were measured the optical transmission and optical reflectance in the UV–Vis–NIR ranges using a spectrophotometer Agilent Cary 5000. The optical transmittance T was measured at normal incidence while optical reflectance R was measured using an absolute specular reflectance accessory with an incident light at 7° to sample surface. From these measurements was obtained the optical absorption coefficient α of each one of samples in the UV–Vis–NIR ranges using the formula $T = (1\text{-}R)^2\exp(\text{-}\alpha L)$ where L is the thickness of the crystal. Next, from the absorption coefficient was evaluated the direct band gap for each one of samples.

Photoluminescence (PL) studies were performed at room temperature using a Horiba spectrofluorometer model Fluorolog-3.

3. Results and discussion

In the growth process of LN crystals was aggregated a quantity of ZnO powder in the melt at several concentrations. Nevertheless, due to there is a solubility limit in $LiNbO_3$:Zn crystals, the Zn content integrated in each sample is much less than the quantity aggregated in the melt. Table 1 shows the Zn content aggregated in melt as well as the quantity incorporated in each sample which was determined by energy dispersive spectroscopy (EDS) on a scanning electron microscope (SEM).

3.1. Raman spectroscopy

Fig. 1 (a) shows the Raman spectra obtained for the six Zn-doped LN single crystals. As is well known, the LN unit cell with 10 atoms has associated 30° of freedom, 27 of which are assigned as phonon modes and the other three as acoustic phonons. The optical modes of LN for R3c symmetry are given by the relation: $\Gamma_{optical} = 4A_1 + 5A_2 + 9E$ [12,16,17]. Only A_1 and E modes are Raman active and therefore only 13 phonon peaks are expected in the spectra as shown with labels at the bottom of Fig. 1 (a). The degeneracy between longitudinal optical (LO) and transverse optical (TO) phonons has been lifted due to the long-range electrostatic fields and the ionic character of LN [17]. The peak parameters of the Raman spectra are known to be very sensitive to the structural changes of LN crystals, particularly those induced by the deviations from stoichiometry and structural defects [18,19]. In fact, it can be observed significant differences in the peak intensities of the recorded spectra. For example the intensity of the line at 186 cm^{-1} is said to be strongly dependent on structural defects [19] and its low intensity for LN may be attributed to the presence of stress in the lattice. The relaxation of the lattice from strains in the Zn-doped LN crystal can lead to increase the intensity of this peak. The increase in the intensity of the other peaks also could have the same origin.

The observed modes in the crystals studied in this work are in agreement with other reports available in the literature [12,17,19–23]. No inconsistency in the spectra due to Zn doping was observed, which reveals no change in the basic structure of the crystal lattice. The E(TO) and A1(LO) modes respectively at ~150 and ~878 cm^{-1} are indicated by arrows in Fig. 1 (a). Fig. 1 (b) and (c) show respectively, magnified views of these modes. The determination of Γ as the linewidth (FWHM) in the mode E(TO) and in the mode A1(LO) was useful to evaluate the Li concentration (C_{Li}) by using the empirical formulae: $C_{Li}[mol\%] = 53.03 - 0.4739\Gamma\ [cm^{-1}]$

Table 1
Left column represents ZnO concentration aggregated in congruent melt for growing $LiNbO_3$ crystals. In right column, ZnO content incorporated in each sample.

ZnO in melt (mol %)	Zn in crystal (mol %)
5.0	0.4718
5.5	0.5345
6.5	0.5549
7.0	0.5359
7.5	0.5669
9.0	0.5935

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