

Dependence of the photoluminescence properties of LiNbO_3 single crystals on the Zn doping concentration

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ABSTRACT:

This work reports the dependence of photoluminescence properties of LiNbO_3 (LN) single crystals, on the Zn doping concentration. The samples were grown by Czochralski technique and were doped with zinc at concentration from 5 to 9 mol %. Structural and photoluminescence (PL) properties were studied by Raman, UV reflectance and fluorospectrometry, respectively. An extraordinary violet luminescence at 425 nm with excitation in UV region (380 nm) was observed. The emission peaks in PL spectra varied in amplitude and in wavelength position according to the level of concentration of Zn in the LN single crystals. It was found an optimal level concentration of Zn in the LN crystals studied in order to obtain a strong PL signal. The PL properties found in the LN crystals studied were related to the ratio of Li/Nb concentration.

Key words: Lithium niobate: Zinc, structural and photoluminescence properties.

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1. Introduction

Lithium niobate (LiNbO_3 ; LNO) is a photorefractive nonlinear optical material with high potential in advanced photonic applications including the store and process of information [1]. This ferroelectric material, at room temperature has a characteristic rhombohedral structure rather than the perovskite structure. The great interest to prepare LNO single crystals is due to its compositional stability during growth. During the melt and the growing crystals are identical with respect to the composition, otherwise the composition of the melt and the crystal vary slightly during the growth, and the crystal becomes compositionally non-uniform, particularly along the growth axis. 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, Zinc (Zn) as a transition metal, efficiently modifies the photo-refraction efficiency and hence improves the data storage capabilities [2]. Zn doping also improves the optical damage resistance significantly above 7 mol % in nominal melt [3] and it is suitable for the recording of holograms at high-speed with long life-time due to the high optical band gap of LNO [4]. Analogous to In doping, Zn doping makes LNO suitable for ultraviolet recording grating applications [2]. Recently, S. K. Kushwaha, et al.[5] made a comparison of structural and vibrational properties between pure and Zn-doped at 1 mol% LNO single crystals. 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. At higher concentrations, 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.

In view of the importance of LNO single crystals doped with Zn in photonic applications, the present work reports the spectroscopy analysis of Zn-doped in a range between 5 mol% up to 9 mol% LNO single crystals growth by the Czochralski (CZ) technique. Raman spectra studies have been performed to reveal the effect of Zn dopant on the modes of vibration. On the other hand, absorption spectra have been recorded in the entire reflectance diffuse UV-Vis region to evaluate the indirect band gap. The stoichiometry (Li/Nb) has been evaluated by Raman and UV-Vis spectroscopy. Finally photoluminescence studies have revealed an extraordinary violet luminescence at 425 nm with excitation in UV region (380 nm).

2. Experimental details

A set of seven LiNbO_3 single crystals with different ZnO concentrations 5, 5.5, 6, 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. ZnO powder was aggregated in the melt at several concentrations. The samples were subsequently cut along the crystallographic axes to obtain rectangular shapes with dimensions $a \times b \times c = (8 \times 1 \times 10) \text{ mm}^3$ for all crystals. Raman spectroscopy was performed using a Micro RAMAN Labram HR VIS-633 Horiba model, equipped with an Olympus microscope with 10x objective, a laser spot diameter $\sim 15 \mu\text{m}$ 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 14mW. The UV-visible absorbance (UV-Vis) by diffuse reflectance was obtained with a Lambda 10 Perkin Elmer UV-Vis spectrometer in diffuse reflectance mode, using Labsphere reflectance patterns in the range of 1100 to 200 nm at a scan speed of 900 nm min^{-1} . Photoluminescence studies were performed at room temperature using a Horiba spectrofluorometer model Fluorolog-3.

3. Results and discussion

3.a. Raman spectroscopy

Fig. 1 (a) shows the Raman spectra obtained for the seven Zn-doped LNO single crystals. As is well known, the LNO unit cell with 10 atoms has associated 30 degrees of freedom, 27 of which are assigned as phonon modes and

the other three as acoustic phonons. The optical modes of LNO for R3c symmetry are given by the relation: $\Gamma_{\text{optical}} = 4A_1 + 5A_2 + 9E$ [6]. 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 LNO. The peak parameters of the Raman spectra are known to be very sensitive to the structural changes of LNO crystals, particularly those induced by the deviations from stoichiometry and structural defects [6]. 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 [6] and its low intensity for LNO may be attributed to the presence of stress in the lattice. The relaxation of the lattice from strains in the Zn-doped LNO 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.

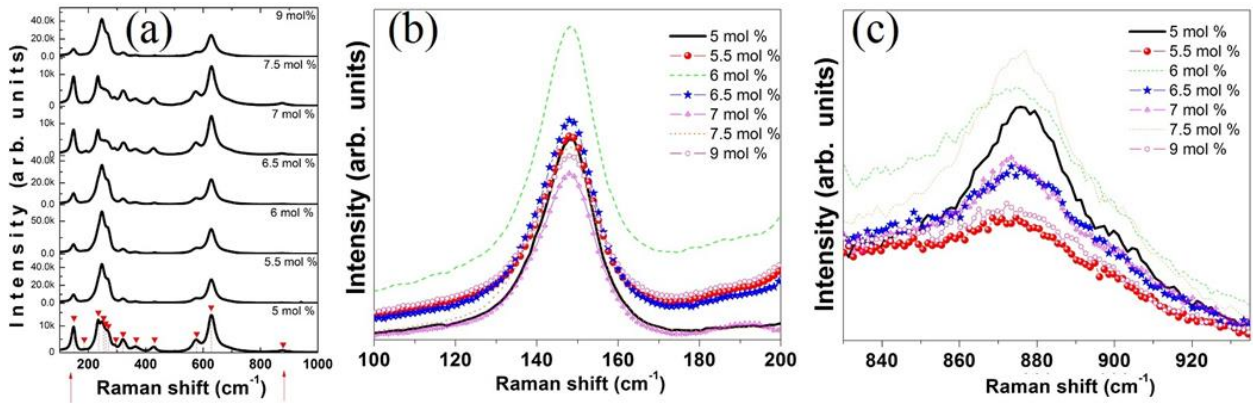


Fig. 1 (a) Raman spectra for the LNO at different concentrations of Zn; (b) magnified view of the peaks at 150 cm^{-1} and (c) 878 cm^{-1} , respectively.

The observed modes in the crystals studied in this work are in good agreement with other reports available in the literature [5,7,8] except by the variation in the intensities of peaks. 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 A_1 (LO) modes respectively at ~ 150 and $\sim 878 \text{ cm}^{-1}$ are indicated by arrows in Fig. 1 (a). Figs. 1 (b) and 1(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 A_1 (LO) was useful to evaluate the Li concentration (C_{Li}) by using the empirical formulae: $C_{\text{Li}}[\text{mol}\%] = 53.03 - 0.4739\Gamma [\text{cm}^{-1}]$ for 150 cm^{-1} and $C_{\text{Li}}[\text{mol}\%] = 53.29 - 0.1837\Gamma [\text{cm}^{-1}]$ for 878 cm^{-1} [9]. The Γ values determined by the deconvolution of Raman peaks are summarized in Table 1. The slight variation in Γ is due to the change in translational symmetry perhaps to the presence of point defects (V_{Li} , Nb_{Li} and Zn_{Li} which stand, respectively, for Li vacancies, Nb at Li and Zn at Li). C_{Li} values also are given in Table I. As is usual for a Li/Nb ratio up to 0.946 the LNO crystals were termed as congruent, and above 0.970 were termed as stoichiometric.

TABLE I
Line widths (FWHM) of the Raman modes E(TO) and A₁(LO), Li concentration (C_{Li}), and Li/Nb ratio.

Zn concentration (mol%)/ Vibrational mode	5	5.5	6	6.5	7	7.5	9
$\Gamma_{E(TO)}$ (cm ⁻¹)	15.4	15.5	15.6	16.2	16.8	17.5	17.1
$\Gamma_{A_1(LO)}$ (cm ⁻¹)	34.0	27.6	29.3	28.6	25.7	30.1	35.8
C _{Li} (mol %) E(TO)	45.7	45.7	45.6	45.3	45.0	44.7	44.9
C _{Li} (mol %) A ₁ (LO)	47.0	48.2	47.9	48.0	48.6	47.7	46.7
Li/Nb	0.941	0.964	0.958	0.961	0.972	0.954	0.934

3.b. UV-Vis spectroscopy

From the UV-visible spectroscopy measurements, the diffuse reflectance in the range of 1100 to 200 nm was obtained. Next, the reflectance diffuse was used to obtain the absorption coefficient α in cm⁻¹ which was used to calculate the indirect band gaps of Zn-doped LN crystals using the relation: $(\alpha h\nu)^2 = A(E_g - h\nu)$. Where ν is the frequency of incident radiation, and h is the Planck's constant. E_g represents the optical band gap and A is a constant. Fig. 2(a) shows the behaviour of $(\alpha h\nu)^2$ as a function of $h\nu$. The E_g values were evaluated by extrapolating the linear part of the plots (see dot line) to the abscissa ($h\nu$). These values were found between 3.93 and 3.98 eV. Fig. 2 (b) shows the dependence of the energy band gap on the Zn concentration. These changes in the energy band gap may be attributed to the distortion of energy band structure. It is known that the optical properties of pure LNO crystals are sensitive to the presence of intrinsic defects, and the structural rearrangement near the defects can change its main non-linear optical effects. In fact, when Nb_{Li} antisites are formed, in order to electrically balance the region, it is very likely to be created near Li-oxygen vacancies, leading to a local structural rearrangement [10]. Since usually the zinc ions substitute the Nb_{Li} antisites [11] the intrinsic defects of LiNbO₃ crystals are altered, and therefore a modification in the indirect optical transition energy values occurs. These results open the possibility that crystals of LNO doped with high concentrations of Zn can be used in photorefraction applications in the UV region of the electromagnetic spectrum.

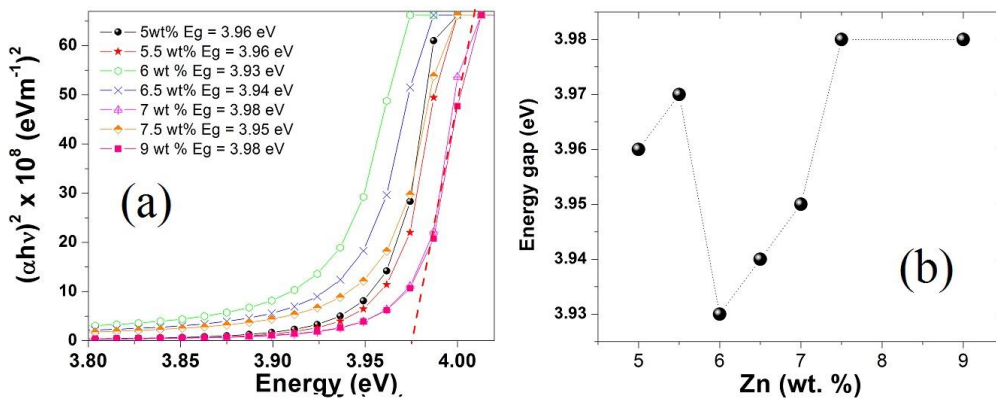


Fig. 2(a) $(\alpha h\nu)^2$ vs $h\nu$ spectra for the calculation of indirect band gap of Zn-doped LNO single crystals, (b) dependence of energy band gap on the Zn concentration.

3.c. Photoluminescence measurements

Luminescence in LiNbO_3 single crystals it has previously explained in terms of charge-transfer in the niobate octahedron, which is strongly affected by the concentrations of Li vacancies [12]. In stoichiometric LiNbO_3 there is an intrinsic blue band at 440 nm which apparently is independent of the excitation wavelength. This band occurs in both pure and doped crystals and has its origin in the intrinsic electron (Nb^{4+}) hole (O^\cdot) recombination at a regular niobate group [12]. On the other hand, in congruent lithium niobate crystals, a strong emission near 520 nm which appears due to the anti-site defect $\text{Nb}_{\text{Li}}^{4+}$ (Nb^{4+} ions located in Li^+ sites) has been found. This proposition is supported by the appearance of the signal in reduced crystals and in those that have lost lithium by heat treatment or changes in the Li:Nb stoichiometry [12].

In the present work it has been found from photoluminescence measurements that $\text{LiNbO}_3:\text{Zn}$ crystals show luminescence in the violet-green spectral region. Fig. 3 (a) shows photoluminescence (PL) spectra of Zn-doped LNO single crystals studied in this research. A broad emission with several emission peaks centred at 410, 419, 440, 530 and 547 nm upon excitation with UV light (380 nm) was observed. Even though the intensity of some emission peaks was very low, it was possible to detect it. In fact, some emission peaks reveals shoulders that suggest the presence of several components as shown in Fig. 3 (b). It is clear that these PL measurements should be refined in all cases with the purpose to carry out a deconvolution process using Gaussian components in order to propose a possible origin of the observed luminescence emission. Nevertheless, from Figs. 3(a) and 3 (b) interesting results about the luminescence properties of the Zn-doped LNO crystals studied in this work are shown. It is observed that all crystals with low concentration of Zn show the well-known blue band centred at 440 nm whose origin was described above and usually is present in pure LNO crystals [8]. Although some of the crystals in addition show other emission peaks centred at 410, 419, 530 and 547 nm. In fact, some of these luminescence emissions only appear for specific Zn concentration values such as occurred in the case of crystal doped with 5.0 mol % of Zn. In this case appears an emission with a peaks centred at 410 nm which was not observed in all other cases. Moreover, there was found an extraordinary high intensity violet emission centred at 419 nm for the crystal doped with 9.0 % mol of Zn. Nevertheless, this emission also appears for the crystal doped with 5.0 mol % of Zn but with a lower intensity as shown in the magnified view of Fig. 3(b).

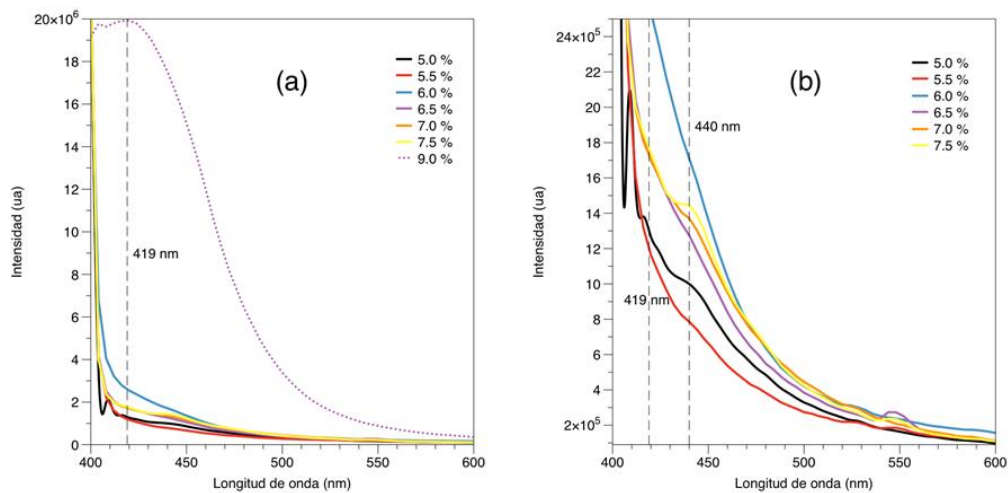


Fig. 3(a) PL spectra of LNO single crystals for different concentration of Zn with an excitation wavelength of 380 nm, (b) magnified view of PL spectra of LNO single crystals for the lower concentrations of Zn.

From the obtained results shown in Figs. 3(a) and 3(b) it is clear that photoluminescence properties of LNO crystals studied in this work strongly depend on the value of Zn concentration. As it was observed, all the crystals presented peaks of photoluminescence emission in the violet-green spectral region. In fact, all the crystals studied presented the blue band emission centred at 440 nm. Nevertheless, in some cases such as the crystal doped with 5% mol of Zn appeared other band emission in the violet region not present in the other crystals. In general terms was observed that the peaks of band emissions tend to shift to the violet region when the Zn concentration is increased as occurred for the crystal with 9% mol of Zn which presents a very high peak emission centred at 419 nm. This behaviour clearly is connected to the magnitude of the Li/Nb ratio present in the Zn-doped LNO crystals obtained from the Raman spectroscopy studies. It is important to note that the LNO crystals with a low Li/Nb ratio showed photoluminescence bands emission with peaks that tend to be centred at lower wavelengths in the violet region than the bands emission of the crystals with a higher Li/Nb ratio.

4. Conclusions

In this work we have shown that the photoluminescence properties of LNO single crystals have a strong dependence on the Zn doping concentration. The studies of Raman and UV-Vis spectroscopies, together with the fluorospectrometry technique have permitted to connect the structural and PL properties of LNO single crystals considered. The emission peaks in PL spectra of the LNO crystals varied in amplitude and in wavelength position according to the Zn level concentration. An extraordinary and high intensity violet luminescence at 419 nm with excitation in UV region (380 nm) was observed in the case of the crystal doped with the higher concentration (9 mol %) of Zn. Nevertheless, at least one of the other crystals (that with 5.0 mol % of Zn) also shown a band emission centred at this wavelength. The crystals doped with the other concentration ranging from 5.0 mol% to 9 mol % presented bands emission in the blue-green spectral region with peaks centred at 440, 530, and 547 nm. A blue-shift in the PL spectra of LNO crystals with an increasing on the Zn concentration was observed. This blue-shift in the PL spectra was related to the existence of a low Li/Nb ratio in the LNO crystals such as was obtained from the Raman studies performed to the samples. These results open the possibility that crystals of LNO doped with high concentrations of Zn can be used in photonic applications in the UV region of the electromagnetic spectrum.

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