Crystalline, Raman, and UV-VIS characterization on Zn-doped LiNbO$_3$ single crystals

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ABSTRACT

Lithium niobate LiNbO$_3$ (LNO) is a photorefractive nonlinear optical material, which exhibits very strong electro-optic behavour and photoconductive effects connected to high optical non-linearity. In this work, we evaluate by Raman and reflectance difusse Uv-vis spectroscopies, the influence of Zn in LNO single crystals. The samples were prepared by Czochralski technique and were doped with zinc at concentration from 5 to 9 mol %. The evolution of the half-widths of E(TO) and A$_1$(TO) Raman bands indicate no variation in lattice vibrations with slight changes in the peak width and intensity. On the other hand, the evolution of ratio Li/Nb concentration was determined by Raman and UV reflectance diffuse spectroscopies, respectively. The evolution of indirect band gap energy of Zn-doped LNO shows that energy values in a range of 3.9 to 4.0 are larger than expected to undoped lithium niobate

1. INTRODUCTION

Lithium niobate (LiNbO$_3$; LNO) is a photorefractive nonlinear optical material. This material has been proved as a potential candidate for advanced photonic applications including the store and process of information.[1] It has a characteristic rombohedral structure rather than the perovskite structure and it is ferroelectric at room temperature. The great interest to prepare LNO single crystals is due to its compositional stability during growth. During the melt and the growing crystal 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. In the optical properties context, Zinc (Zn) as a transition metal efficiently modify the photo-refraction efficiency hence improve the data storage capabilities.[2-4] Zn doping improves the optical damage resistance significantly of roughly above 7 mol% in nominal melt[5]; and it is suitable for the recording of holograms at high-speed with long life-time due to the optical band gap of LNO.[6] Analogous to In doping, Zn doping makes LNO suitable for ultraviolet recording grating application.[2] Recently, S. K. Kushwaha, et al.[7] made a comparison of structural and vibrational properties between pure and Zn-doped at 1 mol% LNO single crystals. The distribution of dopant ions in the lattice matrix of a host single crystal depends on the concentration, size and ionic state of dopant. This one incorporates homogeneously in the lattice only up to a certain concentration.[8] At higher concentrations, high strain develops in the lattice. During this process, defects take place leading to agglomeration of point defects, and dislocations.[9] 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. 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.

2. EXPERIMENTAL DETAILS

Seven $LiNbO_3$ single crystals with different ZnO concentrations from 5 to 9 mol% were acquired from a commercial supplier (Impex High-Tech, Germany). These samples were grown by the conventional 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 $a \times b \times c = (8 \times 1 \times 10)$ mm^3 for all crystals.[10] Raman spectroscopy (Micro RAMAN Labram HR VIS-633 Horiba model, equipped with a Olympus microscope with 10x objective, with laser spot diameter ~15 μm and a CCD detector) was performed with spectra scanned between 180 and 1000 cm^{-1} and five accumulations, using a He–Ne laser at a wavelength of 632.8 nm with 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} and lamp replacement (visible-ultraviolet) at 350 nm.
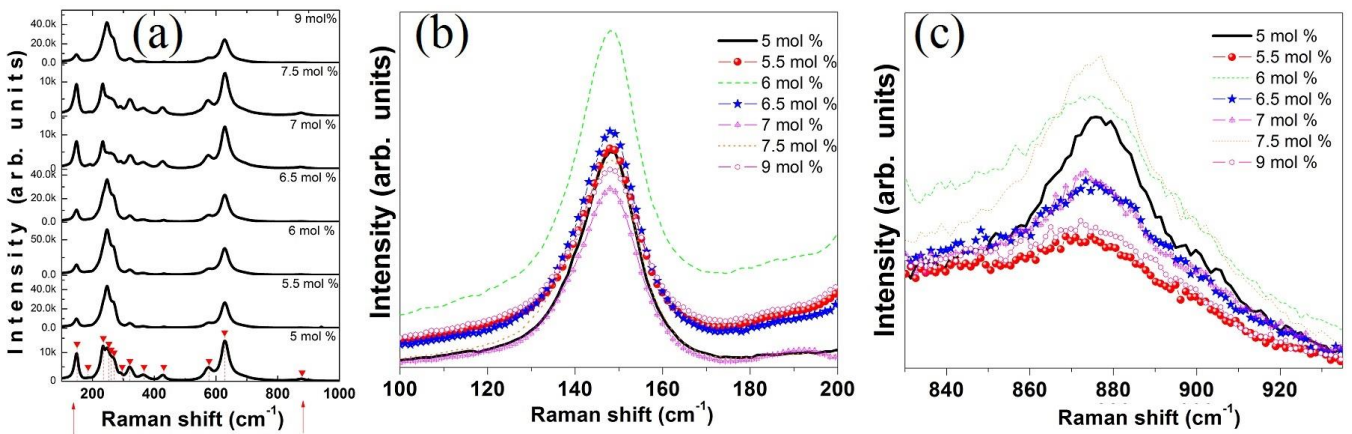
3. RESULTS

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

The Raman spectra recorded for Zn-doped LNO single crystal are shown in Fig. 1 (a) The LNO unit cell with 10 atoms results in 30 degrees of freedom, 27 of which assigned as phonon modes and other three as acoustic phonons. The optical modes of LNO for R3c symmetry are given by the relation: $\Gamma_{optical} = 4A_1 + 5A_2 + 9E$. Only A_1 and E modes are Raman active therefore only 13 phonon peaks are expected in the spectra as one can observe as a 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 due to the ionic character of LNO.[11] 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.[12] One can observe significant differences in the peak intensities of the recorded spectra. The intensity of the line at 186 cm^{-1} is said to be strongly dependent on structural defects[12] and its low intensity for LNO may be attributed to the presence of stress in the lattice. The relaxation of the lattice from strains of Zn-doped LNO crystal might have led to the increase in the intensity of this peak. The increase in the intensity of the other peaks also may be attributed to the same reason. The observed modes in the present crystals are in good agreement with various reports available in the literature.[7, 11, 13, 14] Except variation in the intensities of the 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 ~878 cm^{-1} indicated by arrows in Fig. 1 (a). Magnified views of these modes

are shown in Fig. 1 (b) and (c), respectively. The determination of Γ as the linewidth (FWHM) in the mode E(TO) and for the mode A_1(LO was useful to evaluate the Li concentration (C_{Li}) through the empirical formulae: C_{Li}[mol%] = 53.03–0.4739Γ [cm^{-1}] for 150 cm^{-1} and C_{Li}[mol%] = 53.29–0.1837Γ [cm^{-1}] for 878 cm^{-1}.[12] 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).[14] C_{Li} values also are given in Table. 1. It is important to mention that the Li/Nb ratio up to 0.946 are termed as congruent crystal, and above 0.970 are termed as stoichiometric.

Table 1. Line widths (FWHM) of the Raman modes E(TO) and A_1(LO), the Li concentration (C_{Li}) and the Li/Nb ratio.

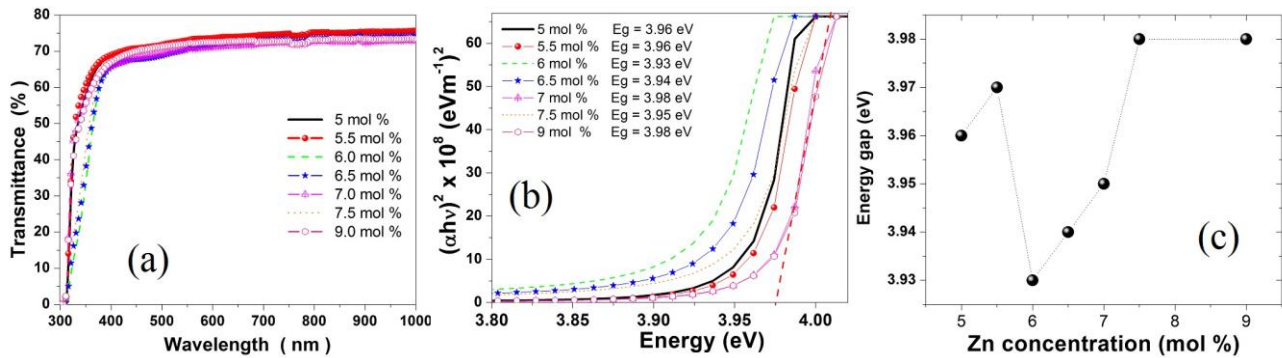| Vibrational mode / Zn concentration (mol %)	5	5.5	6	6.5	7	7.5	9
$\Gamma_{E(TO)}$ (cm^{-1})	15.4	15.5	15.6	16.2	16.8	17.5	17.1
$\Gamma_{A1(LO)}$ (cm^{-1})	34.0	27.6	29.3	28.6	25.7	30.1	35.8
C_{Li} (mol %) E(TO)	45.7	45.7	45.6	45.3	45.0	44.7	44.9
C_{Li} (mol %) A1(LO)	47.0	48.2	47.9	48.0	48.6	47.7	46.7
Li/Nb	0.941	0.964	0.958	0.961	0.972	0.954	0.934

Fig. 2(a) $(\alpha h\upsilon)^2$ vs hυ spectra for the calculation of indirect band gap of Zn-doped LNO single crystals. (b) Evolution of band gap vs Zn concentration.

The optical transmission spectra were recorded in the wavelength range of 300–1000 nm and are shown in Fig. 1(a). The evolution of these results shows that the crystals are highly transparent above a wavelength of 350 nm. The indirect band gaps of Zn-doped LN crystals have been calculated using the relation: $(\alpha h\upsilon)^2 = A(E_g - h\upsilon)$. One can observe in Fig. 2(a), the evolution of $(\alpha h\upsilon)^2$ vs. hυ, where α is the absorption coefficient in cm^{-1}, υ is the frequency of incident radiation, and h is the Plank's constant. Eg represents the optical band gap and A is a constant.[15] The Eg values have been evaluated by extrapolating the linear part of the plots (see dot line) to the abscissa (hυ). The values were found to be between 3.93 and 3.98 eV. Fig. 2 (c) shows the increase in the band gap as increase the Zn concentration. These changes may be attributable 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 structural rearrangement near the defects can change its main linear optical effects. When Nb_{Li} antisites are formed, and in order to electrically balance the region, it is very likely that near the-Li oxygen vacancies are created, obtaining a local structural rearrangement. [10, 16] Because usually zinc ions substitute the Nb_{Li} antisites[17] the intrinsic defects of LiNbO$_3$ 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 the photorefraction applications in the UV region of electromagnetic spectrum.[2]

4. CONCLUSION

The analysis of half-widths of E(TO) and A$_1$(TO) in order to determine the ratio Li/Nb shows that the Zn-doped LNO single crystals are in agreement with termed as congruent crystal, and above 0.970 as stoichiometric.

The optical absorption results for Zn-doped LNO were transformed in Kubelka-Munk units in order to determine the indirect band gap. The evolution of these results was found to be slightly increased with the increase of Zn doping. These results show that the energy band structure is distorted by the presence of zinc such that the energies for these transitions are larger than those of undoped lithium niobate.

5. AKNOWLEDGEMENT

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