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X-ray photoelectron spectroscopy, high-resolution X-ray diffraction and refractive index analyses of Ti-doped lithium niobate (Ti:$LiNbO_3$) nonlinear optical single crystal

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Abstract. Congruent $LiNbO_3$ single crystals with Ti ion dopants (2 and 5 mol%) were successfully grown by Czochralski technique in the automatic diameter control facility. As-grown crystal boules were oriented into (0 0 1) direction cut and optically polished for all measurements. Influence of Ti-ion incorporation into $LiNbO_3$ was studied by core level XPS analysis. Powder X-ray diffraction studies were carried out on doped lithium niobate for phase identification. High-resolution X-ray diffraction technique was used to study the crystalline quality through full-width at half-maximum values. The refractive index values are more for doped samples than for pure sample as determined by prism coupling technique with different laser sources.

Keywords. Lithium niobate; doping; refractive index; X-ray photoelectron spectra; nonlinear optical materials.

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1. Introduction

$LiNbO_3$ single crystal is an excellent material for a variety of applications in nonlinear optics and electro-optics because of its large second-order nonlinearities. Almost all commercially available lithium niobate crystals are grown from a melt of congruent composition by the Czochralski method. The congruent composition is reported to be between 48.35 and 48.60 mol% Li_2O [1–3]. Congruent $LiNbO_3$ (denoted cLN) crystals generally have good optical quality and uniformity. It has

non-stoichiometric composition with many intrinsic defects such as cation vacancies and Nb anti-site defects owing to lack of Li ions [4]. The existence of these defects leads to some restrictions in the desired applications. One of the most effective ways for compensating these defects is to add dopant ions into the cLN melt composition. The physical properties of the crystals are also influenced by the type and amount of dopant ions added [5,6]. Therefore, suitable types of dopant ions and concentrations can be selected based on the required application.

$LiNbO_3$ single crystals can be used for developing optical waveguides with Ti ion diffusion. Metal ion of Ti-diffused $LiNbO_3$ are shown to have a low optical loss and high refractive index values which are important for optical waveguide devices [7]. These optical devices were mainly fabricated using Czochralski-grown $LiNbO_3$ from congruent melt composition. The refractive index increases with the addition of Ti ions and Ti concentrations are important to develop suitable Ti-diffused optical waveguides in cLN. To improve the properties of Ti-diffused waveguides, it is essential to know the influence of Ti ion concentration on the structural and optical properties in cLN optical crystals. In the present communication, we have described the influence of Ti-ion doping in the congruent lithium niobate crystals using X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), high-resolution X-ray diffraction (HRXRD) and prism coupling techniques.

2. Experiment

The starting materials for growing congruent $LiNbO_3$ crystals were 48.6 mol% Li_2CO_3 and 51.4 mol% Nb_2O_5 of high purity from Alfa Aesar. They were mixed thoroughly in an alcohol-wetted zirconia ball mill for 24 h. After the mixture was dried and calcined at 900°C for 24 h solid state reaction and de-carbonization period and different amount of TiO_2 (99.995%) were added to the calcined mixture. The synthesized material was then mixed once again and packed into a platinum crucible of 40×40 mm^2 dimension. Single crystals of $LiNbO_3$ doped with 2 and 5 mol% Ti ions were grown from the melt with congruent composition (48.6/51.4 = Li/Nb). The crystals were grown by conventional Czochralski method using automatic diameter controller (ADC) facility with resistive furnace in air atmosphere. The chosen seed crystal was a pure $LiNbO_3$ crystal with $5 \times 3 \times 60$ mm^3 dimensions and oriented along the C-axis (0 0 1). The crystals were grown with a pulling rate of 0.8 mm/h and rotation rates of about 2–10 rpm. The obtained 2 mol% (denoted cLNT2) and 5 mol% (denoted cLNT5) Ti-doped cLN single crystal were yellow, transparent and crack-free. All the grown crystals were around 20 mm in diameter and 25–30 mm in length. After the crystals were grown, post-growth annealing was carried out at 1000°C for 24 h, then they were cooled to room temperature in air at the rate of 50°C/h.

As-grown crystals were oriented in the z-axis direction (0 0 1) using X-ray goniometer and several wafers of ≈0.7–1 mm thickness were sliced from the grown crystals. Figure 1 shows the photograph of z-axis oriented Ti:$LiNbO_3$. One of the wafers taken from middle part was polished to optical quality to a thickness of 0.8 mm for both cLNT2 and cLNT5. Polished crystals of dimension $10 \times 7 \times 0.8$ mm^3 were used for all measurements. X-ray powder diffraction analysis was carried out

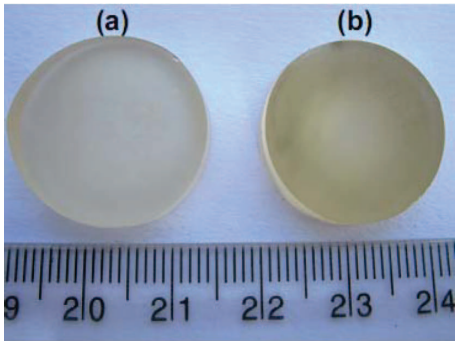

Figure 1. z-axis (0 0 1) oriented (**a**) 2 mol% and (**b**) 5 mol% Ti-doped $LiNbO_3$ samples.

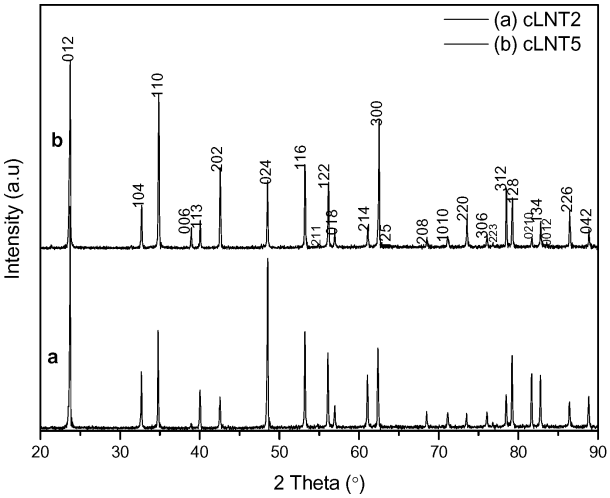

Figure 2. Powder XRD pattern of different $LiNbO_3$ samples: (**a**) cLNT2 and (**b**) cLNT5.

by Rigaku miniflex diffractometer using CuK_α ($\lambda = 1.5405$ Å) as X-ray source for crystalline phase identification. HRXRD analysis was carried out for the samples using a Philips X'pert Pro Materials Research Diffractometer (MRD) in the receiving slit operation mode with a single $CuK\alpha_1$ line of wavelength $\lambda = 1.54056$ Å and angular divergence of $\Delta\alpha = 12$ arc sec. X-rays generated from the monochromator were diffracted from (0 0 6) $LiNbO_3$ atomic planes with the $(+, -, -, +, +)$ geometry [8]. The XPS analysis was taken in a Physical Electronics PHI 5000 Versaprobe^{TM} with monochromatized Al$K\alpha$ (1486.6 eV) X-rays. The energy resolution of this instrument is 0.5 eV FWHM. The measurement was carried out at a base pressure of 5.6×10^{-9} Torr in an analyzer chamber. The prism coupling method was employed to measure the TE mode index values using a Model 2010/M Prism Coupler (Metricon Corporation, USA). In the experiment, different laser sources with wavelengths ranging from 632.8 to 1553 nm were used.

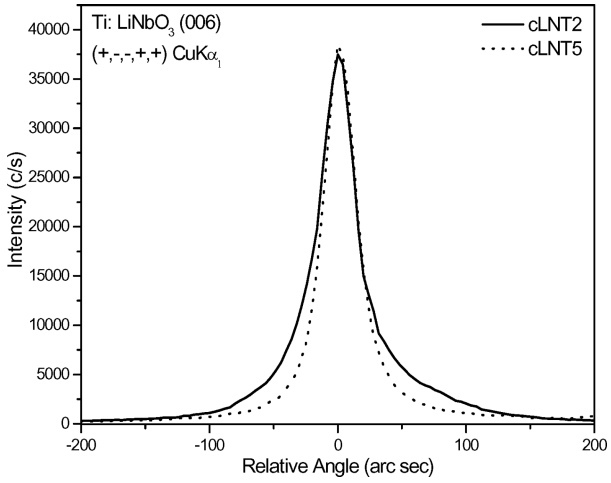

Figure 3. (0 0 6) plane HRXRD spectra recorded for (—) cLNT2 and (···) cLNT5 samples.

3. Results and discussion

Powder X-ray diffraction studies were carried out to confirm the formation of crystalline phase in doped crystals. The obtained XRD patterns of the cLNT2 and cLNT5 crystals at room temperature are shown in figure 2. From powder XRD analyses we confirmed that Ti-doped $LiNbO_3$ crystals were single crystalline phases of $LiNbO_3$. The obtained diffraction peaks were compared with JCPDS card (No. 74-2240) and hkl planes were indexed. The XRD patterns of cLNT2 and cLNT5 were similar and the relative intensity of peaks was changed. The changes may be due to the composition variation in the crystal according to dopant content. No new peak and no peak shifts in the spectra were observed. To know the quality of the crystalline samples of Ti-doped $LiNbO_3$, HRXRD spectra were recorded for samples taken from the middle part. A typical (0 0 6) HRXRD diffraction spectra taken from the (0 0 6) atomic planes of the samples are shown in figure 3. It shows that HRXRD spectra of cLNT2 and cLNT5 samples have well shaped, high intensity sharp peak with no visible distortions and no additional peaks. The measured FWHM values of cLNT2 and cLNT5 were 30.56 and 27.36 arc sec respectively. It reveals that the Ti-doped cLN crystals possess good structural quality of the wafer. Diffraction peak of Ti-doped congruent $LiNbO_3$ samples indicate considerable broadening of (0 0 6) peak, i.e. FWHM, because of the rotation of crystal lattice and strain field [9] in the crystal introduced by the distribution of Ti ions.

A typical photoelectron spectra obtained for Ti:$LiNbO_3$ were shown in figure 4. The binding scale was calibrated using the C1s (284.4 eV) level of adventitious carbon. Curves a and b show pre-clean XPS survey scan of cLNT2 and cLNT5 sample surface. From these spectra the main XPS lines of constituent elements, i.e. O1s, Nb3s, Nb3p, Nb3d doublet, C1s and Ti2p were clearly observed. The presence of Ti peaks, $Ti2p_{3/2}$ and $Ti2p_{1/2}$, can be seen at about 460 eV. Regrettably, intense Nb3s line is partly superimposed on the weak Ti2p doublet and only $Ti2p_{1/3}$

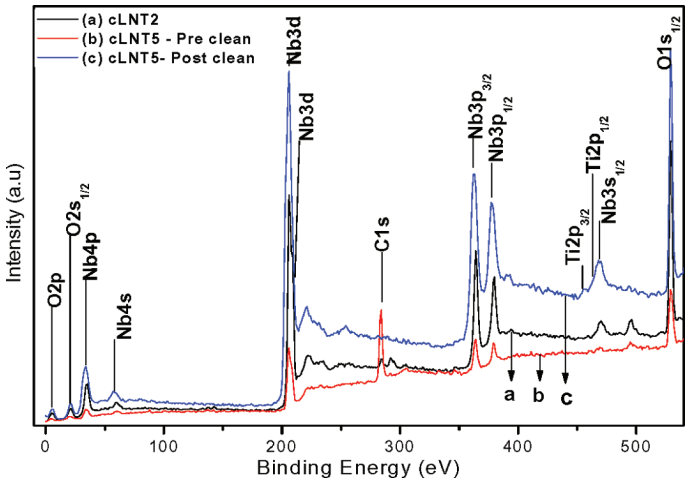

Figure 4. Survey scan of XPS core level spectra of cLNT2 (curve a), cLNT5 pre-clean (curve b) and cLNT5 post-clean (curve c) samples.

peak is clearly visible. The C1s level peak observed at 283.5 eV, results from the trace amounts of organic impurities. All observed core level peak positions of the constituent elements are in good agreement with peak positions reported earlier in [10] for Ti in-diffused $LiNbO_3$.

Curve c of figure 4 shows post-clean spectra of cLNT5 after bombarding it by Ar^+ ions with 2 keV energy for 5 min. After this treatment the adsorbed C1s line was nearly completely removed. Also cLNT5 pre-clean sample shows pronounced shoulder from the higher energy side of O1s (528.6 eV) lines related to the adsorbed carbon oxides. It has been completely removed after Ar^+ ion treatment. From the XPS analysis, it should be noted that our results for binding energy differences between O1s and $Ti2p_{3/2}$, O1s and $Nb3d_{5/2}$ equals to 71.4 and 323.2 eV respectively determined for Ti:$LiNbO_3$ are in good agreement with those reported earlier [10]. The values for O1s-$Nb3d_{5/2}$ (323.2 eV) allows to estimate chemical bond between O and Nb in Ti:$LiNbO_3$ crystal lattice as 200.1 pm [11].

Table 1 shows the measured transverse electric (TE) mode refractive index values for cLNP, cLNT2 and cLNT5 at different wavelengths. The refractive index values were measured at different coupling laser wavelengths upto the third optical window. The wavelengths are 632.8, 825, 1061, 1312 and 1533 nm. During the measurement the intensity of the incident laser light reflected from the prism base–sample interface drops abruptly at a particular angle called critical angle. The refractive index of the prism (n_p) and critical angle are known, and then refractive index of the sample can be measured. From the measured values, it can be seen that TE mode refractive index increased linearly with an increase of Ti concentration (2 and 5 mol%) in doped cLN. Also TE mode refractive index values increasing with decreasing wavelengths were observed.

Table 1. Measured TE mode refractive index values for cLNP, cLNT2 and cLNT5 at different wavelengths. These values are accurate to ±0.0001.

Wavelength (nm)	cLNP	cLNT2	cLNT5
1533	2.2138	2.2145	2.2173
1312	2.2217	2.2230	2.2254
1061	2.2336	2.2350	2.2379
825	2.2536	2.2549	2.2575
632.8	2.2867	2.2900	2.2933

4. Conclusion

In this study, 2 and 5 mol% concentrations of Ti-doped $LiNbO_3$ single crystals were successfully grown by Czochralski method. As-grown crystals studied by different techniques and some structure-related features have been analysed. Crystal powder XRD patterns revealed that as-grown crystals had a single crystalline $LiNbO_3$ phase. HRXRD studies showed the good structural quality of the samples. We examined the electronic structure of the Ti-doped $LiNbO_3$ with XPS to analyse the effects of Ti ions in the crystal lattice. Ar^+ ion bombardment provided complete disappearance of carbon and oxygen-absorbed carbon at the crystal surface. The binding energy difference of Δ(O–Nb) allowed to estimate chemical bond between O and Nb in crystal lattice as 200.1 pm. The TE mode refractive index values were improved by the addition of Ti ions in $LiNbO_3$ which have been favourable for optical waveguide. These characteristics allowed us to conclude that as-grown crystals of Ti:$LiNbO_3$ are good candidates for nonlinear optical waveguide application.

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