# PHOTOREFRACTIVE EFFECT IN LITHIUM NIOBATE CRYSTALS OF VARIABLE COMPOSITIONS AND ITS MANIFESTATION IN RAMAN SPECTRA

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*Results of Raman studies of ordering of the cation sublattice and photorefractive properties of LiNbO₃ single crystals are reported. Photorefraction of crystals containing small concentrations of $Gd^{3+}$ or $Y^{3+}$ and $Mg^{2+}$ is found to be essentially determined by ordering of structural units of the cation sublattice. Intensity of the stretch vibration band of the oxygen bridge between $NbO_6$ $NbO_6$ octahedrons is found to be sensitive to dipole ordering in the cation sublattice of the crystal.*

Recent findings have led to the development of new approaches to growing highly perfect single crystals of compositions close to the stoichiometric (R=Li/Nb=1), revealing a noticeable influence of intrinsic structural defects on photorefractive properties of the crystal [1]. Raman studies of photorefractive effect in lithium niobate crystals of various compositions (including those moderately doped with nonphotorefractive cations) are reported in the paper presented. Photorefraction is revealed in Raman spectra by appearance of forbidden bands [2-7]. It is interesting that intensity of the forbidden bands increases with time, as the optical damage grows.

We have studied the spectra of nominally pure single crystals of congruent (R=0.946) and stoichiometric (R=1) compositions grown from melt (either of stoichiometric composition doped with $K_2O$ or with excess $Li_2O$), congruent single crystals doped with non-photorefractive impurities: LiNbO₃:Gd ($C_{Gd}$=0.002 and 0.44 mass%), LiNbO₃:Y ($C_Y$=0.24 and 0.46), and stoichiometric LiNbO₃:Gd ($C_{Gd}$=0.001 mass %).

Figures 1 (a, b) and 2 show fragments of Raman spectra of crystals of different compositions in the scattering geometry Y(ZX)Z. The spectra are essentially different, and the differences are of fundamental nature determined by ordering of structural units in the lithium niobate cation sublattice. Crystals of stoichiometric composition with a highly ordered cation sublattice were expected to have the least photo-refraction. However, our experiments show a stronger effect in nominally pure, highly-ordered stoichiometric lithium niobate crystals compared to crystals of congruent composition. This is apparent from Figure 1 (a, b) presenting spectra of both the low-frequency region and the region of vibrations of the $NbO_6$ oxygen octahedrons. According to Raman tensor [1, 8, 9], in the absence of photorefraction only the ~150 cm⁻¹ and 580 cm⁻¹ bands corresponding to E(TO) phonons should be active in the regions considered. Appearance of ~172 cm⁻¹ and 605 cm⁻¹ bands (Fig 1 (a, b) corresponding to $A_1$(TO) phonons forbidden in the Y(ZY)Z scattering geometry is caused by photorefraction.

Figure 1 (a,b) points also to relationship between the intensity of forbidden bands (and, consequently, the effects of photorefraction) and the crystal composition. Intensity of forbidden bands is stronger in spectra of stoichiometric crystals either nominally pure or slightly alloyed with $Gd^{3+}$ (curves 1 and 2, respectively) compared to crystals grown from melts of stoichiometric composition alloyed with $K_2O$ (curve 3) and congruent crystals (curves 4). It should be also noticed that within a certain range of impurity concentration (where structural units of the cation sublattice are ordered [1, 8, 10] the intensity of forbidden bands in spectra of congruent crystals (curves 6, 8)

and, consequently, the effect of photorefraction, is considerably smaller than in spectra of nominally pure crystals of stoichiometric and congruent compositions.

Further increase of admixture concentrations in congruent crystals (>0.4 w.%) broadens and increases the intensity of forbidden bands (curves 7, 9) due to increasing photorefraction, and also broadens all the other spectrum lines, apparently as the result of disordering of the cation sublattice brought about by alloying impurities. The effects of photorefraction in stoichiometric or congruent crystals are different depending on the method they are grown. Evaluating the effect of photorefraction by the intensity of forbidden Raman bands (Figure 1 a, b) it is approximately 1.5-3 times stronger in congruent and stoichiometric crystals grown without $K_2O$ admixtures compared with samples grown from similar melts with added $K_2O$.
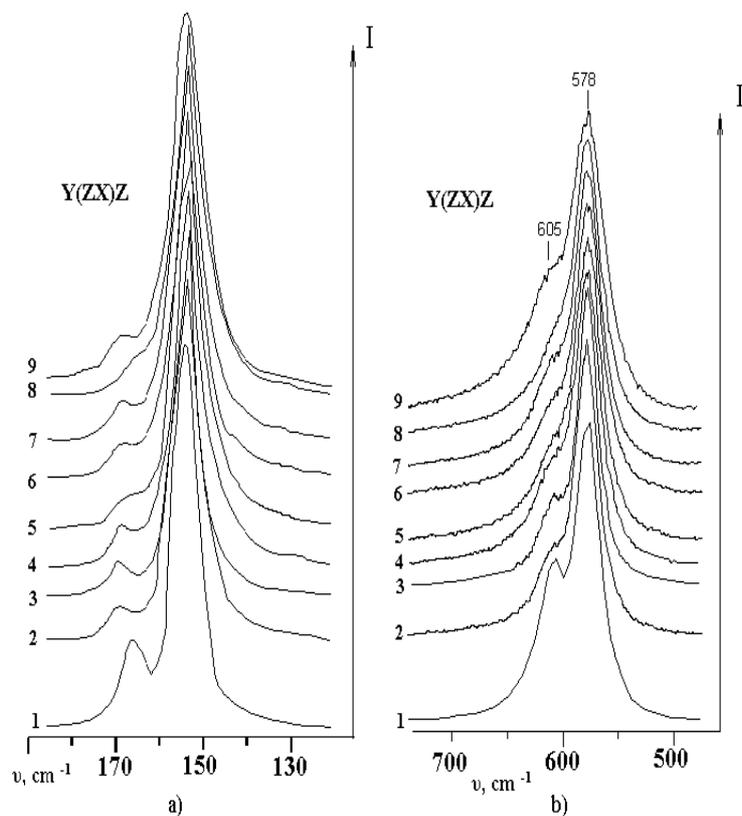


**Fig.1.** Fragments of Raman spectra of diverse lithium niobate single crystals: a) the low-frequency region; b) the region of vibrati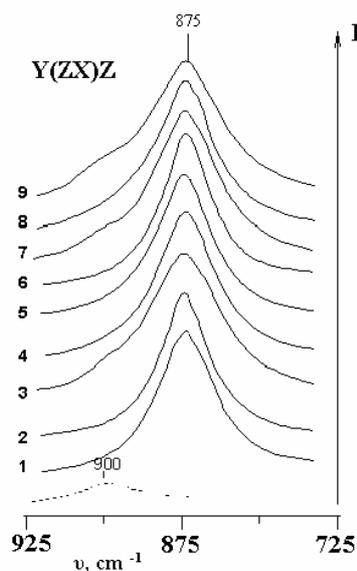ons of the $NbO_6$ oxygen octahedrons. 1.- $LiNbO_3$ stoich. 2.- $LiNbO_3$ stoich.: Gd(0.001%) 3.- $LiNbO_3$ stoich. ($K_2O$). 4.- $LiNbO_3$ cong. 5.- $LiNbO_3$ cong. ($K_2O$). 6.- $LiNbO_3$ cong.: Gd(0.002%). 7.- $LiNbO_3$ cong.: Gd(0.44%). 8.- $LiNbO_3$:Cong.: Y(0.24%):Mg (0.63).9.- $LiNbO_3$:cong.: Y(0.46%).

Whether alloyed or altered in stoichiometry, the lithium niobate crystals invariably demonstrate ordering of structural units in the cation sublattice and dipole moments of the $BO_6$ octahedrons and, consequently, their polarizability. The changes should affect the band corresponding to stretch vibration of the oxygen bridge of $BO_6$ octahedral anions (where B are principal ($Li^+$, $Nb^{5+}$) or impurity cations). The latter is active in Raman spectrum of non-centrosymmetric oxygen octahedrons and forbidden in the spectrum of centrosymmetric (ideal) octahedrons [11]. Figure 2 shows transformation of the band shape of the $B_1$-O-$B_2$ stretch upon the change of crystal composition.

The band has clearly a complex shape. Analysis by band separation software shows existence of only a single band (curves 1, 2, 4-6, 8) in the spectra of crystals with relatively ordered cation sublattices, for instance, those of either congruent or stoichiometric, nominally pure lithium niobate crystals, as well as in the spectra of congruent crystals alloyed with relatively small quantities of $Gd^{3+}$, $Y^{3+}$ ions in the region $B_1$-O-$B_2$ stretch. It is interesting that this band is the narrowest in stoichiometric, i.e. the most ordered crystals. The spectra of both stoichiometric, $Gd^{3+}$-alloyed and congruent crystals, rather heavily alloyed with $Gd^{3+}$ and $Y^{3+}$, clearly exhibit two bands with frequencies 875 and ~900cm$^{-1}$, (curves 3, 7 ,9) in the region of oxygen bridge stretch. A dotted line corresponding to frequency 900 cm$^{-1}$ is shown in Figure 2.

Thus, both stoichiometric and nominally pure congruent lithium niobate crystals may be regarded as single mode crystals. It should be noticed that single mode behaviour of alloyed lithium niobate crystals becomes a manifestation of the slightly alloying impurity concentrations that affect ordering of the cation sublattice of congruent crystals diminishing photorefraction [1, 10]. The photorefractive properties of the crystal can be diminished by admixture of small concentrations (hundredth and thousandth of w.%) of non-photorefractive cations ordering the cation sublattice. Decline of photorefractive properties has been earlier observed only in crystals heavily alloyed (~5 w.%) with non-photorefractive cations [1, 10, 12].

Comparison of Raman spectra of nominally pure stoichiometric lithium niobate crystals grown by different methods shows that both defectness and photorefractive properties are essentially determined by the method employed to grow the crystals. In particular, the difference of forbidden Raman band intensities (about 1.5-3 times) in spectra of stoichiometric crystals grown from melt containing and not containing $K_2O$ (Figure 1a, 1b) point to fine discrepancies in the ordering of structural units of the cation sublattice. The differences may be attributed to the higher purity of the crystal grown from the melt doped with $K_2O$, which results both in decrease of the content of accidental cations with variable valence and difference in the mechanisms of photo-induced excitation of electrons.



**Fig.2.** Fragment of Raman spectrum of different lithium niobate single crystals in the region of stretch of the $NbO_6$ octahedron bridge. 1.- $LiNbO_3$ stoich. 2.- $LiNbO_3$ stoich.: Gd(0.001%) 3.- $LiNbO_3$ stoich. ($K_2O$). 4.- $LiNbO_3$ cong. 5.- $LiNbO_3$ cong. ($K_2O$). 6.- $LiNbO_3$ cong.: Gd(0.002%). 7.- $LiNbO_3$ cong.: Gd(0.44%). 8.- $LiNbO_3$ cong.: Y(0.24%): Mg.(0.63) 9. - $LiNbO_3$:cong.: Y(0.46%).

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