Manifestation of a photorefractive effect in Raman spectra of lithium niobate crystals of different compositions

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Abstract.   **The ordering of structural units in a cation sublattice and the photorefractive properties of lithium niobate single crystals of different compositions: nominally pure with different [Li]/[Nb] ratios and doped with non-photorefractive cations Mg^{2+}, Gd^{3+}, and Y^{3+}, are studied by their Raman spectra. It is shown that at low concentrations of Mg^{2+}, Gd^{3+}, and Y^{3+}, the magnitude of the photorefractive effect is determined by the ordering of the structural units of the cation sublattice. It is found for the first time that the intensity of a Raman line corresponding to the bridge valence vibrations of oxygen atoms in the NbO_6 octahedra is sensitive to the dipole ordering of the cation sublattice.**

Laser radiation induces a change in the refractive index of a lithium niobate crystal ($LiNbO_3$). This phenomenon is called the photorefractive effect or optical distortion effect [1, 2]. This effect prevents the use of these unique crystals in optics for frequency conversion, in electro-optical modulators, etc. [1–4]. The photorefractive effect can be reduced by doping heavily (up to the mass concentration 6 %) the crystal with non-photorefractive cations (for example, Mg^{2+}, Zn^{2+}, In^{2+}, Sc^{3+}, and other cations), which unlike photorefractive cations (Cu, Mn, Ni, etc.), do not change their charge state in a crystal structure upon their illumination [1–4]. In the last years, due to the development of new methods for growing single crystals with the nearly stoichiometric composition ($R = $ [Li]/[Nb] $= 1$), it was found the intrinsic defects of the structure noticeably affect its photorefractive properties [2].

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In this paper, we studied the photorefractive effect in lithium niobate crystals of different compositions (including crystals weakly doped with non-refractive cations) by their Raman spectra. The photorefractive effect is manifested in the appearance of Raman lines, which are forbidden for the given scattering geometry [5–10]. The intensity of the forbidden lines increases with time with increasing optical distortion. We studied the Raman spectra of nominally pure single crystals of the congruent ($R = 0.946$) and stoichiometric ($R = 1$) compositions, which were grown by two methods (from a melt with the excess of Li_2O and a stoichiometric melt with K_2O added), the spectra of congruent single crystals doped with non-photorefractive impurities: $Gd : LiNbO_3$ (the minimum and maximum mass concentrations of gadolinium are $C_{Gd} = 0.002$ % and 0.44 %, respectively) and $Y : LiNbO_3$ ($C_Y = 0.24$ % and 0.46 %, respectively), and the Raman spectra of stoichiometric $Gd : LiNbO_3$ crystals ($C_{Gd} = 0.001$ %). The single crystal growth methods and the preparation of samples for studies are described in detail in papers [11, 12]. The Raman spectra and photorefraction were excited by a 0.2-W, 514.5-nm line from an ILM-120 argon laser. The spectra were recorded with a Ramanor U-1000 and DFS-24 spectrometers at room temperature. Because the spectra of photorefractive crystals can change with time [2, 5, 9], they were recorded within approximately an hour after the beginning of irradiation by the laser, when these variations virtually disappear.

Figures 1 and 2 show the fragments of Raman spectra of crystals of different compositions recorded in the $Y(ZX)Z$ geometry. One can see that the spectra are substantially different. The differences are of a fundamental nature and are determined by the properties of the ordering of structural units in the cation sublattice of lithium niobate. We expected that photorefraction will be minimal in stoichiometric crystals because they have the highly ordered cation sublattice. However, our experiments showed that photoefraction was stronger in nominally pure highly ordered lithium niobate crystals than in congruent crystals. This is clearly demonstrated in Fig. 1, where the Raman spectra in the low-frequency region and in the region of vibrations of the oxygen octahedra NbO_6 are presented. The character of the Raman tensor assumes [2, 12, 13] that in the absence of photorefraction, only Raman lines at 150 and 580 cm^{-1}, corresponding to the $E(TO)$ phonons, should be observed in these spectral regions. However, photorefraction leads to the appearance of the 172-cm^{-1} and 605-cm^{-1} lines, corresponding to forbidden $A_1(TO)$ phonons in the $Y(ZX)Z$ scattering geometry.
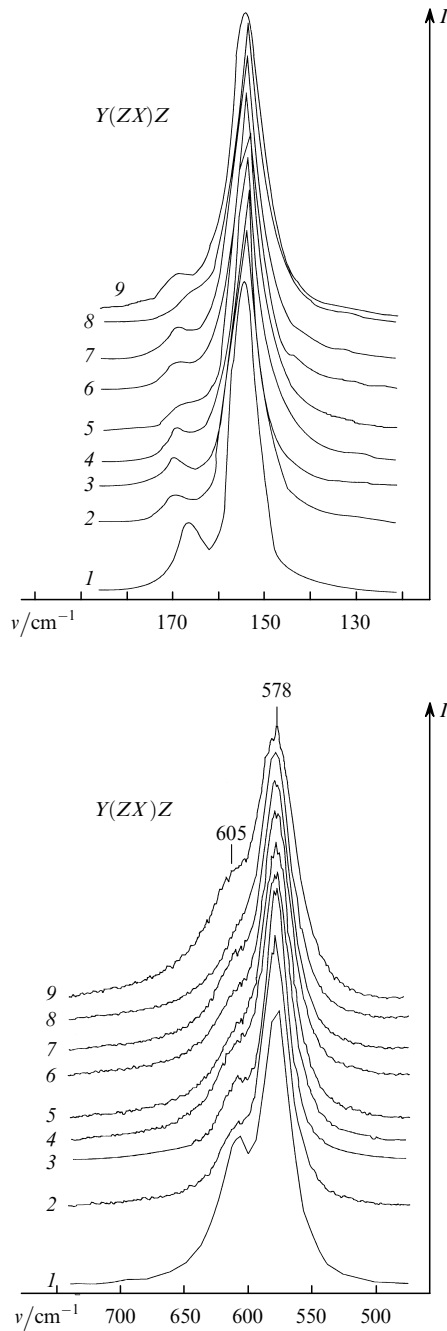
Figure 1. Fragments of the Raman spectra of lithium niobate single crystals of different compositions in the low-frequency region (a) and in the region of vibrations of the oxygen NBO_3 octahedra (b): (*1*) $LiNbO_3$ ($R = 1$); (*2*) $LiNbO_3$ ($R = 1$, $C_{Gd} = 0.001$ %); (*3*) $LiNbO_3$ with the addition of K_2O ($R = 1$); (*4*) $LiNbO_3$ ($R = 0.946$); (*5*) $LiNbO_3$ with the addition of K_2O ($R = 0.946$); (*6*) $LiNbO_3$ ($R = 0.946$, $C_{Gd} = 0.002$ %); (*7*) $LiNbO_3$ ($R = 0.946$, $C_{Gd} = 0.44$ %); (*8*) $LiNbO_3$ with the addition of Mg ($R = 0.946$, $C_Y = 0.24$ %); (*9*) $LiNbO_3$ ($R = 0.946$, $C_Y = 0.46$ %).

It also follows from Fig. 1 that the intensities of the forbidden lines (and, therefore, the photorefractive effect) depend on the crystal composition. The intensity of forbidden lines in the spectra of nominally pure and weakly Gd^{3+}-doped stoichiometric crystals grown from a melt with a substantial excess of Li_2O [curves (*1*) and (*2*)] is higher than the intensity of these lines in the spectra of crystals grown from a stoichiometric melt with the addition of K_2O [curves (*3*)] and of congruent crystals [curves (*4*)].
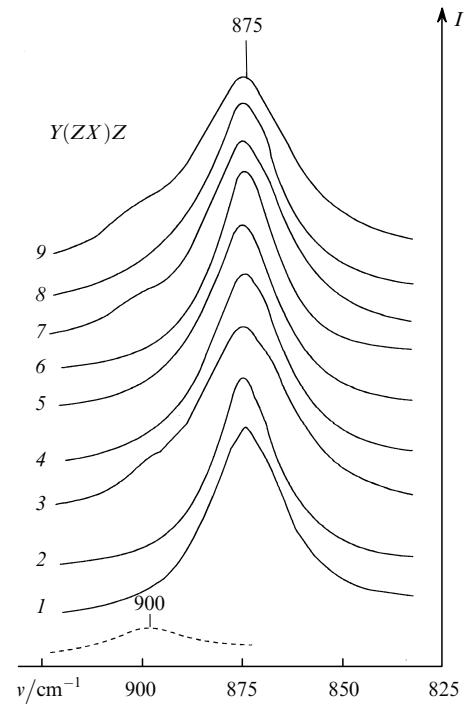

Figure 2. Fragments of the Raman spectra of lithium niobate single crystals of different compositions in the region of valence bridge vibrations of oxygen: (*1*) $LiNbO_3$ ($R = 1$); (*2*) $LiNbO_3$ ($R = 1$, $C_{Gd} = 0.001$ %); (*3*) $LiNbO_3$ with the addition of K_2O ($R = 1$); (*4*) $LiNbO_3$ ($R = 0.946$); (*5*) $LiNbO_3$ with the addition of K_2O ($R = 0.946$); (*6*) $LiNbO_3$ ($R = 0.946$, $C_{Gd} = 0.002$ %); (*7*) $LiNbO_3$ ($R = 0.946$, $C_{Gd} = 0.44$ %); (*8*) $LiNbO_3$ with the addition of Mg ($R = 0.946$, $C_Y = 0.24$ %); (*9*) $LiNbO_3$ ($R = 0.946$, $C_Y = 0.46$ %).

Note also that in a certain region of concentrations of dopants, the intensity of forbidden lines [curves (*6*) and (*8*)] and, therefore, the photorefractive effect in the spectra of congruent crystals are substantially lower than in the spectrum of nominally pure stoichiometric and congruent crystals. As the dopant concentration in congruent crystals is increased (above 0.4 %), the forbidden lines are broadened and their intensity increases [curves (*7*) and (*9*)] due to increasing photorefraction. The other Raman lines are also substantially broadened due to the disordering of the cation sublattice by dopants.

It also follows from our experimental data that the photorefractive effect in stoichiometric and congruent crystals grown by the usual method and with the addition of K_2O into the melt is different. A comparison of the intensities of forbidden lines in the Raman spectra shows that photorefraction in congruent and stoichiometric crystals grown without addition of K_2O is approximately 1.5–3 times higher than in similar crystals grown with the addition of K_2O.

Doping of the lithium niobate crystal or a change in its stoichiometry changes not only the ordering of structural units in the cation sublattice but also the dipole moment of the oxygen BO_6 octahedra and, hence, their polarisability. The intensity of a Raman line corresponding to the valence bridge vibrations of oxygen atoms in the octahedral BO_6 anion should be sensitive to such changes. These vibrations are active in the Raman spectrum of non-centrally symmetric oxygen octahedra and are forbidden in the spectrum of the centrally symmetric (ideal) octahedra [14].

Figure 2 shows the dependence of the shape of the line corresponding to valence $B_1 - O - B_2$ bridge vibrations of oxygen atoms [B_1 and B_2 are the crystal (Li^+, Nb^{5+}) or impurity cations] on the crystal composition. One can see that the line has a complex shape. The analyses of the line shape using the software for separations of line contours shows that the spectra of crystals with a comparatively ordered cation sublattice (for example, the spectra of nominally pure congruent and stoichiometric crystals and the spectra of congruent crystals weakly doped with Gd^{3+} and Y^{3+} ions) exhibit only one line in the region of valence $B_1 - O - B_2$ bridge vibrations [curves (*1*), (*2*), (*4–6*), (*8*)]. This line is the narrowest in highly ordered stoichiometric crystals. Therefore, nominally pure lithium niobate crystals can be treated within the homogeneous region as single mode. This property of doped lithium niobate crystals is manifested at low concentrations of dopants, which produce the ordering of the cation sublattice of a congruent crystal, by decreasing the photorefractive effect [2, 15].

The spectra of stoichiometric lithium niobate crystals weakly doped with Gd^{3+} and the spectra of congruent crystals heavily doped with Y^{3+} and Gd^{3+} exhibit two lines at 875 and ~900 cm^{-1} in the region of valence bridge vibrations of oxygen atoms [curves (*3*), (*7*), (*9*)]. The dashed curve in Fig. 2 corresponds to the ~900-cm^{-1} line.

References

1. Kuzminov Yu.S. *Elektroopticheskii i nelineinoopticheskii kristall niobata litiya* (Electro-optical and Nonlinear-optical Lithium Niobate Crystal) (Moscow: Nauka, 1987).
2. Sidorov N.V., Volk T.P., Mavrin B.N., Kalinnikov V.T. *Niobat litiya: defekty, fotorefraktsiya, kolebatel'nyi spektr, polyaritony* (Lithium Niobate: Defects, Photorefraction, Vibrational Spectrum, Polaritons) (Moscow: Nauka, 2003).
3. Blistanov A.A. *Kristally kvantovoi i nelineinoi optiki* (Crystals for Quantum and Nonlinear Optics) (Moscow: Izd. MISIS, 2000).
4. Rauber A. *Current Topic in Materials Science* (Amsterdam: North-Holland, 1978) Vol. 1, p. 501.
5. Semenov A.E., Cherkasov E.V. *Zh. Fiz. Khim.*, **54**, 2600 (1980).
6. Korotkov P.A., Obukhovskii V.V., Dmitrik G.N., et al. *Opt. Spektr.*, **57**, 572 (1984).
7. Kostritskii S.M., Semenov A.E., Filipov I.V. *Opt. Spektr.*, **57**, 579 (1984).
8. Dmitrik G.N., Korotkov P.A., Radchenko P.S. *Opt. Spektr.*, **58**, 1355 (1985).
9. Semenov A.E., Filipov I.V. *Opt. Spektr.*, **56**, 833 (1984).
10. Malovichko G.I., Grachev V.G., Yurchenko L.P., Proshko Y.Ya., Kokanyan E.P., Gabrielyan V.T. *Phys. Stat. Sol. A*, **133**, K29 (1992).
11. Palatnikov M.N., Sidorov N.V., Stefanovich S.Yu., Kalinnikov V.T. *Trudy III mezhdunarodnoi konferentsii 'Kristally, rost, svoistva, real'naya struktura, primenenie'* (Proceedings of III International Conference on Crystals, Growth, Properties, Real Structure, and Application (Aleksandrov, VNIISIMS, 1997) Vol. 1, p. 349.
12. Palatnikov M.N., Sidorov N.V., Stefanovich S.Yu., Kalinnikov V.T. *Norg. Mater.*, **34**, 903 (1998).
13. Anderson A., Petrov K.I. (Eds) *Primenenie spektrov kombinatsionnogo rasseyaniya* (Application of Raman Spectra) (Moscow: Mir, 1977).
14. Nakamoto K. *Infrared Spectra of Inorganic and Coordination Compounds* (New York: Wiley, 1963; Moscow: Mir, 1966).
15. Sidorov N.V., Serebryakov Yu.A. *Ferroelectrics*, **160**, 191 (1994).