Targeted Changes in the Optical, Electronic, and Elastic Characteristics of Undoped and Doped Crystals of Lithium Niobate

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Abstract—An investigation is performed of low-temperature changes in the electrical conductivity, optical absorption, and velocities of ultrasonic waves in congruent undoped and doped (Fe^{2+}) crystals of lithium niobate during high-temperature annealing in vacuum. The effect electronic (polaron-type) processes in structural and impurity nanoscale complexes $Nb^{5+}-O^{2-}$ and $Fe^{2+}-O^{2-}$ had on their electrical, optical, and elastic characteristics is established. The possibility of changing such characteristics via targeted thermal annealing and optical irradiation is demonstrated.

INTRODUCTION

In [1, 2], we studied features of structural complexes of NbO_6 formed by O^{2-} ions around Jahn–Teller (JT) ions of Nb^{5+} and Fe^{2+} in congruent crystals of lithium niobate (LN) and the parameters of their local deformations. In this work, we present findings from a detailed study of changes in the optical, electronic, and elastic characteristics of LN crystals in a wide range of temperatures (500–77 K) and the possibility of deliberately changing them. Since ways of measuring the physical properties of LN were described in [3–5], we shall focus on our new results and their interpretation.

We studied series of 8 undoped and doped (with concentrations of Fe^{2+} ions ~5×10^{16} cm^{-3}) LN samples annealed for 10 h in vacuum or oxygen at different temperatures. Studies of changes in their physical characteristics depending on the conditions of annealing began as early as the 1990s [4–7], but results were few and often contradictory [8, 9]. The main contradictions concerned processes and mechanisms of electrical conductivity and photo-induced changes in optical absorption and refraction, along with the participation of polarons in such processes. Special attention was therefore given to studying changes in the properties of LN samples in the poorly studied temperature range of 300–77 K.

The most important results were for abrupt changes in the electrical resistivity (ρ), energy of electronic activation (E_a), and optical absorption (α) of

samples, depending on the temperature of annealing and the wavelength of optical irradiation.

It was found that the greatest changes in the electronic (E_a, ρ) and optical (α, n) parameters of all undoped LN samples were observed upon annealing in the range of 700 K < T_{ann} < 1200 K with a maximum near $T_{ann} = 950$ K (Fig. 1). In the 300 K $\leq T_{meas} \leq$ 500 K range of temperature measurements, the nature of temperature changes in the values of E_a, ρ, and α was the same and did not depend on the orientation of
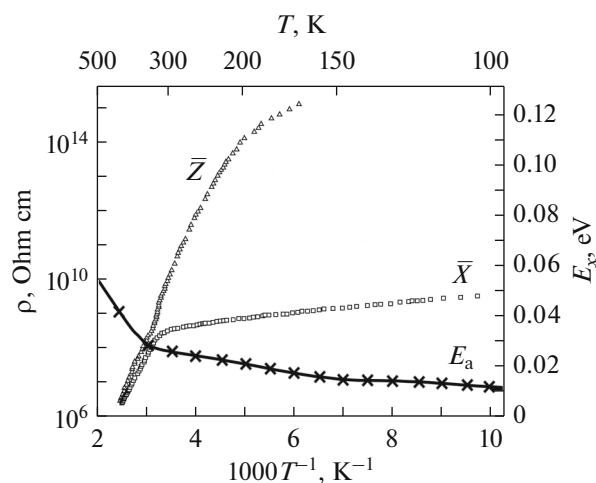

Fig. 1. Temperature dependences of electrical resistivities ρ_x and ρ_z and energy of activation E_a for a sample annealed in vacuum at $T_{ann} = 920$ K.
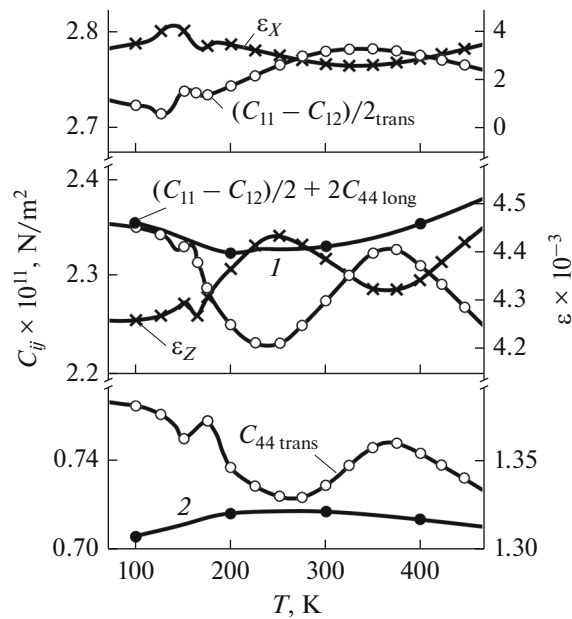
Fig. 2. Temperature dependences of elastic modules C_{ij} and deformations ε_i for a sample annealed in vacuum at 920 K. C_{11} and $(C_{11}-C_{12})/2$ correspond to the distribution of longitudinal and transverse waves, respectively, along $\overline{X}$, and C_{33} and C_{44} correspond to the propagation of longitudinal and transverse waves along $\overline{Z}$. Curve *1* is a projection of the long Nb−O bond onto $\overline{Z}$, and curve *2* is a projection of the short bond in lithium niobate.

samples. When $T_{meas} < 300$ K, however, the same parameters began to depend on orientation of the samples (Fig. 2). The electrical resistance underwent a record change in which the values of ρ_x and ρ_z could differ by five orders of magnitude for a sample with $T_{ann} = 920$ K when T_{meas} was reduced to 100 K. The greatest changes in α in the optical absorption spectrum were also observed in samples annealed at 870 K. Figure 3a shows the absorption spectrum at $T_{meas} = 77$ K, where the bands with photon energy of 2.3 eV correspond to Fe^{2+} ions.

The greatest changes in the optical spectrum were observed upon the optical irradiation of samples with $T_{ann} = 870$ K using filtered beams with different wavelengths. There was simultaneous enhancement of the 3.4 and 1.6 eV bands, the latter of which corresponded to the transition $Nb^{4+} \rightarrow Nb^{5+} + \overline{e}$, and a change in band intensity at 2.3−3.2 eV that corresponded to ion recharge $Fe^{2+} \rightarrow Fe^{3+} + \overline{e}$ (Fig. 3b).

We assumed the undoped and doped LN samples had two temperature ranges for the mechanisms of electrical conductivity, induced optical absorption, and elastic characteristics, which are related to one process of the generation and absorption of several types of polarons, bipolarons and excitons that is controlled by electron−elastic (electron−lattice) interactions within the NbO_6 octahedra containing JT ions of Nb^{5+} and Fe^{2+}.

In the high-temperature range of 500−300 K, the electrical conductivity and change in optical absorption above 300 K were due to the movement of free thermally excited electrons between polarons $Nb^{4+}_{Li} - Nb^{5+}_{Nb}$ in adjacent octahedra of NbO_6. In addition, the maximum in electrical conductivity was reached at T_{ann}, which corresponds to the equality of concentrations of these ions ($Nb^{4+}_{Li} - Nb^{5+}_{Nb} + \overline{e}$) in neighboring octahedra.

An analysis of our results indicated that the wide temperature range of higher conductivity in plane XY below 300 K was associated with the emergence of a low-temperature mechanism in which charge transfer proceeds through quantum tunneling transitions (hops) between localized electron states [9, 10]. Such hopping conductivity is created by the absorption and emission of optical single-frequency phonons [9], contributing to the energy of activation's drop to 0.02 eV. It is obvious that such a low value of E_a prevented us from detecting ultrasmall changes in electrical conductivity by direct means [7].

Such charge hops can in our case occur between electron-hole bound polarons (excitons) formed between closely spaced Nb^{5+} and O^{2-} ions in a NbO_6 octahedron under the conditions of strong electron−lattice interaction. Ions Nb^{5+}_{Nb} and O^{2-}_{Nb} are contained
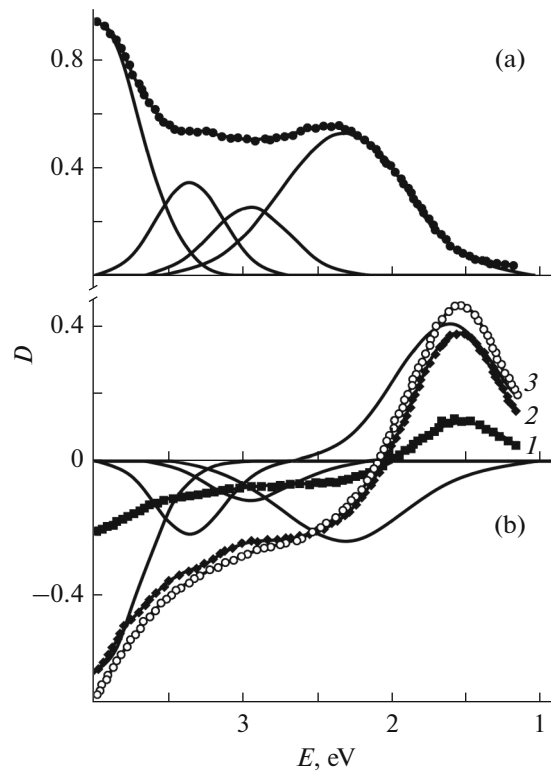
Fig. 3. (a) Optical absorption spectrum and (b) change in the absorption of upon the optical irradiation of LN crystals ($T = 77$ K) annealed in vacuum at $T_{ann} = 870$ K. Wavelengths λ_{irrad} of irradiation were (*1*) 760, (*2*) 546, and (*3*) 365 nm. D is the change in optical absorption, and E is the photon energy.

in NbO_6 octahedra in the form of polaron-type centers $Nb^{4+} + \bar{e}$ and $O^{-} + \bar{p}$ (holes). They form due to bonds with centers of the nearest environment of Nb_{Li}^{4+} and V_{Li} octahedra. Together, the polarons form bipolaron centers strongly related to induced (JT type) deformations of NbO_6 octahedra and deformation of the crystal lattice as a whole, as was first predicted theoretically in [6] for undoped crystals. The formation of bound bipolarons $Fe^{2-} - O^{2-}$ in octahedra is also possible in crystals containing Fe^{2+} ions, which can substitute for Nb^{5+} or Li^{2+} ions. The mechanisms of JT interaction caused by the formation of two types of bipolarons thus participate jointly in $LiNbO_3{:}Fe^{2+}$.

Theoretical calculations show that charge hops are most likely along planes *X* and *Y*, where there are coupled modes (stretching modes) of O−Nb [12] and the shortest distance between O^{2-} and Nb^{5+} in octahedra. According to [11], it is this mode that is responsible for the generation of photoluminescence in a congruent LN sample in the temperature range of 225−20 K with a ~0.1 eV energy of activation. As indicated in [11], the greatest increase in photoluminescence occurs in a relatively narrow temperature range (~100 K) and depends on the concentration of excitons. The authors

assumed that the frequency of exciton hops was an order of magnitude higher than the movement of ordinary polarons in the high-temperature region, according to the oscillatory model of Mott in [10], and was due to the emission and absorption of single-frequency optical phonons.

These conclusions are consistent with changes we observed in the elastic characteristics of ultrasonic waves below 300 K, and similar temperature changes in the intensity of photoluminescence [11], which is proportional to the concentration of excitons.

CONCLUSIONS

Large and abrupt changes in the values of elastic modules and acoustic attenuation in the temperature ranges of 350−200 and 150−170 K and electrical conductivity below 300 K were observed as a result of our experiments performed on the propagation of high-frequency ultrasonic waves and measurements of the electrical conductivity in a congruent undoped LN sample in the temperature range of 450−77 K. It was established that these anomalies were caused by local deformations of NbO_6 octahedra of the JT type and NbO_6 octahedra, along with their smooth variation throughout the temperature range of measurements

below 300 K. Smooth changes in parameters ρ, E_a, and α fully agreed with the theoretical model of molecular crystal dynamics, while abrupt changes can be attributed to the effect polaron carrier transfer inside NbO_6 octahedra has on the balance of elastic and electronic energies described by the JT effect.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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