OPTICAL PROPERTIES OF $LiNbO_3$

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Optical spectrum and spectrum of scattering of lithium niobate of doped 0.03 % by impurity Fe in requirements of impulse excitation by the second harmonic of radiation (532 nm) the laser are observationally investigated YAG:Nd with the continuous illumination from He-Ne the laser (632.8 nm). Presumable theoretical interpretation of the obtained experimental outcomes is given.

1. Introduction

Lithium niobate remains one of most attractive materials with wide spectrum importance technical applications: holographic storage systems, optic components and devices for telecommunications, conversations and processing information, for integrated optics. These applications depend on the photorefractive effects, that are related to the occurrence of some impurities or structural defects acting as donors or acceptors, another words, composition of lithium niobate has contain large deflection from stoichiometry in the direction of deficit Li, that lead to increase thermo-, photorefractive effects. For example, thermal expansions, band gap, UV-luminescence, OH^--vibrational bands in H-doped crystals and etc. have been found to depend from Li/Nb ratio. In present time, wide propagation received "Li – vacancies" and "Nb – vacancies" models, but more experimental results show, that "Li – vacancies" model is more preferable.

The photorefractive effect in $LiNbO_3$ can drastically to enhance by doping with transition metals (for example Fe and Cu being the most widely used ones). While the leading role of these dopants in this as well as the dominance of photovoltaic currents over diffusion and drift processes has been studied intensively, for example in the publications [1]. A detailed description of microscopic mechanisms steering the photorefractive effect is still pending.

The ground limitation for using of lithium niobate crystals in holography bound up with lifetime holograms after process of thermal fixing. In [2,3] was assumed probable methods optimization parameters of process for crystals with concrete ionic concentrations and their ratio to receive maximal values lifetime for high diffraction efficiencies holograms.

In generally, model of process can be describing so: electrons are exciting with light in the determine regions of crystal's volume can be capture on the deep energies levels, so that in process of recording hologram will have been fixing the periodic distribution of intensities interference of waves. We will be receiving "sinusoidal relief" of the occupation the traps, i.e. so name electronic matrix". Following step is process of thermal fixing hologram. It is bound up with thermal heating of crystal, ion current is began dominant, screening of "electronic matrix" and arise non-photosensitive "ionic matrix". Following cooling of crystal to initial temperature and illumination with equipartition intensity light are leaded the process to equalize electronic occupation.

The problem of gratings dynamics extensively considered in [4-5]. However, more questions remain now as before unsolved problems.

The crystal structure of lithium niobate was study in [6-7]. It was determined space group symmetry – *R3c*, hexagonal cell contain six formulas of units and parameters of low-level cell of crystal: $c=13.836\pm0.0004\AA$; $a = 5.14829\pm0.00002\AA$.

A model of the transition of lithium niobate from paraelectric to ferroelectric phase was proposed by [6-8]. In the phase transition, the sublattices of positive ions of Li and Nb displaced relative to the sublattice of oxygen anions. The direction of the displacement of the cations determines the direction of the spontaneous polarization vector, in the ferroelectric phase [0001]. In [8] authors have pointed out that it is position of the metal ions in the structure of the ferroelectric phase that gives rise to dipole moment. At temperature Curie point, where may occur two opposite directions of displacement for metal ions, which correspond to 180° electrical domains. It has been suggested that between the positive and negative ends of crystal by means of etching or from the intensity x-ray reflections. The negative end its x-ray reflection is less distinct. In order to change the polarization of single-domain crystals it is necessary to allow the ions of niobium and lithium to pass through the oxygen layers. At high (1423) this distance is larger than the sum of radii of the ions Li and O.

Composition of lithium niobate crystal can be to represent in form: $(LiNbO_3)_{0.941}(Nb_{Li}NbO_3)_{0.0118}(V_{Li}NbO_3)_{0.0472}$, where first component is usual lithium niobate, second – antisite defects and third – cation vacancies. Usually, lithium niobate crystals are grown with congruent composition Li/Nb ~0.94. Lattice defects stern from non-stoichiometry composition of the crystal and caused occupation Li-locations with Nb and others atoms. Nb_{Li} are most probable electron shallow traps and V_{Li} – are probably hole traps.

One of very importance singularity lithium niobate, which determine optical properties of crystal, is fact, that bounds (O^{2-}-Nb^{5+}) has mainly covalent and (O^{2-}-Li^{+}) - ionic characters. Radii of ions Nb^{5+} and Li^{+} are practically equal. All current models of defects as-grown agree that part of the Li - sites are filled up by excess Nb^{5+} ions accommodate Li deficiency. In original models [15] each Nb_{Li} antisite compensated by four Li vacancies, which are potential hole traps.

Defects of type (Nb_{Li} - Nb_{NB}) with $d \sim 3Å$ are placed in direction along C_3 – axis. Concentration of defects is approximately 2 $10^{20}cm^{-3}$ and $c_{V_{Li}} \sim 8 \cdot 10^{20}cm^{-3}$. Capture one of electrons on (Nb_{Li} - Nb_{NB}) defects (one-electron localization) make "small" polaron (Nb_{Li}^{4+} - Nb_{Nb}^{5+}) with optical band absorption near 1.64 eV. Accordingly, capture two electrons on this defect make Gaitler-London's bipolaron with optical band absorption from 1.7 to 4 eV. Authors of publication showed, that for description optical spectra's of absorption in the interval energies higher than 2.5 eV also need assumption defects of type (Nb_{Li} - Nb_{Li}), minimal distance is 3.76 $Å$, concentration of defects is $\sim 6 \cdot 10^{18}cm^{-3}$. However, computer simulation of bipolaron state (Nb_{Li}^{4+} - Nb_{Li}^{4+}) showed, that this defects do not contribute into optical spectrum for energies high 2.3 eV. In other side, four-electron defect $\begin{pmatrix} Nb_{Nb}^{4+} - Nb_{Nb}^{4+} \\ Nb_{Li}^{4+} - Nb_{Li}^{4+} \end{pmatrix}$, in which on each ions Nb accordance one non-degeneration level and Hamiltonian describe through "four nodes Hamiltonian" in four-electron basis, well explain and describe singularities optical spectrum of lithium niobate crystal for energies high 2.5 eV (model Q-polaron). [19]

Follow type of defects bound up with OH^-, which in $LiNbO_3$ may have two forms: impurity complex and molecular ion. The OH- absorption and Raman-scattering spectrums of congruent, pure and nearly stoichiometric $LiNbO_3$ crystals investigated in publications [16]. Maximum by the 3466 cm^{-1} considered to relate to the stretching vibration of OH^- for protons directly substituted for Li^+ ions and located at 3.36Å (O-O) bonds in oxygen triangles nearest to the Li –site. Maximums by the 3481cm^{-1} and 3486 cm^{-1} are also due to OH^- in 3.36Å (O-O) bonds, but protons suggested occupying V_{Li}^{-} near Nb_{Li}^{5+}. Two different ions environment around V_{Li}^{-} are cause these two absorption maximums. Distance (O-H) is near 0.9896Å, concentration c_{OH^-} is approximately $10^{16} \div 10^{18}$ cm^{-3}, energy of thermal activation is 1.23 eV for $LiNbO_3$ and 1.17 eV for $LiNbO_3$: Fe. [20]

The transport properties in crystal $LiNbO_3$ are of major relevance in connection with the hydrogen doping processes, ionic conductivity, photorefractive fixing etc. Although proposal was first made about possible OH^--molecular migration to explain proton diffusion, in [17] had found a strict proportionality between the proton concentration and conductivity up a similar temperature. H^+ ions are occupying Li-vacancies.

Role donors and traps of electrons in $LiNbO_3$: Fe is ions Fe^{2+} and Fe^{3+}, respectively, [18] and they are deeper then Nb_{Li}^{4+} and Nb_{Li}^{5+} with respect to condition band edge.

Summarizing the XSW measurements, the lattice position for an assumed single – site occupancy of Fe atoms in $LiNbO_3$ structure is determined to be (0.18±0.07) Å above the ferroelectric Li –site in direction of "c" axis of crystal. However, due to the systematic differences in coherent fractions for $(00\bar{6})$ and $(1\bar{1}\bar{4})$measurements, spread of positions in range up to ±0.7Å is conceivable.

Thermal reduction of lithium niobate with iron used to change the charge state of the impurity and so adjust the ration between concentrations Fe^{2+} and Fe^{3+} states. Usually ratio is $c_{Fe^{2+}}/c_{Fe^{3+}} \approx 0.05$ for case $c_{Fe} \approx 56\cdot 10^{18}cm^{-3}$ and $c_{Fe^{2+}} \approx 2.5\cdot 10^{18}cm^{-3}$, where $c_{Fe} = c_{Fe^{2+}} + c_{Fe^{3+}}$.

2. Optical spectra and spectra of scattering.

Experimental researches of optical spectra of absorption $LiNbO_3$ published in many works. On fig. 1 our experimental results are shown only in connection with a context of article. We shall notice only, that in spectral area in which our researches (is area of a transmission of a crystal) were carried out, values of factor of absorption are small.

On fig. 2 plotted spectral dependence of volume photogalvanic current for $LiNbO_3$.

Curves of two-refraction *Δn* changes on diameter of the area of a crystal covered by light given on fig. 3. With increase of time of an exposition, the area of changes Δn grows.

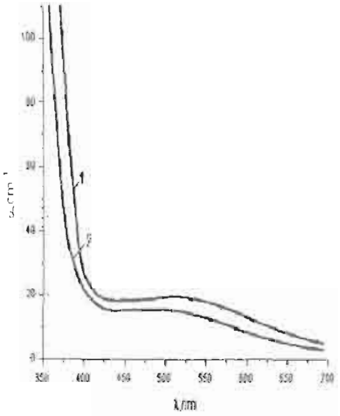


Fig.1 Optical spectra of absorption $LiNbO_3$ for two polarizations: 1- $E_{light}\perp c$ and 2- $E_{light}\parallel c$.

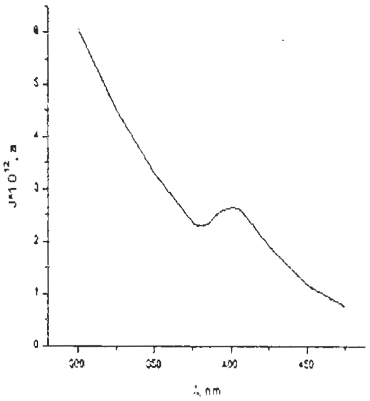


Fig.2 Spectral dependence of volume photogalvanic current for $LiNbO_3$

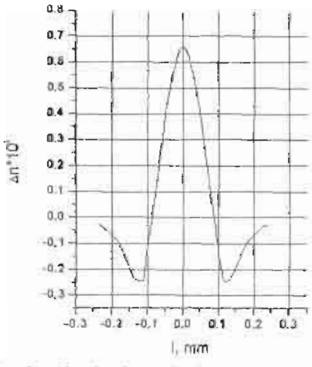


Fig.3. Optically induced changes of factor refraction Δn on diameter of the covered area of a crystal.

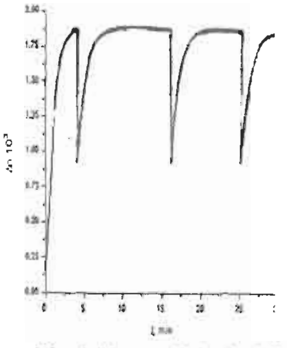


Fig.4 "Jumps" Δn in $LiNbO_3$ +Fe.

At achievement of some critical size $\Delta n \approx 1.7 \cdot 10^{-3}$ on dependence Δn (fig. 4) are observed "jumps" (effect partial polarization reversal) which quantity is defined by density of capacity (~8 W/cm^2).

This result earlier published in article [10] and explained in authors of paper [14].

Investigations of spectral dependences of Raman-scattering by frequency ω scattering cross-sections, allow studying time-development of process. As well known, parameter of line width directly connected with time-delay between processes absorption and radiation photons. The scattering cross-section defines from expression:

$$d_1\sigma(k_1\lambda_1;\Theta\lambda_2) = \left(\frac{\left|M_{fi}M_{i0}\right|^2}{\hbar^2\left[(\omega_1-\omega_i)^2+\gamma_i^2\right]} \right)\left(\hbar\omega_1 - E_f\right)^2 \frac{d\Omega}{\left(4\pi^2\hbar^4c^4\right)} .$$

M$_{fi}$ and M$_{i0}$ are matrix elements and $\tau_i = 1/\gamma_i$.

Therefore, we have two cases: slow $|\omega_l - \omega_i| << \gamma_i$ (depend on lifetimes) and fast $|\omega_l - \omega_i| >> \gamma_i$ (depend on experimental conditions) processes. For slow processes:

$$I(t) \sim \begin{cases} \gamma_i^2\left\{ - exp\left(-\frac{\gamma_i}{2}t \right) \right\}^2 & t < T_L \\ I(T_L)\, exp\left[-\gamma_i\left(t - T_L \right) \right] & t > T_L \end{cases}$$

For fast processes:

$$I(t) \sim \begin{cases} \left(\Delta\omega_i\right)^{-2}\left\{ 1 - exp\left(-\frac{t}{\tau_L} \right) \right\}^2 & t < T_L \\ I(T_L)\, exp\left[-2\frac{\left(t - T_L\right)}{\tau_L} \right] & t > T_L \end{cases}$$

Here t=0 and t=T_L are leading edge and trailing edge of impulse, correspondingly.

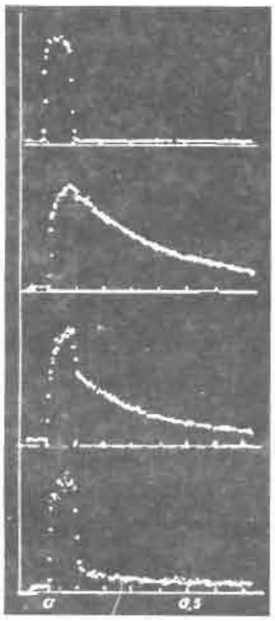


Fig. 5 Study lifetime of states in LiNbO$_3$ (here x-axis is t, μs):
Impulse of laser:
a. λ=532 nm, 100 ns

b. Case ω_l = ω$_i$

c. Case ω_l = ω_0 + 1.2 GHz

d. Case ω_l = ω_0 + 2.2 GHz

The received results show, that at a resonance with a line of absorption (case "*b*") intensity of radiated light slowly grows (an interval $0 \le t \le T_L$) and then (in an interval $t > T_L$) slowly decreases with time of attenuation about ~14 μs.

In cases "*c*" and "*d*" in intensity of radiated light "slow" and "fast" components, and amplitude slow components are well observed is less, than in a case "*b*".

Time-delay between processes of absorption and radiation of photons are approximately ten nanoseconds.

These investigations will well be coordinated with relaxation changes of factor of the absorption, in this case reflecting recombination processes (see fig. 6). The received experimental results easily can be approximated function $\alpha(t)=\alpha_1(0)exp(t/\tau_1)+\alpha_2(0)exp(t/\tau_2)+\alpha_3(0)exp(t/\tau_3)$ with parameters $\alpha_1(0)=4.13$, $\tau_1=0.016$ ms; $\alpha_2(0)=0.972$, $\tau_2=0.95$ ms; $\alpha_3(0)=2.19$ and $\tau_3 = 0.144$ms (see fig. 6a). They also can be approximated with function $\alpha(t)=\alpha_1(0)exp(t/\tau_1)+\alpha_2(0)exp(t/\tau_2)$ with parameters $\alpha_1(0)=2.536$, $\tau_1=0.3$ ms, $\alpha_2(0)=4.848$ and $\tau_2=0.016$ ms (see fig. 6b). Points give experimental data.

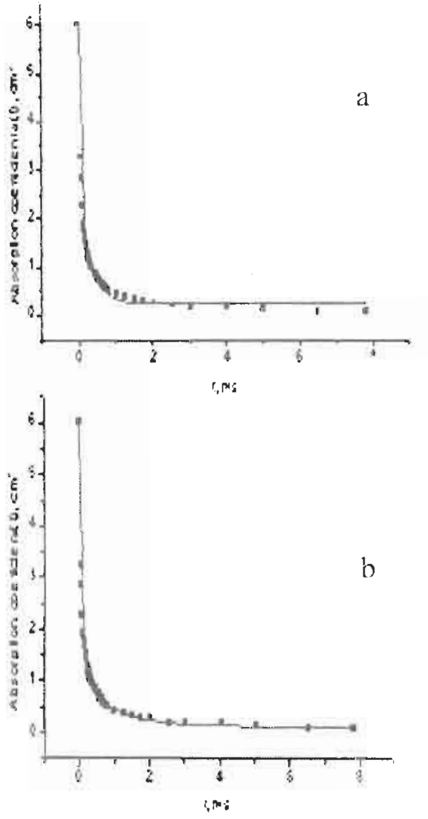


Fig. 6 (See comments in the text)

On fig. 6 results of adjustment in experimental dependence relaxation processes which estimate on change of factor of absorption, which will be coordinated to results of work [11] is given. Want to remind, that in [11] was defined light-induced absorption changes vs time. In same work it is possible to find the data on dependence of maximum α_{li}^{max} of light-induce absorption, lifetime τ, stretching factor β changes from intensity of pump light (see also [12]), and, for excellent description of the complete evolution of $\alpha_{li}(t)$ is obtained by function $\alpha_{li}(t)=\alpha_l(t=0)exp[(t/\tau)^{\beta}]$. Here $f_{KWW}(t)=exp[[(t/\tau_{KWW})^{\beta}]$ is "stretched" exponential function, known as the Kohlrausch-Williams-Watts relaxation function [13]. This function applicable only for times long compared molecular vibration periods. Laplace transform resolves $f_{KWW}(t)$ into a linear superposition of simple exponentials $(A(\tau) \ge 0)$:

$f_{KWW} = \int_0^\infty A_\beta(\tau)\exp\left(-\frac{t}{\tau}\right)d\tau$. Each dynamical region has a simple exponential relaxation (approximately) with its own characteristic time scale for relaxation. Boundaries and contents of dynamically distinct regions change with passage of time. As known, that value of β usually decreases from "≈1" to "≈1/3". Use by authors [11] these functions is connected with made by them the assumption, that during absorption and recombination of electrons in $LiNbO_3$:Fe properties small polaron are badly taken into account and dependence of optical absorption should not have simple monoexponential form. The investigation of the dynamics of the light-induced absorption changes in $LiNbO_3$ crystals reveals: the recombination of electrons from small polarons (Nb_{Li}^{4+}) with deep traps (e.g., Fe^{3+}) follows a stretched-exponential behavior (this result from the fact that lifetime of an individual polaron depends on the distance to the next deep trap) and, thus, for all polarons together, a spectrum of lifetimes instead of a single time constant is obtained [11].

Excitation and recombination of the electrons for $LiNbO_3$:Fe can be described by the two-center charge model, which introduced in [15, 18]. Electrons can be excited from Fe^{2+} by light either into the conduction band or into Nb_{Li}^{5+} forming Nb_{Li}^{4+}. Direct excitation into Nb_{Li} centers requires that there are always some these centers close to each Fe^{2+}. In this case, because Nb_{Li} is an intrinsic defect that occurs in a very high concentration [16, 17]. The electrons in the Nb_{Li}^{4+} traps can be excited to the conduction band by light or thermally. The conduction-band electrons can be recombine either with Fe^{3+} or Nb_{Li}^{5+}.

Completely in this model, excitation and recombination of the electrons describe by the equations:

$$\frac{\partial c_{Fe^{2+}}}{\partial t} = -\left[q^s_{Fe^{2+}\to cb} + q^s_{Fe^{2+}\to Nb_{Li}^{4+}}(c_{Nb_{Li}} - c_{Nb_{Li}^{4+}})\right]\cdot I_L c_{Fe^{2+}}$$
$$+ (\gamma_{cb\to Fe^{2+}} n + \gamma_{Fe^{2+}\to Nb_{Li}^{4+}} c_{Nb_{Li}^{4+}})(c_{Fe} - c_{Fe^{2+}})$$

$$\frac{\partial c_{Nb_{Li}^{4+}}}{\partial t} = -\left[\beta_{Nb_{Li}^{4+}\to cb} + q^s_{Nb_{Li}^{4+}\to cb} I_L + \gamma_{Nb_{Li}^{4+}\to Fe^{3+}}(c_{Fe} - c_{Fe^{2+}})\right]$$
$$\cdot c_{Nb_{Li}^{4+}} + (\gamma_{cb\to Nb_{Li}^{5+}} n + q^s_{Fe^{2+}\to Nb_{Li}^{4+}} I_L c_{Fe^{2+}})(c_{Nb_{Li}} - c_{Nb_{Li}^{4+}})$$

Here: $q^s_{Fe^{2+}\to cb}$, $q^s_{Fe^{2+}\to Nb_{Li}^{4+}}$ - absorption cross-section of Fe^{2+} for absorption and excitation of an electron from Fe^{2+} into conduction band (cb) and Nb_{Li}^{4+}, correspondingly; $q^s_{Nb_{Li}^{4+}\to cb}$ - absorption cross-section of Nb_{Li}^{4+} for absorption and excitation of an electron from Nb_{Li}^{4+} into conduction zone; c_{Fe} , $c_{Nb_{Li}}$ – are total concentration of Fe and Nb_{Li}, correspondingly; $c_{Fe^{2+}}$ and $c_{Nb_{Li}^{4+}}$ - concentration of Fe^{2+} and Nb_{Li}^{4+}, correspondingly. I_L – intensity of the spatially homogeneous light; $\gamma_{cb\to Fe^{2+}}$ - coefficient of recombination of conduction band electrons with Fe^{2+}; $\gamma_{cb\to Nb_{Li}^{5+}}$ - coefficient of recombination of conduction band electrons with Nb_{Li}^{5+}; $\gamma_{Nb_{Li}^{4+}\to Fe^{3+}}$ - coefficient of recombination of electrons from Nb_{Li}^{4+} with Fe^{3+}.; n – density of free electrons in the conduction band; $\beta_{Nb_{Li}^{4+}\to cb}$-rate of thermal excitation of electrons from Nb_{Li}^{4+} into the conduction band. It is impossible to forget, that in real crystals $LiNbO_3$:Fe as it was specified above, always there is a concentration of ions Fe^{3+} and Nb^{5+}_{Li}. In table 1 the experimental values published in paper [15] which are used quality of initial calculations given for carrying out have been reduced.

Table 1

Quality, unit	Value	Notes
$q^s_{Fe^{2+}\to cb}$, m^2/J	1.0×10^{-5}	Light wavelength 532 nm
	0	Light wavelength 632.8 nm
$q^s_{Nb^{4+}_{Li}\to cb}$, m^2/J	5.0×10^{-5}	Light wavelength 532 nm
	5.2×10^{-5}	Light wavelength 632.8 nm
$q^s_{Fe^{2+}\to Nb^{4+}_{Li}}$, m^5/J	3.22×10^{-30}	Light wavelength 532 nm, 632.8 nm
c_{Fe}, m^{-3}	1.2×10^{25} or 5.6×10^{25}	$c_{Fe} = c_{Fe^{2+}} + c_{Fe^{3+}}$
$c_{Nb_{Li}}$, m^{-3}	1.0×10^{26}	
$c_{Fe^{2+}}$, m^{-3}	Variable; initial data 2.5×10^{24} for $c_{Fe} = 5.6\times10^{25}$	published in paper [1]
$c_{Fe^{2+}} / c_{Fe^{3+}}$	Variable; initial data ≈ 0.05 for $c_{Fe} = 5.6\times10^{25}$	Typically ratios in the range from 0.01 to 1
$c_{Nb^{4+}_{Li}}$, m^{-3}	variable	
I_L, W/m^2	Variable	$I_{YAG:Nd}$; $I_{He\text{-}Ne}$ to 3×10^4 ($I_{YAG:Nd}$)
$\gamma_{cb\to Fe^{2+}}$, m^3/s	1.65×10^{-14}	
$\gamma_{cb\to Nb^{5+}_{Li}}$ m^3/s	0	
$\gamma_{Nb^{4+}_{Li}\to Fe^{3+}}$ m^3/s	1.14×10^{-21}	
$\gamma_{Nb^{4+}_{Li}\to Fe^{3+}}$ m^3/s	1.14×10^{-21}	
n, m^{-3}	variable	
$\beta_{Nb^{4+}_{Li}\to cb}$, s^{-1}	0	
μ, m^2/Vs	$\approx 7.4\ 10^{-5}$	Very small value of mobility of electrons specifies that fact, that electrons in this case cannot be considered as the free particles.
r_{13}, m/V	10.9×10^{-12}	Electrooptic coefficient, Light wavelength 632.8 nm
ε	28	Dielectric coefficient
n_0	2.286	Refractive index. Light wavelength 632.8 nm

First of all we shall remark, that in this case experiments were carried out in geometry when impulse radiation from YAG:Nd with a wave length 532 nm and intensity $I_{YAG:Nd}$ was guided under an angle 20° to a surface of a crystal while radiation from He-Ne the laser with a wave length 638,8 nm and intensity $I_{He\text{-}Ne}$ has been oriented perpendicularly to the same surface

Such experiment allowed observing of a modification of absorption stipulated by absorption of transitions $Fe^{2+} \rightarrow Nb_{Li}^{4+}$, $Nb_{Li}^{4+} \rightarrow cb$ and a recombination of electrons from a conduction band on levels Nb_{Li}^{4+} and Fe^{2+}.

Measuring optically induced modifications of a refractivity in $LiNbO_3$:Fe at use He-Ne of the laser such as ЛГ-31 with wave length of radiation 632,8 nm have shown, that magnification of exposure time results in propagation of a refractivity (in particular, see a fig.3. The more a power density the more strongly a steepness of effect. This outcome is not new and early described in [10], [14]).

After light transformations, we can write out the kinetic equations for both cases. However, two-center charge model basically be not capable to explain the modifications of absorption factor observed in experiments (for example, [11]). In paper [21] the data on formation of an electric field in earlier shined field which magnitude as appeared can exceed 10^5 V·cm are published. Such field can reduce in an electrical breakdown and should be taken into account at interpretation, for example optical, experiments. The estimation of a field of a photorefraction on observationally observable values of a modification of a two-refraction with the equation of electrooptical effect gives 680 V/cm for $\delta\Delta n = 5\ 10^{-5}$ and T=300K.

In ferroelectric materials - photoconductors on boundaries of uniformly irradiated field the space charge is formed. The modification of spontaneous polarization at illumination of the crystal, happening as a result of a modification of concentration of the free carriers [22], calls occurrence of a depolarization electric field. Due to photoconductivity this field screens, that is at enough long-lived illumination the field in the field of a light stain is close to null. Magnitude Δn in the field of a light stain, in this case, is determined by the formula [23]. After removal of illumination there can be rather fast relaxation of excited states of impurities therefore, magnitude of spontaneous polarization is returned to an equilibrium value. Thus there is a modification and magnitudes Δn which, however, does not tend to zero. The space charge on boundaries of irradiated area can be maintained long enough and after a relaxation of spontaneous polarization. Therefore, after lockout of light, in earlier irradiated field there is a built-in field which defines a quantity Δn, maintained long enough. This magnitude essentially depends on the shape of a stain. The modification Δn is easy for finding from the equation of electro-optical effect:

$$\Delta n = \frac{n^3}{2}(m + 2MP_s)\left[\frac{(\alpha^* f^2 - g)c}{4\pi(c+g)}P_s + \alpha^* fP_s\right]N^0 + \frac{2\pi N^0 \alpha_0}{n} \tag{1}$$

$$\Delta n = \frac{n^3}{2}(m + 2MP_s)\frac{\varepsilon - 1}{\varepsilon}\left[\frac{(\alpha^* f^2 - g)c}{4\pi(c+g)}P_s + \alpha^* fP_s\right]N^0 \tag{2}$$

where ***m*** - the linear electrooptical coefficient, ***P_s*** - spontaneous polarization, *N* – concentration of impurities, α - polarizability, *f*-Lorenz's factor, *M* – electrooptical coefficient, *g* – coefficient of deformation potential.

Presence of two relaxation times *Δn*, the reference for the given mechanism photorefractive effect, is well-known from operations [21, 24-26,]. In the beginning of illumination for small time, restricted only the velocity of a photo-ionization of an impurity, mounts magnitude Δn, defined by expression:

$$\Delta n = \frac{n^3}{2}(m + 2MP_s)\left[\frac{(\alpha^* f^2 - g)c}{4\pi(c+g)}P_s + \alpha^* fP_s\frac{1-\varepsilon}{\varepsilon}\right]N^0 + \frac{2\pi N^0 \alpha_0}{n}$$

Association *n* from *Φ (x)* - allocation of light intensity and *T* - temperatures is determined by the concrete mechanism of drive of impurities. If under an operation of light there is a recharge of impurities this association is given by formulas:

$$N^{0} = S\Phi N\{(S + S_{i}^{'})\Phi + [WN_{c}\, exp(-I / kT)N_{i}^{-1} + W_{00}\,]N_{0}^{'}\}^{-1}$$

where $S_{i}^{'} = S_{i}W / W_{i}$ и

$$N^{0} = 2(S\Phi)^{1/2} NN_{i}\{(N_{i} + N)(S\Phi)^{1/2} + \{(N_{i} - N)^{2} S\Phi +$$

$$+ 4N_{i}N[S_{i}^{'}\Phi + WN_{c}\, exp(-I / kT) + W_{00}N_{i}]\}^{1/2}\}^{-1}$$

The relaxation time of an excited state is not enough at major impurity concentrations. Shelf time of space charge, defined a thermal ejection of electrons from traps and the pickup on them of the free carriers, is determined by expression:

$$\tau_{s}^{-1} \approx W_{i}N_{c}\, exp(-I / kT) + Wn_{0} \qquad (3)$$

When the photoexcitation of an impurity does not reduce in ionization, concentration of the excited centers in stationary state can be spotted expression:

$$N^{0} = \frac{N\tau S\Phi}{1 + \tau S\Phi}$$

As a rule, the relaxation time of an excited state is not enough. A unique reason of effect of a photorefraction in this case is formation of space charge which time of maintenance is determined by expression (3).

Let's estimate a reference length of shielding of a field l that is thickness of a stratum of a space charge. Division of charges happens due to ionization of impurity centers, the subsequent electron drift in an electric field and their capture on the free trap. The area in which the electric field is distinct from zero less, the energetically more favorable is the relevant condition. Therefore in the field of the positive space charge there is the complete ionization of deep impurity centers, and in the field of the negative - the complete recharge of traps. Thus, we have $\rho=eN$ and $\sigma=eNl$. Guessing, that the light stain has the homogeneous allocation of illumination and estimating P as we shall discover, that on an order of magnitude $l=\Delta P_{s}/eN=\alpha^{*}fd^{2}\approx 10^{-6}cm$.

It is obvious, that allocation $\Delta n(x)$ during illumination noticeably differs from $\Delta n(x)$ after removal of illumination, more precisely, after relaxation of excited states of impurities. Besides from model follows, that sensitivity induction of photorefraction should have spectral maxima. For $LiNbO_3$:Fe such association has been found out in [27].

As well known, small polarons and bipolarons absorb radiation when a self-trapped carrier is exited from severely localized state to another well-localized state at an adjacent site. The widths of the absorption spectra of small polarons and bipolarons are due to variations of the energy differences between these well-localized states caused by atomic displacements. That is, phonon broadening provides the predominant broadening mechanism for small-polaronic absorption spectra. Therefore, small-polaronic absorption spectra are generally temperature depend. Small-polaronic absorption spectra are generally asymmetric. The absorption on the low-energy side of the peak is greater than that on the high-energy side of the peak.

The absorption coefficient per unit density of small polaron is given by [28, 29]:

$$\frac{\alpha}{n_{p}} = \frac{2\pi^{3/2} \cdot e^{2} \cdot t^{'}}{m^{'} \cdot \omega \cdot c \cdot \Delta} exp\left[\frac{-\left(2E_{b} - \hbar\omega\right)^{2}}{\Delta^{2}}\right] \qquad (4)$$

where t' is the intersite electronic transfer energy and the electronic effective mass is defined by relation $t^{'} \equiv \frac{\hbar^{2}}{2m^{'}a^{2}}$; $\Delta \equiv \sqrt{8E_{b}E_{vib}}$. At low temperature E_{vib} is just the zero-point vibrational energy $\frac{\hbar\omega_{ph}}{2}$, at high enough temperatures for the vibrational motion to be treated classically, $E_{vib}=k_BT$. Derivations of (4) presume that $E_b>>\Delta>t'$, this factor reduces the absorption. This reduction factor occurs because the transfer related absorption requires the electronic energies of initial and final sites be within t' of one another while motion broadens the local energy levels by larger amount Δ. The efficacy of the absorption is reduced when the time required for the electronic transfer $\frac{\hbar}{t'}$ is longer than the time interval during which the electronic energies remain coincident, $\frac{\hbar}{\Delta}$. If $E_b>>t'>\Delta$, $\frac{t'}{\Delta}$ should be replace by unity in (4).

For a small bipolaron, two carriers occupy a common site since the depth of electronic well that self-traps the carriers at equilibrium is twice as deep as that for a small polaron, $-4E_b$, rather than $-2E_b$. The electronic energy of the two self-trapped carriers is then $-2(4E_b)+U$, where U is the on-site Coulomb repulsion energy. A small bipolaron is stable with respect to separation into two separated small polarons, if its electronic plus deformational energy, $-4E_b+U$, exceeds that of two separated polarons $-2E_b$. Absorption spectra of small bipolaron are similar to those of small polarons. But energies of the absorption maximums small bipolarons tend to be even higher than those small polarons.

Very small value of mobility of electrons ($\mu\approx7.4\ 10^{-5}\mathrm{m^2/Vs}$) in $LiNbO_3$ specifies that fact, that electrons in this case cannot be considered as the free particles, e.g. polarons are strongly located. Conductivity here carries jump character, i.e. the free length about the lattice constant can exceed time of a recombination essentially 10^{-8} s.

All aforesaid allows making improvements for two-center models:

1. to take into account association of cut of an absorption on an energy of incident photons and on allocation of intensity of light in the field of a light stain;
2. to take into account singularities of recombination processes.

On fig.7 results of calculations of change of absorption after the termination of action of a pulse of light from the YAG:Nd laser (532 nm) on the modified model which show the good consent with experiment (see. Fig.6) are submitted (dashed line is theoretical calculations).

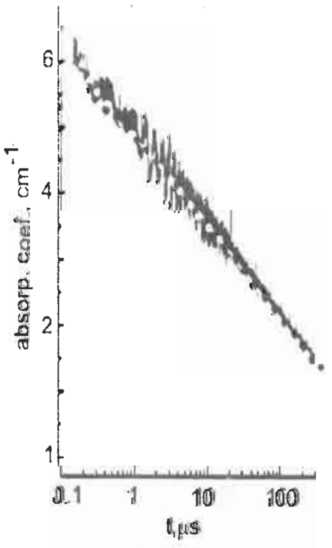


Fig.7

Before discussing the results of calculations, we shall pay attention to the following experiments.

Thin plates of crystals $LiNbO_3$ and Fe(0.03 %): $LiNbO_3$, annealed during one hour at temperature near 500K, are positioned in the vacuum lightproof camera, in which they are anchored on a thin thread above a semitransparent metal plate. Oscillations of a crystal are checked on a diversion of an optical beam from the light pocket mirror anchored on a thread (the mass of a crystal is many times greater than mass of pocket mirror). The control of distance changes between a crystal and a plate, at appearance of a charge on a surface of a crystal, is carried out with the help of the interference microscope with the accuracy up to 0.5 micron. The temperature, during recording of a diffraction grating, is determined by measuring of an optical trajectory in dark area of a crystal.

In all cases, radiation from laser He-Ne (λ=6328Å, power of 30 Watt/cm^2) is created by the standard methodics for crystals $LiNbO_3$. Recordings of diffractograms from a crystal, in a time dependence of an exposure, have fixed changes of diffraction strips forms in the area of a light stain (fig. 8a, b), and also distribution of Δn on amplitude and section in one (fig.3.). It is necessary to note, that intensity distribution on the area of a light stain was created uniform one practically no more than 0,03%. Maximal values Δn are observed, when radiation from the laser is directed perpendicularly to an axis "C" of a crystal. The further experiments have shown that distribution Δn during lightning appreciably differs from distribution after removal of lightning. During investigations of relaxation time Δn, the quick and slow components are observed.

The observable effect is the result of appearance of an electric field in a crystal (strength about 10^5V/cm), causing Δn change and the appearance of a charge on a crystals surface depending on temperature, intensity and a wave length of laser radiation.

It is necessary to note, that there is no new effects in the obtained results, because in 1966 in paper [25] the observation of the effect of photoinduced change of the index of refraction and after that [26] on a possibility of the use this effect for the recording phase holograms with high efficiency [31-36]. Results of similar observations, but in an electric field (by electrical compass method) also have been published in paper [30]. The fact is known, that the spatial charge is formed in ferroelectrics - photoconductors, on boundaries of uniformly lightning area. Change of spontaneous polarization of crystal P_s in a place of lightning causes the appearance of depolarization electric field E which can save it self long-lived time at the low conductance of a crystal (in case of the mobility for $LiNbO_3$ is approximately equal to 10^{-4}cm$^2\cdot$s$^{-1}\cdot$V^{-1} [39]). This electric field strength is the magnitude of interatomic interactions degree and, therefore, leads to deformations of electronic configurations not only the impurity centers, but also in atoms constituting this crystal structure. This consequence is a result of observable changes of P_s and Δn. The change P_s on the other hand, causes the appearance of a depolarization electric field. Due to a photoconduction this field is screened, i.e. the electric field inside the light stain area will have zero value at long enough time of lightning. At this moment the quantity Δn can be calculated, as it has been done in paper [23].

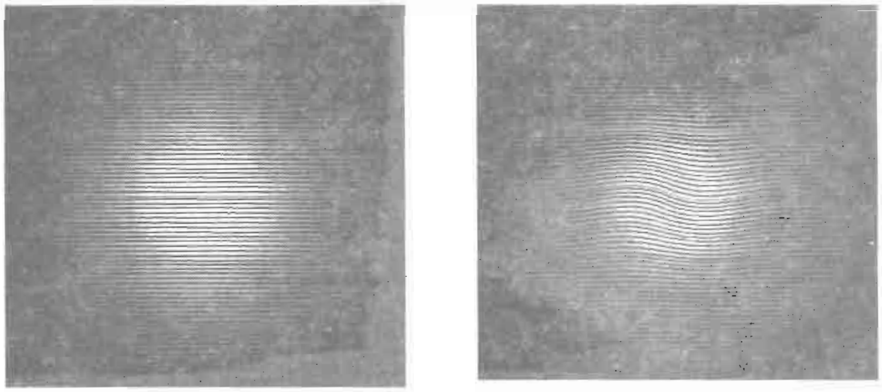


Fig.8. a. The diffraction pattern, when effect on crystal it is not observed yet;
b. Contortions of the diffraction strips in area light stain

In calculations by cluster method of electronic structure $LiNbO_3$ it has been received the data on spontaneous polarization P_s (0,77cm^{-2}) [37], taking place in the consent with the experimental results 0,71cm^{-2} [38]. Ionization or excitation of an impurity increases its polarizability in two times and so the ferroelectric impurity is polarized by a macroscopic field so the dipole moment of an impurity changes also. The deformation lattice near the impurity causes of the dipole moment change of the impurity centre [43].

In [23] the expression of distribution function $P(r)$ is obtained taking into consideration [44]. From this we have the following expression

$$\Delta P_s \approx \frac{\alpha^* f P_s N}{4\pi}(f+1),$$

where f is the Lorentz factor; $E=fP_s$ is a macroscopic field; α^* is a polarizability of an impurity; $\alpha f P_s$ is change of the dipole moment of an impurity. For the case $a_B < r_c$ (shallow impurities) f is equal to zero. Thus, quantity of change ΔP_s and consequently Δn, are obtained by deep levels. The macroscopic field leads to zero at the homogeneous lightning of the short-circuited crystal. In this case the change of **n** is caused by change of the polarizability α of the impurity centers. The value $\Delta\alpha_0$ depends on the optical polarization of the same impurity atoms and the deformation area of the crystal. After stopping of the lightning, because of relaxation process of excited states of impurities, P_s returns to an initial equilibrium value. However, Δn does not return to an initial value. That means that the inducted field with very large relaxation time appears in the earlier lightning area (fig.9).

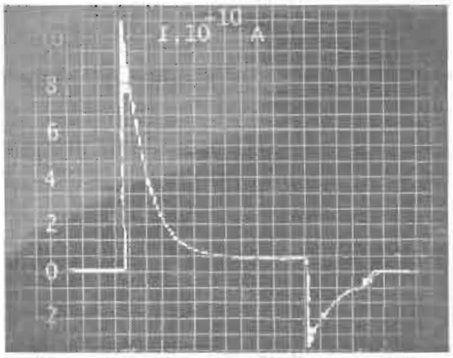
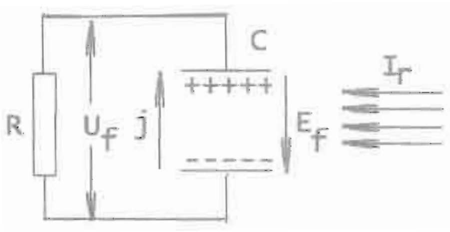


Fig.9. Changes of a photoelectric of a short circuit in crystal Fe: LiNbO$_3$.

Time of scan of a signal is 250s. The first emission of a signal corresponds to insert of light, second - to lockout.

The electric field at the non-homogeneous lightning (so it is possible for itself to present a problem on distribution of light on o a crystal taking into consideration of lightning and non-lightning areas) is determined by concentration of free electrons. It is necessary to take into account that concentration of free electrons is, less, than the trapped electrons one. Thus, the photoinduced field E is defined by the charge distribution on traps and as follows from the above mentioned, leads to the unreturning of Δn to the initial value after stopping of lightning. On the other hand, the photoinduced field can be obtained using the equivalent circuit:



where R is the loading resistor, R_c in internal resistance of a crystal ($R_c << R$), U_f is a voltage drop on the loading resistor, I_r is the intensity light, impinging on a crystal, j is spatial component of a current $\bar{j}$, directed to normal to an face surface of the plane-parallel plate thickness d, E_f is photoinduced field strange in the capacitor C. The induced field strange is determined by charge density ρ on the capacitor plates which have arisen as a result of lightning of a crystal by light, more over $\frac{d\rho}{di} = j - \sigma E$, σ is an admittance. As $E = \frac{4\pi\rho}{\varepsilon_l}$, where ε_l - longitudinal component of dielectric constant, then we, taking into account the time of the dielectric relaxation $t_d = \frac{\varepsilon_l}{4\pi\sigma}$, obtain $\frac{dE}{dt} + \frac{E}{t_d} = -\frac{4\pi j}{\varepsilon_l}$. It follows that $E_f = -\frac{j}{\sigma}$ and $E(t) = E_f\left(1 - exp\left(-\frac{t}{t_d}\right)\right)$. At $t >> t_d$, $j = -\sigma E_f$. Here it is possible to present σ as the total of the some two contributions: σ_f - a photoconductivity and σ_d - eigen conductivity, more over σ_f is not a small value in comparison with σ_d. Defining j as αGJ, where α is an absorption constant; G is Glass coefficient and $\sigma_f = \alpha K_f J$ where K_f is a conductivity coefficient, we have:

$$E_f = -\frac{G}{K_f\left(\frac{\sigma_d}{\sigma_f} + 1\right)}$$

and, if $\sigma_f >> \sigma_d$, then E_f is defined only by a material plate parameters, i.e. by the relation $\left(-\frac{G}{K_f}\right)$. For Fe:LiNbO$_3$ the values of Glass's constants are given by the relation in [45]:

$$G^L_{33} \approx G^L_{31} = 2 - 4;\ G^L_{22} \approx 0.1 - 0.3;$$
$$G^c_{12} \approx 0.1 - 0.5 >> G^L_{15}$$

At $t << t_d$ and the minor current j, the charge separation will be only because of photovoltaic field. In the case of niobate lithium, it is necessary to take into account also, that there is a dependence of cross spatial orientation of a polar axis of the crystal $\bar{C}$ and the current $\bar{j}$. The quantity of a photorefraction field, estimated in the experiment on LiNbO$_3$, is equal to 850 V/cm. Also the storage charge is equal to $4 \cdot 10^{-12}$ Q, and field of a spatial charge - 1800 V/cm. For Fe:LiNbO$_3$ value of photorefraction field is equal to $\approx 1.5 \cdot 10^4$ V/cm.

The solution of distribution problem of a spatial charge and the field near the boundary of homogeneously lighted area at the presence and absence of the external electric field is well-known [1]. The size of area of a spatial charge at presence of the external field E_o is defined by following expression:

$$l = \frac{2kT}{eE_0}\left(\sqrt{1 + \left(\frac{2kT}{eE_0 l_D}\right)^2} - 1\right)$$

where l_D is a screening distance of Debye which at presence of the concentration traps N, is defined by the expression $l_D = \sqrt{\frac{\varepsilon kT}{4\pi e^2 N}}$. Under conditions $E_0 > \frac{kT}{el_D}$ the character size of area of the spatial charge will be expressed from. $l = \frac{\varepsilon E_0}{4\pi e N}$. For $E_o \approx 10^4$ V/cm and $N \approx 10^{18}$ cm^3 the character size of area is approximately equal 10^{-7} cm that it is less, than the character size of area of the non-homogeneous lightning, which is equal to the wave length or more. It allows to use a quasi-neutrality condition analyzing photorefraction effect at which it can be proposed that local electron concentration is defined by the light intensity in the given point (it usually means that Δn connects with an intensity distribution weakly at the enough strong lightning and is defined only by value of an external field). The diffusion field appears usually at the external field absence at the non-homogeneous lightning, for example at recording holograms on $LiNbO_3$ in [41]. Its value is expressed by $\frac{kT}{eL}$, where L is a character length of light intensity change, for example the character wave is defined by the sinusoid wave length for the sinusoidal spatial distribution of light intensity. It is confirmed by the experimental results on hologram recording in which it is shown, that the first Fourier-component value of a diffusion field is equal to $\frac{2\pi kT}{\lambda}$ (but only it is of interest at calculations of the hologram diffraction efficiency). This value is equal to $1.5 \cdot 10^3$V/cm at room temperature and $\lambda \approx 10^{-4}$cm.

In ref. [40] it is informed about investigations of temperature and spectral dependences of photovoltaic current in ferroelectrics, in $LiNbO_3$ particularly. It has been shown, that a photoconductivity and photovoltaic effect in $LiNbO_3$ are connected to interband or impurity to band transitions. The appearance of the photovoltaic current can be consequence of volumetric photovoltaic effect in the homogeneous and homogeneously lighted $LiNbO_3$ [45.] In this case the current direction is defined by the axes direction of spontaneous polarization, even in the absence of the electric field. At ionization of the impurity centre in a polar crystal, as it is shown in ref. [42], the free made electrons have a privaled velocity direction on spontaneous polarization direction or against one, i.e. the probability of the appearance of electrons as a result of ionization, which has the velocity direction parallel to P_s, differs from the probability of the appearance of the electron having an opposite direction of velocity. It is connected with the distortion of wave functions in an unsymmetrical field of the impurity centre. The application of this model has difficulties because of small carriers mobility in $LiNbO_3$ (conductivity must have the jump character), and the recombination time essentially exceeds 10^{-8} s, but quite agrees to Fe: $LiNbO_3$ in which the supplier of electrons is the impurity atom Fe^{2+} in a conduction band.

Thus, the expression for a current, determining the volumetric photovoltaic effect $j=\sigma E+K\alpha\Phi$ where K is the proportional coefficient of spontaneous polarization P_s, α is an absorption constant of light, is applicated completely in the case of Fe: $LiNbO_3$ and if we use the our results, then j will explain the fact and character of changes of an absorption constant completely. On the other hand, the presence of 90°-phase shift between lattices at hologram recording on $LiNbO_3$ [41] is a necessary condition of realization of the diffusion mechanism of recording.

The long-range development of these operations will be submitted in the follow part of paper.

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LiNbO$_3$ OPTİK XÜSUSİYYƏTLƏRİ

TƏLƏT R. MEHDİYEV

YAG:Nd lazerin (532 nm) HeNe lazerindən (632.8 nm) arasıkəsilməyən şüalandırmayla ikinci şüalanma harmonikası ilə impuls oyanması şəraitində 0.03% Fe aşqarı ilə aşqarlanmış litium niobatın optik və yayılma spektrləri eksperimental araşdırılmışdır. Alınan eksperimental nəticələrin ehtimal ediləcək nəzəri interpretasiyası verilmişdir.

ТАЛАТ Р. МЕХТИЕВ

ОПТИЧЕСКИЕ СВОЙСТВА LiNbO$_3$

Экспериментально исследованы оптические спектр и спектр рассеяния ниобата лития легированного 0.03% примесью Fe в условиях импульсного возбуждения второй гармоникой излучения (532 nm) лазера YAG:Nd с непрерывной подсветкой от He-Ne лазера (632.8 nm). Дана предположительная теоретическая интерпретация полученных экспериментальных результатов.