

OPTICAL PROPERTIES OF LiNbO₃. PART ONE.

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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 LiNbO₃ 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: $c=13.836\pm 0.0004\text{Å}$; $a = 5.14829\pm 0.00002\text{Å}$.

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: $(\text{LiNbO}_3)_{0.941}(\text{Nb}_{\text{Li}}\text{NbO}_3)_{0.0118}(\text{V}_{\text{Li}}\text{NbO}_3)_{0.0472}$, 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 stem 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 ($\text{O}^{2-}\text{-Nb}^{5+}$) has mainly covalent and ($\text{O}^{2-}\text{-Li}^+$) - 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 ($\text{Nb}_{\text{Li}} - \text{Nb}_{\text{NB}}$) with $d \sim 3\text{Å}$ are placed in direction along C_3 – axis. Concentration of defects is approximately $2 \cdot 10^{20}\text{cm}^{-3}$ and $c_{\text{V}_{\text{Li}}} \sim 8 \cdot 10^{20}\text{cm}^{-3}$. Capture one of electrons on ($\text{Nb}_{\text{Li}} - \text{Nb}_{\text{NB}}$) defects (one-electron localization) make "small" polaron ($\text{Nb}_{\text{Li}}^{4+} - \text{Nb}_{\text{NB}}^{5+}$) 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 ($\text{Nb}_{\text{Li}} - \text{Nb}_{\text{Li}}$), minimal

distance is 3.76 Å, concentration of defects is ~6·10¹⁸cm⁻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 $\left(\begin{matrix} \text{Nb}_{\text{Nb}}^{4+} - \text{Nb}_{\text{Nb}}^{4+} \\ \text{Nb}_{\text{Li}}^{4+} - \text{Nb}_{\text{Li}}^{4+} \end{matrix} \right)$, 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 LiNbO₃ may have two forms: impurity complex and molecular ion. The OH⁻ absorption and Raman-scattering spectrums of congruent, pure and nearly stoichiometric LiNbO₃ 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 10¹⁶⁻¹⁸ cm⁻³, energy of thermal activation is 1.23 eV for LiNbO₃ and 1.17 eV for LiNbO₃: Fe. [20]

The transport properties in crystal LiNbO₃ 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 LiNbO₃: Fe is ions Fe²⁺ and Fe³⁺, 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 LiNbO₃ 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 $\bar{1}$ 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 Fe²⁺ and Fe³⁺ states. Usually ratio is c_{Fe²⁺}/c_{Fe³⁺} ≈ 0.05 for case c_{Fe} ≈ 56·10¹⁸cm⁻³ and c_{Fe²⁺} ≈ 2.5·10¹⁸cm⁻³, where c_{Fe} = c_{Fe²⁺} + c_{Fe³⁺}.

2. Optical spectra and spectra of scattering.

Experimental researches of optical spectra of absorption LiNbO₃ published in many works. On fig. 1 our experimental results are shown 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 LiNbO₃.

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.

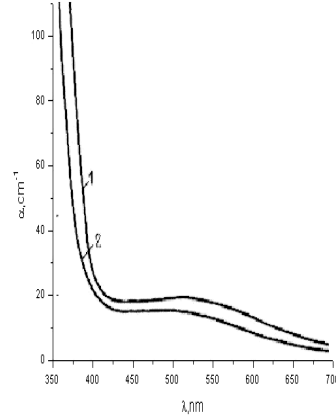


Fig. 1 Optical spectra of absorption LiNbO₃ for two polarizations: 1- E_{light}⊥c and 2- E_{light}||c.

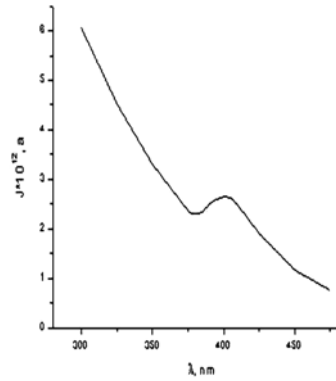


Fig. 2 Spectral dependence of volume photogalvanic current for LiNbO₃

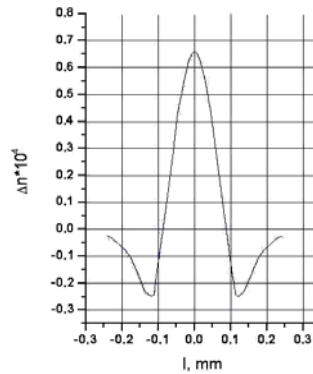


Fig.3. Optically induced changes of factor refraction Δn on diameter of the covered area of a crystal.

At achievement of some critical size Δn ≈ 1.7·10⁻³ on dependence Δn (fig. 4) are observed "jumps" (effect partial polarization reversal) which quantity is defined by density of capacity (~8 W/cm²).

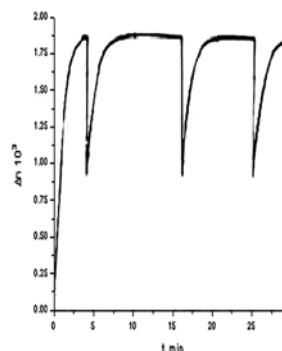


Fig.4 "Jumps" Δn in LiNbO₃+Fe.

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:

$$d_I \sigma(k_I \lambda_I; \Theta \lambda_2) = \left(\frac{|M_{fi} M_{i0}|^2}{\hbar^2 [(\omega_I - \omega_i)^2 + \gamma_i^2]} \right) (\hbar \omega_I - E_f)^2 \frac{d\Omega}{(4\pi^2 \hbar^4 c^4)}$$

M_{fi} and M_{i0} are matrix elements and $\tau_i = 1/\gamma_i$. Therefore, we have two cases: slow $|\omega_I - \omega_i| \ll \gamma_i$ (depend on lifetimes) and fast $|\omega_I - \omega_i| \gg \gamma_i$ (depend on experimental conditions) processes. For slow processes:

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

For fast processes:

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

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

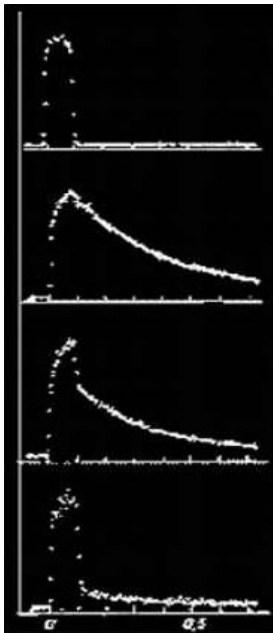


Fig. 5 Study lifetime of states in LiNbO₃ (here x-axis is t, μs):

Impulse of laser:
a. $\lambda=532$ nm, 100 ns

b. Case $\omega_I = \omega_i$

c. Case $\omega_I = \omega_0 + 1.2$ GHz

d. Case $\omega_I = \omega_0 + 2.2$ GHz

The received results show, that at a resonance with a line of absorption (case "b") intensity of radiated light slowly grows (an interval $0 \leq t \leq T_L$) 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.

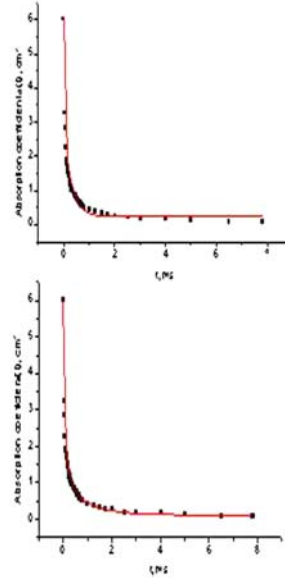


Fig. 6 (See comments in the text)

a

b

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_{ii}^{\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 $\alpha_{ii}(t)$ is obtained by function $\alpha_{ii}(t) = \alpha_i(t=0) \exp[(t/\tau)^\beta]$. 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

$$(A(\tau) \geq 0): f_{KWW} = \int_0^\infty A_\beta(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau$$

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 LiNbO₃: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 LiNbO₃ crystals reveals: the recombination of electrons from small polarons (Nb_{Li}⁴⁺) with deep traps (e.g., Fe³⁺) 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 LiNbO₃:Fe can be described by the two-center charge model, which introduced in [15, 18]. Electrons can be excited from Fe²⁺ 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 Fe²⁺. 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 Fe³⁺ or Nb_{Li}⁵⁺.

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

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

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

Here: $q_{Fe^{2+} \rightarrow cb}^s$, $q_{Fe^{2+} \rightarrow Nb_{Li}^{4+}}^s$ - absorption cross-section of Fe²⁺ for absorption and excitation of an electron from Fe²⁺ into conduction band (cb) and Nb_{Li}⁴⁺, correspondingly; $q_{Nb_{Li}^{4+} \rightarrow cb}^s$ - 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 Fe²⁺ and Nb_{Li}⁴⁺, correspondingly. I_L - intensity of the spatially homogeneous light; $\gamma_{cb \rightarrow Fe^{2+}}$ - coefficient of recombination of conduction band electrons with Fe²⁺; $\gamma_{cb \rightarrow Nb_{Li}^{4+}}$ - coefficient of recombination of conduction band electrons

with Nb_{Li}⁵⁺; $\gamma_{Nb_{Li}^{4+} \rightarrow Fe^{3+}}$ - coefficient of recombination of electrons from Nb_{Li}⁴⁺ with Fe³⁺; n - density of free electrons in the conduction band; $\beta_{Nb_{Li}^{4+} \rightarrow cb}$ -rate of thermal excitation of electrons from Nb_{Li}⁴⁺ into the conduction band. It is impossible to forget, that in real crystals LiNbO₃:Fe as it was specified above, always there is a concentration of ions Fe³⁺ and Nb_{Li}⁵⁺. 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
$q_{Fe^{2+} \rightarrow cb}^s, m^2/J$	1.0×10^{-5}	Light wavelength 532 nm
	0	Light wavelength 632.8 nm
$q_{Nb_{Li}^{4+} \rightarrow cb}^s, m^2/J$	5.0×10^{-5}	Light wavelength 532 nm
	5.2×10^{-5}	Light wavelength 632.8 nm
$q_{Fe^{2+} \rightarrow Nb_{Li}^{4+}}^s, m^5/J$	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 $c_{Fe} = 5.6 \times 10^{25}$	published in paper [1]
$c_{Fe^{2+}} / c_{Fe^{3+}}$	Variable; initial data ≈0.05 for $c_{Fe} = 5.6 \times 10^{25}$	Typically ratios in the range from 0.01 to 1
$c_{Nb_{Li}^{4+}}, m^{-3}$	variable	
$I_L, W/m^2$	Variable	$I_{YAG:Nd}; I_{He-Ne}$ to 3×10^4 ($I_{YAG:Nd}$)
$\gamma_{cb \rightarrow Fe^{2+}}, m^3/s$	1.65×10^{-14}	
$\gamma_{cb \rightarrow Nb_{Li}^{4+}}, m^3/s$	0	
$\gamma_{Nb_{Li}^{4+} \rightarrow Fe^{3+}}, m^3/s$	1.14×10^{-21}	
$\gamma_{Nb_{Li}^{4+} \rightarrow Fe^{3+}}, m^3/s$	1.14×10^{-21}	
n, m^{-3}	variable	
$\beta_{Nb_{Li}^{4+} \rightarrow cb}, s^{-1}$	0	
$\mu, m^2/Vs$	$\approx 7.4 \cdot 10^{-5}$	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 $I_{\text{He-Ne}}$ has been oriented perpendicularly to the same surface.

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

Measuring optically induced modifications of a refractivity in $\text{LiNbO}_3:\text{Fe}$ at use He-Ne of the laser such as ЛП-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 photorefractive on observationally observable values of a modification of a two-refraction with the equation of electrooptical effect gives 680 V/cm for $\delta\Delta n = 5 \cdot 10^{-5}$ and $T=300\text{K}$.

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:

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

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

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:

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

Association n from $\Phi(x)$ - 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

$$N^0 = 2(S\Phi)^{1/2} N N_i \{ (N_i + N)(S\Phi)^{1/2} + (N_i - N)^2 S\Phi + 4N_i N [S'_i \Phi + WN_c \exp(-I/kT) + W_{00} N_i] \}^{1/2} \}^{-1}$$

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:

$$\tau_s^{-1} \approx W_i N_c \exp(-I/kT) + W n_0 \quad (3)$$

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 photorefractive 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 $l = \Delta P_s / eN = \alpha^* f d^2 \approx 10^6 \text{cm}$.

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 LiNbO₃: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]:

$$\frac{\alpha}{n_p} = \frac{2\pi^{3/2} \cdot e^2 \cdot t'}{m' \cdot \omega \cdot c \cdot \Delta} \exp \left[\frac{-(2E_b - \hbar\omega)^2}{\Delta^2} \right] \quad (4)$$

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, $E_{vib} = k_B T$. Derivations of (4) presume that $E_b \gg \Delta > t'$, 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 $E_b \gg t' > \Delta$, $\frac{t'}{\Delta}$ 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 ($\mu \approx 7.4 \cdot 10^{-5} \text{ m}^2/\text{Vs}$) in LiNbO₃ 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).

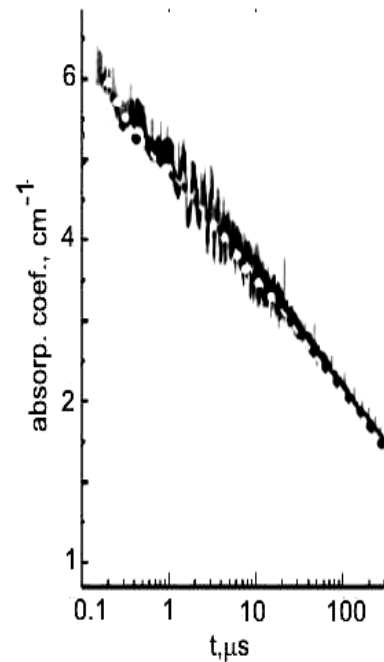


Fig.7

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

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LiNbO₃ OPTİK XÜSUSİYYƏTLƏRİ. BİRİNCİ HİSSƏ

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

Талат Р. Мехтиев

ОПТИЧЕСКИЕ СВОЙСТВА LiNbO₃. ЧАСТЬ ПЕРВАЯ

Экспериментально исследованы оптический 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.

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