

Comparative study of composition dependences of photorefractive and related effects in LiNbO₃ and LiTaO₃ crystals

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Abstract. The results of a comparative study of composition dependences of the light-induced refractive index change, photorefractive sensitivity, polaron luminescence, and intrinsic optical absorption in nominally pure LiNbO₃ and LiTaO₃ crystals are reported. Our investigation demonstrates that the particular light-induced defects traced by the photoluminescence are secondary photorefractive centers themselves. The experimental results obtained are well described by light-induced dissociation of bipolarons into small polarons that are unstable at room temperature.

Keywords: lithium niobate, lithium tantalate, photorefractive effect, luminescence, polaron.

1. INTRODUCTION

Lithium tantalate (LiTaO₃) and lithium niobate (LiNbO₃) are attractive host materials for various applications due to their large electro-optic and nonlinear coefficients. Recently, a new interest to LiNbO₃ and LiTaO₃ crystals was stimulated by the study of small polarons and bipolarons [1-5]. Besides of fundamental aspects, polarons are very perspective entities for practical purposes. Polaron states can be used in two-color holography as intrinsic photorefractive centers in chemically reduced crystals [6,7]. At the same time, suppression of the photorefractive damage, known to be the main limiting factor for a variety of high-throughput applications of nominally pure LiNbO₃ and LiTaO₃ crystals [1,2], necessarily requires a detailed knowledge of light-induced charge transport governed by polarons related to the particular intrinsic defects [1-7]. These practical aspects mentioned above require some new effective method for quantitative evaluation of such intrinsic defects. The recent publications [8,9] show that photoluminescence technique is promising for getting more information about polarons. Another current problem is related to the fact that despite the general idea no detailed explanation was given up to now for the significant difference between photorefractive properties of nominally pure LiNbO₃ and LiTaO₃ crystals.

In this paper we employ the photoluminescence technique to trace the intrinsic photorefractive centers along a comparative study of photorefractive properties of nominally pure LiNbO₃ and LiTaO₃ crystals.

2. SAMPLES AND EXPERIMENTAL METHODS

We have investigated nominally pure single domain LiNbO₃ and LiTaO₃ crystals with different compositions: 9 LiNbO₃ samples with lithium concentrations C_{Li} ranging from 48.4 mol% (congruently melting crystals) to 49.96 mol% (nearly stoichiometric composition obtained by vapor-transport-equilibration (VTE) technique [2]), and 5 LiTaO₃ samples with C_{Li} ranging from 47.2 mol% (so-called under congruent composition [10]) to 49.97 (nearly stoichiometric composition). Among these there are two nearly stoichiometric LiNbO₃ samples fabricated by the two different techniques: K₂O-assisted growth [11,12] and double-crucible method [13,14]. Furthermore, single-domain LiNb₃O₈ crystals were studied. The C_{Li} values were estimated by precision measurements of the fundamental absorption edge, the birefringence, the temperature where the birefringence disappears as well as by measuring the linewidth of

phonon bands in the Raman spectra of all the samples [2,10,11]. All these methods yield a compositional resolution of 0.05 mol% Li₂O. The use of a difference optical spectroscopy method enabled us to resolve the weak absorption bands connected with the intrinsic defects.

Light-induced changes of the extraordinary refractive index Δn of our crystals have been measured at light intensities J between 10^4 and 10^8 W/m². The focused extraordinary polarized beam of a He-Ne ($\lambda = 632.8$ nm), He-Cd ($\lambda = 441.6$ nm), or Kr⁺ ($\lambda = 676.4$ nm) laser has been used. In order to evaluate the steady state value Δn_s , the laser beam induced trajectory changes, due to photorefractive defocusing, have been studied. The intensity distributions (shape and the magnitude) at the focus and at a long distance after crystal were recorded with the aid of a photodiode array. It is known [15] in fact, that such investigation allows measuring the photorefraction with reliable precision.

We have used a simple model [16] for evaluation of Δn_s from the laser-beam trajectory: $\Delta n_s = 4n_e\{(y/y_0)-1\}(x/y_0)^2$, where n_e is the extraordinary refractive index, x is the path length of the laser beam in sample, y is the radius of the laser spot at a half intensity in steady state; y_0 is the radius of the laser spot at a half intensity in initial state (at exposition time $t = 0$).

Moreover, the measurement of the time dependence of the radial shape of the output beam provides us with the information on specific time τ of temporal growth of Δn , i.e. the photorefractive sensitivity S . We define S as:

$$S = \frac{1}{J} \left. \frac{\Delta n}{\Delta t} \right|_{t \rightarrow 0} \cong \frac{\Delta n_s}{J\tau} . \quad (1)$$

Holographic measurements are carried out with a standard two-beam interference setup. Two beams of either a He-Ne laser ($\lambda = 632.8$ nm) or an Ar⁺ ion laser ($\lambda = 488$ nm) are superimposed inside the crystal. Low light intensities ($\leq 1.6 \times 10^5$ W/m²) were achieved within the interference pattern for both cases.

A search was made also for luminescence because it was thought that this might help towards understanding the photorefractive effect, which appears to involve a new electron transport mechanism, specific for LiNbO₃ and LiTaO₃ crystals. Absorption of light directly produces a photocurrent, rather than by merely liberating electrons, which then produce photovoltaic currents. The samples were excited at room temperature using radiation at 632.8, or 676.4 nm from a He-Ne or a Kr⁺ laser with light propagation along the c -axis. The luminescent radiation was collected with a confocal microscope and focused on the entrance slit of a LabRam Yobin-Ivon spectrometer. Alternatively, detection by a 90° scattering optical system of a DFS-24 spectrometer is used. Filters were used to prevent laser light entering the monochromator and, also, to eliminate incoherent light from the exciting laser beam.

3. EXPERIMENTAL RESULTS

The measurements of diffraction efficiency for the two-beam holographic recording scheme indicate that steady-state light-induced refractive index changes Δn_s and photorefractive sensitivity S depend on crystal composition C_{Li} of LiTaO₃, Fig. 1. These dependences have a drastic character similar to the one observed in LiNbO₃ in previous investigations [6,11-15]. Our data lead to the conclusion that intrinsic defects play a significant role in photorefraction for both LiNbO₃ and LiTaO₃ crystals. However, the mechanism of their contribution to the photorefractive effect remains an open question, as there is no easily explainable dependence of both Δn_s and S on C_{Li} , i.e. on the intrinsic defect concentration N ($N \sim 50C_{Li}$), in near stoichiometric ($C_{Li} > 49.50$ mol%) and other composition ranges of LiTaO₃ crystals, Fig.1. For example, up to a Li concentration of 49.5 mol% Li₂O, Δn_s exceeds 1×10^4 and increases with increase of C_{Li} . If the Li concentration is larger than 49.5 mol%, Δn_s is decreasing sharply: $\Delta n_s \approx 2 \times 10^6$ at $C_{Li} = (49.97 \pm 0.05)$ mol%.

In the case of LiNbO₃ crystals, the situation of composition dependence of Δn_s based on the previously published data [6,11-15] is not so clear because of a significant contradiction between data for near stoichiometric crystals ($C_{Li} \geq 49.90$ mol%) fabricated by

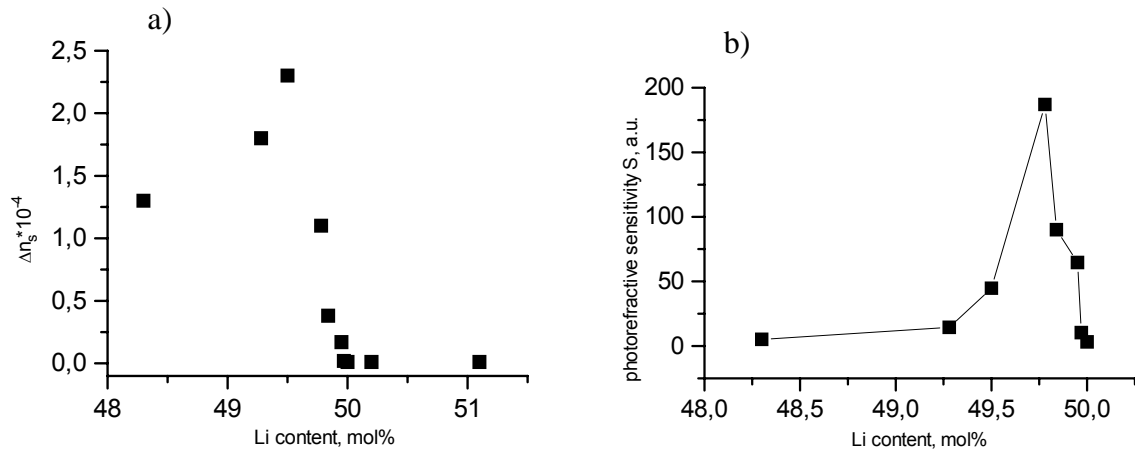


Fig.1. Composition dependences of steady-state light-induced refractive index change Δn_s **(a)** and photorefractive sensitivity S **(b)** in nominally pure LiTaO_3 crystals fabricated by VTE technique, using a congruent crystal as starting material.

different techniques: VTE, double-crucible and K_2O -assisted growth. Our measurements of photorefractive defocusing show that the influence of C_{Li} on Δn_s values differs for various levels of J , see Fig. 2. Moreover we observed a threshold value J_t for input light intensity J , where the dependence $\Delta n_s(C_{\text{Li}})$ changes qualitatively. Thus, if $J < J_t$, Δn_s increases with the increase of C_{Li} (i.e. with decrease of N), however for $J > J_t$ the opposite dependence is observed. In the case when J has a value close to J_t , no clear correlation between Δn_s and the C_{Li} was observed. At the same time, a close correlation occurs between the J_t value and the optical absorption coefficient α for the weak absorption band near 500 nm related to the so-called bipolaron absorption, i.e. to intrinsic defects [1,6,17]. It has been previously established [15], that a nominally pure crystal may be regarded as slightly reduced LiNbO_3 , if this crystal has been obtained under standard fabrication conditions. In our samples the actual value of J_t depends on laser wavelength λ : the shorter λ the smaller is J_t . However, in any case the smallest Δn_s value has been observed for near stoichiometric crystals with largest C_{Li} ($C_{\text{Li}} = 49.96 \pm 0.05$ mol%).

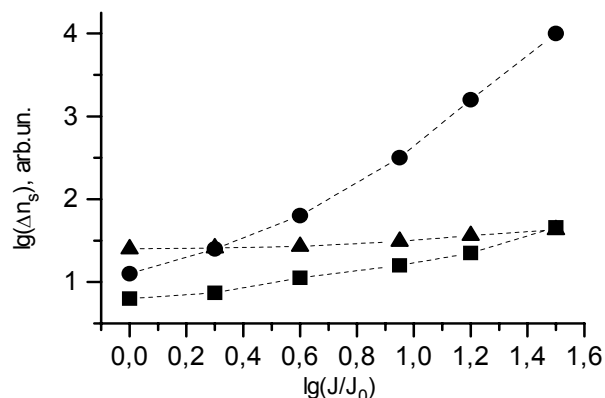


Fig. 2. Extraordinary refractive index change Δn_s vs light intensity J (where $J_0 = 10^4 \text{ W/m}^2$) in crystals with different composition C_{Li} : 1 - 49.02 ± 0.05 mol%; 2 - 48.50 ± 0.05 mol%; 3 - $C_{\text{Li}} = 49.30 \pm 0.05$ mol%. The accuracy of a measurement of the relative changes of Δn_s is $\pm 10\%$. The value of 4 [arb.un.] for Δn_s corresponds to an absolute value of $\Delta n_s = (0.4 \pm 0.3) \times 10^{-3}$, which is derived from a comparison with holographic data for $\text{LiNbO}_3:\text{Fe}$ crystals [15].

According to the data shown in Fig. 2, the comparison of the amplitude values of photorefraction Δn_s for crystals with different C_{Li} , grown either from different raw materials or using different technologies (i.e. crystals have different levels of optical absorption α related to different degrees of residual chemical reduction), may show any Δn_s dependences on N , e.g., with a maximum of Δn_s at arbitrary values of C_{Li} intermediated between congruent and stoichiometric compositions.

Our measurements indicate a strong increase of photorefractive sensitivity S with the growth of light intensity J for all the $LiNbO_3$ and $LiTaO_3$ crystals studied here, excluding only the stoichiometric crystals fabricated by VTE technique, see Fig. 3. This increase is in contradiction to an expected intensity independent sensitivity S which is typical for the one-centre photovoltaic model. The slope of the S dependence on J increases with the growth of the C_{Li} value in the crystals. This increase of S with the growth of light intensity J is a clear evidence of significant contribution of some secondary centres in photorefractive response. Note, that previous findings allow to assume that the secondary photorefractive centres are polarons related to the intrinsic antisite defects $Nb_{Li}(Ta_{Li})$ [1-4,6,7,14,15].

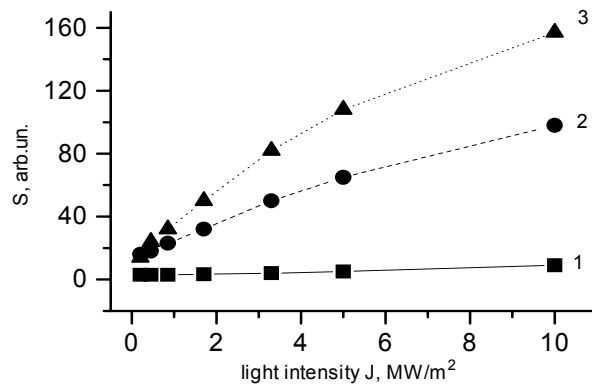


Fig.3. Intensity dependence of photorefractive sensitivity S in $LiNbO_3$ crystals with different compositions C_{Li} : 1 - $C_{Li} = 49.50 \pm 0.05$ mol%; 2 - 48.72 ± 0.05 mol%; 3 - 48.50 ± 0.05 mol%. Excitation wavelength is 632.8 nm.

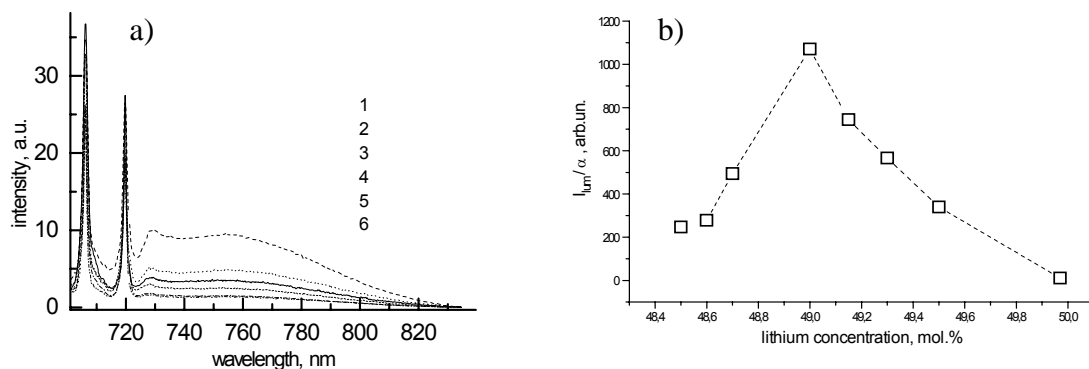


Fig. 4. (a) Photoluminescence spectra of $LiNbO_3$ and $LiTaO_3$ crystals at 300 K (a): 1- $LiNbO_3$, $C_{Li} = 49.02 \pm 0.05$ mol%; 2- $LiNbO_3$, $C_{Li} = 49.30 \pm 0.05$ mol%; 3- $LiNbO_3$, $C_{Li} = 49.50 \pm 0.05$ mol%; 4- $LiNbO_3$, $C_{Li} = 48.50 \pm 0.05$ mol%; 5- $LiTaO_3$, $C_{Li} = 48.30 \pm 0.05$ mol%; 6- $LiNbO_3$, $C_{Li} = 49.97 \pm 0.05$ mol%. Sample notation is given in accordance with sequence of their luminescence intensity at 760 nm from largest (#1) to smallest (#6). **(b)** Composition dependence of luminescence intensity normalized to optical absorption coefficient α for bipolaron absorption band. All these crystals were fabricated with either growth from Li-rich melts (#1 - 4), or VTE-technique (#5 - 6). The excitation wavelength was 676.4 nm with a power of about 70 mW. In this figure no correction has been made for the photomultiplier response and filters.

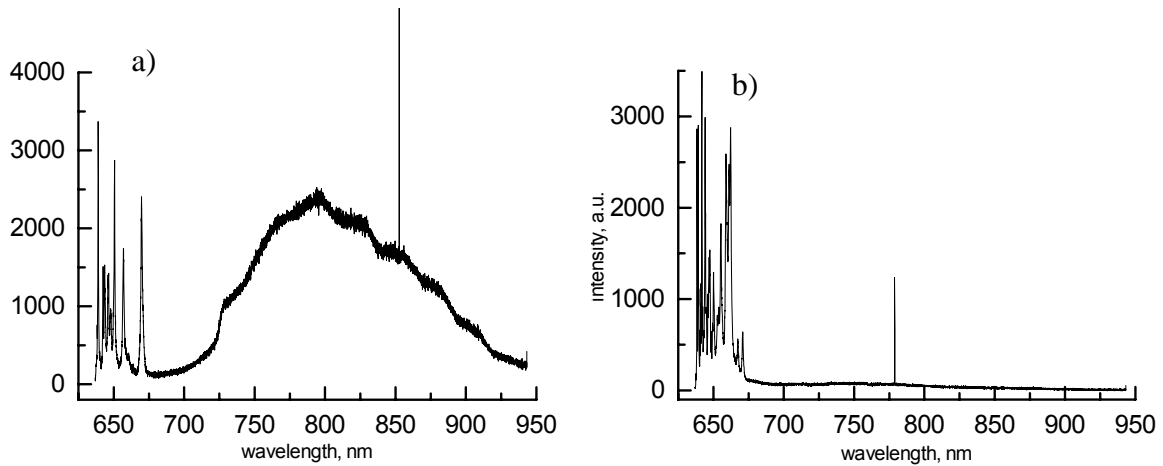


Fig. 5. Photoluminescence spectra of the congruently melting LiNb_3O_8 crystals **(a)** and single crystal of LiNb_3O_8 **(b)**. The excitation wavelength was 632.8 nm with a power of about 2 mW, corresponding to the high-intensity excitation regime as confocal microscope with microscope objective $\times 100$ was used to excite and to collect luminescence emission. Measurement was made at 300 K.

Figure 4(a) shows the luminescence spectra observed with DFS-24 spectrometer at 676.4 nm excitation for LiNbO_3 and LiTaO_3 crystals with different compositions. In Fig. 4(b) the composition dependence of luminescence intensity in nominally pure LiNbO_3 crystals shows the same behavior as the composition dependence of S . The luminescence spectra observed with the LabRam Jobin-Yvon spectrometer at 632.8 nm are shown in Fig. 5. The difference between the shapes of the luminescence band for these two kinds of experiments is caused by the different spectral selectivity of the photodetectors for DFS-24 and LabRam. The rough calibration of these photodetectors shows that the LabRam gives more appropriate information about the shape of any band in the range from 600 to 900 nm. However, the information obtained with DFS-24 is useful for a comparative study of luminescence intensities in different samples. Thus, we conclude that we observe the same luminescence band in both experiments and this band has an intensity maximum near 800 nm in the strongly nonstoichiometric ($C_{\text{Li}} < 49.50$ mol%) LiNbO_3 and LiTaO_3 samples. In near stoichiometric LiNbO_3 crystals ($C_{\text{Li}} \geq 49.90$ mol%) fabricated with either double-crucible or K_2O -assisted growth techniques, the luminescence band has an intensity maximum near 880 nm, see Fig. 6.

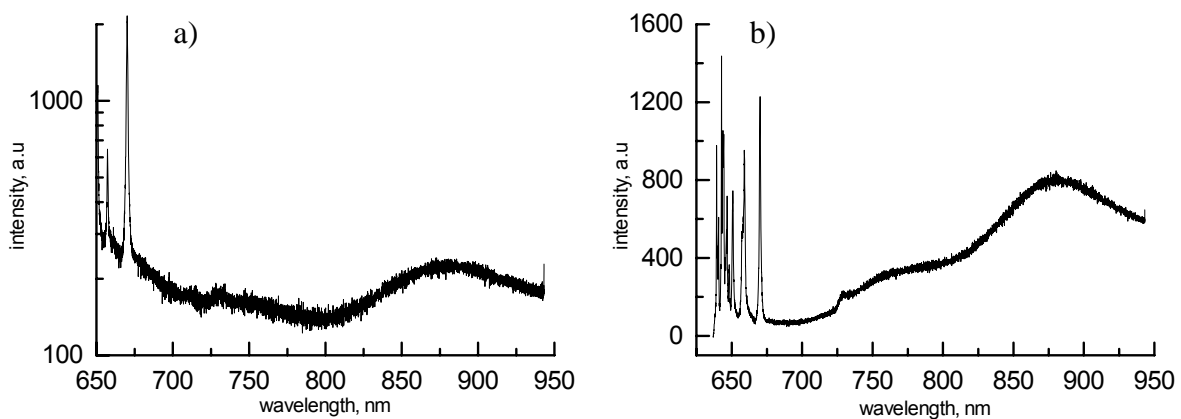


Fig. 6. Photoluminescence spectra of near stoichiometric LiNbO_3 crystals fabricated with double crucible technique **(a)** and K_2O -assisted growth technique **(b)**. The excitation wavelength was 632.8 nm with a power of about 10 mW. Measurement was made at 300 K.

In the case of near stoichiometric LiNbO₃ crystals the luminescence intensity is strongly attenuated, excluding only LiNbO₃ crystals fabricated with K₂O-assisted growth technique: Here the attenuation factor A , comparatively with the I_{lum} value in congruently melting LiNbO₃, is > 50 in LiNbO₃ crystals fabricated with VTE technique, and $A \approx 12$ for LiNbO₃ crystals fabricated with double-crucible technique, Fig. 6. The polaron luminescence was not detected in the near stoichiometric LiTaO₃ as well as in LiNb₃O₈ crystals. A comparative study of the strongly nonstoichiometric LiNbO₃ and LiTaO₃ crystals ($C_{Li} < 49.50$ mol%) demonstrates that luminescence intensity is always smallest in LiTaO₃.

Additional chemical reduction annealing in H₂ atmosphere has been established to introduce a large amount of extra luminescence at 800 nm in LiNbO₃ and LiTaO₃ crystals, presumably corresponding to the large bipolarons concentration in these crystals. This luminescence growth correlates closely with a marked increase of the so-called bipolaron absorption band [1,6,17], having its center at ~ 500 nm. Thus, according to the previous data [8,9], we conclude that the 800 nm peak is caused by the polaron luminescence.

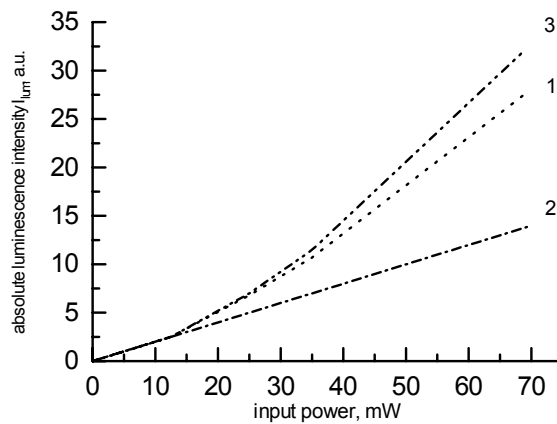


Fig. 7. Dependence of luminescence intensity I_{lum} on exciting laser-beam power P in nonstoichiometric LiNbO₃ crystals ($C_{Li} = 49.30 \pm 0.05$ mol%) – (1). The excitation wavelength is 676.4 nm for slightly focused beam of Kr⁺ ion laser. Theoretical curves are plotted for linear law $I_{lum} = AP$ (2) and super-linear law $I_{lum} = AP^{3/2}$ (3), both theoretical curves are normalized to experimental value I_{lum} observed at $P = 12$ mW.

It is important to note, that the luminescence intensity I_{lum} demonstrates a nonlinear dependence on exciting light intensity J at moderate intensity excitation regime, see Fig. 7. It may be regarded as a clear evidence of the two-photon excitation of this luminescence. Note, that because of the super-linear dependence of I_{lum} on J it was impossible to detect the luminescence signal at low-intensity excitation with our set-ups. As it has been established experimentally (see Fig. 2), the change of excitation regime from the low-intensity range to moderate intensities one induces the significant shift of maximum position at the dependences $\Delta n_s(C_{Li})$ and $S(C_{Li})$ to smaller C_{Li} values, and it become rather correlated with the composition dependence of I_{lum} (see Fig. 4).

4. DISCUSSION

Our data show that intrinsic defects are responsible for the appearance of secondary photorefractive centres. In LiTaO₃ it may be caused, similar to well-established findings in LiNbO₃ [3,4], by the photo dissociation of bipolarons ($Ta_{Li}^{3*}-Ta_{Ta}'$) into two short-living single polarons at room temperature, which are themselves filled secondary centres. The existence of secondary photorefractive centres is confirmed by the close correlation between the composition dependences of S and I_{lum} at excitation wavelengths of 632.8 nm and 676.4 nm used in our experiments. Thus, the photorefractive properties of nominally pure LiNbO₃ and LiTaO₃ have been consistently explained by assuming that $Nb_{Li}^{3*}-Nb_{Nb}'$ (or $Ta_{Li}^{3*}-$

Ta_{Nb}) bipolarons are formed as shown by optical measurements [1,17-21]. Bipolarons may be considered as pairs of small polarons stabilized by joint lattice distortion and covalence. They can be broken into single (small) polarons again by illumination via photo-dissociation process. At room temperature polarons are short-living (several milliseconds) because of small activation energy (0.3 eV) of their annihilation. Kinetics of the dissociation-annihilation process can indeed be described by a second order reaction [17]: $B \leftrightarrow P + P$.

With densities N_B of bipolarons and N_P of polarons the kinetics can be described by the following rate equation taking into account generation and recombination of polarons:

$$dN_P/dt = g'N_BJ - rN_P^2 \quad (2)$$

If the concentration of bipolarons changes only slightly during illumination, $\Delta N_B \ll N_B$, the term $g'N_B$ in Eq. (2) can be replaced by a constant g . At cw laser intensities typical for our luminescence experiments, utilizing 676.4 nm excitation, this is a good approximation and the term gJ can be used instead of $g'N_BJ$ in Eq. (2) as generation rate [17]. The concentration N_P can be evaluated from data on light-induced changes of optical absorption α_{li} , as $\alpha_{li} = sN_P$ with $s = s_P - 0.5s_B$, where s_P denotes the absorption cross section of polarons and s_B that of bipolarons. Solving the rate equation (2), one obtains for steady-state absorption changes during illumination: $\alpha_{li}^s = s(gJ/r)^{1/2}$, where $1/r \sim \tau_P$, and τ_P is the polaron lifetime limited by fast thermal relaxation to bipolaron states or other deep traps.

The existence of these polarons in cw-illuminated crystals can be monitored by measuring the luminescence spectra, as polarons can be further excited, i.e. photo ionized, if it will absorb a second photon $h\nu$ during its short lifetime within the absorption band at 780 nm. Electron elaborated by this way relaxes to the bottom of the conduction band, attends to photovoltaic current, captured onto a locally distorted site and after relaxes either vibrationally or radiatively to a level of the localized polaron "defect" within the band gap. Along the latter non-phonon relaxation process a photon $h\nu'$ ($h\nu' < h\nu$) is emitted, giving the luminescence signal. The possibility of such a transition has been demonstrated within the frame of the two-centres configuration model of small polarons, treating the luminescence as the result of thermalization of charge carriers captured into the ground state of a polaron, and confirmed experimentally for e-irradiated $LiNbO_3$ crystals [8]. Radiative non-phonon transition from a locally distorted site, formed via thermalization of hot conduction electron, to ground polaron state is possible if a configuration coordinate of an excited quasi localized state in the conduction band would be same with the ground state of a polaron within the energy gap. Of course, the probability of this process is small and, indeed, the polaron luminescence is relatively weak and can be observed only at moderate and high excitation intensities.

Combined solution of equations, describing the dissociation-annihilation process and the luminescence gives the following results for the dependence of polaron luminescence intensity I_{lum} on exciting laser intensity J :

$$I_{lum} = \alpha_{li}^s \gamma J = s (gJ/r)^{1/2} \gamma J = A\gamma (sN_B\tau_P)^{1/2} J^{3/2} \quad (3)$$

where γ is the quantum efficiency of luminescence, A is some proportionality coefficient related also to a geometrical factor of the experimental measurements.

At further growth of excitation intensity J we will have:

$$I_{lum} = A\gamma \{sN_B\tau_P(1 - \exp(-J/J_s))\}^{1/2} J. \quad (4)$$

In this case, when N_P has the same order of magnitude as N_B , such an input intensity law is caused by a significant depletion of bipolaron states, relating to a decrease of instant bipolaron concentration N_B in the illuminated crystals.

To explain the peculiarities observed experimentally, we consider that the spectral dependence of light-induced absorption differs significantly from the intrinsic optical absorption spectrum of $LiNbO_3$ and $LiTaO_3$, as electrons trapped in shallow secondary centres increase the optical absorption in the red and infrared. These composition dependences are not monotonous: S , I_{lum} and Δn_s have maximum values at an arbitrary composition, depending on light intensity J , intermediate between congruent and

stoichiometric, Fig. 4. Such a particularity can be explained considering distance-dependent excitation and recombination rates [18,19], i.e. the lifetime τ_P of an individual small polaron depends on the distance to the next available deep electron trap, decreasing with the intrinsic defects concentration at composition variations. According to the model proposed in Eqs. (3,4), polaron luminescence intensity I_{lum} is expressed by the product of intrinsic defect concentration $[Nb_{Li}]$ ($N_B \sim [Nb_{Li}] = B(1-C_{Li})$ for standard crystals) and polaron lifetime τ_P , that allows to explain all the composition dependences observed here. Moreover, the nonquadratic-intensity dependence of two-photon absorption luminescence (see Fig. 7) is well described in frame of this model (3,4). Therefore, it should be expected that the photorefractive sensitivity S , i.e. the photovoltaic current density i_{pv} normalized to J , is proportional to the luminescence intensity I_{lum} , as both effects have the same microscopic origin: two-photon excitation of polarons. Thus, luminescence measurements may be regarded as an effective tool for the evaluation of optimal composition of nominally pure crystals for a desired photorefractive application (e.g., holographic memory cells [6]), according to a chosen wavelength and input intensity range.

Besides, based on these new insights, much lower values of I_{lum} , as well as S and Δn_s , in nominally pure LiTaO₃ crystals with any composition can be regarded as an evidence of a much smaller polaron lifetime in comparison with LiNbO₃. This conclusion is in good agreement with recent data on polaron relaxation in LiTaO₃ [20,21].

Our data allow to conclude that measurements of polaron luminescence intensities provides highest resolution among all the known methods for evaluation of composition at comparative study of different near stoichiometric crystals. For example, no difference was observed between the near stoichiometric LiNbO₃ crystals fabricated with double-crucible and VTE techniques at measurements of fundamental absorption edge, birefringence, and Raman bandwidths. At the same time, the polaron luminescence intensities differs by 4.1 times, which allows to conclude a big difference of relative concentrations of intrinsic defects $[Nb_{Li}]$ in these crystals: $[Nb_{Li}]_{DCr}/[Nb_{Li}]_{VTE} \geq 4.1$, while the absolute values of these concentrations are much lower in comparison with all other LiNbO₃ crystals studied, according to data on C_{Li} obtained with the other standard methods, which are giving the same figure of $C_{Li} = 49.96 \pm 0.05$ mol.% for the both kinds of near stoichiometric crystal. Thus, our rough estimation shows that the compositional resolution of polaron luminescence spectroscopy is better than 0.01 mol% in near stoichiometric range of crystal compositions.

In conclusion, we have supplemented our measurements by a search for correlation between the photoluminescence and photorefractive effect. Our results indicate that in nominally pure LiNbO₃ and LiTaO₃ the particular light-induced defects traced by the photoluminescence are the secondary photorefractive centres themselves.

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