Gated luminescence in as-grown and reduced undoped LiNbO₃ crystals

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Abstract. The results of comparative study of the gated two-color luminescence and intrinsic optical absorption in as-grown and chemically reduced nominally pure LiNbO₃ crystals are reported. A powerful laser beam at 514.5 nm was used as gating radiation, and a laser weak beam at 632.8 nm was used to probe the luminescence. The dependences of luminescence spectra on the power of gating radiation and crystal composition have been investigated. The luminescence intensity correlates with the bipolaron absorption band in the chemically reduced crystal. We conclude that this gated luminescence at 800-950 nm is caused by the radiative transitions involving polaron states and it may be directly correlated with the two-color photorefractive sensitivity used for gated holographic recording.

1. Introduction
Lithium niobate (LiNbO₃) has been extensively studied for holographic data storage media since the discovery of photorefractivity in this material [1]. One of the critical issues in the implementation of holographic data storage is to fix the stored information. Due to the dynamic nature of photorefractive effect, the stored information is gradually erased during readout. Several techniques have been developed to overcome this volatile readout, including thermal fixing and electrical fixing [2]. Thermal processes or applications of high external electric fields required for these methods might be impractical. One promising method is to use two-color recording, in which a gating beam (usually of higher photon energy than the recording beams) is present during recording for sensitizing the material. This gating light just aids the recording process but is not at the recording wavelength, thereby making the readout at a longer wavelength nonvolatile. In addition, the stored information can be erased with the gating beam (or gating beam plus one of the recording beams). This approach is attractive in that it is an all-optical process.

The holographic storage system that uses the two-photon gated recording method has been recently reported: High diffraction efficiency is achieved when a cw near-IR laser (800 nm) is used for writing and a green/blue incoherent light for gating [3,4]. There are many hints that short-living (order of ms at room temperature) small (single) polarons strongly influence photorefractive sensitivity. At room temperature almost all of these polarons are paired forming the bipolarons in equilibrium. Bipolarons can be broken into single polarons again by illumination within visible range. The dissociation of bipolarons changes the optical absorption spectrum of the crystals. The broad absorption band near 500 nm has been attributed to the presence of the bipolarons and a narrower band at 760 nm has been...
assigned to the formation of single polarons under illumination with proper wavelength [4,5]. The second important source of small polarons is two-photon band-to-band excitation of an electron, forming a pair of the electron and hole polarons within bandgap [6]. To optimize the crystal properties for two-color holography, it is necessary to study the efficiency of small polarons excitation with recording red/near-IR light in different crystals. The usual approach consists of direct measurement of photovoltaic current density at two-color excitation [3,7]. However, this approach is rather sophisticated technically. As alternative approach, we propose to use the measurements of two-photon luminescence, as it has been established [5], that two-photon photorefractive sensitivity is correlated with this photoluminescence (PL) intensity, as both effects have the same microscopic origin: the photoexcitation of small polarons.

2. Experimental techniques

Nominally pure LiNbO₃ crystals with different composition were used in this study. Some samples of the congruent crystal were annealed in pure hydrogen atmosphere at 500 °C or in vacuum 10⁻³ Torr at 500-700 °C for various times in range from 0.5 to 11 hours. As can be seen from the corresponding absorption spectra, the strength of the bipolaron absorption band depends on the reduction temperature in a strongly nonlinear way. This fact makes it difficult to control the reduction process and may lead to arbitrarily different results for slightly altered experimental conditions. Since the dependence of bipolaron concentration on the reduction conditions in nominally pure LiNbO₃ is not known in general, the most convenient characterization is given by the properties of the bipolaron band itself [2]. We will therefore refer to the steady-state absorption at λ=500 nm, i.e., the maximum of the bipolaron absorption band, as the degree of reduction. The two near-stoichiometric samples have slightly different composition, as it were fabricated by various techniques: double crucible CZ (DCCZ) growth and vapor-transport-equilibrium (VTE) treatment. According to our previous study, the deviation (Δx_c = 50 - x_c) from true stoichiometric composition is larger in the DCCZ sample than in the VTE one by factor of 4.1, while composition parameter x_c = ([Li2O]/([Li2O] + [Nb2O5]))×100% has been found to have almost same value of 49.96±0.05 % in the both crystal, according to the Raman data [5].

To investigate the contribution of small polarons to PL, the samples was irradiated by a focused beam of 514.5 nm from an argon-ion laser for pumping (gating), or/and by another focused laser beam of 632.8 nm from a helium-neon laser for probing. The on/off statuses of these two beams were controlled by two shutters. To focus both pump and probe beams, a high-NA microscope objective (×50) was used. This objective is part of a confocal microscope within a “LabRam” spectrometer. Therefore, a microscope confocal hole allows extract luminescence and Raman signal from an area, where overlapping between pump and probe beams is largest. To calibrate a spectral dependence of sensitivity of the LabRAM Jobin-Yvon spectrometer in red and near-IR ranges (640-1000 nm), a NIST calibrated halogen lamp were used as the standard quasi-white light source. This calibration of the both photodetector and monochromator responses has provided possibility to use the LabRam in obtaining of appropriate information about the PL bands in the near-IR range.

3. Experimental results and discussion

The PL spectra excited by probe beam of a He-Ne laser in as-grown nominally pure LiNbO₃ crystals contain a weak band, which has intensity depending strongly on the crystal composition and degree of residual chemical reduction. This broad luminescence band is observed to be centred around 800-820 nm in the raw spectra measured by the LabRAM spectrometer [5]. Calibrating the spectrometer’s spectral sensitivity, we conclude that these PL spectra consist of the two broad bands centred at 835 and 950 nm, Fig. 1. Note that this result is in satisfactory agreement with the previously reported data on position of the PL bands (840 and 953 nm) [8].

Integral PL intensity, I_pl, as well as ratio between intensities of two PL bands depends drastically on composition of as-grown crystals: at decrease of x_c, i.e. increase of intrinsic defect concentration,
the sharp growth of absolute intensity of 835-nm PL band is observed at slight increase of 950-nm band intensity, e.g. ratio $I_{PL}(835\text{nm})/I_{PL}(950\text{nm}) \approx 1.6$ in as grown congruent crystals.

![Figure 1. PL spectra of a slightly reduced DCCZ crystal excited by: single 10-mW-514.5-nm beam (a), single 10-mW-632.8-nm beam (b), both beams (c-e) at constant power (10 mW) of 632.8-nm beam and different powers of pump 514-5-nm beam: 20 mW (c), 40 mW (d) and 50 mW (e).](image1)

These bands were observed also in PL spectra measured at two-color excitation, when second green pump beam of Ar+-laser is used to increase PL excitation efficiency. Green and red beams were aligned to overlap inside the crystal so that the change of PL in the presence of green light could be monitored. As seen in figure 1, as-grown crystals show significant increase of PL intensity in the presence of green light. The green-induced increment of PL intensity disappears immediately, when the green pump beam was turned off. Note, that one-color PL excited by single green pump beam has much smaller intensity in comparison with one-color PL excited by red probe beam, Fig. 1.

![Figure 2. PL intensity versus pump power $P_{pump}$ in the as-grown congruent (1) and near-stoichiometric VTE crystals (2).](image2)

Figure 2 shows the PL intensity variation with the pump power at a constant probe 632.8-nm-beam power (10 mW) in the as-grown congruent and near stoichiometric VTE crystals, i.e. in samples with
different residual lithium deficiency. \( I_{PL} \) demonstrates a marked growth with power \( P_{pump} \) of the pump 514.5-nm-beam in the both crystals. It may be regarded as a clear evidence of the two-color (gated) excitation of this luminescence. The slope of power dependence of PL intensity, \( \partial I_{PL}/\partial P_{pump} \), as well as the maximum value of \( I_{PL} \) increase with \( \Delta xc \), i.e. there is clear correlation between \( \partial I_{PL}/\partial P_{pump} \) and intrinsic defects concentration. The dependence of \( I_{PL} \) on \( P_{pump} \) tends to saturation at higher pump powers in congruent crystal, Fig.2(1), while no the tendency to saturation is observed in VTE crystal, Fig.2(2). The spectral shape and absolute intensity of PL differ slightly with the specimens of as-grown congruent LiNbO\(_3\) crystal.

Additional chemical reduction via annealing in vacuum or H\(_2\) atmosphere has been established to introduce a large amount of extra luminescence at 835 nm, presumably corresponding to the large bipolarons concentration in these crystals. This growth of PL intensity correlates closely with a marked increase of the bipolaron absorption band [1,5,9], having its center at ~ 500 nm. Both \( I_{PL} \) and \( \Delta I_{PL} \) (measured at 835 nm) increase monotonically with the increase of the optical absorption coefficient \( \alpha \) at 500 nm within \( \alpha \) range from 0.2 to 3 cm\(^{-1}\). Thus, the maximum value of normalized increment of PL intensity (\( \Delta I_{PL} / I_{PL} \)) is evaluated to be on the order of 0.1 in the slightly and moderately reduced congruent crystals at \( P_{pump} = 50 \) mW, Fig. 2. The dependence of \( I_{PL} \) on \( \alpha \) shows an evident saturation in the more deeply chemically reduced crystals with larger \( \alpha \), while \( \Delta I_{PL} \) sharply decreases with the further increase of \( \alpha \) and \( \Delta I_{PL} = 0 \) in the reduced crystal with the largest value of \( \alpha \) (8.1 cm\(^{-1}\)) among studied samples. Besides, the PL spectra of deeply reduced crystals have pronounced difference from the spectra of all other crystals, as the 950-nm band is not observed, Fig. 3.

Figure 3. PL spectrum obtained by two-color excitation at \( P_{pump} = 20 \) mW in the strongly reduced congruent crystal with \( \alpha = 8.1 \) cm\(^{-1}\).

It has been found that the some important features of the PL spectra of the reduced nominally pure LiNbO\(_3\) can be consistently explained by photoexcitation of the (Nb\(_{Li}^\bullet\)-Nb\(_{Li}^\bullet\)) bipolarons [5,8]. Bipolarons may be considered as pairs of small polarons stabilized by a joint lattice distortion and covalence. They can be broken into single (small) polarons by illumination with a proper wavelength via a photo-dissociation process. At room temperature single polarons are short-living (\( \leq \) ms) because of their small activation energy (0.3 eV) for annihilation. The kinetics of the dissociation-annihilation process may be described by a second order reaction [9]: \( B \leftrightarrow P + P \). The existence of these single polarons in continuous wave (cw) illuminated crystals manifests itself in the luminescence spectra, as the polarons can be further excited by absorption of a photon with energy corresponding to the single
polaron absorption band centred at 780 nm. Electrons elaborated in this way relax to the bottom of the conduction band, captured at a locally distorted site and after relaxes either vibrationally or radiatively to a level of a localized polaron defect below the band edge, i.e. within the band gap. Along the latter non-phonon relaxation process a photon with smaller energy is emitted, giving the luminescence signal at $\lambda > 800$ nm. Such a radiative (non-phonon) transition from a locally distorted site to the ground polaron state is possible if the configuration coordinate of the excited quasi-localized state in the conduction band would be the same as that of the ground state of a polaron [10]. Of course, the probability of this process is small and, indeed, the polaron luminescence is relatively weak and can be observed only at relatively high excitation intensities specific for strongly focused laser beams obtained by the high-magnification objectives used in the confocal microscope of a LabRam spectrometer [5,8].

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 [11]:

$$\frac{dN_p}{dt} = g'N_B \rho_{pump} - rN_p^2$$  \hspace{1cm} (1)

If the concentration of bipolarons changes only slightly during illumination, $\Delta N_B << N_B$, the term $g'N_B$ in Eq. (1) can be replaced by a constant $g$. At cw laser intensities typical for our luminescence experiments this is a good approximation and the term $gJ_pump$ can be used instead of $g'N_B\rho_{pump}$ in Eq. (1) as generation rate [11]. The concentration $N_p$ can be evaluated from data on light-induced changes of optical absorption $\alpha_{li}$, 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 (1), one obtains for steady-state absorption changes during illumination:

$$\alpha_{li} = s(gJ_pump/r)^{1/2}$$  \hspace{1cm} (2)

where $1/r \sim \tau_P$, and $\tau_P$ is the polaron lifetime limited by fast thermal relaxation to bipolaron states or other deep traps. 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 probe laser intensity $J_{prob}$:

$$I_{lum} = A\gamma(sN_B\tau_P(1 - \exp(-J_{pump}/J_s))^{1/2})J_{prob}$$  \hspace{1cm} (3)

where $J_s$ is specific saturation parameter: In the case $J_{pump} > J_s$, $N_p$ has the same order of magnitude as $N_B$, and a pump intensity law of $I_{lum}$ is caused by a significant depletion of bipolaron states, relating to a decrease of instant bipolaron concentration $N_B$ in the crystals illuminated by a high-intensity pump beam.

At the same time, such experimental conditions (light wavelength and intensity) allow for appearance of marked generation of electron free polaron - hole polaron pairs due to the two-photon interband absorption [6,12]. According to the data on PL of polarons in SrTiO$_3$ [6], the sequent recombination of these polarons should be sufficient to give rise of luminescence in LiNbO$_3$, too. The recent data [12] on competition of the two light-induced processes (photodissociation of bipolarons, and two-photon interband absorption) in small polarons generation has been used as a key argument for assignment of 835-nm and 950-nm bands to the different radiative transitions between polaron states. For example, significant increase of 835-nm band accompanied by evident suppression of 950-nm band with growth of $x$ in deeply reduced crystals gives evidence of dominating role of the bound Nb$_{Li}^{+}$ polarons, appearing due to the bipolarons photodissociation, in PL at 835 nm. The PL at 950 nm is, hence, assigned to the recombination of free electron and O$^-$ hole polarons. Note that existence of 835-nm band in the PL spectra of as-grown samples is strongly related to $x_c$, i.e. to intrinsic antisite defects Nb$_{Li}^{+}$ concentration, and, therefore, may be assigned either to a residual
bipolarons content in as-grown crystals, since these crystals grown in standard conditions may be regarded as slightly reduced LiNbO$_3$ [13], or to formation of the bound Nb$_{Li}^{5+}$ polarons due to electrons trapping at unoccupied Nb$_{Li}^{4+}$ ions during hopping transport of electrons, occurs via free Nb$_{Nb}^{4+}$ polarons [14]. Eventually, an involvement of impurity Fe$^{2+}$/3+ ions in the recombination and excitation process in nominally pure LiNbO$_3$ would yield much weaker effects than the polaronic one [12], in contrast to the situation reported for PL in the reduced iron-doped LiNbO$_3$ crystals [15,16].

Similar behaviour with respect to chemical reduction degree and crystal composition was observed for the two-photon gated holographic recording via bound polarons/bipolarons in the reduced nominally pure LiNbO$_3$ [3-4]. Thus, the data on PL intensity may be used for rough estimation of efficiency of the gated holographic sensitivity of nominally pure crystals with given composition and chemical reduction degree. Besides, PL spectroscopy gives valuable insight on charge transport governed by free polarons that must have some practical importance, as such a transport is very perspective to use for dynamic holographic recording with light in the infrared spectral range [14].

Two-color gated luminescence from the pre-exposed states has not been completely analyzed yet. The dependence of bleaching rate on the gating wavelength should also be taken into account. Optimization of the recording conditions might enable further improvements to be achieved.

4. Summary

We have reported the data on measurement of the gated two-photon luminescence upon background shorter-wavelength illumination in as-grown and reduced nominally pure LiNbO$_3$ crystals. The gating-light power, composition and bipolaron concentration dependences of this weak photoluminescence in the near IR-range allow for conclusion, that the light-induced generation of free and bound small Nb$_{Nb}^{4+}$ and Nb$_{Li}^{4+}$ electron polarons and bound small O$^-$ hole polarons is responsible for this gated luminescence in the nominally pure LiNbO$_3$ crystals. It has been shown, that the data on the luminescence intensity may be used for rough estimation of the gated holographic sensitivity of the reduced nominally pure LiNbO$_3$ crystals.

5. References

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