

Transient and stable color centers in pure and Cu-doped LiNbO₃

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The present work is devoted to investigation of stable and transient color centers that are induced by radiation and temperature in pure and Cu-doped LiNbO₃ single crystals. The transient changes of absorption of the crystals induced by pulsed electron beam ($E=0.25$ MeV) are studied in 0-5000 ns time range, as well as stable changes of absorption induced by reducing annealing and irradiation with γ -quanta, high energy electrons or fast reactor neutrons.

1 Introduction

Lithium niobate LiNbO₃ (LNO) is a ferroelectric crystal having important applications in laser, electrooptic, acoustooptic, nonlinear optics and optical storage devices [1-3]. Rare-earth-doped LNO has attracted attention [1] as self-frequency-doubled and self-Q-switched lasers. The photo-refractive effect, which is used for storage of volume phase holograms, is due to the presence of transition metal impurities (Fe, Cu etc.) and intrinsic lattice defects [3, 4]. Lattice defects, Fe²⁺ (Fe³⁺) and Cu⁺ (Cu²⁺) ions are sources and traps of electrons in LNO and Fe- or Cu-doped LNO. That is why study of recharging processes of defects and dopants under external influences (thermal treatment, ionizing irradiation) is of interest. Purpose of the present work is investigation of stable and transient color centers induced by radiation and temperature in LNO and LNO:Cu crystals.

2 Samples and experimental

Pure LNO, LNO:Cu (0.03 mol%) and LNO:Cu (0.05 mol%) crystals were grown from congruent melt in the Institute of Electronic Materials Technology (ITME) by the Czochralski technique [5]. Samples for the stable color centers (SCC) investigations were made in the form of plane-parallel polished plates of 0.5-1 mm thickness. The samples were irradiated with gamma quanta (1.25 MeV) from ⁶⁰Co source and high energy electrons (1.3 and 3.5 MeV) with absorbed doses 10⁴-10⁷ Gy as well as fast reactor neutrons with fluence up to 10¹⁸ cm⁻². Optical absorption spectra were recorded with SPECORD-M40 and UNICAM 340 spectrophotometers. The additional absorption (AA) was determined as difference between optical absorption coefficient after and before treatment.

Samples for the transient color centers (TCC) investigations were prepared as cubes 10×10×10 mm³ oriented along the crystallographic axes with polished faces. The induced optical density was measured after

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crystal excitation with pulsed electron beam, and decay kinetics were measured in 0-5000 ns time range after end of excitation. The electron beam energy was about 250 keV and the pulse duration 10 ns. Experimental procedure of measuring of transient absorption induced by electron beam in details is presented in Ref. [6].

3 Results and discussion

3.1 Stable absorption induced in LNO and LNO:Cu crystals

The absorption spectra of pure LNO and LNO:Cu crystals are shown in Fig. 1. The fundamental absorption edge of pure LNO crystal is above 31000 cm^{-1} , in the region below the crystal is transparent. In LNO:Cu crystals the wide and intensive band centered at 25000 cm^{-1} is present. This band is associated with the intervalent transition $\text{Cu}^+ \rightarrow \text{Nb}^{5+}$ [7, 8]. Besides, the much less intensive band near 10000 cm^{-1} is observed in LNO:Cu crystals. This absorption band corresponds to ${}^2\text{E} \rightarrow {}^2\text{T}_2$ transition in Cu^{2+} ions [8, 9].

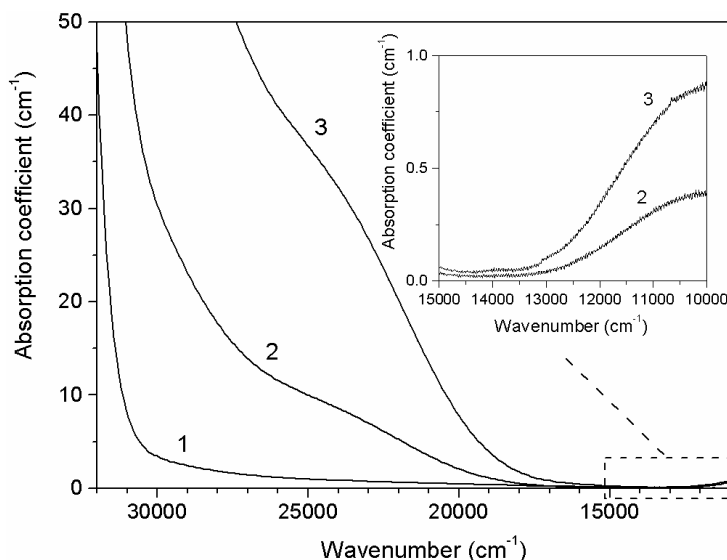


Fig. 1 Optical absorption spectra of as-grown crystals: (1) pure LNO; (2) LNO:Cu (0.03%); (3) LNO:Cu (0.05%).

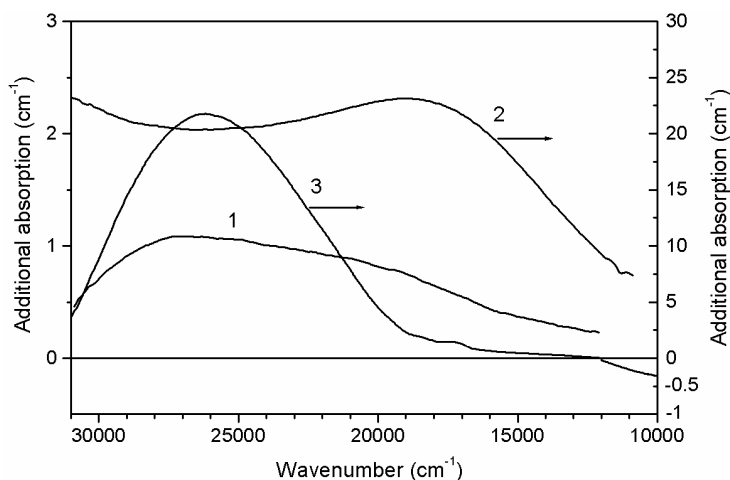


Fig. 2 AA spectra of (1, 2) pure LNO after annealing in (1) vacuum (700 K; 1 h) and (2) hydrogen (700 K; 1 h); and (3) LNO:Cu (0.03%) after annealing in vacuum (900 K; 2 h).

High temperature air annealing of LNO crystals at temperature up to 1300 K practically does not influence on optical absorption of the crystals. Annealing of LNO crystals in reducing atmosphere (Fig. 2) leads to the intensive greyish coloration of the crystals with complex AA band in the 32000-10000 cm^{-1} region with two

weakly pronounced maxima near 28000 cm^{-1} and 20000 cm^{-1} . These results agree with the results reported in Ref. [7, 10]. Annealing in hydrogen atmosphere leads to much intensive coloration in comparison with annealing in vacuum at the same temperature. In accordance with Ref. [11] the AA at 20000 cm^{-1} of reduced crystals is attributed to bipolarons (two electrons captured by the $(\text{Nb}_{\text{Li}})^{4+}-\text{Nb}_{\text{Nb}}$ trap). The absorption band centered at 28000 cm^{-1} present in reduced crystals is attributed to F-type centers created on the basis of oxygen vacancies [12]. Electrons required for recharging of Nb ions are created as a result of the process: $2\text{O}^{2-} \rightarrow \text{O}_2\uparrow + 2\text{V}_{\text{O}} + 4e^-$. At the same time both absorption bands (near 28000 cm^{-1} and 20000 cm^{-1}) in the crystals annealed in reducing atmosphere are caused by F-type centers [7].

The AA spectrum of LNO:Cu crystal after annealing in vacuum represents an intensive wide band with maximum near 25000 cm^{-1} . This agrees with results obtained in Ref [7]. The long-wave edge of this band stretches up to 15000 cm^{-1} (see Fig. 2). Besides, some clearing near 10000 cm^{-1} is observed. Such a character of AA spectrum indicates that after the annealing of LNO:Cu crystals an increase in the absorption band caused by Cu^+ ions (at 25000 cm^{-1}) and a decrease of absorption of Cu^{2+} ions (at 10000 cm^{-1}) take place. This means that reducing of Cu^{2+} ions to Cu^+ ions ($\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$) occurs under such annealing conditions. The electrons required for the recharging of copper ions obviously are created as a result of the process: $2\text{O}^{2-} \rightarrow \text{O}_2\uparrow + 2\text{V}_{\text{O}} + 4e^-$. As it was mentioned above, the absorption of F-type centers created on the basis of V_{O} can also contribute to the AA in this region.

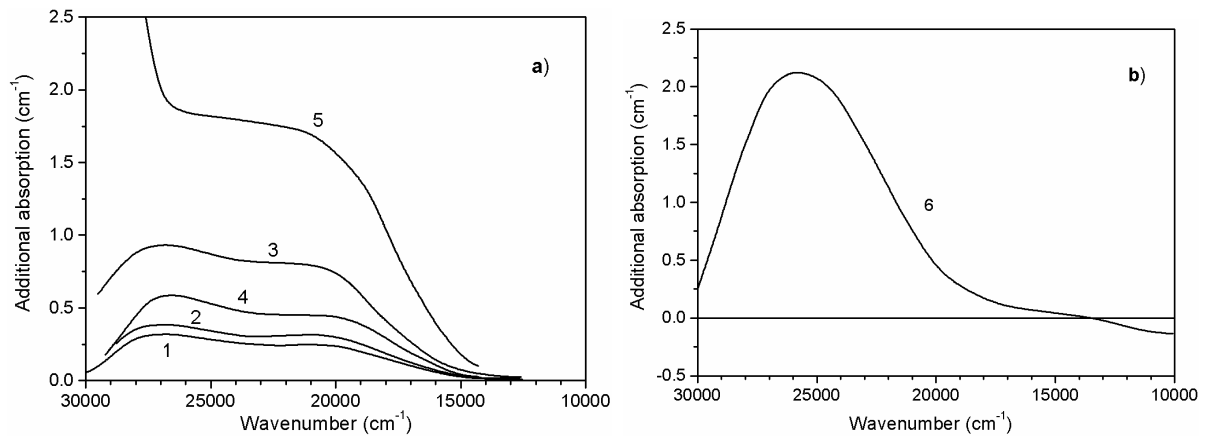


Fig. 3 AA spectra of (a) pure LNO after γ -irradiation ($D=10^6\text{ Gy}$) (curve 1), electron irradiation (curve 2 – $E=1.3\text{ MeV}$, $D=10^6\text{ Gy}$; curve 3 – $E=3.5\text{ MeV}$, $D=10^6\text{ Gy}$) and neutron irradiation (curve 4 – $F=10^{16}\text{ cm}^{-2}$; curve 5 – $F=10^{18}\text{ cm}^{-2}$) and (b) LNO:Cu (0.03%) after γ -irradiation ($D=10^5\text{ Gy}$) (curve 6).

Irradiation of pure LNO crystals with γ -quanta or electrons (Fig. 3) causes stable induced absorption in the $30000\text{-}15000\text{ cm}^{-1}$ region with two weakly pronounced maxima at 27000 cm^{-1} and 21000 cm^{-1} . The same changes of absorption are observed after irradiation of the crystals with fast reactor neutrons of fluences lower than 10^{16} cm^{-2} . The AA value after the neutron irradiation (neutron fluence $10^{14}\text{-}10^{16}\text{ cm}^{-2}$) is similar to AA after irradiation with γ -quanta or electrons (1.3 MeV) at absorbed dose $10^4\text{-}10^6\text{ Gy}$ (see Fig. 3). In this case the observed AA is caused by recharging of point defects available in the crystal. The absorption band centered at 21000 cm^{-1} in the crystals after ionizing irradiation is attributed to bound small polarons i.e. O^- centers stabilized by lattice distortion [11]. Irradiation of pure LNO crystals with high energy electrons (3.5 MeV with dose 10^6 Gy and higher) or fast reactor neutrons (fluences 10^{17} cm^{-2} and higher) cause much intensive coloration of the crystals in the same $30000\text{-}15000\text{ cm}^{-1}$ region as well as broadening of fundamental absorption edge after neutron irradiation. In this case the observed changes of absorption are caused by recharging of available point defects as well as creation of radiation displacement defects, in particular, oxygen vacancies on the basis of which F-type centers are formed [13, 14].

Gamma-irradiation of LNO:Cu crystals leads to the same, but less intensive, stable changes of absorption as after reduction annealing. This testifies the same recharging process of copper ions ($\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$) during irradiation. Similar results were obtained in Ref. [5, 7] after X-ray and γ -irradiation of LNO:Cu crystals. In addition to the absorption band caused by copper ions, a shoulder in the region $17000\text{--}22000\text{ cm}^{-1}$ can be distinguished in the AA spectrum of the γ -irradiated LNO:Cu crystal. Considering that this band corresponds to absorption of O^- hole centers [11], it can be supposed that formation of the hole centers is a source of electrons required for the $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ recharging during irradiation. After air annealing ($T \geq 600\text{ K}$) of the irradiated LNO or LNO:Cu crystals the crystals coloration goes back to the previous unirradiated state.

3.2 Transient absorption induced in LNO and LNO:Cu crystals

The spectra of the transient absorption induced in pure LNO and LNO:Cu crystals measured at the end of irradiation pulse are presented in Fig. 4. The transient AA spectrum of the investigated crystals at room temperature covers a wide region from 30000 to 8000 cm^{-1} and reveals two peaks (near 22000 and 13000 cm^{-1} for pure LNO; near 18000 and 13000 cm^{-1} for LNO:Cu). Nearly the same AA spectra in both crystals are observed at liquid nitrogen temperature.

A transient induced absorption with maxima at 27000 , 20000 and 13000 cm^{-1} were observed in Ref. [15] for undoped LNO crystals. Decay kinetics of transient absorption induced by X-ray or laser radiation (532 nm) were investigated at wavelength 1061 nm (9400 cm^{-1}) for LNO and LNO:Mg crystals [16], as well as at 633 nm (16000 cm^{-1}) for LNO:Fe crystals [17]. Spectra of transient induced absorption in these works were not presented.

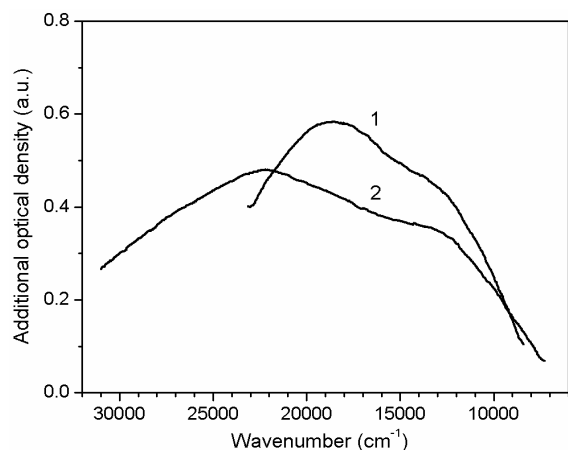


Fig. 4 AA spectra of (1) LNO:Cu (0.05%) and (2) pure LNO measured just after the end of electron pulse excitation.

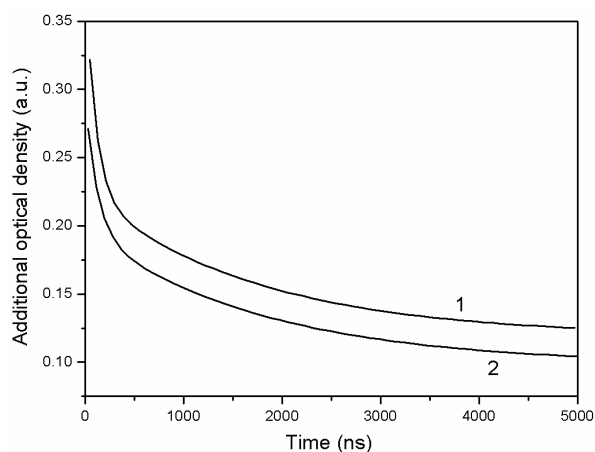


Fig. 5 Decay of induced absorption in (1) LNO:Cu (0.05%) measured at 11300 cm^{-1} and (2) pure LNO measured at 12000 cm^{-1} .

An increase of observed induced absorption occurs during the irradiation pulse creating centers responsible for this absorption via very fast nanosecond process. The absorption band at 13000 cm^{-1} in both crystals is considered to be caused by small electron polarons in Nb_{Li} site [11], and the band at 22000 cm^{-1} in pure LNO is attributed to O^- hole centers. The transient absorption band at 18000 cm^{-1} in LNO:Cu crystals is obviously caused by O^- hole centers, possibly the hole trapped on oxygen ions in neighborhood of Cu^+ . The induced absorption below 12000 cm^{-1} in LNO:Cu crystals does not show a well-resolved band. Therefore, trapping of holes by Cu^+ and formation of Cu^{2+} ions is not effective sufficiently during the irradiation pulse.

Decay kinetics for the long-wave band (13000 cm^{-1}) were measured at 12000 cm^{-1} for pure LNO and 11300 cm^{-1} for LNO:Cu. Decay of the short-wave band was measured at 20000 cm^{-1} for pure LNO and 19000 cm^{-1} for LNO:Cu. Decay kinetics for long-wave bands are shown in Fig. 5. Analysis of these decay kinetics shows that

approximation with sum of two exponents is satisfactory. Thus, centers of two types with substantially different lifetimes contribute to the both absorption bands. The room temperature decay kinetics can be described as:

$$D(t) = D_0 + D_1 \exp(-t/\tau_1) + D_2 \exp(-t/\tau_2), \quad (1)$$

where $D(t)$ is the optical density value at time t , D_0 is the optical density at the time $t \gg \tau_2$, D_1 and D_2 are the maximal optical density values for the first and second types centers at the beginning of measuring, and τ_1 , τ_2 are the lifetimes of the first and second types centers, respectively. The numerical values of the equation parameters are listed in Table 1. It should be pointed out that the time constants for the fast and slow decay components are very close to each other for LNO and LNO:Cu. So, the transient processes of releasing and migration of electrons are slightly affected by Cu dopant.

The values of D_1 and D_2 show that the concentration of the centers responsible for fast and slow components is different for LNO and LNO:Cu crystals. Some fraction of electron and hole polarons in both crystals decays very slowly or possibly is stable, since after 5 μ s the optical density in the crystals remains 40% from the initial value.

Table 1 Decay parameters for the transient absorption bands observed in LNO and LNO:Cu crystals.

pure LNO		
Wavenumber of registration	12000 cm^{-1}	20000 cm^{-1}
D_0	0.110	0.10
D_1	0.096	0.21
D_2	0.098	0.15
τ_1	123 ns	410 ns
τ_2	1.80 μ s	7 μ s
LNO:Cu		
Wavenumber of registration	11300 cm^{-1}	19000 cm^{-1}
D_0	0.13	0.30
D_1	0.155	0.16
D_2	0.100	0.11
τ_1	104 ns	200 ns
τ_2	1.7 μ s	2.7 μ s

4 Summary

Stable color centers as well as transient ones are formed in LNO crystals under irradiation. The induced stable absorption is characterized by two maxima at 27000 cm^{-1} and 21000 cm^{-1} . The transient induced absorption is characterized by two maxima at 22000 cm^{-1} and 13000 cm^{-1} . The induced coloration is caused by recharging of point defects present in as-grown crystals. The absorption band at 13000 cm^{-1} is caused by small electron polarons that are unstable at room temperature. The band at 21000–22000 cm^{-1} is caused by formation of O^- hole centers part of which recombine rapidly and the rest ones remain stable at room temperature. Copper ions also participate in the recharging processes under ionizing irradiation and act as traps for electrons ($\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$) and can stabilize O^- centers. Under neutron irradiation at fluences higher than 10^{17} cm^{-2} along with recharging of available point defects the formation of radiation displacement defects (oxygen vacancies and F-type centers on its basis) occurs.

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