Thermal and radiation stability of pure and doped with Cu, Fe and Cr ions lithium niobate single crystals for optical applications

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THERMAL AND RADIATION STABILITY OF PURE AND DOPED WITH Cu, Fe AND Cr IONS LITHIUM NIOBATE SINGLE CRYSTALS FOR OPTICAL APPLICATIONS

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The results of investigations of the influence of gamma and proton radiations on absorption, luminescence and birefringence of either pure or Cu, Fe and Cr doped $LiNbO_3$ single crystals were presented. A method of birefringence dispersion testing on the entire areas of plane-parallel plates of $LiNbO_3$ crystals has been illustrated by the influence of both types of irradiation on pure and Fe, Cr and Cu-doped $LiNbO_3$ wafers. It was found that LN:Cu single crystal shows different behavior to the other investigated crystal. First of all it exhibits lower susceptibility to γ-rays, the absence of 500 nm additional absorption, and strong proton susceptibility observed in polarimeter measurements.

1. INTRODUCTION

Metal oxides have a wide-ranging importance in many areas of the physics and technology. They are applicable as ceramics, high-T_c superconductors or substrates for the latter and have relevance to microelectronics and especially for laser materials. Irradiation of these materials by energetic particles leads to recharging of existing point defects as well as to the displacement of an atom into an interstitial position, forming what is commonly called a Frenkel defect [1]. In the oxygen sublattice this could result in the formation of three kinds of Frenkel defect pairs: neutral interstitial O_j atom and V_o vacancy, or a vacancy with one or two trapped electrons (the so-called F^+ and F center) and their complementary

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O_j^- and O_j^{2-} defects. Current understanding of the defects in oxides have been given in [2].

A survey of recent theoretical studies of radiation-induced point defects in simple oxides with emphasis on highly ionic MgO, partly-covalent corrundum (Al_2O_3) and ferroelectric $KNbO_3$ have been presented in [3].

Influence of X-rays on the absorption spectrum of ferroelectric pure $LiNbO_3$ and doped with transition metal ions (Cu, Mn, Ni) was firstly investigated in [4]. Three main bands with peaks at 1.6eV (polaron Nb^{4+}), 2.5eV and 3.2 eV (holes trapped at Li vacancies) have been observed in pure crystals or Mn-, Ni- and Eu-doped crystals after low temperature (10 K) irradiation. For the Cu- doped samples, a competition is apparent between the production of these bands and the conversion of Cu^{2+} (1.2 eV band) into Cu^+ (3.1 eV band).

In this paper we present results of the influence of gamma and proton radiations on optical properties of either pure or Cu, Fe and Cr doped $LiNbO_3$ single crystals.

2. EXPERIMENTAL

$LiNbO_3$ single crystals were pulled in Y direction by the Czochralski technique from the congruent melt (51.4 mol. % LiO_2: 48.6 mol. % Nb_2O_5) in the Institute of Electronic Materials Technology [7]. The specimens of the following compositions were prepared: $LiNbO_3$ (LN), LN:Fe (0.1at.%), LN:Cu (0.05at.%, 0.06at.% and 0.07 at.%), LN:Cr (0.3at.%).

The samples were cut out from the crystals parallel to the Y growth direction, and perpendicularly to Z and than polished to the thickness of about 3 mm. They were irradiated by gamma photons immediately after the crystal growth process. The ^{60}Co gamma source with a power of 1.5 Gy/sec was used. Annealed at 800°C in the air for 5 hours samples were subsequently irradiated by protons (p^+) in the C30 cyclotron, the proton fluency was varied between 5^*10^{12} to about 1.2^*10^{16} protons/cm^2. To avoid the sample overheating the average beam current was kept at approximately 200 nA. Collimated to about 10 mm in diameter external proton beam passed through the few cm long air gap, where the crystal samples were placed. Effective proton energy at the entrance face of the sample was ca. 21 MeV.

Optical transmission was measured before and after γ,.p^+ and annealing treatments using LAMBDA-900 Perkin-Elmer spectrophotometer in UV-VIS range and FTIR-1725 in the IR range. Additional absorption was calculated according to the formula:

$$.\Delta K(\lambda) = (1/d)\ln(T_1/T_2) \tag{1}$$

where K is the absorption, λ is the wavelength, d is the sample thickness and T_1 and T_2 are transmissions of the sample before and after a treatment, respectively.

Photoluminescence using 514.5 nm argon laser excitation at 10 K was measured only for LN:Cr single crystal. Luminescence spectrum was registered using GDM-1000 monochromator and EMI 9684B photo multiplayer.

In such a way the samples had underwent a series of treatments including: gamma irradiation (10^5 Gy), thermal annealing (air, 400°C, 5 hours), 2nd gamma irradiation (10^6 Gy), consecutive 2nd thermal annealing (air, 800°C, 5 hours), 3rd gamma irradiation (10^7 Gy), and the final 3rd thermal annealing (air, 800°C, 5 hours). On the end the crystals were consecutively undertaken to irradiation with p$^+$ with fluencies up to 1.2^*10^{16} cm^{-2}.

Before and after irradiating the sample we have been examined changes in the birefringence and birefringence dispersion coefficient. It was measured and calculated by the formula:

$$BRD = \frac{\Delta n(\lambda_i)}{\Delta n(\lambda_{i+1})} \tag{2}$$

for λ = 670 nm step 10 nm.

A TV camera and video frame grabbing techniques were used for collecting the input data from the whole surface of the investigated wafer, and hence birefringence inhomogeneity maps obtained [8].

3. RESULTS

Fig. 1 presents absorption measurements for three investigated crystals. As one can see fundamental absorption edge shifts towards longer wavelengths from pure LN by LN:Cr, LN:Fe to LN:Cu, changing from 320 nm to 420 nm.

Absorption of LN:Cr single crystal exhibit clear bands peaked at 464, 659, 731, 1265 and 2871 nm. Broadband absorption corresponds to the transitions $^4A_2\rightarrow^4T_1$, $^4A_2\rightarrow^4T_2$. They occur in the red-orange and green-blue regions respectively, giving rise to the characteristic colors of Cr^{3+} doped crystals. 731 nm band is $^2E\rightarrow^4T_2$ transition giving rise to R lines, 1265 nm band may be Cr^{4+} or Cr^{5+} absorption and 2871 nm band is the absorption of OH$^-$ ions.

Absorption of LN:Fe shows characteristic for Fe^{2+} transitions peaked at 482 nm and 1062 nm [9]. The first is probably Fe^{2+} d$\rightarrow$d transition which is assigned usually to Fe$^{2+}\rightarrow$Nb^{5+} intervalence transfer, and the second is $^5A\rightarrow^5\gamma E$ transi-
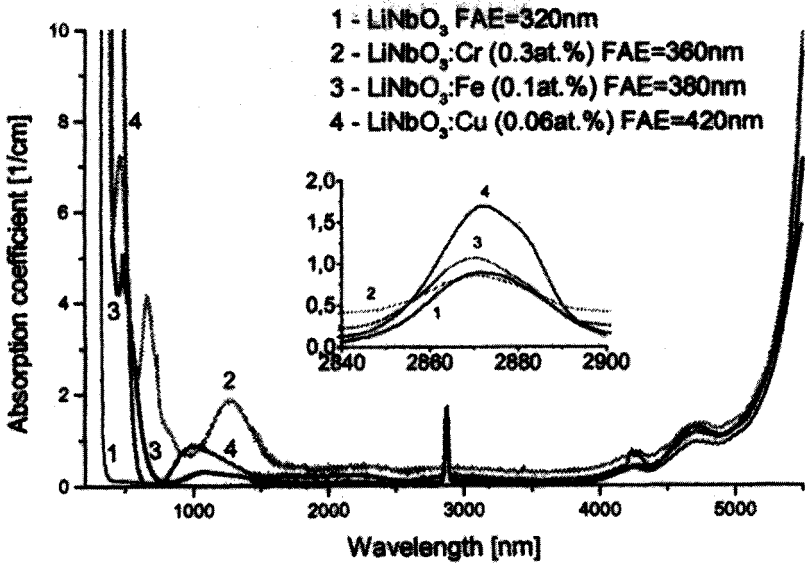
FIGURE 1 Absorption curves of LN (1), LN:Cr (2), LN:Fe (3) and LN:Cu (4) single crystals (See Color Plate III at the back of this issue)

tion. Nevertheless, the shape of this band and intensity of OH⁻ band at 2871 nm suggest Fe^{3+} ions presence.

Absorption of LN:Cu shows 460 nm band which give rise to red-yellow color of the crystal, asymmetric band peaked at about 1000 nm which at low temperatures exhibit three different bands and 2000 nm symmetric band. 460 nm band may be connected with $Cu^{+} \rightarrow Nb^{5+}$ intervalence transfer, 1000 nm and 2000 nm bands are $^2E \rightarrow ^2T_2$ and ^2E transitions in Cu^{2+} [10].

Luminesence of LN:Cr single crystal at low temperatures (Fig. 2) exhibit broad emission band peaked at about 950 nm and R-lines peaked at 730.7 nm and 734.4 nm with linewidths of about 2 nm. The first line is connected with Cr^{3+} (Nb) site while second one with Cr^{3+} (Li) site [11] (or reciprocal interpretation presented in [12] and [13]). Luminescence of the other LN:Fe and LN:Cu crystals was not measured but taking into account absorption measurements (2871 nm band) it may be assumed that in the case of the crystals Fe and Cu substitutes Nb and also Li octahedral sites (see insert of Fig. 1).

Fig. 3 show transmission (a) and absorption (b) changes in LN crystal under gamma, thermal and proton treatments. As one can see annealing at 400°C (a.3) of previously gamma 10^5 Gy irradiated LN sample (a.2) leads to returning of the

transmission to the shape before irradiation (a.1). Next annealing treatments were performed for higher (800°C) temperature and it is seen that the shape of transmission of 800°C annealing (a.5, a.7) significantly differs from 400°C case (1, 3). An increase in gamma dose (a.4 and a.6) leads to a saturation of transmission and absorption changes.

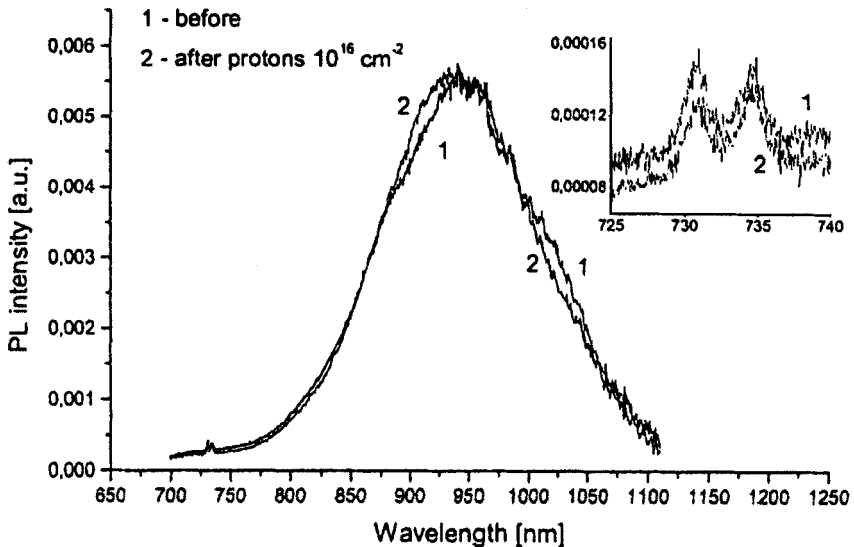FIGURE 2 Photoluminescence of LN:Cr (0.3at.%) single crystal before (1) and after (2) proton irradiation with a fluency of 10^{16} cm^{-2} (See Color Plate IV at the back of this issue)

As one can see from Fig. 3b proton irradiation gives almost the same changes in the absorption spectrum as in case of gamma's. From Fig. 3b. it fallows that in the additional absorption of LINbO$_3$ single crystals irradiated with gamma and protons there arises at least two additional bands peaked at about 384 and 500 nm.

Irradiation of Fe, Cr and Cu doped LN crystals with gamma rays lead to some new, interesting changes in absorption. Annealing should generally restore optical features of each doped crystal previously gamma irradiated (see e.g. Fig. 4 curves 3,6 and Fig. 5 curves 1, 4 and 3, 6). But in the case of 10^5 Gy and 10^6 Gy doses we are dealing with abnormal change in the absorption – bleaching phenomenon (curves 2, 5). In the case of LN:Fe crystal the annealing at 400°C for 3 h after 10^5 Gy irradiation do not restore initial transmission (curves 1, 4) while

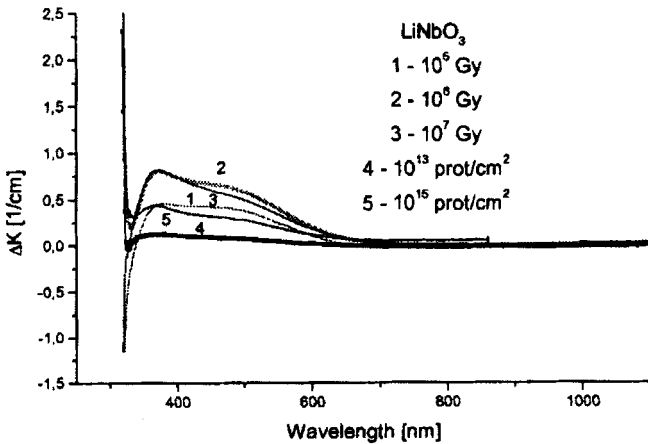**a)**
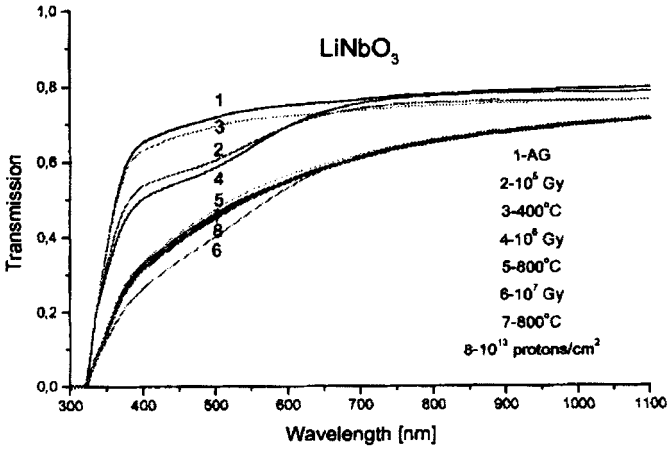
b)

FIGURE 3 Changes in the transmission (a) and absorption (b) after gamma and thermal treatments (See Color Plate V at the back of this issue)

10^6 Gy irradiation (curve 2) and 800°C annealing for 3h (curve 5) bleached the crystal. In the case of LN:Cu samples, as one can see from Fig. 5, 10^6 Gy is a dose for which some saturation of absorption changes is observed (curve 2 as

compare to curve 1) and the bleaching after 800°C annealing for 3h (curve 5). With increasing dose up to 10^7 Gy further increase of additional absorption is observed for both LN:Fe and LN:Cu crystals (Fig. 4 curve 3 and Fig. 5 curve 3).
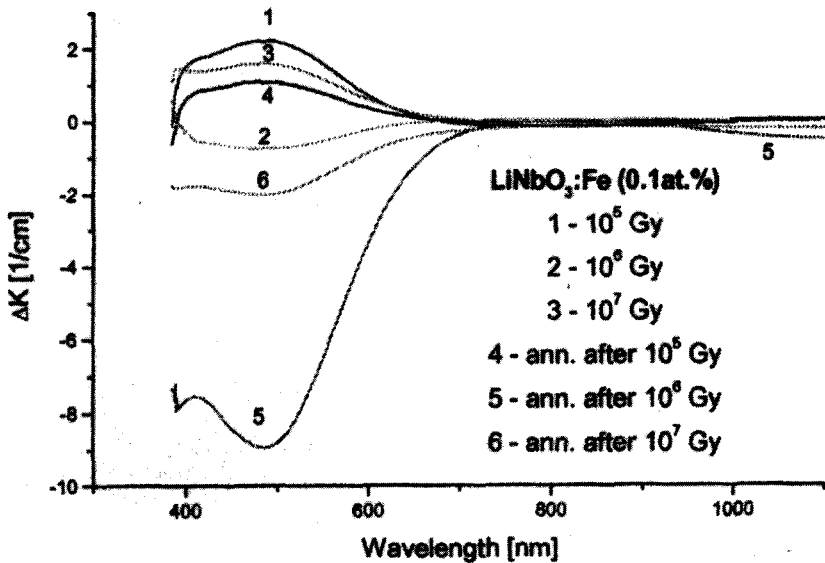

FIGURE 4 Additional absorption in LN:Fe single crystals after gamma and thermal treatments (See Color Plate VI at the back of this issue)

In case of LN:Cr crystal it was observed that the annealing at 400°C for 3h also does not restore initial transmission.

As one can see from Figs 3, 4, 5 and 6 shapes of the additional absorption of LN:Fe and LN:Cr crystals after gamma irradiation are almost similar as in the case of pure LN (exclude relative intensity of the two mentioned bands), while corresponding shape of LN:Cu crystal is significantly different. In the latter case, for doses up to 10^7 Gy, there is not observed 500 nm band. As was shown in Fig. 6 fitting procedure using Gauss curves gives at least four additional absorption bands peaked at 373 nm, 402 nm, 451 nm and 526 nm.

Different shape of the additional absorption after proton irradiation in LN:Cu crystal with respect to other crystals is confirmed in Fig. 7 where changes in the absorption (mainly on the fundamental absorption edge and inside Cu^{2+} bands) after proton irradiation with fluencies from 10^{13} (2) cm^{-2} to 10^{16} cm^{-2} (6) are shown. As one can see only in the case of 10^{16} cm^{-2} fluency there arises in the LN:Cu absorption spectrum additional absorption at about 500 nm. In fluency
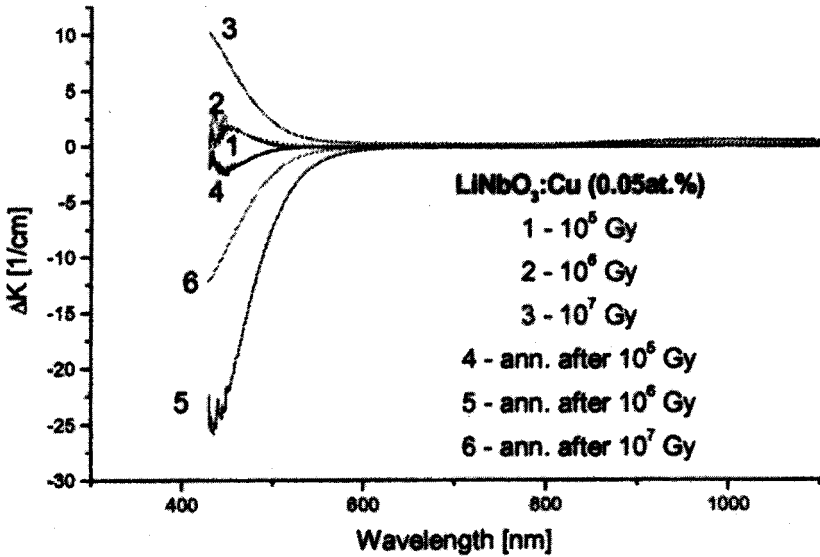
FIGURE 5 Additional absorption in LN:Cu single crystals after gamma and thermal treatments (See Color Plate VII at the back of this issue)

dependence of additional absorption (b) at least three regions are seen. First one for fluencies below 10^{14} cm^{-2} second one for fluencies between 10^{14} and $5^{*}10^{14}$ cm^{-2} and third one over $5^{*}10^{14}$ cm^{-2}. The shape of this dependence is characteristic of all the crystals.

Different behavior of LN:Cu samples was confirmed also by birefringence dispersion measurements. Fig. 8a-c presents changes in polarimeter image (analyzer and polarizer were parallel) of LiNbO$_3$ wafers doped with Cu (0.06at.% and 0.07at.%). In the irradiated by protons samples two crescents one can see (b, c) which characterize shape of a proton beam (it was focused). The contrast of the image is larger for higher doping (c). Moreover, the image changes in the time due to a relaxation process. It means that the above image is influenced also by color centers formed in the samples by protons.

Fig. 8d shows horizontal cross-section of BRD coefficient after protons 10^{13} cm^{-2} in LN:Cu (0.07at.%). One can see clear extremes correlated with changes induced by protons. Pure LiNbO$_3$ samples and doped with Fe and Cr ions (up to 0.3at.%) did not exhibit such strong effect for this value of fluency. For larger values of fluency (up to 10^{16} cm^{-2}) all these crystals clearly show decrease in birefringence dispersion in the range of proton beam (see Fig. 8e-h).
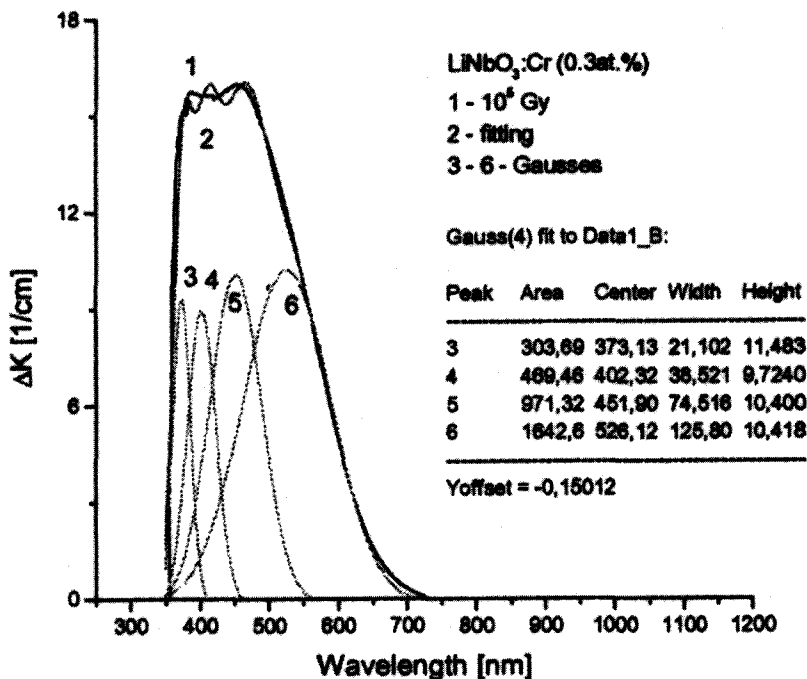
FIGURE 6 Fitting procedure of the additional absorption in LiNbO$_3$:Cr single crystal after 10^5 Gy γ-rays using Gauss curves (See Color Plate VIII at the back of this issue)

4. DISCUSSION AND CONCLUSIONS

In contrast to stoichiometric crystals [14] in the absorption spectrum of LN:Cr there was observed 1260 nm (curve 2) band associated probably with Cr^{4+} or Cr^{5+} absorption. In Cr^{3+} doped lithium niobate congruent single crystal there were stated Nb^{5+} sites in which substitution of an ion of higher than 3+ valency is possible [12]. But up to now nobody has measured luminescence of these centers. Fig. 1 clearly show the possibility of existence of higher than 3+ chromium ions absorption in LN crystals but we can not find any evidence. OH$^-$ absorption seen in this figure do not exclude substitution of both octahedral sites: Nb and Li in all of the investigated crystals. This fact was confirmed e.g., by luminescence measurements of R-lines in LN:Cr crystal (Fig. 2).

In Fig. 3a a very important property of LN crystals was stated. Namely optical characteristics are not stable with respect to temperature. It is possible that after
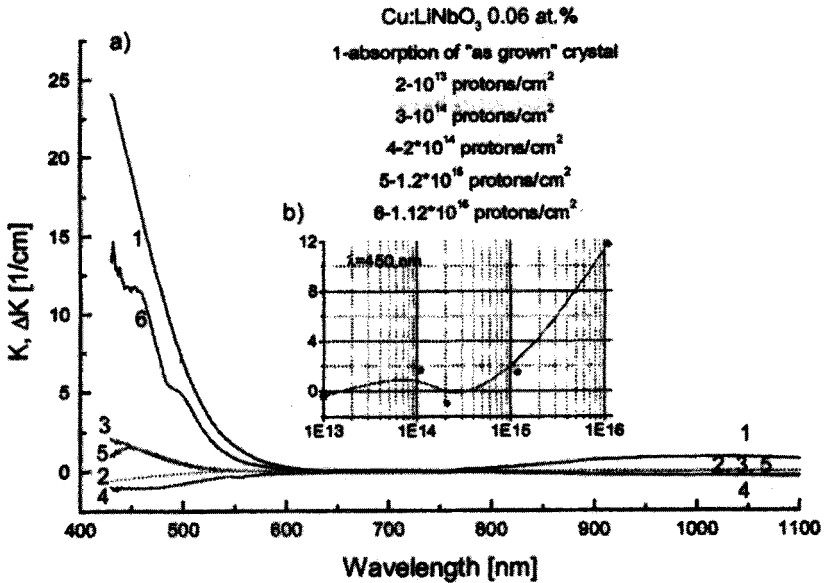
FIGURE 7 Absorption (1) and the additional absorption (2–6) of LN:Cu single crystal after proton irradiation with fluencies 10^{13}-10^{16} prot/cm^2 – (a) and fluency dependence of additional absorption in this crystal – (b) (See Color Plate IX at the back of this issue)

growth of these crystals residual stresses are staying. From this figure it follows that annealing at 400°C and 800°C give two different initial optical states (transmission curve). Dose dependence of the additional absorption after γ-rays seen in Fig. 3b (curves 1–3) suggests that in case of pure LN crystal we deal with saturation phenomenon with respect to radiation defects. No further increase in additional absorption (or in the amount of radiation defects) takes place when one exceed a dose of 10^6 Gy. It means that for this value all point defects existing in the crystal (of the order of about 10^{17} cm^{-3}) are recharged by gamma's. The shape of the additional absorption exhibit presence of at least two bands one of which being connected with F-type color centers (384 nm). Second one (500 nm) seems to be associated with Nb^{4+}-Nb^{4+} bipolarons described early in [15] for reduced $LiNbO_3$. It is confirmed by absorption of pure not-irradiated LN crystal where a weak one 500 nm band is also observed. Moreover, dissociation of these centers is observed after annealing process giving additional absorption near 650 nm (polarons Nb^{4+}). Presented in Fig. 3b additional absorption of LN crystal after proton irradiation (curves 4, 5) shows the same features as previously for gamma's. It means that in the case of interaction of protons with LN crystals, for

fluencies below 10^{15} cm^{-2}, the main rule in forming of radiation defects play recharging processes of existing after growth point defects. It may be ionization of lattice and impurity ions and/or recombination of these ions with delta electrons formed by protons [16].

Changes in additional absorption of LN:Fe and LN:Cu single crystals under gammas and thermal annealing (Figs 4 and 5) confirm early observed for pure LN (Fig. 3a) unstable optical properties under thermal treatment. The only difference is that in the case of former crystals one can observe some critical dose of γ–rays (10^6 Gy) for which drastic bleaching in absorption is observed. It may be due to residual stresses annealed by gamma's. Comparing Fig. 4 and Fig. 5 one can see that the shape of the additional absorption differs significantly for both crystals. In the case of LN:Cu crystals there is not observed bipolarons band peaked at about 500 nm. 460 nm additional absorption band seems to be connected mainly with Cu$^+$ ions formed by recharging of Cu^{2+} (Cu$^+$→Nb^{5+} intervalence transfer). Such supposition is confirmed by corresponding changes in the 1000 nm Cu^{2+} band. This may be a reason for which 500 nm band is absent. Other investigated crystals exhibit similar shapes of the additional absorption differing only by magnitude of the additional absorption (greater for LN:Cr – 16 cm^{-1}, smaller for LN:Fe – 2 cm^{-1}) and relative intensity of the two above mentioned peaks (384 and 500 nm).

Detailed analysis of the shape performed for LN:Cr additional absorption (Fig. 6) have not shown two but four bands which are responsible for this absorption. First two bands are well known F$^+$ and F centers [4]. Third band means increase in the Cr^{3+} absorption. It may be due to e.g. recombination of Cr^{4+} ions with Compton electrons. Fourth band is associated with bipolarons Nb^{4+}-Nb^{4+} absorption. In the case of LN:Fe crystals third band, centered at about 480 nm, means increase in Fe^{2+} absorption. This supposition is confirmed by corresponding changes observed for magnitude of 1062 nm absorption after gamma (increase) and annealing (decrease) treatments.

Fig. 7 presents characteristic for all the investigated LN crystals shape of the additional absorption and fluency dependence in the case of proton irradiation of LN:Cu single crystal. Fluency dependence of the additional absorption exhibit characteristic shape with maximum at about 10^{14} cm^{-2}, minimum at about 10^{15} cm^{-2} and further sharp rise for higher fluencies. Monotonic increase of the additional absorption up to 10^{14} cm^{-2} is associated with recharging processes of point defects. The probable reason of the decrease of the additional absorption in the region 10^{14} cm^{-2} – 10^{15} cm^{-2} could be mutual interaction of the cascades from different proton trajectories [17]. Strong increase of the additional absorption above 10^{15} cm^{-2} is characteristic for Frenkel defects formation. Also in the case of proton irradiation LN:Cu crystal differs from others. Namely additional
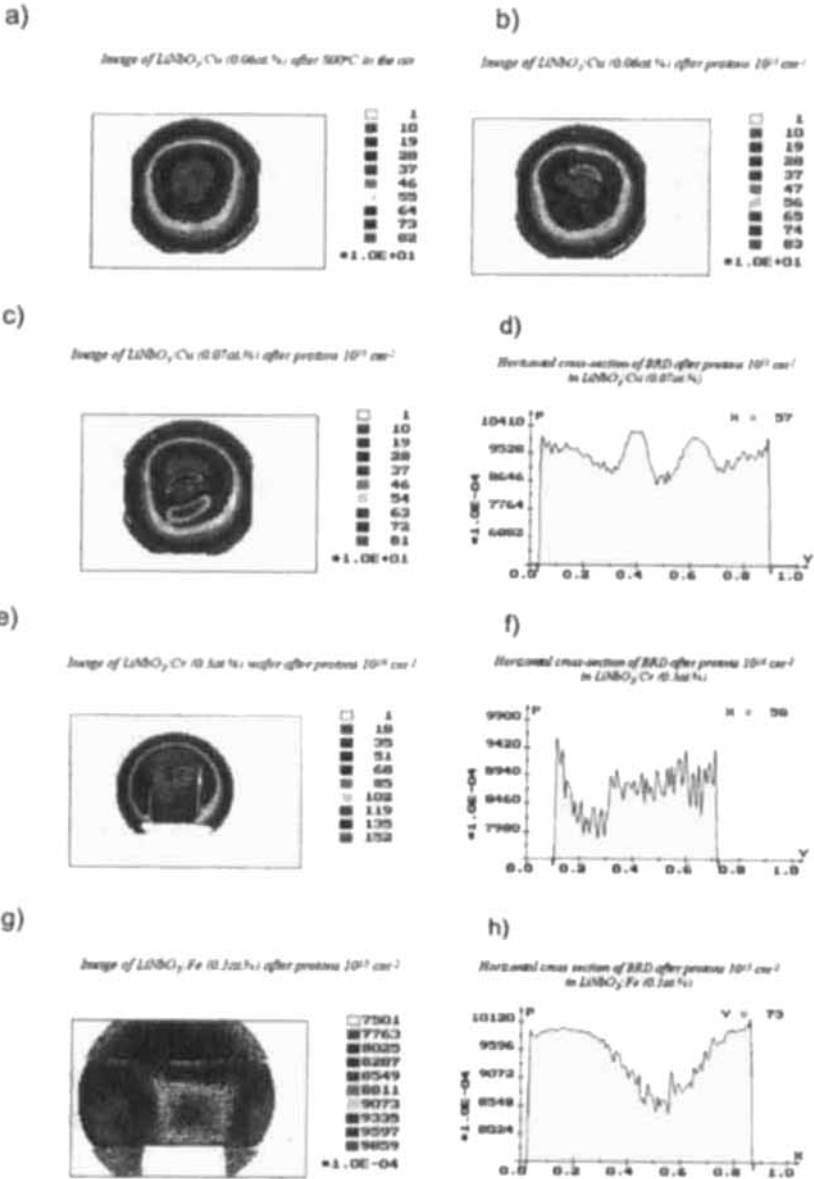
FIGURE 8 Images of LN:Cu (0.06at.%) – (a, b) and LN:Cu (0.07at.%) – (c) samples before (a) and after (b, d) proton irradiation with a fluency of 10^{13} cm^{-2}; horizontal cross-section of BRD coefficient (eq. 2) after protons 10^{13} cm^{-2} in LN:Cu (0.07at.%) – (d); image of LN:Cr (0.3at.%) sample (rectangle) after 10^{16} protons/cm^2 – (e) and horizontal cross-section of BRD coefficient for this crystal – (f); image of LN:Fe (0.1at.%) sample (rectangle) after 10^{15} protons/cm^2 – (g) and horizontal cross-section of BRD coefficient for this crystal – (h) (See Color Plate X at the back of this issue)

absorption characteristic for Nb^{4+}-Nb^{4+} bipolarons arises only for a fluency as high as 10^{15} cm^{-2}.

Luminescence measurements of LN:Cr crystal at low temperatures have shown that proton irradiation leads to change in relative luminescence intensity from Cr^{3+} (Nb^{5+}) and Cr^{3+} (Li^{+}) sites. We observed increase in luminescence associated with the latter (see Fig. 2).

Polarimetric measurements (Fig. 8b-d) have shown that LN:Cu crystal exhibit strong susceptibility to proton irradiation. Even for such small fluencies as 10^{13} cm^{-2} the observed changes in polarimetric image and BRD coefficient are very significant. Moreover (investigations were performed for λ = 670 nm and 760 nm) there are not only due to color centers but also due to some other changes, e.g. in band gap. Similar investigations were performed for gamma irradiated and thermally annealed the samples. It had been observed rather unexpectedly that classical thermal annealing can lead to a decrease in optical homogeneity in the majority of cases. It may be attributed to generation of an internal electric field by the pyroelectric effect, and to the electrooptic effect involved thereafter. The secondary electrons which are homogeneously generated by gamma irradiation in the investigated crystals are believed to increase the optical homogeneity, also by canceling this field. Birefringence dispersion seems to be a good key parameter in manufacture of e.g. retardation plates, 2nd harmonic generators or polarizers.

Acknowledgements

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