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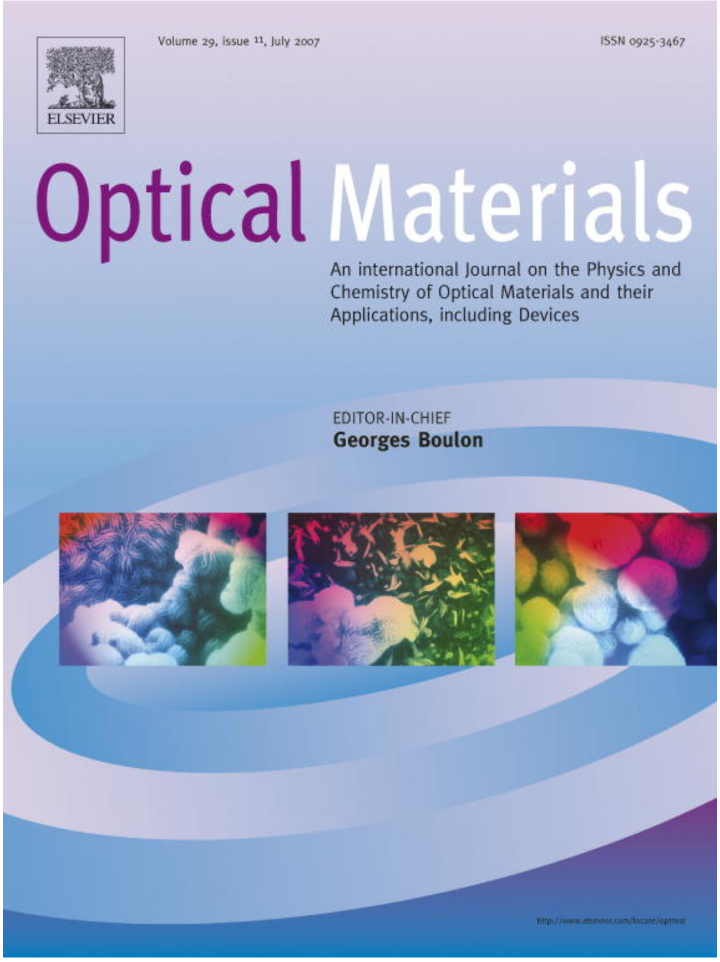

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Recharging processes of active ions and radiation defects in some laser crystals doped with RE and TM ions under proton irradiation

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Abstract

Recharging processes of transition metal ions (Cr, Fe, Cu) and rare-earth ions (Dy, Nd, Er, Pr) in some oxide laser crystals: $Y_3Al_5O_{12}$, $LiNbO_3$, $SrLaGa_3O_7$, $Gd_3Ga_5O_{12}$ and $YAlO_3$, and, also radiation defects arising in these materials under influence of gamma, electron and proton irradiations and annealing were analyzed. Special attention was paid to proton irradiations that were did for fluencies of 10^{12}–10^{16} cm^{-2}. To show changes in optical properties of the materials additional absorption spectra were obtained and analyzed. To avoid different initial defect structure of the crystals, we annealed them in the air or in hydrogen against proton irradiation. The same type of color centers after proton irradiation we found for all investigated oxides as previously registered for gamma irradiated the crystals. But the limit was found of the behavior, 1–5×10^{14} cm^{-2} (dependently on the crystal) fluency, over which Frenkel defects are formed. We found crystals more resistant to proton irradiation (GGG) and dopants very sensitive to the type of ionizing radiation (Fe, Cu, Cr).

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Keywords: γ-Rays; Proton irradiation; Additional absorption

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1. Introduction

Changes of optical properties of various crystals induced by ionizing radiation are of big importance because many optical instruments are dedicated to work in radiation fields. Except of pure military applications, optical instruments are installed on satellites and spacecraft missions, as well as in scientific laboratories, working on-line with accelerators. In the cosmic space there arise charged particles, such as electrons, protons, high energy cosmic rays, and bremsstrahlung photons. High energy protons (>30 MeV) have very long penetration depths and are thus difficult to protect against [1,2]. Laser systems based in the space will be subjected to these form of radiation and thus, due to damage, lost their initial parameters.

Characterization of high energy particles acting with a matter is limited by the availability of suitable sources. So, in many papers mainly γ-irradiation sources are used to characterization of the laser materials. Irradiation with low and medium energy protons seems to be the less exploited, in spite of big importance of that kind of irradiation. Relative facility of getting large proton fluxes, in comparison e.g. with fast neutrons, makes such studies attractive.

Main features of the interaction of the ionizing particles with solids can be summarized as follows:

(i) charged particles, contrary to neutral ones, passing through the matter loose continuously their energy mainly due to the ionization of the medium atoms;
(ii) interaction of particles can be treated as interaction with two atomic separate sub-systems: electronic and nuclear one. To a good approximation these two interactions are decoupled;
(iii) fast incident particles initialize a stochastic cascade. There is essential difference between cascades initiated by photon or electron (electromagnetic cascade

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caused by electromagnetic interactions) and protons or other heavy particles (hadronic cascade, caused by electromagnetic and nuclear interactions);
(iv) after the fast cascade is finished, much slower interactions with the medium still take place.

Defects in crystals can be produced by ionizing radiation as well as destroyed or modified. The last effects concern also defects which were initially present in the sample, before its irradiation. One can list many kinds of produced defects such as (i) ionized atoms constituting original lattice in the interstitial positions, (ii) vacancies, (iii) intruder atoms or ions (knocked-out atoms of the lattice, stopped products of nuclear reactions, etc.). The original defects can be further modified by recombination or by evolution driven by the interaction with the lattice. Several early papers were done on the proton influence on various materials [3,4] but up to now there was not performed a systematic analysis.

In the next sections of this work we report the most important effects recently found by us during our study of the influence of the irradiation by 20 MeV protons on the optical absorption spectra of some oxide materials. We try to get general and detailed conclusions on the type of defects, its fluency dependence and the sensitivity to protons of some well known laser hosts.

2. Experimental

From the single crystals obtained in the Institute of Electronic Materials Technology the parallel plate samples of 1–3 mm thick were cut-out and both sides polished: $Y_3Al_5O_{12}$ (YAG–Nd^{3+} (1 at.%), Cr^{4+} (0.1 at.%)), $SrLaGa_3O_7$ (SLG–Dy (1 at.%), Cr (0.1 at.%)) and $LiNbO_3$ (LN–Cu (0.06 at.%), Cr (0.3 at.%), Fe (0.1 at.%)). Proton exposures were done in the C30 cyclotron in INP Świerk, Poland. The proton fluency was varied between 5×10^{12} and 1.2×10^{16} protons/cm^2. Each time the fluency was measured with a charge integrator. To avoid the sample overheating the average beam current was kept at approximately 200 nA. External proton beam collimated to about 10 mm in diameter 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. 20 MeV.

The absorption spectra were taken at 300 K before and after proton irradiation in the spectral range between 190 and 25000 nm using LAMBDA-900 and FTIR 1725 of PERKIN–ELMER spectrophotometers. Values of $\Delta K(\lambda)$ factors which describe an additional absorption (AA) due to the irradiation were calculated according to the formula

$$\Delta K(\lambda) = \frac{1}{d} \cdot \ln \frac{T_1}{T_2}, \tag{1}$$

where K is absorption, $\Delta K(\lambda)$ is the additional absorption, λ is the wavelength, d is the sample thickness, and T_1 and T_2 are the transmissions of the sample measured before and after irradiation, respectively.

Against irradiation with protons the samples were annealed at 673 K, 1673 K for 1 (3) h, in the oxidizing atmosphere or at 1200 °C for 1 h in reducing atmosphere.

3. Results and discussion

In Fig. 1, AA spectra of the pure YAG and YAG:Nd single crystals irradiated with protons are shown. As one can see, for low fluencies (up to 10^{14}), very well known shape of the AA is observed. Previously we reported the shape for AA bands obtained for the crystals irradiated with gamma quanta [5]. It is characteristic for recharging of intrinsic defects in the crystals. There are seen characteristic for YAG matrix radiation defects, e.g. 255, 276 nm, 300 nm (Fe^{2+} and Fe^{3+} ions) and 385 nm (F-centers). Fast protons penetrating the crystal sample lose continuously their energy. Part of this energy is transferred to the secondary delta electrons which become the source of the recharging effect of ions present in the crystal.

With increase of proton fluency from 10^{14} to 10^{16} the AA increase and its shape strongly changes suggesting the presence of new type defects. Because the intensity of AA versus proton fluency exhibit linear increase in this range, we think the new defects are Frenkel defects. As one can see from the insets of Fig. 1a and b, the protons fluency dependence of the additional absorption exhibits characteristic minimum at about 10^{14} protons/cm^2. Not depicted curve no. 8 in Fig. 1b represents AA next to 10^{16} protons/cm^2 measured on the reverse side of the sample as compare to the measurement represented by curve 6. So, due to specific interaction of protons with matter, the measurement of the transition of the irradiated sample may give different results for its both sides.

Curve 5 in Fig. 1b shows additional absorption band of YAG:Nd single crystal after electron irradiation with a fluency of 5×10^{16} electrons/cm^2. Comparing curves 4 and 5 one can see that the difference between the two irradiations is the type of recharging process. It seems that for protons, ionization fraction is larger than for electrons (shallower minimum of additional absorption for about 255 nm).

In Fig. 2 absorption (K) and changes in the absorption (ΔK) of YAG:Cr^{3+} single crystal, obtained by annealing of YAG:Cr^{4+} single crystal in reducing atmosphere for 1 h, after subsequent proton irradiations are presented. Small fluencies of protons lead to an increase (curves 2–4) in Cr^{3+} ion concentration while the fluency of 10^{14} protons/cm^2 leads to an increase in Cr^{4+} ion concentration (curve 5 with a maximum at about 480 nm). Thus, change in a fluency of protons changes mechanism of protons interaction with YAG:Cr^{3+} crystal; from recombination processes of the type $Cr^{4+} \rightarrow Cr^{3+}$ to ionization $Cr^{3+} \rightarrow Cr^{4+}$. It may be due to not all Cr^{4+} ions were reduced to Cr^{3+} after annealing process of YAG:Cr^{4+} single crystal in reducing atmosphere. In the inset of Fig. 2 dose dependence of the additional absorption after proton irradiation is presented; the minimum attributed to a change of the mechanism of interaction of protons with

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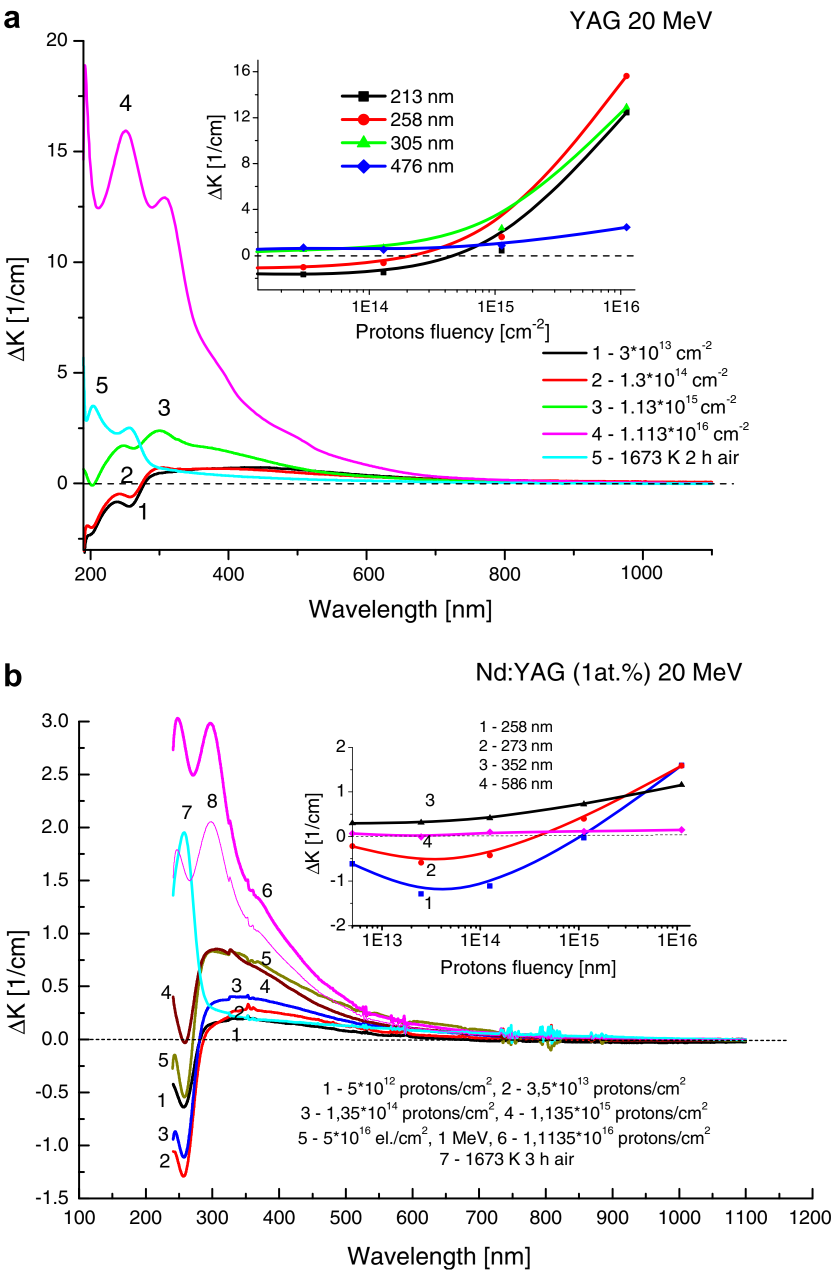

Fig. 1. Additional absorption spectra of pure YAG (a) and YAG:Nd (1%) (b) single crystals irradiated with protons with fluencies from 10^{12} to 10^{16} cm^{-2}. In the inset of each figure the AA dependence versus fluency is shown.

YAG:Cr^{3+} single crystal is observed. From the dependence one can distinguish two dose ranges: (1) fluencies less than 5×10^{14} cm^{-2} where recharging effects dominate, and, (2) fluencies larger than 5×10^{14} cm^{-2} where the presence of Frenkel defects is expected.

In Fig. 3, AA spectra after subsequent proton irradiations are shown for fluencies 10^{14}–10^{16} cm^{-2}. Against proton irradiation, gamma irradiation (dose of 10^5 Gy) and next annealing at 673 K in the air were did. So we can clearly compare the types of defects arising in the crystal after both types of irradiation. From the figure it results the radiation defects are of the same type for both irradiations (exclude Frenkel defects, so for fluencies lower than 10^{14} cm^{-2}) and they are only recharged intrinsic point defects. Changes in the AA band observed after gamma and proton irradiations are mainly related to the charge exchange of Fe^{2+}, Fe^{3+} (234–260, 303–315 nm), cation vacancies and F-type centers (385 nm) [$F^+ \rightarrow V_0 + e^-$, $F \rightarrow V_0 + 2e^-$] [6]. Annealing at 673 K entirely removes radiation defects introduced to YAP:Er crystal by γ-quanta. As compare to YAG crystals AA versus protons fluency dependence shows tendency to saturation (see inset of Fig. 3).

To check in which way different temperature of the annealing affect the defect structure of YAP crystal we performed some experiments. They are summarized in Fig. 4a and b.

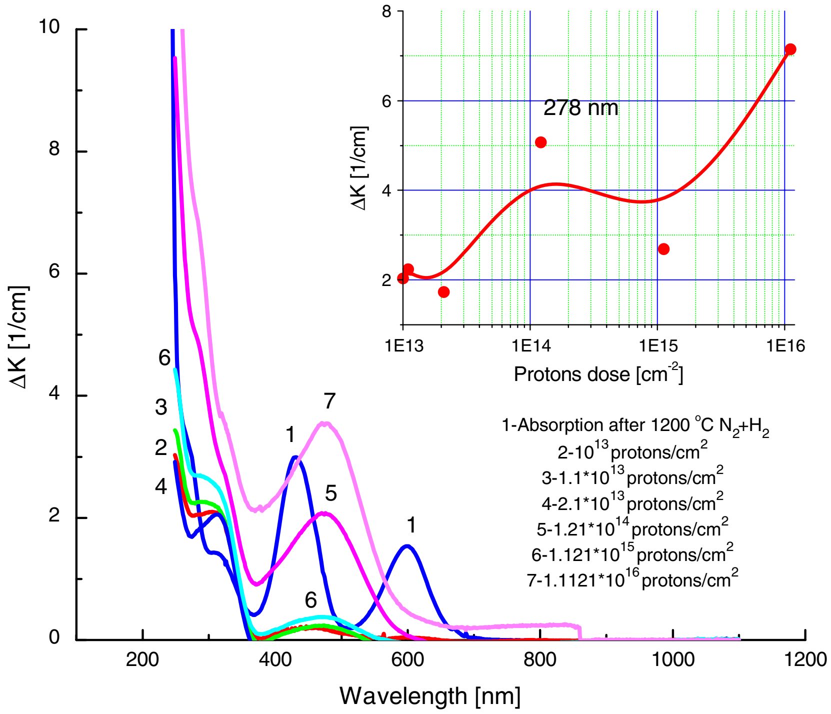

Fig. 2. Additional absorption spectra of YAG:Cr^{3+}, Cr^{4+} (0.1%) single crystal irradiated with protons with fluencies from 10^{13} to 10^{16} cm^{-2}. In the inset the AA dependence versus fluency is shown.

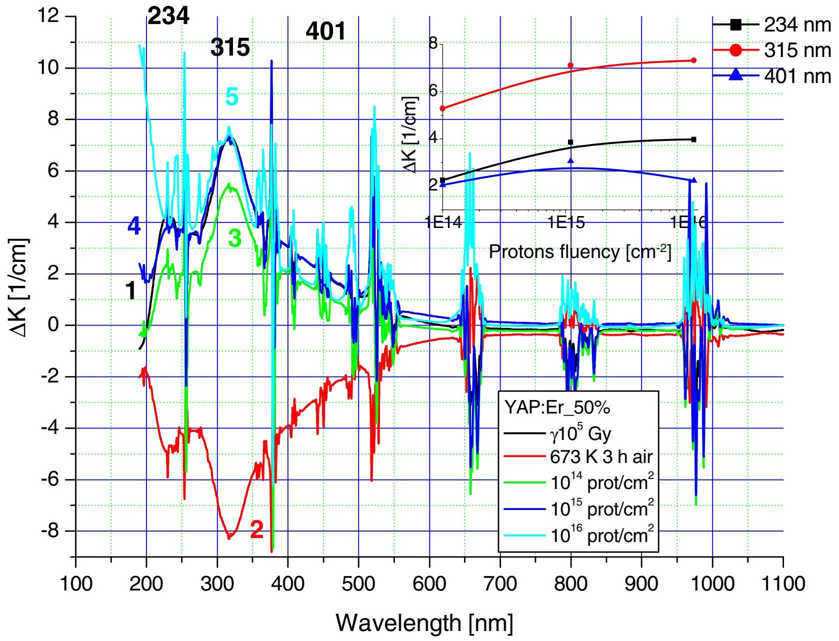

Fig. 3. Additional absorption spectra of YAP:Er^{3+} (50%) single crystal irradiated with protons with fluencies from 10^{13} to 10^{16} cm^{-2}. In the inset the AA dependence versus fluency is shown.

From the figures it results: annealing in the air at 673 K for 3 h is enough to obtain initial optical absorption of the crystal when irradiated with gammas (10^5 Gy), annealing in the air at 1073 K introduce additional defects (430 nm band, may be oxygen ions at interstitials), annealing in the air at 1673 K introduce some additional defects (260, 358, 487 nm – recharging of Fe un-controlled ions and oxygen ions), annealing in hydrogen at 1473 K completely bleaches the crystal. So, if we irradiate the crystal with gammas or protons we should know about actual defect structure of the crystal. As one can see from Fig. 4a although the shape of the AA after gammas registered

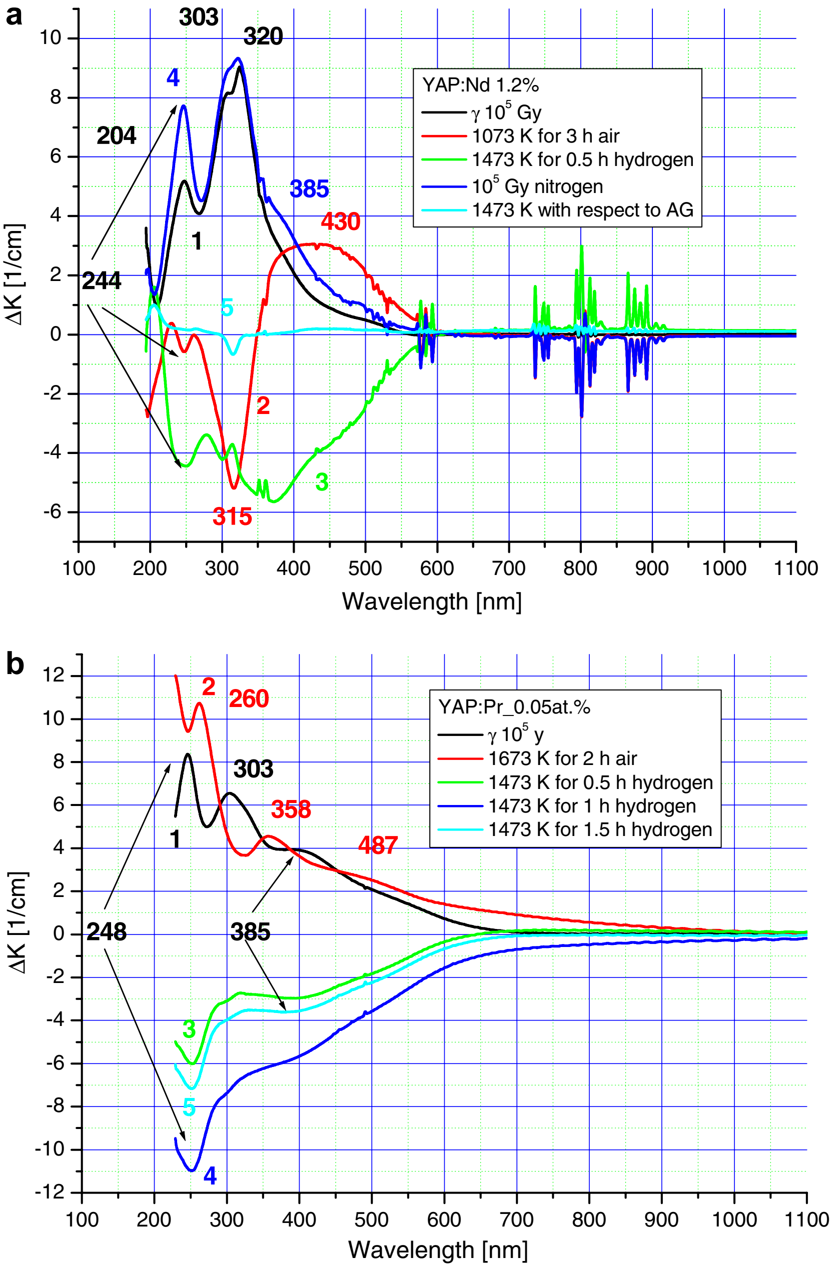

Fig. 4. AA spectra of YAP:Nd (1.2%) (a) and YAP:Pr (0.05%) (b) single crystals next to γ-irradiation and subsequent annealing.

for the crystal irradiated just after growth (curve 1) and the AA of crystal irradiated next to annealing in hydrogen (curve 4) are generally the same, some distinct differences are clearly seen. From Fig. 4b one can see the time is limiting factor of the bleaching of the crystal as an effect of the annealing in hydrogen.

When analyse the influence of gammas and protons with fluencies from 10^{12} to 10^{16} cm^{-2} on the absorption of GGG single crystal, three main centers are observed both after γ- and proton (for fluencies lower than 10^{14} cm^{-2}) irradiations: 255, 340 and 465 nm being attributed to the presence of Ga and O vacancies as well as Fe ions (255 nm), $Ca^{2+}F^{+}$ complex centers and hole O-centers (340 nm), and, F-centers (465 nm) [7].

Fig. 5a and b shows the influence of protons with fluencies from 10^{12} to 10^{16} on the Cr doped SLG and SGG single crystals. Similarly as in case of YAG:Cr crystal (see Fig. 2), beside radiation defects characteristic for gallates (290 nm – Ga^{2+} centre ($O^{2-} + p^{+} \rightarrow O^{1-} + e^{-}$; $Ga^{3+} + e^{-} \rightarrow Ga^{2+}$) and 380 nm – F-centre [8]) and Frenkel defects, one can observe recharging of Cr ions. For SLG crystal doped with Co ion we observed ionization of Co^{2+} ions and arising of Co^{3+} ($^5T_2$–^5E transition at 1223 nm) [9].

In Fig. 6 one can see AA bands after proton irradiation with fluencies 10^{13}–10^{16} of $LiNbO_3$:Fe (a) and $LiNbO_3$:Cu (b) single crystals and (in the inset of each figure) AA dependence versus fluency. The latter one seems to be of

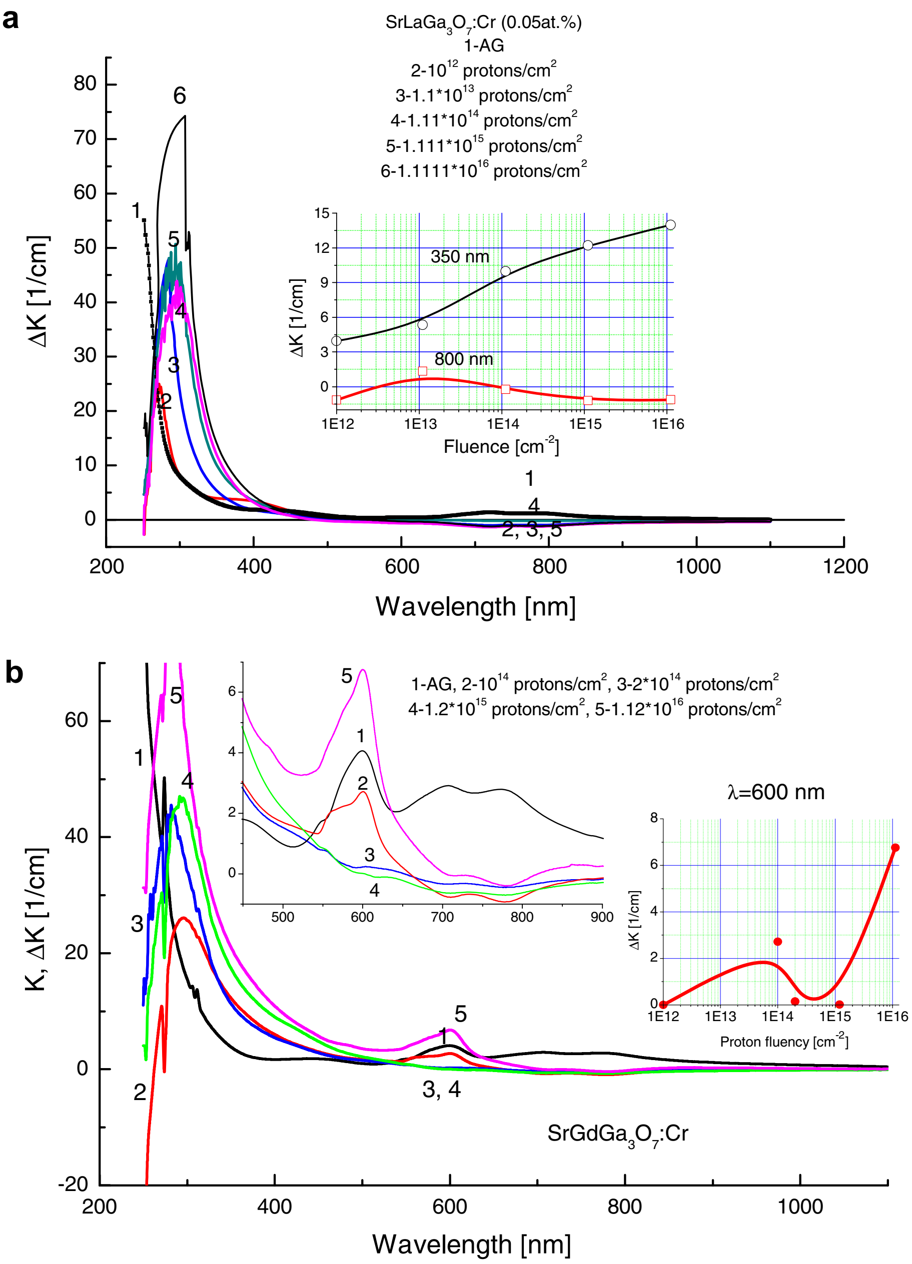

Fig. 5. AA bands of $SrLaGa_3O_7$:Cr (SLG:Cr) (a) and $SrGdGa_3O_7$:Cr (SGG:Cr) (b) gallate crystals next to proton irradiation.

the same type for both crystals but Fe doped LN crystal show higher susceptibility to proton irradiation. In the additional absorption of $LINbO_3$ single crystals, pure and doped, irradiated with gamma and protons there arises at least two additional bands peaked at about 384 (F-type color centers) and 500 nm (Nb^{4+}–Nb^{4+} bipolarons). For the crystals annealed in the air additional absorption arises near 650 nm (polarons Nb^{4+}).

It had been observed rather unexpectedly that classical thermal annealing can lead to a decrease in optical homogeneity of LN crystals in the majority of cases [10]. 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 or proton (for fluencies lower than 10^{14} cm^{-2}) irradiation in the investigated crystals are believed to increase the optical homogeneity, also by canceling this field.

As compare to LN crystals doped with other TM ions, LN:Cu reveals lack of 500 nm AA band for all doses of gammas and for fluencies of protons as high as 10^{15} cm^{-2}. Polarimetric measurements 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 birefringence coefficient are very significant [10].

Fig. 7 presents AA spectra after proton irradiation of LN:Cr single crystal. From Figs. 6a and b and 7 one can

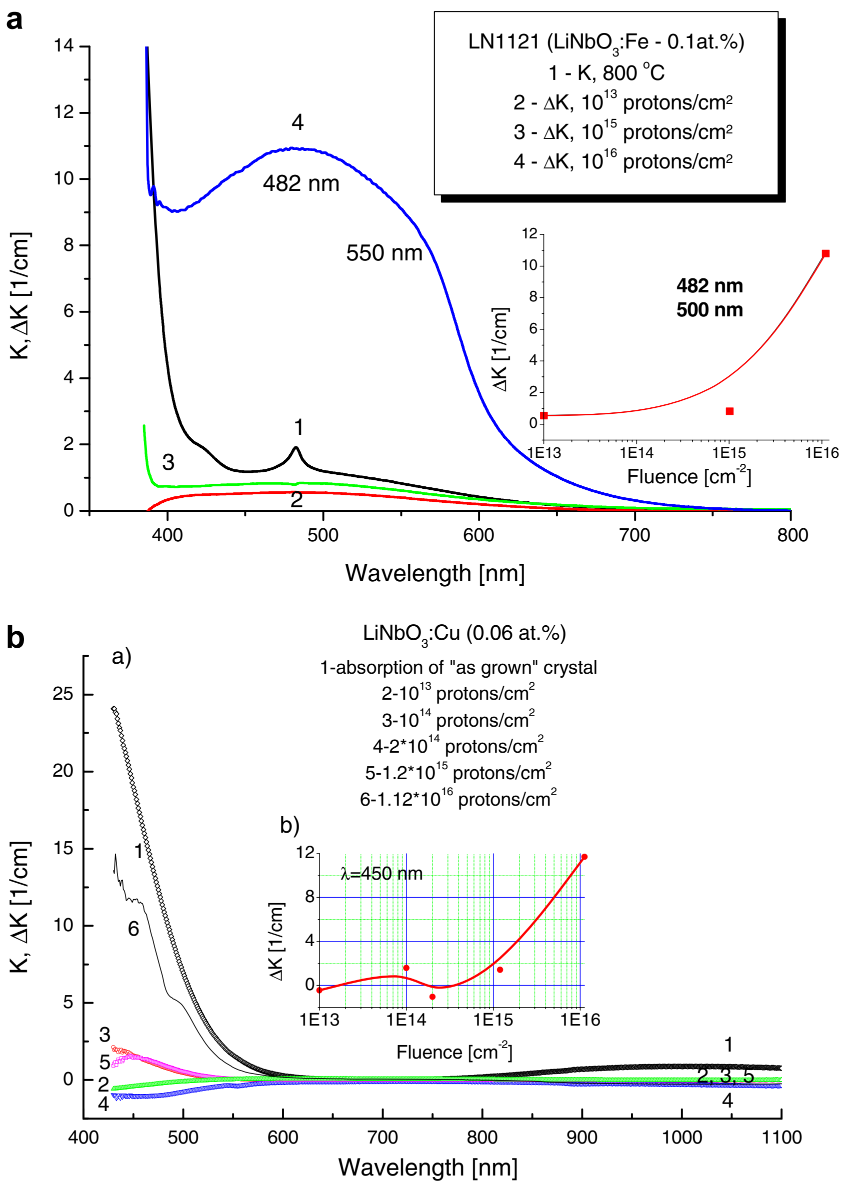

Fig. 6. AA bands of LiNbO$_3$:Fe (a) and LiNbO$_3$:Cu (b) single crystals irradiated with protons with fluencies of 10^{13}–10^{16}. In the inset of each figure AA dependence versus fluency is shown.

observe changes in the concentration of TM active ions (Fe^{2+}, Cu^{2+} and Cr^{3+}) after the irradiation (recharging of active ions). In fluency dependence of additional absorption at least three regions are seen: first one for fluencies below 10^{14} cm^{-2} (recharging effects), second one for fluencies between 10^{14} and 5×10^{14} cm^{-2} (mutual interaction of the cascades from different proton trajectories) and third one over 5×10^{14} cm^{-2} (Frenkel defects).

4. Conclusions

For given growth conditions (growth method, purity of the starting material, growth atmosphere, technological parameters) some definite sub-system of point defects appears in the crystal (e.g. active ions, vacancies, antisite ions, active ions, un-controlled and controlled impurities or interstitial defects). At the end of the growth it is electrically balanced and is left in a metastable state. Some external factors, like irradiation or thermal processing, may lead to the transition of this sub-system from one metastable state to another. During this transition point defects may change their charge state.

The type of the radiation defects arising in the crystal and glasses strongly depends on whether the material was obtained, or next annealed, at oxidizing or reducing atmosphere.

Irradiation can induce numerous changes in the physical properties of a crystal or a glass. This may originate from atomic rearrangements which take place powered by the energy given up when electrons and holes recombine non-radiatively, or could be induced by any sort of radiation or particle bombardment capable of exciting

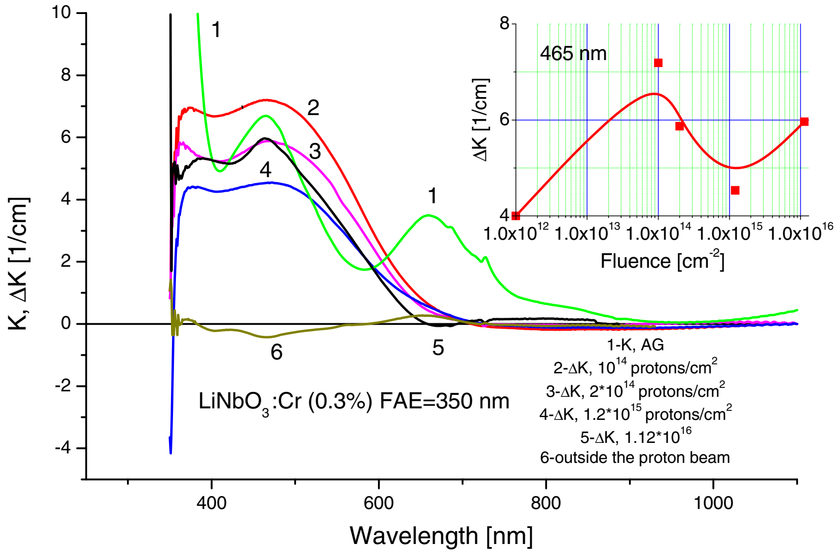

Fig. 7. AA bands of $LiNbO_3$:Cr single crystal next to proton irradiation with fluencies of 10^{14}–10^{16}. In the inset AA dependence versus fluency is shown.

electrons across the forbidden gap E_g into the conduction band.

The similarity of some radiation defects that arises after gamma and proton irradiation in the investigated laser materials results from the physics of proton irradiation with matter. Passing through the matter, protons produce secondary δ-electrons which may acts with ions or vacancies in the same way as electrons produced by Compton effect in case of gamma irradiation. The essential difference between these two kinds of irradiations is almost homogeneous distribution of the electrons in a bulk material in case of gammas and possibility of creating of Frenkel defects by protons (gammas with energy of 1.25 MeV can not form the defects).

In protons fluency dependence of additional absorption of laser materials at least three regions are seen: first one for fluencies below $10^{14}\,\mathrm{cm}^{-2}$ (recharging effects), second one for fluencies between 10^{14} and $5\times10^{14}\,\mathrm{cm}^{-2}$ (mutual interaction of the cascades from different proton trajectories) and third one over $5\times10^{14}\,\mathrm{cm}^{-2}$ (Frenkel defects).

All forms of the irradiations: exposure to ^{60}Co gamma rays, over threshold electrons (1 MeV) and high energy (20 MeV) protons, and, annealing in the air or hydrogen create damage centers in laser materials which may reduce optical output of the lasers. The observed in the absorption spectrum changes after ionizing radiation or annealing treatment can have important influence on the performance of optoelectronic devices applied in e.g. outer space. The obtained results point to the direct influence of color centers on the processes of inverse population formation of many lasers.

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