Stability of color centers in LiYF₄ crystals at low temperatures

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Abstract. This paper presents the results of examining the stability of induced radiation defects in crystals at 15K. The following regularities have been established. Defects induced at low temperatures in pure and Nd³⁺ doped LiYF₄ crystals are unstable: upon termination of radiation, even at 15K induced color centers are visibly destructed, exposure to the halogen lamp light increases the destruction speed significantly. Heating crystals up to 80K results in complete destruction of color centers induced at 15K.

1. Introduction

LiYF₄ crystals doped with rare-earth ions are promising materials for creating active optical elements on their base. Rare-earth ions enter crystals by substituting Y³⁺ ions, thus they can be introduced in big concentrations. One of the main features of optical materials is their radiation resistance. Changes in crystal clarity during exposure result in disastrous change of limits and efficiency of generation of optical media forced radiation. Thus the main focus of this paper is establishing the nature of processes causing the radiation changes of clarity in optically active materials and finding a way to create radiation resistant materials.

It is understood that exposure of LiYF₄ crystals provides additional optical absorption in the wide spectral range. Figure 1 shows electron irradiation at room temperature in undoped LiYF₄ crystals induces absorption bands with maximum limits of 4.5; 3.7; 2.8 and 2 eV. Transition absorption measured with high time resolution, is significantly different in central spectral range. Radiation at 80K results in induction of bands in regions 4.1; 3.7 and 2.7 or 2.1 eV depending on the orientation of crystal in relation to polarization plane of the probing light. Figure 2 shows that γ - radiation of LiYF₄ crystals at room temperature results in induction of absorption bands in region 260; 330; 440; 640 nm (4.7; 3.7; 2.8; 1.95 eV, respectively). Band 3.7 eV is believed to be due to F-centers induced in the crystal. Doping with ytterbium and neodymium reduces the efficiency of induction of these centers in the crystal. Figure 3 calculates the positions of bands corresponding to absorption F (3.9 eV) and Vₖ (3.02; 2.99; 2.88 eV) – centers close to experimentally measured band positions and supposedly accountable for these bands. It is known that in the course of time, after the exposure, the type of spectra change, due to transformation of defects into more stable forms [4].

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This paper focuses on research of kinetics of spectrum change of induced optical absorption in nominally “pure” and Nd doped LiYF₄ crystals when exposed to electron flows at low temperatures, 15K.

2. Experimental results and discussion

Pure and Nd³⁺ doped LiYF₄ crystals, made in INKROM CJSC, have been examined. Samples have been cut out from single crystals, alongside and perpendicular to optical axis c, then they have been polished. The absorption spectra of examined crystals had narrow absorption lines in region 1.3 – 2.3 eV, which is normal for LiYF₄ with Nd³⁺. Absorption in Nd³⁺ bands region becomes higher as concentration of feed impurity increases: 0; 0.7; 1.5; 2 at%, respectively.

Electron radiation was applied, with high-current pulse accelerator as an exposure source; it generated electron flow with the following specifications: mean electron energy 0.2 MeV, pulse length -10 ns, energy absorbed by crystal per pulse 10⁻² Gy. Pulse optical spectrometer was used for exposure and measurement of induced absorption, see the description in [5].

The following procedure was used to measure the spectra of radiation induced absorption in crystals at super-low temperatures. The sample was placed into the crystal holder of cryostat and was cooled down to the set temperature. Probing light from the exposure source was directed toward the sample. Light went through the sample, through monochromator and onto a CCD matrix, spectrum of the light that went through the sample was registered in PC. Then sample was exposed to a series of radiation pulses from small-scale pulsed electron accelerator. Then the radiation from the same source of probing light was directed toward the sample. The spectrum of the light that passed through the irradiated sample is different to the spectrum obtained when passing through unexposed sample. The result of measuring the spectrum that passed through the irradiated sample was also saved in PC. Ratio of spectrum values of probing light flows that passed through the sample before and after radiation exposure are obviously the spectral ratios of radiation induced transmission. Spectrum values of transmission rates were then converted into spectral values of transmission density of absorption factors. The corresponding spectra of radiation induced additional absorption in the sample were constructed based on calculated spectral values of transmission, optical density or absorption factors.

Typical spectra of extra absorption, induced by radiation by a series of pulses from electron flow from accelerator, in nominally pure LiYF₄ crystals and crystals with approx. 2at% Nd are represented in Fig. 1, a and b. Crystals have not been exposed before, and were transparent in the examined spectrum range. In the spectrum of induced absorption at 15K of pure and doped crystals, there are visible well-defined absorption bands at 2.1 and in 3.7 eV region, less defined band in 2.8 eV region, ill-defined band in 4.5 eV region. In doped crystals, 2.1 eV band is slightly widened into the short-wave region.
With increase of radiation dose, the size of additional absorption grows in the whole region of the spectrum, appearance of induced absorption spectra does not change visibly, but increment decreases with increase of dose. At radiation doses higher than 200 pulses, and corresponding \( \sim 2 \cdot 10^4 \) Gy, it tends to saturate the growth of induced absorption.

Pause in exposure, and pause in a series of sequential pulses results in diminution of the size of induced absorption. When LiYF\(_2\) crystal + 2at\% Nd, pre-exposed to a series of 200 subsequent pulses, is kept at constant temperature of 15K, decline of absorption in the whole spectrum range is observed, which reaches 25\% relative to initial one, in 100 minutes. The decline of induced absorption when keeping the crystal at low temperature depends on the history of the crystal. Some crystals can show the decline of induced absorption up to 50\%.

![Figure 2. Spectra of induced and measured at 15K extra absorption in pure LiYF\(_4\) crystals, exposed to radiation dose of 3.5 \( \cdot \) 10\(^4\) Gy and exposed to halogen lamp radiation for 10, 50, and 150 min. The inserted image shows the kinetic curve of crystal bleaching.](image)

Further exposure of crystal after the pause in radiation in a series of consecutive pulses results in recovery of initial form of kinetics of growth of optical absorption in the whole spectral region.

Reduction of induced absorption size during the pause between series of radiation pulses in the band in 2.1 eV region is notably bigger than in the band in 3.7 eV region for all examined crystals.

Induced at 15K additional absorption is sensitive to the effect of radiation in optical spectrum. Exposure to radiation of halogen lamp of typical light of “Avantes” spectrometer of pure and doped LiYF\(_4\) crystals, previously irradiated with series of electron pulses at 15K, results in decline of induced absorption in the spectral region. Figure 2 shows changes in spectrum of induced absorption with dose of 3.5 \( \cdot \) 10\(^4\) Gy at 15K in pure LiYF\(_4\) crystal, with time of exposure of crystal to halogen lamp radiation. Partial bleaching of crystal was observed in the whole examined spectrum region. Appearance of spectrum remains unchanged, but the ratio of absorption in bands changes. Kinetics of decline of absorption is shown on inserted image on Figure 2. After 150 min of exposure to halogen lamp, absorption in the band of 2.1 eV region decreased \( \sim 4 \) times, band in 3.7 eV region \( \sim 2 \) times. Such effect is observed when previously irradiated Nd doped crystals were exposed to halogen lamp radiation. For instance, photoexcitation of previously irradiated at 15K with a dose 2\( \cdot \)10\(^4\) Gy of LiYF\(_4\) + 2 at\% Nd crystal, absorption band in 2.1 eV region is reduced threefold, whereas band in 3.7 eV region only by 25\%.
Figure 3 represents the results of examining the thermal stability of radiation induced color centers at 15K in LiYF$_4$ crystals. Experiment was conducted as follows. The crystal was exposed to a series of electron pulses up to dose of $10^4$ Gy, the spectrum of induced absorption was measured at this temperature. Then crystal was heated to certain temperature $T_i > 15K$, cooled to 15K, then induced absorption spectrum was measured again. Afterwards crystal was heated to $T_j > T_i$, cooled, spectrum measured at 15K, etc. This procedure was repeated until induced absorption disappeared. Resistance of induced color centers was examined for pure and Nd doped crystals. Figure 3 shows curves color center annealing, normalized for initial optical density at 25K, liable for bands in 3.7 and 2.1 eV regions. It should be noted that these bands are annealed absolutely likewise. The appearance of annealing curves is unaffected by the level of purity of crystal.

Research results show that when heating up to 45K, induced absorption remains almost unchanged. When temperature rises above 45K, absorption drops abruptly, centers start breaking. Maximum destruction speed occurs at 60K. By 80K induced centers and corresponding absorption disappears completely.

Preliminary irradiation of crystals at 15K, this is especially shown in doped crystals, and further annealing up to room temperature does not restore the initial defect structure of the sample completely. Exposure of crystals to doses up to 400 ... 1000 pulses at 15K results in generation of characteristic spectra of additional absorption, given on Fig. 1. According to results given on Figure 3, further heating results in complete bleaching of crystals at 100K. Clarity of the crystal heated to room temperature can be compared to the initial one. Crystal remains clear when stored in darkness, from several days to one year. However, further exposure of such crystal (irradiated at 15K by a series of radiation pulses, annealed to room temperature and kept at this temperature for a long period) results in induction of additional absorption spectrum at 15K, which is visibly different to the one induced in crystal without preliminary radiation exposure.

Figure 3. Temperature dependence of stability of radiation induced absorption bands at 15K in ranges 3.7 and 2.1 eV in pure and Nd doped LiYF$_4$ crystals.

Figure 4. Spectra of absorption induced at 15K in LiYF$_4$ crystal doped with 2a at% of Nd, preliminarily exposed to $7.2 \cdot 10^4$ Gy radiation dose, then heated to room temperature and kept at this temperature for 15 days and exposed at 15K to radiation doses of $1 \cdot 5 \cdot 10^2$, $2 \cdot 3 \cdot 10^3$, $3 \cdot 8 \cdot 10^3$, $4 \cdot 1.2 \cdot 10^4$, $5 \cdot 2 \cdot 10^4$ Gy.
Figure 4 shows results of research of absorption induced at 15K in crystal LiYF$_4$ with 2at% of Nd, previously exposed to 720 radiation pulses ($7.2 \cdot 10^4$ Gy), then heated to room temperature and kept at this temperature for 15 days. Absorption spectra were measured after exposure of such crystals to different doses of radiation pulses.

The band in 2.1 eV region of the induced absorption spectrum in such crystal has a significantly different shape and size from the one induced in the initial crystal. Band in 2.1 eV region grows slower with increase of radiation dose, compared to the band in 3.7 eV. Band in 3.7 eV is obviously dominating band in the spectrum.

Thus, doped crystal keeps the data about the previous exposure at 15K even after annealing, and storage at room temperature. Note that the described effect is not observed or is insignificant when annealing pure crystals, they do not save the data on previous exposure at low temperatures after annealing and storing at room temperature.

3. Conclusions

Exposure of pure and Nd doped LiYF$_4$ crystals to electron flows at 15K results in induced color centers in them, which emerge in absorption bands in 2.1 and 3.7 eV, and in ill-defined bands of 2.8 eV and 4.5 eV regions. The view of spectra of additional absorption, induced in pure and doped crystals is similar. Efficiency of coloring of doped crystals is slightly lower. When increasing the radiation dose, the absorption also increases in the whole examined spectral range – 1.5...5.5eV, growth speed tending to slow down with radiation dose. After termination of radiation exposure, even at 15K, absorption drops. In 100 minutes, absorption can drop to 25% from initial value. Influence of halogen lamp light results in significant acceleration of decline of induced absorption. In 150 minutes of influence of light flow onto irradiated at 15K with $2 \cdot 10^4$ Gy LiYF$_4$ crystal + 2 at% Nd, there is threefold reduction of the absorption band in region 2.1 eV, when the band in 3.7 eV region – only by 25%. Within the same period of exposure to halogen lamp light, absorption in band in 2.1 eV of pure LiYF$_4$ crystal reduced by ~ 4 times, when band in 3.7 eV - ~ 2 times. Thus, radiation induced pure and LiYF$_4$ crystals color centers are unstable at 15K. Decomposition speed of centers responsible for bands 2.1 eV and 3.7 eV is different. This indicates that these centers are of different nature.

Heating crystals results in decomposition of induced color centers. When heating to 45K, induced absorption remains almost unchanged. When temperature rises above 45K, absorption drops abruptly, and center start to break. Maximum speed of decomposition of centers is at 60K. By 80K, induced centers and corresponding absorption disappear completely. Curves of decomposition of centers responsible for absorption in 2.1 eV and 3.7 eV regions are absolutely similar. This means that these centers decompose under the influence of same processes.

The following observation is of interest. If LiYF$_4$ crystal with 2at% Nd, is exposed to high doses of radiation, and then heated to room temperature and kept at room temperature for a long time, crystal restores its clarity completely. But the reaction of such crystal to further exposure at 15K is absolutely different to the reaction to exposure of a crystal without pre-treatment. The band in 2.1 eV region in the induced absorption spectrum of such crystal is different in shape and size from the band induced in a crystal that has not been exposed. Band in 2.1 eV region grows slower with increase of radiation dose, compared to the band in 3.7 eV. Band in 3.7 eV is obviously dominating band in the spectrum.

Thus, doped crystal keeps the data about the previous exposure at 15K even after annealing, and storage at room temperature. Note that the described effect is not observed or is insignificant when annealing pure crystals, they do not save the data on previous exposure at low temperatures after annealing and storing at room temperature.

This effect can possibly be explained as follows. In the radiation field at low temperature, there is a transformation of the crystal structure in the region of impurity ion. The generated defective region is a competitive center of trapping carriers, involved in the formation of color center, responsible for band in 2.1 eV.
References
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