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Pulsed cathodoluminescence of $YLiF_4$ crystals at 15 K

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ABSTRACT

Here, we study pulsed cathodoluminescence of "pure" and Nd^{3+} doped $YLiF_4$ crystals. Luminescence spectrum covers two short-lived bands with maxima at 4.3 and 3.2 eV and a halfwidth of 0.9 eV each. Irradiated at 15 K, "pure" and Nd^{3+} doped crystals of $YLiF_4$ have induced color centers that provide for the absorption band reaching maxima of 2.1 and 3.7 eV in the main bands.

1. Introduction

$YLiF_4$ crystals doped with rare-earth ions hold potential in becoming a basis for forming active optical environment and scintillator with a high light yield. A key feature of optical materials is their resistivity to radiation as induced color centers may degrade spectral parameters and kinetics of crystals with impurities. Here, we study pulsed cathodoluminescence and (PCL) absorption spectra of $YLiF_4$ crystals within a wide range of radiation absorbed doses ($\leqslant 10^5$ Gy).

Non-activated "pure" and Nd^{3+} doped $YLiF_4$ crystals grown at INCROM Ltd were cut out of single crystals at 45° angle to the optic axis of crystal C and then were polished.

Fig. 1 shows absorption spectra of the crystals before being irradiated. In the absorption spectra of non-irradiated crystals doped with Nd^{3+} the characteristic absorption bands of Nd^{3+} could be observed in a range of 1.3–2.3 eV (Fig. 1). In the Nd^{3+} band area the rise of absorption is linearly dependent on the concentration of impurity added to the melt ranging from 0.7 to 2 mol.%.

2. Methods

Pulsed cathodoluminescence and absorption spectrum were taken at temperature range of 15–300 K using nanosecond time-resolved pulse spectrometer [2,3]. High-current pulsed electron accelerator was used able to generate a beam with the following parameters: average electron energy 0.2 MeV, pulse duration 10 ns, absorbed dose per pulse 10^2 Gy.

The following procedure was used to measure the spectra of radiation induced absorption in crystals at 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 was registered in pulsed spectrometer. 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 that passed through the irradiated sample is different to the spectrum obtained when passing through unexposed sample. The result was also saved in pulsed spectrometer 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 optical density. The corresponding spectra of radiation induced additional absorption in the sample were constructed based on calculated spectral values of optical density.

3. Results and discussion

Fig. 2 illustrates spectra of pulsed cathodoluminescence (PCL) measured with 10 ns pulse duration in relation to the end of electron pulse irradiation of undoped $YLiF_4$ crystals (samples 1 and 2) and of neodymium-doped $YLiF_4$ crystal (sample 3). At 15 K in the PCL spectrum of $YLiF_4$ crystals under study there are two bands

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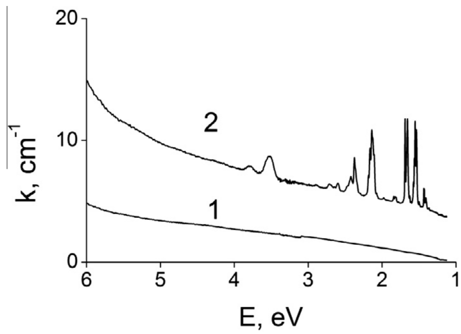

Fig. 1. Absorption spectra of $YLiF_4$ crystals non-activated (1) or Nd activated (2).

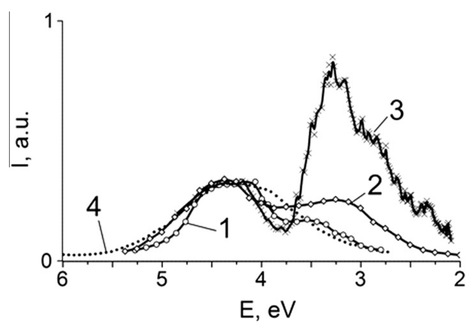

Fig. 2. PCL spectra measured at 15 K and 10 ns pulse duration of $YLiF_4$ crystals with various prehistory: pure $YLiF_4$ crystals (1 and 2), $YLiF_4$ crystal with 2 mol.% Nd dopant (3) and X-ray luminescence spectra of $YLiF_4$ crystal at 4 K (4) in accordance with [1].

reaching maximum at 4.3 and 3.2 eV and with halfwidth of 0.9 eV each. Correlation between the two bands depends on the prehistory of a sample and it increases in favors of the longwavelength band in Nd doped $YLiF_4$ crystals. The same figure shows the spectrum of stationary X-ray luminescence of pure $YLiF_4$ crystals at 4 K in accordance with [1]. A comparison of our findings with those of Hayes shows that the longwavelength band in the PCL spectrum is visible due to the luminescence of Tr^{3+} dopant, while the shortwavelength band, as in the Hayes' investigations, is caused by self-trapped excitons.

That the bands we observed at 4.3 and 3.2 eV in the PCL spectrum had different natures was confirmed by dissimilarities in the kinetics curves (Fig. 3). Findings demonstrate that the luminescence build-up at 3 eV is inertialess. The buildup of luminescence at 4.3 eV is inertial, with characteristic time of build-up equal to 40 ns at 15 K and decreasing to 25 ns at 200 K.

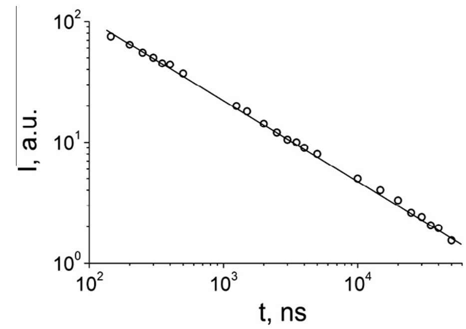

Fig. 4. Dependence of luminescence intensity at 4.4 eV on decay time at 80 K.

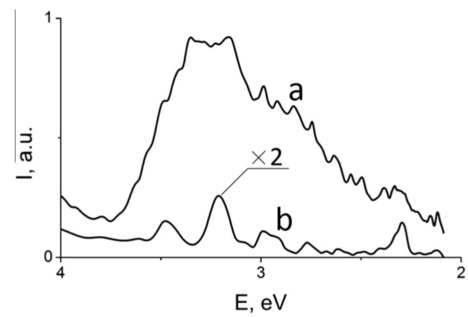

Fig. 5. PCL spectrum of $YLiF_4$ crystal doped with 2 mol.% of Nd measured at 15 K 10 ns (a) and 200 ns (b) after the end of pulsed excitation.

Dependence of luminescence intensity at 4.4 eV on the decay time at 80 K has been identified as having a bimolecular nature and represents a straight line in co-ordinate lgJ = f(lgt) (Fig. 4).

Luminescence spectra of all $YLiF_4$ crystals under study ("pure" and doped) measured with a ms delay consist of a number of narrow luminescence bands at 2–3.8 eV originating from various radiative transitions of Nd^{3+} ion. For example, Fig. 5 shows a fragment of PCL spectrum measured with various pulse durations, of a neodymium-doped crystal. Research showed that band intensity in doped crystals depends on crystallographic orientation of crystal as regards to the axis of investigation and on temperature of crystal irradiate.

Fig. 6a and b shows typical absorption spectra of $YLiF_4$ crystals, with radiation-induced electrons, that are nominally "pure" or containing about 2 mol.% of Nd. In the spectrum of pure and doped crystals can be seen strong absorption bands at 2.1 and 3.6 eV and poor resolution band at 3 eV. As can be seen from findings that spectral image of a radiation-induced crystal does not depend on

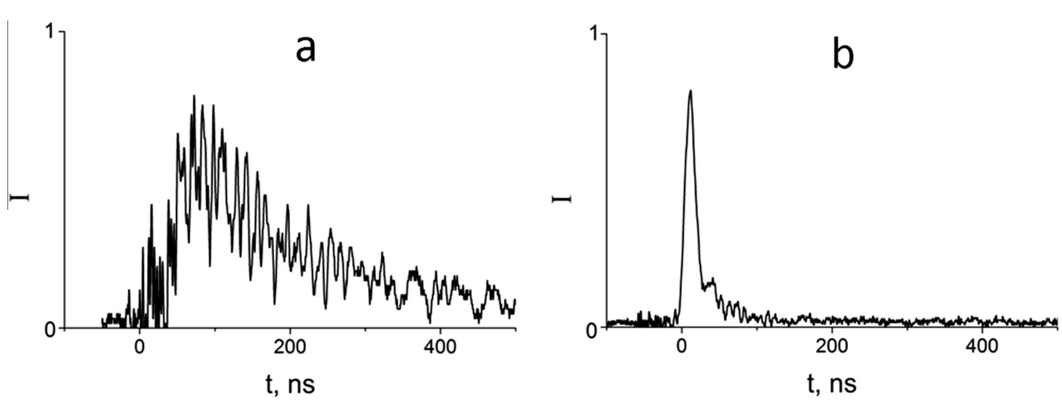

Fig. 3. Luminescence relaxation kinetics of bands peaking at 4.4 eV (a) and 3.2 eV (b) at 15 K.

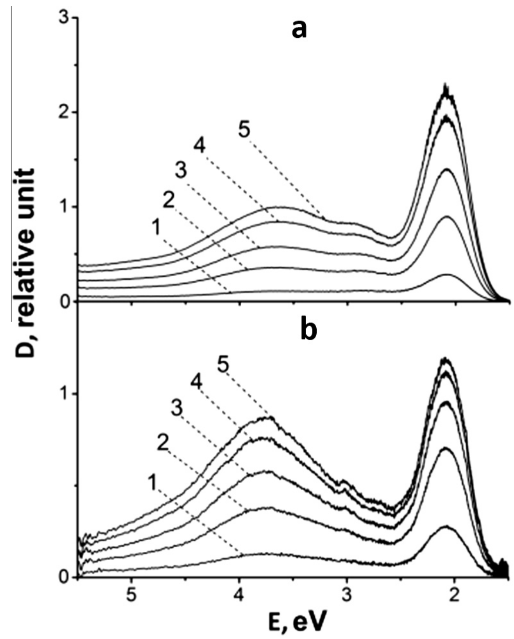

Fig. 6. Spectra of induced and measured at 15 K absorption of $YLiF_4$ crystals, pure (a) and doped with 2 mol.% of Nd (b) under various doses of series of electron pulses: 5×10^2 (1), 2×10^3 (2), 4×10^3 (3), 8×10^3 (4), 1.2×10^4 Gy (5).

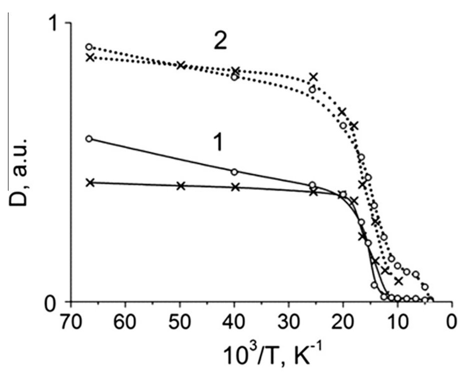

Fig. 7. Temperature dependence of optical density at maximum of 3.7 eV (1) and 2.1 eV (2) in absorption spectra of irradiated "pure" $YLiF_4$ crystal (×) and the 2 mol.% Nd doped $YLiF_4$ crystal (○) ($D = 6 \times 10^4$ Gy).

the presence of activator and is, therefore, determined by radiation-induced defects in crystal lattice.

Increase of radiation dose leads to the increase of absorption value with saturation at 5×10^4 Gy. The increase of radiation dose has no effect on spectral image of induced absorption.

After the irradiation a decrease in absorption is observed even at 15 K. This decrease can be as low as 25% of the original value in a 100 min-long exposure. There is a similarity between the curves showing thermal decay of centers contributing to absorption at 2.1 and 3.7 eV. This means that the both centers decay as a result of the same process.

Fig. 7 illustrates findings of a study into thermal stability of color centers induced by irradiation at 15 K in $YLiF_4$ crystals. The experiment was performed as follows. A crystal is irradiated by electron beam up to a dose of about 10^4 Gy and a spectrum of induced absorption at this temperature is measured. The crystal is then heated up to a temperature of $T_i > 15$ K, cooled to 15 K, with the spectrum of induced absorption measured again. Then, the crystal is heated up to a point of $T_{i+1} > T_i$, cooled, and the spectrum is measured at 15 K, etc. Repetition of the procedure is completed once the induced absorption fully disappears.

Fig. 7 shows no induced absorption is present up to 45 K while at 45 K a sharp fall in absorption and decay of centers can be noticed. At 60 K decay rate reaches its maximum and at 80 K centers fully disappears with their corresponding absorption lines.

Stability of induced absorption does not depend on the concentration of Nd^{3+} dopant in the crystal. Thermal decay of radiation-induced defects, contributing to the bands peaking at 2.1 and 3.7 eV, occurs by different energies that are equal to 15×10^{-3} eV and 7×10^{-3} eV.

It was shown that after the exposure to a halogen lamp КГМ 6.3-15 (300–1000 nm) there was a noticeable acceleration in the decrease of induced absorption. After a 150 min exposure to the illumination of light in the 2 mol.% Nd $LiYF_4$ crystal, irradiated at 15 K with a dose of 2×10^4 Gy, there was a threefold decrease in the absorption band at 2.1 eV, while the band at 3.7 eV decreased by approximately 25%. Exposure to halogen lamp resulted in in fourfold decrease pure $LiYF_4$ crystal at 2.1 eV and twofold decrease at 3.7 eV. These results suggest also instability of radiation-induced color centers in pure and doped $LiYF_4$ crystals at 15 K.

4. Conclusion

Pulsed cathodoluminescence spectrum of $YLiF_4$ crystals consists of two short-lived bands with maxima at 4.3 and 3.2 eV and a half-width of 0.9 eV each. Presence of neodymium in the crystal has no impact on the view of the short-lived spectrum; however the correlation between the bands changes in favors of the short-lived band at 3.2 eV. Presence of a band at maximum of 4.3 eV is likely to be attributed to selftrapped excitons. Radiative transitions of Nd^{3+} ion appear as a total of narrow luminescence bands at 2–3.8 eV in the spectra measured with a millisecond pulse duration after excitation.

Irradiated at 15 K, "pure" and Nd^{3+} doped crystals of $YLiF_4$ have induced color centers that attribute to the appearance of absorption bands at 2.1 and 3.7 eV and low resolution band at 3 eV. "Pure" and doped crystals have similar spectra of additional absorption. Our results also suggest different structures of radiation-induced center.

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