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THE MEASUREMENTS OF PHOTOSTIMULATED LUMINESCENCE IN ALKALI DOPED BaFBr:Eu^{2+} AT LIQUID NITROGEN TEMPERATURE

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Considerable increase of the photostimulated luminescence (PSL) intensity and red shift of the excitation spectrum was obtained by alkali doping of BaFBr:Eu^{2+} crystals [1]. The band of the $F_A(Br^-)$ centers about 0.1 eV shifted to low energy side against the "normal" $F(Br^-)$ centers. The $F_A(Br^-)$ centers are destroyed after heating to 330 K.

Keywords: BaFBr:Eu^{2+}; Storage phosphors; Photostimulated luminescence; F-center

BaFBr crystals activated with europium are an important storage phosphor in which X-ray produced images are stable for long periods in the dark at room temperature. We gained effectuality improvements of PSL in this material by alkali doping (Na^+, K^+, Rb^+) [1]. In the alkali doped BaFBr:Eu^{2+} a considerable increase of PSL intensity was observed. Upon Na doping the intensity of the PSL increased by a factor of 15 in contrast to undoped samples. At one the PSL peak shifted 0.08 eV in the red region of the spectrum upon Na doping. The potassium and rubidium doping results in the same facts, but with less efficacy [2]. It is perhaps the substitution of Ba^{2+} ions by the small percentage of alkali impurities that results in the generation of charge compensating Br^- vacancies caused by alkali doping of BaFBr:Eu^{2+}. The $F_A(Br^-)$ centers are produced by X-irradiation at room temperature. The optical absorption band at 2.2 eV of the $F_A(Br^-, Na^+)$ centers is broadened to lower energies, compared to the regular $F(Br^-)$ centers, by about 0.2 eV. This is in agreement with the red shift of the PSL excitation spectra of BaFBr:Eu^{2+}:Na. Apparently, the $F_A(Br^-, Na^+)$ centers are dominated in the PSL spectrum at low energy [2]. However recently Inoue *et al.* [3] reported that $F_A(Br^-)$ centers are stable at liquid nitrogen temperature (LNT), they can be thermally activated and move away from the Na^+ ions at room temperature (RT), transforming into isolated $F(Br^-)$ centers. This conversion was observed from annealing temperature dependence of $F(Br^-)$ center in BaFBr:Eu^{2+} [3].

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We carried out measurements of PSL excitation spectra of BaFBr:Eu^{2+} samples with alkali doping at 80–500 K temperature region. BaFBr:Eu^{2+} and BaFBr:Eu^{2+}:Na^{+} crystals with and without oxygen contamination were used for spectral measurements. BaFBr crystals were grown with the Shtoeber method in a graphite crucible. Stoichiometric mixtures of $BaBr_2$ and BaF_2 were used. All samples were doped with 0.1 mole % of Eu^{2+}, the concentrations of alkali in the crystals were 0.0002–0.01%. The growing was carried out in helium-fluorine atmosphere for preclusion of oxygen contamination and helium atmosphere without fluorine for crystals with oxygen. The samples were irradiated with X-ray source operating at 30 kV, 10 mA during 30 s at room temperature. The excitation spectra were made with a MDR2 grating monochromator and a halogen lamp. The UV luminescence was detected by a FEU39

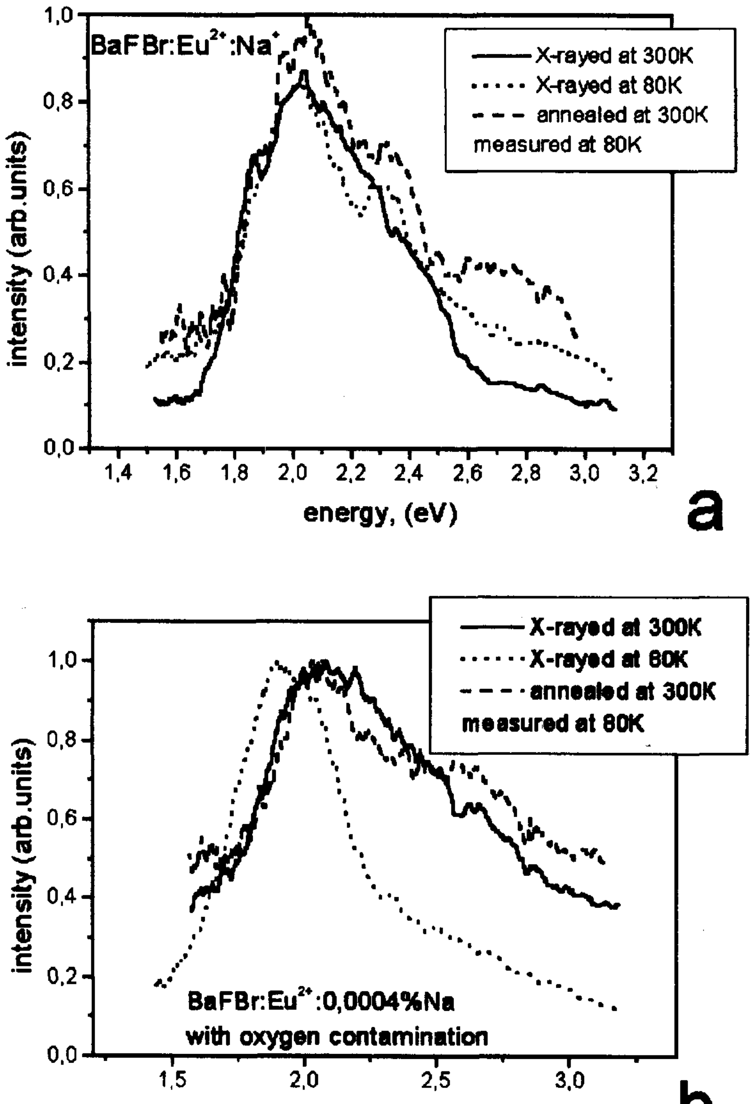

FIGURE 1 Annealing-temperature dependence of excitation spectra of BaFBr:Eu^{2+}:Na^{+} (a) and BaFBr:Eu^{2+}:Na^{+} with oxygen contamination (b). Each spectrum was measured at LNT after being heated to 300 K.

photomultiplier. The crystals were X-irradiated at liquid nitrogen temperature and the PSL spectra were measured. Then samples were annealed to room temperature and the PSL spectra were measured at LNT again. Absorption annealing-temperature dependence is also analysed.

The PSL peak at 2.06 eV observed in the excitation spectra of X-rayed at 80 K BaFBr:Eu^{2+}:Na^{+} crystal after annealing to 300 K in crystals (Fig. 1a). The shift of this peak to 2.14 eV remarked at rising of temperature to 330 K (Fig. 2a). The PSL disappeared at rising of temperature to 430 K.

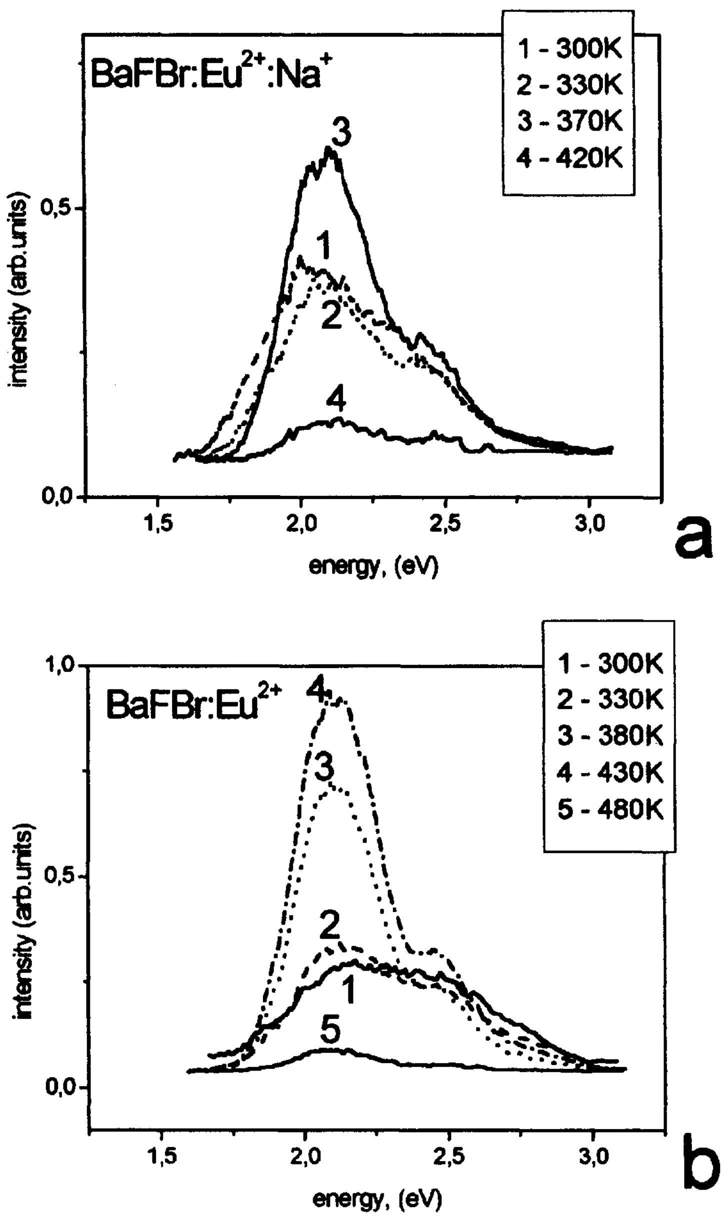

FIGURE 2 PSL excitation spectra of X-ray irradiated BaFBr:Eu^{2+}:Na^{+} (a) and BaFBr:Eu^{2+} (b) crystals without oxygen contamination with heating. Each spectrum was measured at 300 K.

The PSL spectra shifts to a higher energy above 250 K in samples with oxygen contamination (Fig. 1b). The optical absorption band at 2.1 eV is shifted to high energy by about 0.1 eV after annealing to 300 K in X-rayed BaFBr:Eu^{2+}:Na^+ crystals with oxygen contamination. And optical absorption spectra shifts are not observed in the non-oxygen samples after annealing. It is known that oxygen impurity greatly influences the PSL process in BaFBr:Eu^{2+} and spatially correlates with Eu^{2+}-F(Br^-) centers [4]. Therefore the excitation spectrum shift at annealing may be due to oxygen contamination in crystal, not F_A(Br^-) center transformation.

When the temperature of BaFBr:Eu^{2+}:Na^+ crystal without oxygen contamination was raised to 330 K after the X-ray irradiation, the excitation spectrum shifted to a higher energy side. The F_A(Br^-) centers transformed to isolated F(Br^-) centers, moving away from the pinning Na^+ ion. This regular F(Br^-) center fully destroyed at 430 K (Fig. 2a). Such shifting is not observed in PSL spectra of BaFBr:Eu^{2+} crystals without alkali doping (Fig. 2b). The PSL intensity increase detected in PSL excitation spectrum of BaFBr:Eu^{2+} crystals after heating to 330 K is presently unclear (Fig. 2b).

CONCLUSION

The F_A(Br^-) centers are stable at room temperature and caused a red shift of PSL excitation spectrum in alkali doped BaFBr:Eu^{2+} crystals. This F_A(Br^-) center transformed to isolated F(Br^-) center, moving away from the pinning Na^+ ion to 330 K.

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