

# PHOTOSTIMULATION RED SHIFT FOR BaFBr:Eu<sup>2+</sup> WITH ALKALI DOPING

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**Abstract** — The X ray storage phosphor BaFBr:Eu<sup>2+</sup> doped with Na<sup>+</sup> gives a photostimulability shifted to lower photon energy. The photostimulation luminescence intensity considerably increases compared to BaFBr:Eu<sup>2+</sup> upon room temperature X irradiation. This red shift of the photostimulation spectrum is caused by formation of F<sub>A</sub> (Na<sup>+</sup>) centres on the Br<sup>-</sup> sub-lattice as electron traps.

## INTRODUCTION

Barium fluorobromine doped with Eu<sup>2+</sup> is an important storage phosphor in which X ray produced images are stable for long periods in the dark at room temperature. Currently it is widely applied for production of the imaging plates for radiography. Medical imaging plates are used in X ray diagnostics, replacing conventional photographic film. This results in a greatly reduced X ray dose for patients. The imaging plates are composed of a plastic support plate coated with fine BaFBr:Eu<sup>2+</sup> grains mixed uniformly with a binder, and with a protective transparent film on top. The photostimulated luminescence (PSL) is excited usually by light with a He-Ne laser (633 nm) for the readout process. This gives the blue emission of Eu<sup>2+</sup> at 390 nm. It is known that doping with some impurities (for example Ca<sup>2+</sup>, Sr<sup>2+</sup>) shifts the photostimulation spectrum towards the infrared region. This could allow the use of light-emitting diodes, instead of gas lasers, for the readout process<sup>(1,2)</sup>.

The red shift of photostimulation spectrum for BaFBr:Eu<sup>2+</sup> crystals with alkali doping (Na<sup>+</sup>) is reported.

## METHODS

For the PSL measurements BaFBr:Eu<sup>2+</sup> crystals with, and without, NaF doping (up to 5%) were grown. The crystals were grown with the Shteber method in a graphite crucible in a helium-fluorine atmosphere in order to reduce oxygen contamination. The stoichiometric mixtures of BaBr<sub>2</sub> and BaF<sub>2</sub> were used. All samples were doped with 0.1 mol % of Eu<sup>2+</sup>. In the case of BaFBr:Eu<sup>2+</sup>, samples of good quality with big blocks were obtained. After doping of Na<sup>+</sup> the samples grew as chaotic small blocks for the largest concentration of NaF.

The samples were irradiated with an X ray source operating at 30 kV, 10 mA during 30 s at room temperature for PSL measurements. Low energy X rays were filtered out with an Al filter (thickness 1 mm). The excitation spectra were made with a MDR2 grating mono-

chromator and a halogen lamp. The UV luminescence was detected by a FEU39 photomultiplier. The absorption spectra were measured in the visible and ultraviolet regions with a Specord UV VIS apparatus. The X irradiation was made at 40 kV, 40 mA for 20 min at room temperature for measurements of the absorption spectra.

## RESULTS

Figure 1 shows the PSL spectra of the BaFBr:Eu<sup>2+</sup> and BaFBr:Eu<sup>2+</sup>:Na<sup>+</sup> crystals (1.5% and 5% NaF). The peak of the photostimulated luminescence spectrum at 2.06 eV (599 nm) after X irradiation at 300 K in the samples of BaFBr:Eu<sup>2+</sup> was observed. Upon 5% NaF doping, this peak shifted to 1.99 eV (621 nm), the half-width of spectrum was widened on the red side from 1.89 eV (657 nm) to 1.84 eV (672 nm) and also the peak intensity increased about thirteenfold. Upon 1.5% NaF doping, the PSL spectrum widened further (to 1.8 eV (687 nm)) towards the infrared region, but its intensity was less than at 5% NaF doping.

The absorption bands at 2.65 eV (467 nm) and 2.2 eV

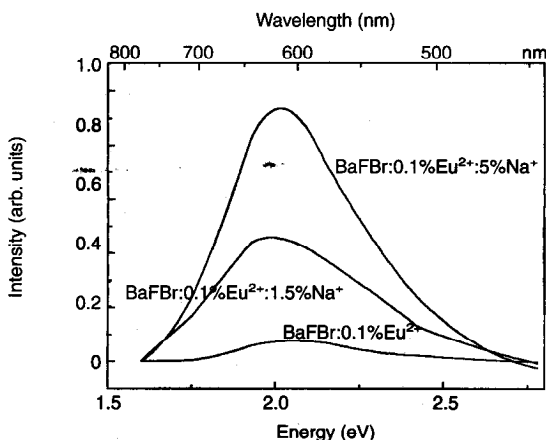


Figure 1. PSL spectrum of BaFBr:Eu<sup>2+</sup> and BaFBr:Eu<sup>2+</sup> with NaF doping, X irradiated at 300 K.

(563 nm) and excitation spectra (Figure 2) appeared after X irradiation of BaFBr:Eu<sup>2+</sup>. These are ascribed to F(F<sup>-</sup>) and F(Br<sup>-</sup>) centres<sup>(3)</sup>. The doping with Na<sup>+</sup> causes a broadening of the band at 2.2 eV (563 nm) on the lower energy side to about 1.99 eV (621 nm). The absorption bands are shifted, like the PSL peak, to 1.99 eV for BaFBr:Eu<sup>2+</sup>:5%Na<sup>+</sup> after X irradiation at room temperature.

## DISCUSSION

BaFBr:Eu<sup>2+</sup> like PbFCl has matlockite structure: with the fluorine layers and the double layers of bromine separated by the barium layers, and the Eu<sup>2+</sup> ions replace the Ba ions in a random way. The luminescence and

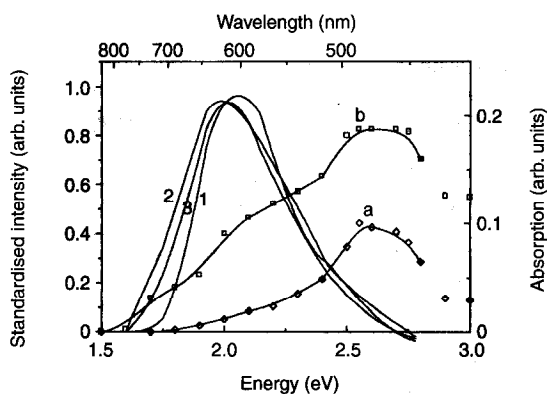


Figure 2. Normalised excitation spectra of Eu<sup>2+</sup> luminescence PSL spectra of BaFBr:Eu<sup>2+</sup> (curve 1), BaFBr:Eu<sup>2+</sup> + 1.5% NaF (2) and BaFBr:Eu<sup>2+</sup> + 5% NaF (3) and absorption spectra of BaFBr:Eu<sup>2+</sup> (a), BaFBr:Eu<sup>2+</sup> + 5% NaF (b). Spectra measured at room temperature.

## REFERENCES

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storage mechanisms of BaFBr:Eu<sup>2+</sup> phosphors have been the subject of several studies; but the exact mechanism of the PSL process is still not very clear. There are few models which describe the PSL process in BaFBr:Eu<sup>2+</sup>. All models identify F centres as electron traps. The electron is excited to the conduction band leaving the holes in the valence band on X irradiation of this material. The free electrons are trapped both by the fluorine or bromine anion vacancies making F(F<sup>-</sup>) and F(Br<sup>-</sup>) centres (the absorption peaks at 2.65 eV and 2.2 eV on Figure 2, respectively). The F(F<sup>-</sup>) centres do not play any role in the PSL process of BaFBr:Eu<sup>2+</sup><sup>(3)</sup>. The annihilation of F(Br<sup>-</sup>) centres during photostimulation is radiative, since the electron-hole recombination in this case takes place near the Eu<sup>2+</sup> sites. The above conclusions were arrived at on the basis of analogy with alkali halides. The replacement of Ba<sup>2+</sup> ions by the small percentage of Na<sup>+</sup> results in the generation of charge compensated vacancies of Br<sup>-</sup> at NaF doping of BaFBr:Eu<sup>2+</sup>. The F<sub>A</sub>(Br<sup>-</sup>, Na<sup>+</sup>) centres are produced after X irradiation at room temperature. The optical absorption band at 2.2 eV (563 nm) of the F<sub>A</sub>(Br<sup>-</sup>, Na<sup>+</sup>) centres is broadened to lower energy, in contrast with the regular F(Br<sup>-</sup>) centres, by about 0.2 eV (Figure 2). This is in agreement with the red shift of the PSL spectra of BaFBr:Eu<sup>2+</sup>:Na. Apparently, the F<sub>A</sub>(Br<sup>-</sup>, Na<sup>+</sup>) centres are dominant in the PSL spectrum at low energy (Figure 2). Possibly the increase of photostimulated luminescence is due to the presence of charge compensating bromine vacancies that lead to the creation of more F centres.

In conclusion, the Na<sup>+</sup> doping leads to the formation of F<sub>A</sub>(Br<sup>-</sup>, Na<sup>+</sup>) centres, a photostimulation red shift, and an intensity increase. Possibly, the doping by other alkali impurities (K, Rb, Cs) will also produce more efficient BaFBr:Eu<sup>2+</sup> phosphors.