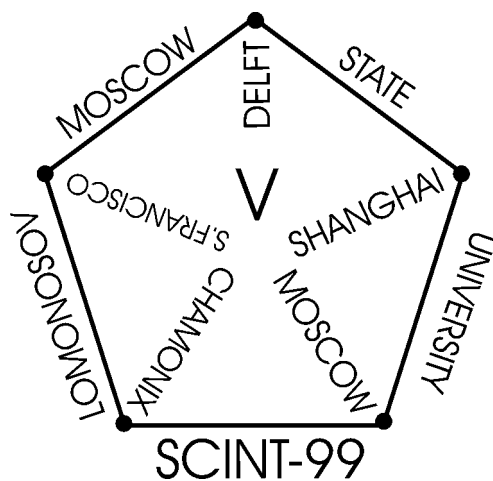


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The Influence of Alkali Impurities on the BaFBr:Eu²⁺ Photostimulated Luminescence.

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Abstract. The X-ray storage phosphor BaFBr:Eu²⁺ doped with alkali impurities (Na⁺, K⁺, Rb⁺) gives a photostimulated spectrum shifted to lower photon energies. The photostimulation luminescence intensity considerably increases compared to BaFBr:Eu²⁺ upon room-temperature X-irradiation. This red-shift of the photostimulation spectrum is caused by formation of F_A centers on the Br⁻ sublattice as electron traps.

Keywords: BaFBr:Eu²⁺, storage phosphors, photostimulated luminescence, F-center.

Introduction

Barium fluorobromine doped with Eu²⁺ 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 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 Eu²⁺ at 390 nm. It is known that doping with some impurities (for example Ca²⁺, Sr²⁺) 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 [1,2]. This paper reports the redshift of photostimulation spectrum for BaFBr:Eu²⁺ crystals with alkali doping (Na⁺, K⁺, Rb⁺).

Experimental

For the PSL measurements we prepared undoped BaFBr:Eu²⁺ crystals and those doped with varied concentrations of NaF, KF, RbF. The crystals were grown with the Shteber method in a graphite crucible in helium-fluorine atmosphere in order to reduce oxygen contamination. Stoichiometric mixtures of BaBr₂ and BaF₂ were used. All samples were doped with 0.1 mole % of Eu²⁺.

For the PSL measurements the samples were irradiated with an X-ray source (30 kV, 10 mA) for 3 min. at room temperature. Low-energy X-rays were filtered out with an Al filter (thickness 1 mm). The excitation spectra were performed with a MDR12 grating monochromator and a halogen lamp. The light from a halogen lamp passed through an optical filter allowing only wavelengths longer than 500 nm to be transmitted. This was necessary to separate the stimulating light from Eu²⁺ emission. The UV luminescence was detected by a FEU106 photomultiplier through an optical filter appropriated for Eu²⁺ emission. The absorption spectra were measured in the visible and ultraviolet regions with a "Specord UV VIS" apparatus. For the absorption investigations, X-irradiation was carried out at RT (40kV, 40 mA, 20 min).

Figure 1 shows the PSL spectra of undoped BaFBr:Eu²⁺ and BaFBr:Eu²⁺ with alkali doping (2% K⁺, 2%Rb⁺ and 1.5%Na), X-irradiated at room temperature. In undoped BaFBr:Eu²⁺ the prominent peaks of the PSL spectrum at 2.18eV and 2.45eV were observed.

Upon 2% K and 2% Rb doping, the intensity of the PSL peak at 2.18 eV is increased by a factor of about 2. Moreover, in the case of 2% Rb doping the PSL peak was redshifted from 2.18 to 2.09 eV. Best results were obtained for sodium doping. Upon 1.5% Na doping the intensity of the PSL is increased by a factor of 12 in contrast to undoped samples; the PSL peak shifted to 2.06 eV.

The results for BaFBr:Eu²⁺ with various alkali doping are listed in table 1:

Table 1.

Storage phosphor	PSL peak position (ev)	Redshift of PSL spectrum (eV)	PSL intensity ratio of alkali doped to undoped phosphors
BaFBr:0.1%Eu ²⁺ :5%Na ⁺	2.06	0.08	13
BaFBr:0.1%Eu ²⁺ :4%K ⁺	2.06	0.04	4
BaFBr:0.1%Eu ²⁺ :2%Rb ⁺	2.09	0.06	2
BaFBr:0.1%Eu ²⁺	2.18	0	1

An increased impurity concentration leads to an increased PSL intensity. The largest PSL intensity is obtained for 5% NaF doping; the peak intensity is increased by a factor of 13.

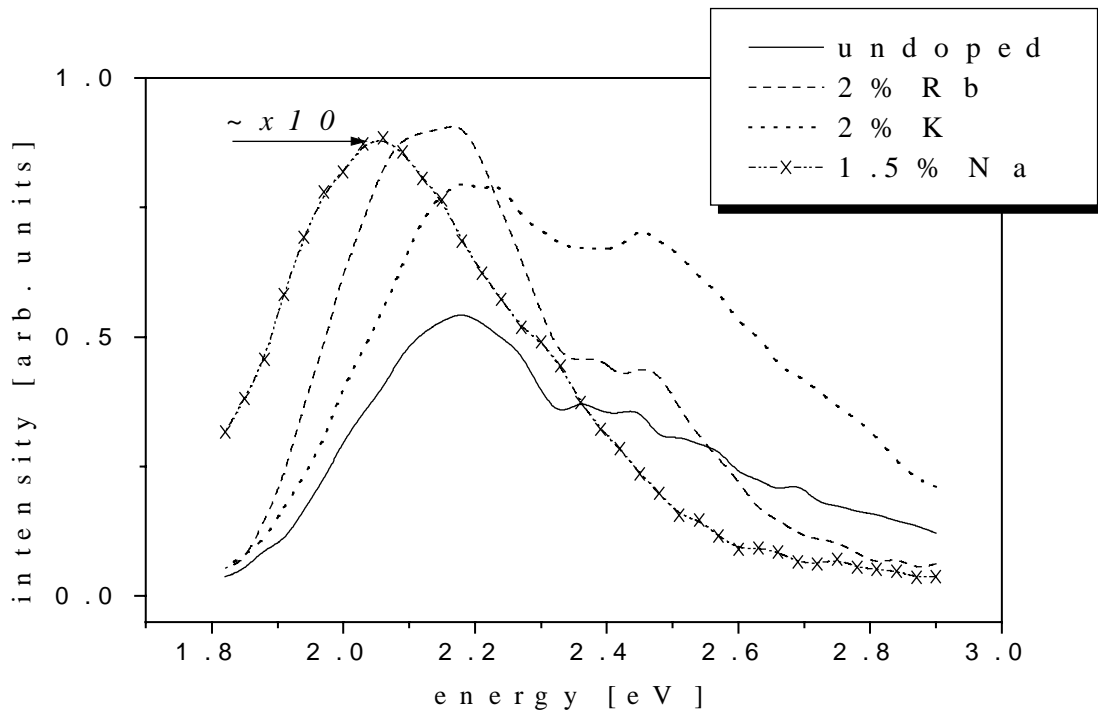


Fig1. PSL spectra of undoped BaFBr:Eu²⁺ and BaFBr:Eu²⁺ doped with various alkali ions (2%Rb, 2%K, 1.5%Na), X-irradiated at 300K. The PSL intensity of BaFBr:Eu²⁺:1.5%Na (the curve with cross (x)) is scaled up by a factor of 10.

The absorption bands at 2.65 eV and 2.2 eV and excitation spectra (fig.2) appeared after X-irradiation of BaFBr:Eu²⁺. They are ascribed to F(F⁻) and F(Br⁻) centers [3]. The doping with Na⁺ (or other alkali impurities) causes a shift of the PSL band at 1.98 eV to lower energies of about 1.9 eV. The absorption bands are shifted, as the PSL peak, to 1.99eV for BaFBr:Eu²⁺:5%Na⁺ after X-irradiation at room temperature.

An increased impurity concentration leads to a decreased stimulation energy. The stimulation energy is the energy required for the readout of the active centers. The stored energy is released faster in BaFBr:Eu²⁺ with alkali doping then in undoped BaFBr:Eu²⁺, by using the same intensity for the excitation light.

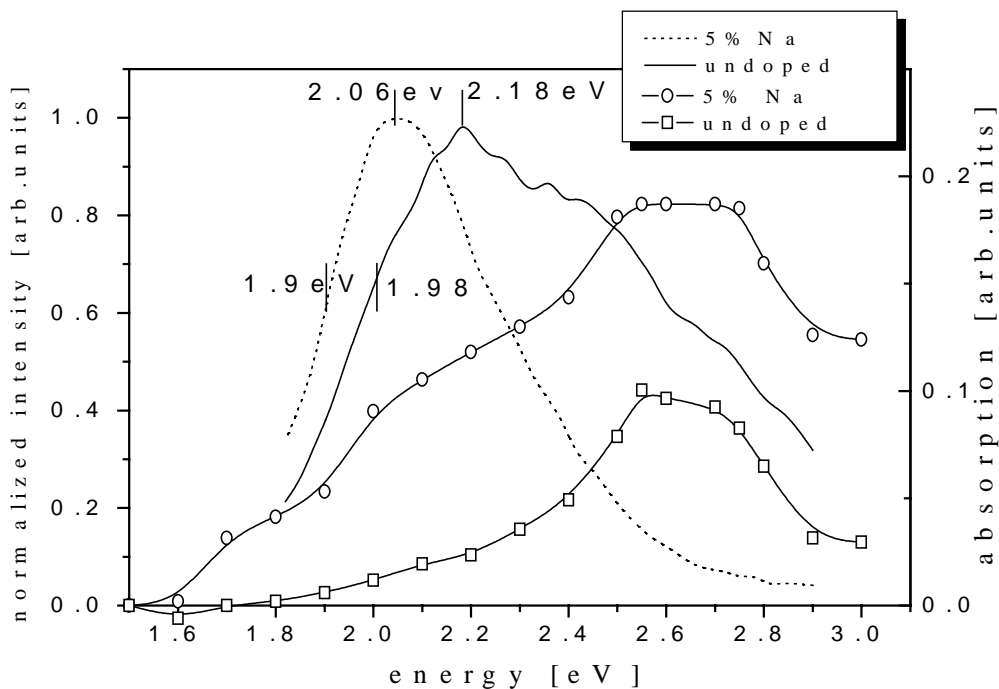


Fig.2. Normalized PSL spectra of BaFBr:Eu²⁺ and BaFBr:Eu²⁺+5%NaF; absorption spectra (the curves with the squares and circles) of BaFBr:Eu²⁺ and BaFBr:Eu²⁺+5% NaF. Spectra measured at room temperature.

Discussion

BaFBr:Eu²⁺ like PbFCl has matlockite structure: the fluorine layers and the double layers of bromine are separated by the barium layers. The doped Eu²⁺ ions replace Ba ions. The luminescence and storage mechanisms of BaFBr:Eu²⁺ 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:Eu²⁺ [4,5]. All models identify F centers as electron traps. The electron excites 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⁻) and F (Br⁻) centers (the absorption peaks at 2.65 eV and 2.2 eV on fig.2, respectively). The F (F⁻) centers do not play any role in the PSL process of BaFBr:Eu²⁺ [3]. The annihilation of F (Br⁻) centers during photostimulation is radiative, since the electron-hole recombination in this case takes place near the Eu²⁺ sites. The above conclusions were derived in analogy to alkali halides. The substitution of Ba²⁺ ions by the small percentage of alkali impurities results in the generation of charge compensating Br⁻ vacancies caused by alkali doping of BaFBr:Eu²⁺. The F_A(Br⁻, Na⁺) 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 (fig.2). This is in agreement with the red shift of the PSL spectra of BaFBr:Eu²⁺:Na. Apparently, the F_A(Br⁻, Na⁺) centers dominate in the PSL spectrum at low energies (fig.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 centers. It is not clear why the sodium impurity leads to a better redshift than the potassium or the rubidium doping. One reason could be that the Na⁺ ions have a smaller ionic radius (Na⁺ - 0.98Å^o, K⁺ - 1.33Å^o, Rb⁺ - 1.49Å^o [6]). The size of the Na-ion is smaller than the size of the replaced Ba-ion. Due to lattice relaxation the ions surrounding the F_A(Br⁻, Na⁺)-center move slightly inwards to the vacancy. Thus, they are reducing the diameter of the vacancy. That leads to a broadening of the absorption band of the F(Br⁻) center at 2.2 eV to 1.99 eV for the F_A(Br⁻, Na⁺) centers.

In conclusion, the alkali doping leads to the formation of $F_A(Br^-)$ centers, a photostimulation redshift, and an intensity increase. The best results were obtained for sodium impurity, but the potassium and rubidium doping greatly improves the PSL properties of $BaFBr:Eu^{2+}$ as storage phosphor too.

References

1. C. Dietze, T. Hangleiter, P. Willems, et. al., Appl. Phys. **80(2)** (1996) 1074-1078
2. S. Schweizer, P. Willems, P. J. R. Leblans, L. Struye, and J.-M. Spaeth, J.Appl.Phys.**79(8)** (1996) 4157-4165
3. A. R. Lakshmanan, Phys. Stat. Sol. **A 153** (1996) 3-27
4. F. H. Koschnik, J.-M. Spaeth, R. S. Eachus, W. G. McDugle, and R. H. D. Nuttal, Phys. Rev. Letters **67** (1991) 3571
5. H. H. Ruter, H. von Seggern, R. Reininger, and V. Saile, Phys. Rev. Letters **65** (1990) 2438
6. I. A. Parfianovich, E. E. Pensina, The electron color centers in the ionic crystals, ISU, Irkutsk, 1977