

EU²⁺ PHOTOIONIZATION IN BAFBR CRYSTALS

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Abstract. The absorption, excitation spectra and creation of thermoluminescence spectra of BaFBr and BaFBr:Eu²⁺ in vacuum ultraviolet region 5-10 eV at temperatures 6-300 K were studied. The decay of emission as well as the influence of additive coloration on Eu²⁺ absorption were studied. The oxygen-free BaFBr crystals as well as BaFBr contained around 100 and 1000 ppm of Eu²⁺ were studied.

A new excitation band at 6.7 eV, related with europium, was observed in spite of absence of the band in absorption spectrum. The decay of Eu²⁺ luminescence at 6-8 eV excitation is several times longer than the decay of 5d¹4f⁶-4f⁷ transitions (or simply 5d-4f). The decay time increased from one-two μs at room temperature to 6.8 μs at 6 K. The creation of V_k peak of thermoluminescence was observed when irradiated the crystal with vacuum ultraviolet photons above 6 eV. Creation of V_k and Eu⁺ centers followed by 6-7 eV irradiation were proposed.

INTRODUCTION

X-ray storage phosphors are currently used for digital medical radiography. The best-known storage phosphor is Eu-doped BaFBr. Upon x irradiation defects are formed to allow a readout process of the stored x-ray information. The electron- and hole-trap centers are involved in the image formation process. It is not clearly known how the energy is transferred to the activator Eu²⁺ which emits at 390 nm. The stimulation processes leading to the recovery of the stored image are of significant interest. The role of Eu in photostimulation process is not clear yet. The transformation of Eu²⁺ to Eu³⁺ during x-ray irradiation was assumed (1,2). However the appearance of Eu³⁺ luminescence induced by x-irradiation was not observed by other investigators. The triple photostimulable defect consisted of Eu²⁺, some hole and F centers was proposed to be created by x-irradiation of BaFBr:Eu (3,4).

Usually BaFBr crystals contain a large amount of oxygen. To investigate the Eu related processes only, we prepare the oxygen-free BaFBr-Eu crystals and study the Eu²⁺ luminescence and photoionization by vacuum ultraviolet photons.

EXPERIMENTAL

The crystals were grown in helium fluorinated atmosphere (5). No traces of oxygen absorption or photoluminescence bands were found in crystals. Undoped crystal as well as crystals contained Eu²⁺ ions with 4.5 eV absorption coefficient near 10 and 100 cm⁻¹ were studied. Using known calibration constant for determining Eu²⁺ concentration in alkali halides (6), the europium concentration in our BaFBr crystals can be estimated as 100 and 1000 ppm respectively. We designate these crystals as low and highly doped crystals. Usual Eu concentration in commercial BaFBr:Eu is a few hundreds of ppm.

Decay of photoluminescence was measured by single photon technique using CAMAC time-to-digital converters or by the usual technique using CAMAC analog-to-

digital converter. The spectra in 4-10 eV region were measured with vacuum monochromator VMR2. In thermoluminescence studies the crystal was irradiated by light of VMF25 a 25W hydrogen discharge lamp dispersed by VMR2 monochromator a few minutes at 78K. The creation spectra were corrected on spectral response of monochromator and discharge lamp.

The additive coloration was done in calcium vapor in vacuum at temperature 800°C during 1 hours. The pieces around 10x10x5 mm were dark blue after coloration. Piece was cut to desirable size and annealed at 500°C before measurement.

RESULTS

The excitation spectra for Eu^{2+} emission show bands at 4.5 eV, 5.8 eV, which is known as 4f-5d bands, and 6.7 eV (Fig.1). The 6.7 eV band was not observed in BaFBr:Eu at room temperature earlier (7,8) possibly due to presence of oxygen. The dips at 7.6, 8.1 (see Fig.1)

well coincide with exciton peaks at 7.64, 8.15 eV observed in absorption spectra of BaFBr thin film (9). The excitation spectrum of Eu luminescence in exciton region 7-8 eV are coincide with those of exciton 4.2, 5.15 eV bands, which were observed in pure crystals and lightly Eu doped crystals (Fig.1). The exciton luminescence was suppressed in crystals heavily doped with Eu.

The luminescence excited within 4-6 eV region shows a known 5d-4f Eu^{2+} exponential decay (10) with lifetime decreased from 700 ns at room temperature to 550 ns at 78 K and below. The Eu^{2+} luminescence lifetime becomes to be equal to a few microsecond excitation with photons above 6 eV (Fig.2).

The decay of Eu^{2+} luminescence was sufficiently different when excited in 4-6 eV (4f-5d region), 6-7 eV (photoionization region), 7-8 eV (exciton region) and above 8 eV (band-to-band region) (Fig 2). It seems that the long components near 100 μs at 6.3 K at 7.2 and 8.2 eV excitation belongs to the 5.1 eV excitons with similar decay time. The rise time in 0.1-0.5 μs range was observed for excitation in the range of exciton and band to band transitions (see inset on Fig.2). The decay at 6.5 eV excitation was exponential within two decades of magnitude and accompanied by weak long time phosphorescence. Additionally at low temperatures the 0.6 μs component was appeared.

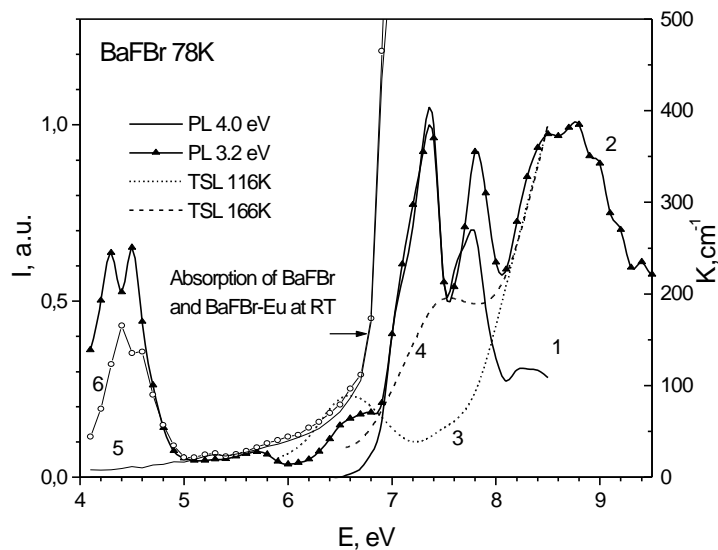


Fig.1 Absorption (5,6), excitation spectra of 3.2 eV Eu^{2+} (2) and 4.3 eV exciton luminescence (1) in BaFBr-Eu crystal at 78K as well as creation spectra of thermally stimulated luminescence peaks at 116 K (3), 166 K (4).

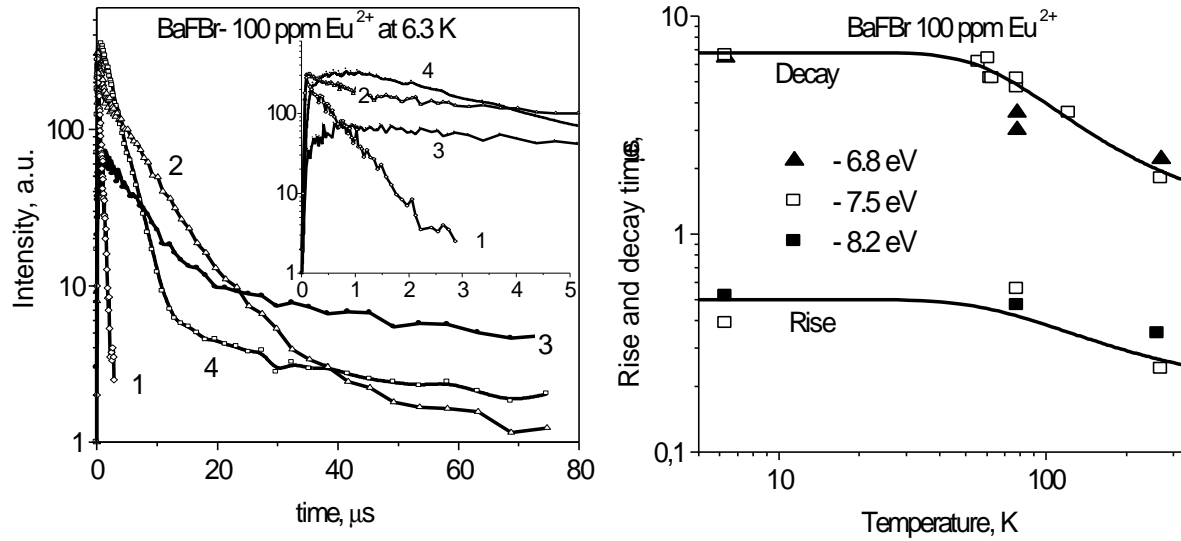


Fig.2 Decay of 3.2 eV Eu^{2+} luminescence of BaFBr:Eu at 6.3 K irradiated by 4.6 eV (1), 6.7 eV (2), 7.2 eV (3) and 8.2 eV photons. Inset shows the initial stage of decay curve.

Fig.3 Rise and decay times of 3.2 eV Eu^{2+} photoluminescence in low doped BaFBr:Eu.

The lifetime of microsecond component at 6.5, 7.2 eV excitation increased with decreasing temperature (Fig.3), except the lifetime of 8.2 eV excitation, which is nearly constant. The dependence can be described with following assumption. The decay of Eu^{2+} luminescence after 6-8 eV excitation depends on population rate of Eu 5d excited level. It seems that the 5d level can be populating from two states, one of them dominates below a liquid nitrogen temperature while the other prevails above room temperature. Observed dependence especially for 7.2 eV excitation can be satisfactory explained by the following:

$$\tau(T)^{-1} = \tau(\text{low } T)^{-1} + \exp(-E/kT) * \tau(\text{high } T)^{-1} \quad [1]$$

The decay curve was fitted with parameters: $\tau(\text{low } T) = 6.8 \mu\text{s}$, $\tau(\text{high } T) = 1.3 \mu\text{s}$, $E = 0.017 \text{ eV}$. More attractive physical picture is that the 5d excited states populate from one state with tunnel transitions at low temperatures and transitions over potential barrier at high temperatures.

The creation thermoluminescence peaks at 116 K and 166 K were observed after irradiation with photons with energies above 6 eV. At 6-6.8 eV region of photon energies only sharp 116 K peak was observed with halfwidth 11 K. At higher photon energy the 116 K peak became wider with halfwidth 16 K and second peak was appeared. Both thermostimulated luminescence peaks show an increase above 7.8 eV. This growth undoubtedly related with band to band transition and creation of free electrons and holes. The creation spectrum of 116 K peak shows a maximum at 6.6 eV while peak 166 K shows maximum at 7.5 eV. The shape of 116 K thermostimulated luminescence peak was satisfactory simulated with an activation energy 0.28 eV and frequency factor $1.3 * 10^{11} \text{ s}^{-1}$ (Fig.4).

We try to search an Eu^{3+} emission after 6.5 eV irradiation at 78K. The sharp red lines, which can be attributed to Eu^{3+} , in 2-1.8 eV region under excitation 3-2 eV light

was not found.

The additively colored BaFBr show a several absorption bands in vicinity of F bands. After annealing at 500°C and quenching to room temperature the F(Br) bands only was observed in absorption spectra. To prevent the F-center aggregation we irradiated the crystal into F-band at 80K. F-center photobleaching lead to decrease the F-band by 2-3 times, while several bands at both sides of F band appeared. Upon heating the F-band was recovered around 120-150K. After heating up to room temperature the F band was almost completely recovered in pure BaFBr, while in BaFBr-1000 ppm Eu^{2+} about 20% of F band was not recovered yet. These facts possibly point on electron capturing by Eu^{2+} and creation Eu^+ stable at room temperature. Taking into account difference in oscillator strengths of Eu and F bands one can estimate that a few percent of initial Eu^{2+} can transform to Eu^+ . No additional absorption specific for Eu-doped crystal, which can be related with Eu^+ was observed.

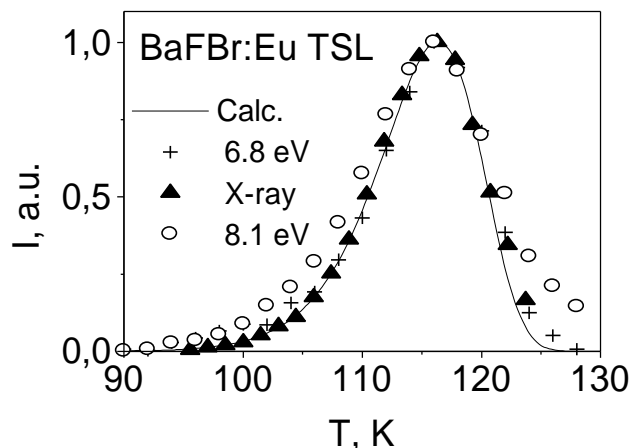


Fig.4 Thermostimulated luminescence curves of low doped BaFBr:Eu after vacuum ultraviolet and x-ray excitations at 78 K. Calculated curve fitted with parameters: $E=0.28$ eV, $\nu=1.3 \cdot 10^{11}$ s⁻¹

DISCUSSION

The results show that after excitation into 6.7 eV band the charge (electron or hole) from Eu^{2+} ion go away from europium and trap onto at least two types of traps. The shallow trap with depth near 18 meV lead to elongation of Eu^{2+} luminescence. Sufficiently deeper traps capture a few percent of all charges. This process leads to appearance of 116 K thermostimulated luminescence peak. The largest glow peak 116 K in x-irradiated BaFBr crystals (Fig.4) can be assigned to recombination of moving self trapped holes (V_k centers) with trapped electrons. The V_k centers are diffuse above about 120 K (11). The shape of peak of thermoluminescence 116 K was the same with x-irradiation and 6.8 eV irradiation (see Fig.4). So it is very reasonable that the V_k centers as well as trapped electrons are created by 6-7 eV irradiation of BaFBr:Eu²⁺ at 78 K.

Under the excitation of BaFBr-Eu²⁺ crystal into exciton region 7-8 eV the more widen 116 K thermoluminescence peak (see Fig.4) and new peak 166 K of thermostimulated were observed. It seems V_k center created rather far from trapped electron. In this case some part of self-trapped holes can be trapped by some defects during heating. One can assume the 166 K peak to elaboration of V_{kA} type centers. Possibly the 7-8 eV photons create a more energetic hole and hole runs a more distance from Eu before self-trapping.

Generally two photoionization reactions are possible:





The observation of V_k glow peak after 6.7 eV irradiation as well as absence of Eu^{3+} luminescence pointed out that the second reaction is performed. Transitions from Br 4p-zone to Eu lead to creation of Eu^+ and V_k centers. The additional electron has to be captured on 6s Eu orbital. The ground state of Eu^+ ion have to lie a several eV higher than those of Eu^{2+} due to its lower ionization potential. Therefore, the 4p Br - 6s Eu transition energy has to be slightly less than the energy of exciton transitions in BaFBr.

The mechanism of luminescence at 6.7 eV excitation can be explained as follows. After 6.7 eV photon absorption the Eu^+ and nearest V_k centers created. The electron tunneled from Eu^+ to V_k center and recombine with it. The energy of recombination transferred to Eu^{2+} and excites it. Intensity of tunnel recombination of randomly distributed trapped electrons with V_k centers in alkali halides usually following the hyperbolic decay law. In the case of BaFBr:Eu it seems that the most of V_k centers created on nearest position from Eu^+ , so the decay is exponential on the first stage (see Fig.2).

Similar type of transitions, followed by creation of self trapped holes, are known for CsI doped with Pb or Tl impurity (12,13). The impurity ions with trapped electrons as well as ESR of V_k centers were observed (12). The V_k center thermoluminescence peaks were observed also (13). It was concluded that the higher the excitation energy of photons, the longer the trapped electron - V_k center distances (13). Also the formation of V_k centers by ultraviolet light excitation in alkali iodides and bromides containing MnO_4^- ions was observed (14).

Eu^{2+} ion was assumed to capture the electron during additive coloration or x-ray irradiation of NaCl, KCl, KI. The of Eu^{2+} emission in KI after treatment was decrease several times (15) but the Eu^+ ion was not observed directly. The capture of electron by Eu^{2+} and creation of Eu^+ is more favorable in alkali halides than in crystals with double charged cations. Possibly this is a reason of rather low concentration of Eu^+ in additively colored BaFBr:Eu. Caption of electron by Eu^{2+} ion and following recombination of V_k with Eu^+ accompanied by emission of 5d-4f of Eu^{2+} was discussed to be rather probable in x-irradiated KBr:Eu (16). Thermoluminescence of crystals doped with Eu^{2+} was observed after irradiation by UV light when the photon energy is insufficient to induce band to band transitions (17-19). All these results point on possibility of the Eu^+ creation in different crystals.

CONCLUSION

The experimental results show that V_k centers and possibly Eu^+ are created in BaFBr: Eu^{2+} during irradiation by 6-8 eV photons. The significance of Eu^+ centers for photostimulated luminescence need to be investigated.

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