

# Kinetics of Photostimulated Luminescence in BaFBr:Eu

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## ABSTRACT

Europium-activated barium halides, especially BaFBr:Eu are used as photostimulable x-ray phosphors in computerized radiography. The kinetics of the photostimulated luminescence (PSL) has been investigated. The measurements support the mechanism of PSL involving  $F^+ \leftrightarrow F$  and  $Eu^{2+} \leftrightarrow Eu^{3+}$  centers as proposed by Takahashi *et al.* (1, 2). Values for the cross section of optical excitation of trapped electrons and for the calculated oscillator strength have been determined.

Conventional x-ray radiographs usually are produced by combination of a photographic film and an intensifying screen. The screen converts the x-ray energy into visible light and an image is formed on the exposed film. This technique is hampered by the limited latitude of the film.

Superior images have been reported by using computerized radiography (3). This system utilizes an imaging plate which consists of the photostimulable phosphor BaFBr:Eu (4). During x-ray exposure part of the electrons and holes created in the phosphor by the x-ray is trapped. This charge is subsequently read out by scanning the imaging plate with a focused He/Ne laser beam. During readout the intensity of the resulting blue  $Eu^{2+}$  emission (5) is proportional to the trapped charge.

A mechanism for the photostimulated luminescence (PSL) in europium-activated barium halides has been proposed by Takahashi *et al.* (1, 2). Based on optical, ESR, and photoconductivity measurements, they concluded that during x-ray irradiation, part of the electrons are trapped at halide vacancies forming the so-called F centers, and that  $Eu^{2+}$  ions are converted into  $Eu^{3+}$  ions. Upon stimulation, the electrons are promoted to the first excited state of the F centers and subsequently trapped by neighboring  $Eu^{3+}$  centers. The resulting excited  $Eu^{2+}$  ions decay to the ground state by photoemission (5).

A definite improvement in performance of this computerized radiography technique can be achieved if the readout time is shortened. For a certain laser power density, the readout time depends on the cross section for optical excitation of the trapped electrons. To determine the value of the cross section, the kinetics of PSL in BaFBr:Eu has been investigated. Our measurements support the mechanism of PSL as proposed by Takahashi *et al.* (1, 2). Values for the optical cross section and for the calculated oscillator strength have been determined. Large improvements in these values for europium activated barium halides are shown to be improbable.

## Experimental

BaFBr:Eu phosphors activated with 0.05-1 mole percent Eu and coactivated with 0.1-1% Al, Ga, Li, Na, Sc, Y, La, Gd, or Lu were made by firing intimate mixtures of raw materials in a  $H_2/N_2$  atmosphere at 700°C. The phosphors were ground and refired. Before firing, the materials were dried at 200°-300°C. Care was taken to avoid oxygen during firing.

Infinitely thick phosphor powder layers were irradiated in a Radifluor 150 x-ray unit (Torr X-ray Company). The peak voltage was 120 kV, the current 3-5 mA, and the irradiation time 0.2-12 min.

The photostimulated luminescence was transmitted through a monochromator and fed into a photon counting system. The data could be displayed on a multi-channel analyzer (Canberra, 35+) and stored on floppy disk. PSL excitation spectra were measured at low excitation density to prevent significant depletion of stored energy during the measurements. This point was checked by assuring that the PSL spectra were independent of the scan direction of the excitation monochromator.

## Results and Discussion

PSL excitation spectra of the europium-activated BaFBr phosphors were independent of both europium content and the type and concentration of additional impurity ions. In mixed barium halides such as BaFBr:Eu, the PSL spectrum is equal to the sum of  $F(F^-)$  and  $F(Br^-)$  absorption spectra (1).

Any impurity ion hardly influences the optical properties of the F centers and hence there is hardly any change in the shape of the PSL spectra. The addition of impurity ions only changes the concentration of F centers and hence the amount of stored energy.

To investigate the kinetics of the readout process, the decay of the PSL intensity with time was measured after x-ray irradiation under continuous excitation with stimulating light. The decay was measured as a function of x-ray doses, wavelength and intensity of stimulating light and temperature (100-300 K). The decay is characterized by the  $1/e$  decay time.

The measurements were done at low x-ray doses where the reflection coefficient of the phosphor did not significantly change upon x-ray irradiation. Additional absorption of the stimulating light could then be disregarded. The intensity of the stimulating light is constant in time.

Under these irradiation conditions, the photostimulated peak intensity and the amount of stored energy are proportional to the x-ray doses. However, the decay time ( $\tau_{1/e}$ ) is constant.

The decay time of the photostimulated luminescence as a function of the intensity of stimulating He/Ne radiation at 633 nm is presented in Fig. 1 on a double logarithmic scale.

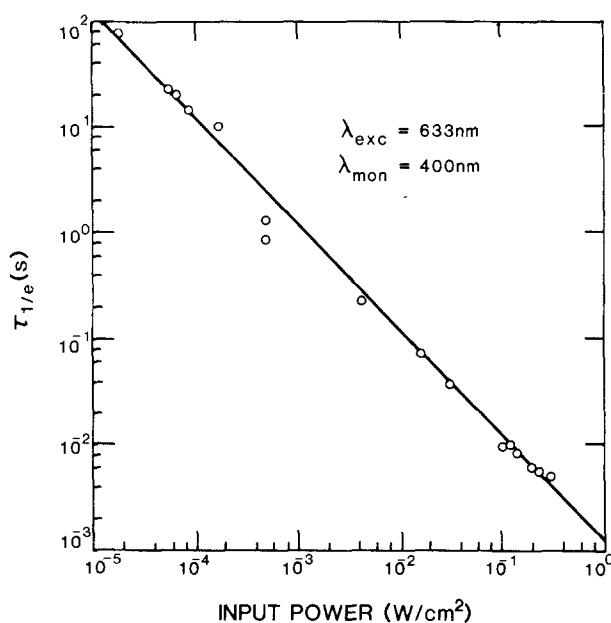


Fig. 1. Decay rate of photostimulated  $Eu^{2+}$  luminescence of x-ray irradiated BaFBr:Eu plotted on a double logarithmic scale as a function of excitation density. The luminescence was stimulated with He/Ne laser light of 633 nm. The monitor wavelength was 400 nm.

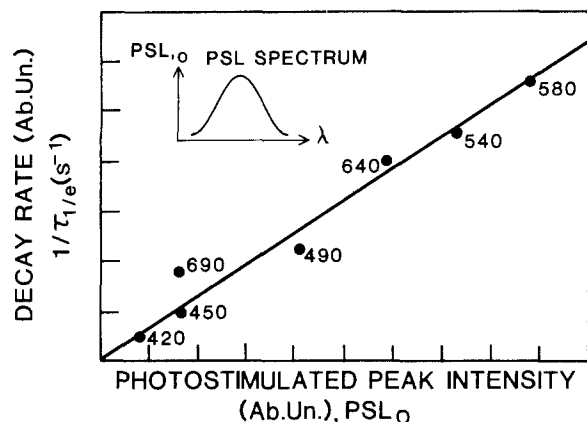


Fig. 2. Decay rate of photostimulated luminescence of x-ray irradiated BaFBr:Eu plotted as a function of photostimulated peak intensity. Values of wavelengths of stimulating light are indicated (nm). The photostimulated peak intensity is obtained from the PSL excitation spectrum.

mic scale. Similar results were obtained for other wavelengths of stimulating light. A linear relationship is obtained with slope equal to unity. The decay rate is proportional to the excitation density. This result combined with a decay rate independent of the x-ray doses suggests that the decay rate can be given by

$$\tau_{1/e}^{-1} = \sigma_0 I \quad [1]$$

where  $I$  is the optical excitation density (photons/cm<sup>2</sup> s) and  $\sigma_0$  is the optical excitation cross section (cm<sup>2</sup>).

As mentioned above, the decay rate for all stimulation wavelengths depends on the optical cross section and not on the density of states. This is verified by measuring the decay rate as a function of the wavelength of the stimulating light. The result is presented in Fig. 2 where the decay rate is plotted as a function of photostimulated peak intensity,  $PSL_0$ . The photostimulated peak intensity is obtained from the PSL excitation spectrum. As shown in Fig. 2, a linear dependence is obtained which means that the decay rate is given by

$$\tau^{-1} \propto PSL_0$$

and

$$PSL_0 = \sigma_0 IT \quad [2]$$

where  $T$  is the peak concentration of electrons trapped at

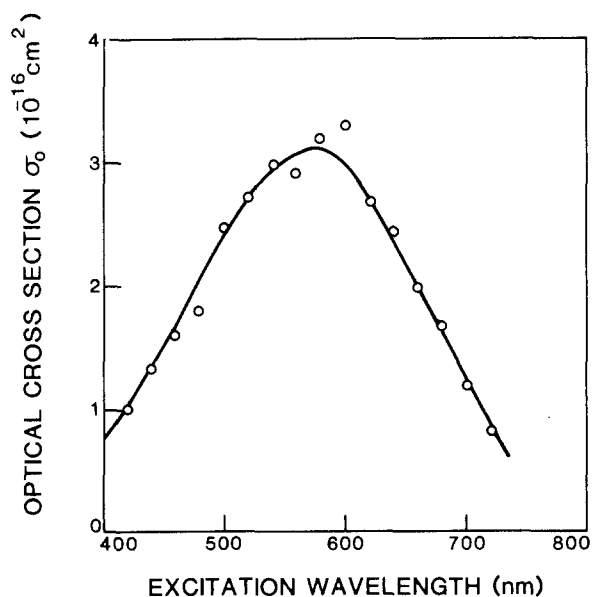


Fig. 3. Cross section for optical excitation of electrons to the first excited states of F(Br<sup>-</sup>) centers in BaFBr:Eu plotted as a function of wavelength of stimulating light.

F centers. In these experiments the excitation density,  $I$ , was equal for all stimulation wavelengths. Combination of Eq. [1] and [2] then implies that a change in light output in the PSL excitation spectra caused by a change in wavelength of the stimulating radiation is due to a change in cross section of only one type of color center. As indicated by the PSL spectrum, in the present phosphors mainly F(Br<sup>-</sup>) centers are present (1) which is in good agreement with a [F<sup>-</sup>]/[Br<sup>-</sup>] ratio larger than unity by about 5% as determined by chemical analysis. Also for the present phosphor, significant hole burning effects could not be detected; the PSL spectrum did not change during readout.

Determination of the optical cross section from decay rate measurements using Eq. [1] requires an estimation of the excitation density,  $I$ . Due to light scattering in the phosphor layer, the excitation density strongly varies with the depth in the phosphor screen. However, no significant differences in decay rates of monolayers and thick powder layers have been detected. Therefore, the excitation density was taken equal to the incident photon flux, which was measured with a calibrated photodiode.

The calculated optical cross section as a function of excitation wavelength is presented in Fig. 3. The oscillator strength calculated from the integrated cross section (6) is about 1.5. This is a typical value for the investigated BaFBr:Eu phosphors. Since the maximum value of the oscillator strength can be unity, the inaccuracy in the calculated value may be due to either assumption related to the excitation power density, or to the exponential nature of the decay time. As will be discussed below, the decay is not exponential but hyperbolic.

Measurements of the decay of the photostimulated luminescence with time can be summarized in the following way. In Fig. 4 the normalized intensity is plotted on a double logarithmic scale as a function of normalized time, the time divided by the decay time. A universal function is obtained which is independent of x-ray doses, temperature and wavelength, and intensity of stimulating light. The decay of the PSL intensity with

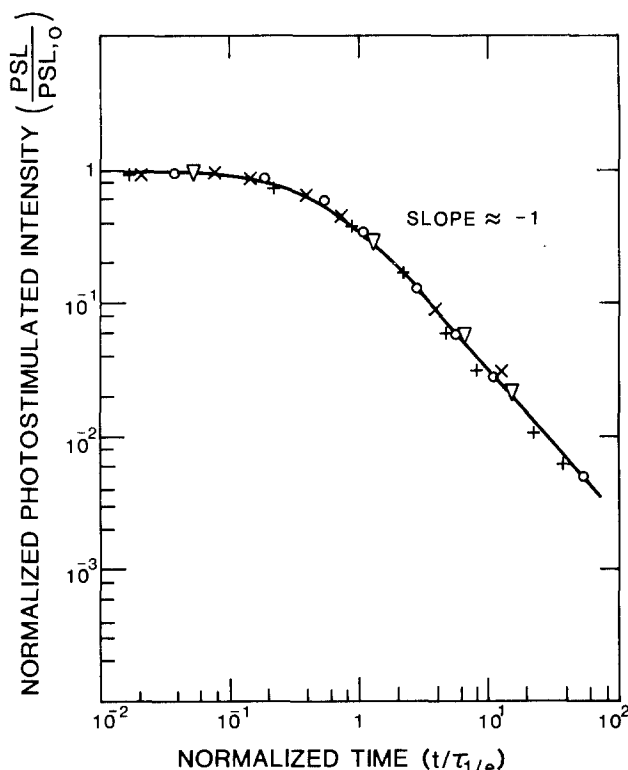


Fig. 4. Normalized photostimulated luminescence intensity of x-ray irradiated BaFBr:Eu plotted on a double logarithmic scale as a function of normalized time, the time divided by the decay time. A universal function is obtained independent of x-ray doses, wavelength and intensity of stimulating radiation and temperature between 100 and 300 K.

time is not pure exponential, but hyperbolic. The assumption of an exponential decay therefore yields values for the oscillator strength which are too high.

The decay behavior of Fig. 4 is typical for electron transfer between two types of species whose concentration decreases in time. The donors are the F(Br<sup>-</sup>) centers. Takahashi *et al.* (1) have presented experimental evidence that the acceptors are Eu<sup>3+</sup> ions which are produced from Eu<sup>2+</sup> ions upon x-ray irradiation. At high density UV excitation the characteristic Eu<sup>3+</sup> luminescence has been detected (1). They found that the intensity of the Eu<sup>3+</sup> luminescence decreased upon illumination. We have obtained similar results.

Electrons can be transferred from excited states of F centers directly to Eu<sup>3+</sup> ions if the wavefunctions of the excited states of F centers and Eu<sup>3+</sup> overlap sufficiently. At the same time, electrons can thermally be liberated from excited states of F centers into the conduction band and subsequently be captured by Eu<sup>3+</sup> ions. Upon illumination photoconductivity has been observed (1, 2) which means that at least part of electrons are promoted to the conduction band. However, the decay of the PSL was measured to be independent of temperature between 100 and 300 K, which indicates that free electrons have only a minor contribution to the PSL. We note that unambiguous conclusions require measurements at lower temperatures.

Summarizing, the value of the oscillator strength is high, of the order of unity. This high value is typical for color centers. Because the peak value of the oscillator strength is close to unity, large improvements in optical cross section for photostimulated luminescence in BaFBr:Eu phosphors are improbable.

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## Preparation of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>-Based Phosphor Powders

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#### ABSTRACT

Phosphor materials are important in cathode ray tube (CRT) and electroluminescence display technologies. Phosphor materials based on Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> garnet are used extensively because of their high optical emission intensity and long life. In this study, we prepared cerium-doped YAG powders by freeze drying of precursor solutions and by mechanically mixing the constituent oxide powders. The freeze dried powders, due to a homogeneous distribution of cations in their precursor solutions, formed the garnet phase at 1300°C, 300°C lower than that required for the constituent oxide mixtures, and they also had a higher optical emission intensity than those prepared from oxide mixtures. Furthermore, Ce-doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> powder was heat-treated in molten Li<sub>2</sub>SO<sub>4</sub> salt to increase the particle size and to give a more equiaxed particle shape such that their subsequent packing density in CRT faceplate could be increased. However, the Li<sub>2</sub>SO<sub>4</sub> molten salt treatment introduced a small amount of the distorted tetragonal phase among the cubic garnet phase and decreased the optical emission intensity.

The rapid increase in video display terminals (VDT) has generated significant interest in display technologies. Among the existing display technologies, the cathode ray tube (CRT) display is the prevailing technology in providing large area, high resolution, color display. In CRT displays, phosphor powder is deposited on the faceplate of CRT tubes and visual images are induced by the fluorescence of phosphor powder excited by electron beams. The introduction of projection displays has fostered a need for high intensity phosphors.

Phosphor powders are also used in other display technologies. For example, in electroluminescent (EL) displays, phosphor powders are placed between two electrodes and an applied electric field between the electrodes leads to electroluminescence. Both powder and thin film phosphors can be used in EL displays. However, the use of powdered phosphor has the advantage of a better control of chemical stoichiometry and crystal perfection, which are essential to good luminescent properties. The use of powdered phosphor also avoids the problem of low optical output in thin film EL displays resulting from the internal reflection between

the thin film phosphor layer and the electrode, even though recent development has increased the optical output of certain thin film devices to a level above that of powdered phosphor displays. Furthermore, a large area ( $\geq 100$  cm<sup>2</sup>) display in powdered EL technology can be achieved by depositing a uniform layer of defect-free phosphor powder between electrodes. However, such a large area structure is difficult to achieve by the existing thin film technology.

Most commercial phosphor powders, especially the garnet-based phosphors, are rather expensive because of the stringent requirements on high purity, precise stoichiometries, exact crystalline phases and controlled particle sizes and morphologies. Furthermore, the performance of CRT and EL display systems is critically dependent on the quality of the phosphor powder. Thus, it is desirable to develop preparation techniques such that phosphor powders with novel compositions, crystalline phases, and particle morphologies can be prepared to yield quality phosphor powder and to give competitive edges in display systems.

Phosphor material based on cerium-doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> was chosen for projection CRT applications because it