

Creation of Photostimulable Centers in BaFBr:Eu²⁺ Single Crystals by Vacuum-Ultraviolet Radiation

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Several experiments were performed in order to understand the creation and readout mechanisms of photostimulable (PS) centers in BaFBr:Eu²⁺ single crystals. PS centers can be efficiently created starting from 6.7 eV, i.e., the minimal energy required to excite the first valence exciton. This exciton relaxes to an e - V_k (Br₂⁻) pair. The relaxation of such a defect in the neighborhood of Eu²⁺ yields a PS center, namely, an F - H (Br₂⁻) pair. An additional decay channel of the e - V_k pair results in Eu^{2+*} emission due to the energy match between the emission of this pair and an absorption band of Eu²⁺.

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Since their introduction several years ago, erasable image plates containing powdered BaFBr:Eu²⁺ crystals have found a wide range of applications as two-dimensional x-ray detectors in medicine, physics, and biology.¹ The main advantages of this novel sensor as compared with conventional x-ray films are their dynamical range of more than 5 orders of magnitude and their fast processing time. For readout, the films are scanned by red light, mostly by a HeNe laser ($\lambda = 633$ nm). The material emits in this photostimulation process violet light ($\lambda = 390$ nm) with an intensity proportional to the absorbed x-ray dose.

Several models have been proposed for the storage mechanism. According to Takahashi *et al.*² UV or x rays ionize Eu²⁺ into Eu³⁺ and the free electrons are subsequently captured by existing Br⁻ vacancies and thus form F centers.³ A different model based on F - H pair (an F center along with an interstitial halogen ion) production as in alkali halides⁴ was suggested by von Seggern *et al.*⁵ These authors assumed that the high-energy radiation creates free excitons which subsequently decay at lattice imperfections, e.g., an Eu²⁺ ion. The decay of the trapped exciton finally generates an F - H pair. In contrast to the model of Takahashi *et al.*,³ the latter model implies that the vacancies are generated by the irradiation process itself, and that the components of the photostimulation (PS) center are in close proximity to each other.

Two different readout mechanisms have been proposed, associated with the two different storage mechanisms. In both models irradiation by visible light excites an electron trapped in an F center; emission in both models is due to the electronic transition from the $4f^{65d}$ Eu²⁺ level to the $4f^7$ ground state. The models differ in the way in which the electron is transferred from the F center to the trapped hole. Takahashi *et al.*² suggested a band model which assumes that upon excitation the elec-

tron in the F center is liberated into the conduction band and subsequently trapped by the Eu³⁺. On the other hand, de Leeuw, Kovats, and Herko⁶ and von Seggern *et al.*⁵ proposed that since the electron and hole centers are spatially correlated, the electron is transferred upon stimulation by tunneling from the relaxed excited state of the F center to the Eu³⁺ or to an Eu²⁺-hole complex.

The experiments to be described were planned to resolve the above controversy. We show for the first time that photostimulable centers can be efficiently created in the vacuum-ultraviolet (VUV) spectral region, which comprises the excitonic region and the interband transitions of the host.⁷⁻⁹ From these results we propose a model that explains both the generation of PS centers as well as the intermediate step in the photostimulation process. The model is based on the F - H pair formation mechanism proposed by Williams *et al.*^{10,11}

The experiments were carried out at HASYLAB, DESY, employing synchrotron radiation dispersed by the HONORMI monochromator¹² working at a resolution of 0.1 nm. The measurements were performed on single crystals of BaFBr doped with 500 ppm of Eu²⁺.

The reflectivity spectrum between 6 and 28 eV is displayed in Fig. 1(a). The two prominent peaks with maxima at 7.41 and 7.97 eV can be assigned to the energetically lowest excitons in BaFBr as confirmed in undoped BaFBr crystals.⁷ They correspond to the excitation of the spin-orbit-split Br⁻- $4p$ -derived valence-band electrons into bound excitonic states. A small peak in the reflectivity at the low-energy side of the excitons (at around 6.6 eV) has been observed in BaFCl and SrFCl as well by Nicklaus⁷ and is presumed to be caused by intrinsic lattice defects. The features in the energy range up to 10 eV were attributed⁷ to higher excitons. The features dominating the spectral range between 10 and 15 eV are most probably due to fluorine $2p$ excitations. The energy range between 17 and 20 eV is assigned to

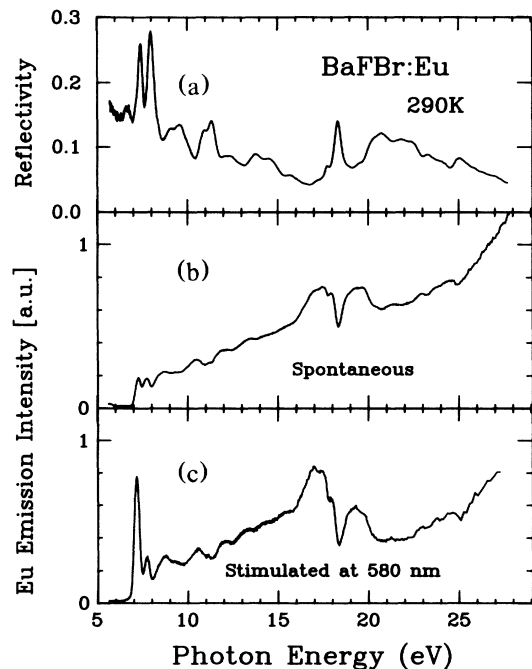


FIG. 1. (a) Reflectivity of BaFBr:Eu²⁺; (b) spontaneous and (c) stimulated emissions of Eu²⁺ ($\lambda = 390$ nm).

the core ($5p$) excitons of Ba²⁺ (Ref. 8) in analogy to those observed in BaF₂ crystals.¹³

The excitation spectrum of the Eu²⁺ spontaneous emission ($\lambda = 390$ nm) is shown in Fig. 1(b). A comparison between this spectrum and the reflectivity spectrum reveals that there is a one-to-one correspondence between peaks in the reflectivity and dips in the emission. This is due to the high reflectivity and low penetration depth of the radiation into the sample at the reflectivity maxima. In addition, it is seen from the figure that, apart from the dips, the emission intensity increases with increasing photon energy. We note in passing that Mikhaylin and Terekhin^{8,9} recently reported luminescence excitation spectra of the spontaneous Eu²⁺ emission in BaFBr which are very similar to the results presented in Fig. 1(b).

The spectrum of photostimulated luminescence (PSL) center formation is displayed in Fig. 1(c). This spectrum was taken in the following way. The synchrotron radiation was continuously scanned and the crystal was subjected to pulses of a dye laser (580 nm, maximum of the photostimulation spectra, see below). Emitted light (Eu²⁺ emission, 390 nm) was recorded only while the laser pulse was "on." The laser intensity per pulse was sufficient to depopulate all the PS centers created by the VUV radiation in the time between two laser pulses. Thus the experiment records the efficiency of the VUV photons in creating stimutable centers. Note that the spontaneous [1(b)] and stimulated [1(c)] emissions exhibit the same spectral components but there are clear differences in the heights of the various peaks.

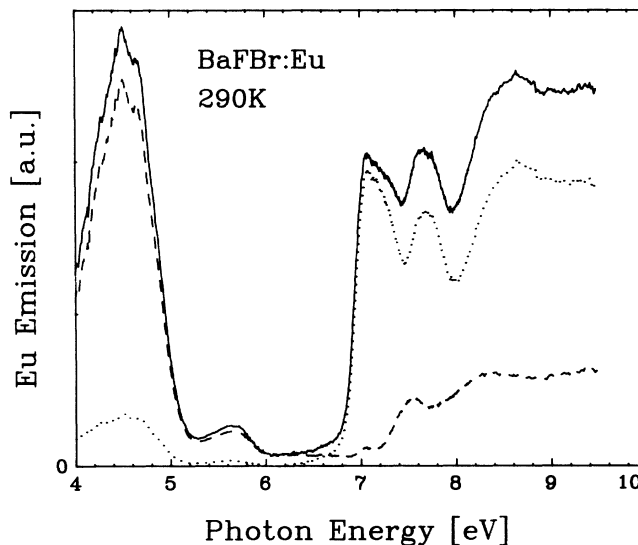


FIG. 2. Excitation spectra of the Eu²⁺ emission ($\lambda = 390$ nm). Dotted and dashed lines: recorded in coincidence and in anticoincidence with laser light modulated at 500 Hz, respectively. The laser light illuminates the sample for 250 μ sec in each period. Solid line: total emission.

Figure 2 presents more excitation spectra experiments of the Eu²⁺ emission recorded when irradiating the sample with synchrotron radiation. An Ar-ion laser modulated at 500 Hz, by means of an acousto-optical crystal, irradiated the sample for $\frac{1}{8}$ of the modulated period. The laser wavelength ($\lambda = 514$ nm) can photostimulate existing centers (see Fig. 3). The dotted and dashed lines correspond to the spectra obtained in coincidence and anticoincidence with the 250- μ sec pulse of the Ar-ion laser light pulse, respectively. The broad

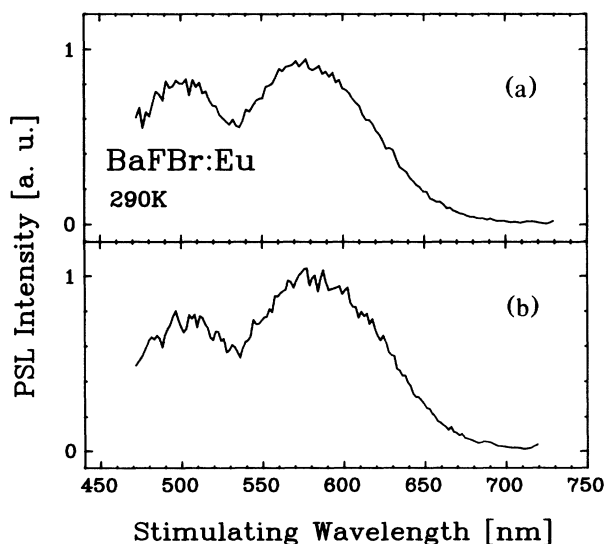


FIG. 3. Dependence of the Eu²⁺ emission on the wavelength for the stimulation process. (a) Charged at 7.1 eV; (b) charged at 11 eV.

band centered at 4.5 eV corresponds to the direct excitation of Eu^{2+} . As can be seen from the figure, the intensity of this band recorded in anticoincidence with the laser pulse is 7 times higher than the one recorded in coincidence. This indicates that the laser light does not have any effect on this emission band; i.e., the emission is not due to the reading of a PS center. This stands, however, in strong contrast to the spectral features above 6.6 eV. In this spectral region the emission is mostly in coincidence with the laser light pulse despite the fact that the crystal is irradiated by synchrotron radiation 7 times more when the laser light is off. Therefore, during this time the synchrotron radiation is mostly creating PS centers at the expense of spontaneous Eu^{2+*} emission. The structures in the anticoincidence spectrum presented in Fig. 2 are, most probably, caused by the change in the light penetration depth as a function of the photon energy. A shorter penetration depth implies less Eu^{2+} available for the creation of centers and therefore a higher probability for obtaining spontaneous Eu^{2+*} emission. The spectrum displayed by the solid line in Fig. 2 gives the total emission intensity. A comparison between this spectrum and the excitation spectrum of the spontaneous Eu^{2+*} emission presented in Fig. 1(b) reveals, nevertheless, that they are very similar.

Stimulation spectra were recorded by "reading out" the PS centers that have been previously stored by means of exposing the sample to VUV monochromatic radiation. The readout was performed by scanning chopped monochromatic visible light (470–740 nm) and recording the Eu^{2+*} ($\lambda = 390$ nm) emission intensity at the frequency of the chopped light using a lock-in amplifier. These spectra allow us to judge the nature of the electron trap (defect) since the stimulation spectrum resembles very closely the absorption spectrum of the defect.³ Figures 3(a) and 3(b) display stimulation spectra recorded after irradiating the sample for a few minutes with 7.1 and 11.0 eV, respectively. As discussed above, these photon energies correspond to the creation of excitons associated with the Br^-4p - and F^-2p -derived valence bands, respectively. From the figure it is clear that the stimulation spectra are very similar in spite of the fact that different excitons are at play. Again, the same spectrum was obtained when PS centers were created with zero-order radiation from the monochromator. Takahashi *et al.*³ showed that the stimulation spectra of $F(\text{Br}^-)$ and $F(\text{F}^-)$ centers in x-ray-irradiated BaFBr: Eu^{2+} crystals differ significantly. A comparison with their results³ reveals that our stimulation spectrum corresponds to the $F(\text{Br}^-)$ center. Therefore, it can be concluded that the electron storage center is an $F(\text{Br}^-)$ center regardless of the VUV photon energy employed in the storing process.

A comprehensive study of the VUV excitation and emission spectra of pure and Eu^{2+} -doped BaFBr at several temperatures reveals the existence of two broad

emission bands centered at 4.3 and 2.5 eV.¹⁴ These two emissions were also observed after x-ray excitation of BaFBr by Crawford, Brixner, and Somaiah.¹⁵ The onset for the excitation of the 4.3-eV emission band corresponds to the red wing of the first Br^- -derived exciton (6.7 eV). Therefore, we assigned¹⁴ the 4.3-eV emission band to the recombination luminescence of the $e + V_k(\text{Br}_2^-)$ center. Since the 4.3-eV emission band is resonant with the Eu^{2+} direct excitation (see Fig. 2), the excitation spectra of both emissions should be very similar beyond 6.7 eV as observed experimentally.¹⁴ One should mention that the $e + V_k(\text{Br}_2^-)$ emission was not detected above 250 K.^{14,15}

The experimental results presented in this Letter can be consistently explained in terms of a model invoking, as a first step, the relaxation of the free exciton (or the free hole and consequently the trapping of the electron) in the neighborhood of a lattice distortion induced by the Eu^{2+} as proposed by von Seggern *et al.*⁵ This leads to an $e + V_k$ center. From the results presented in Fig. 3 it can be assumed that the V_k center corresponds to a Br_2^- molecule, even after direct excitation of the fluorine- (or Ba-) related excitons. This is most probably due to an efficient Auger-type decay in which the hole is transferred from the fluorine (or Ba) to the Br.

The $e + V_k$ center can decay radiatively or evolve into an off-center self-trapped exciton. The former case results in spontaneous Eu^{2+*} emission as explained above. The results presented in Fig. 2 show that after the annihilation of the (VUV-created) PS centers by the previous laser pulse, the amount of spontaneous emission is very small as compared to the stimulated emission. This observation points to the fact that the VUV photons absorbed after bleaching mainly create new PS centers.

The off-center self-trapped exciton has been identified in alkali halides as an unstable $F-H$ pair, namely, a nearest-neighbor $F-H$ pair.¹⁰ We propose that the presence of the Eu^{2+} substitutional ion, with a smaller ionic radii than the replaced Ba^{2+} , actually stabilizes the $F-H$ pair even at room temperature, otherwise, the storage would not be possible. The $\text{Eu}^{2+}-F-H$ complex is, therefore, the PS center and it can be created with photon energies starting at the red wing of the first exciton of BaFBr as shown in Fig. 1(c). It should be pointed out that this model implies that the electron and hole centers are correlated, confirming the results of von Seggern *et al.*⁵

The photostimulation of the PS centers upon F -center excitation can be explained using the same model. As is well known, the excited F center induces a crystal relaxation. We propose that this relaxation destabilizes the H center trapped in the neighborhood of the Eu^{2+} . The $H-e^*$ complex then becomes an excited $e + V_k$ center, with the same decay channels as described above. Since the photostimulation is usually performed with a laser, the process is repeated many times, finally depleting the

stored information, as clearly demonstrated in the coincidence spectrum displayed in Fig. 2.

In conclusion, we have presented experimental evidence showing that PS centers are created with high efficiency upon exciting the crystal with photon energies larger than that of the first intrinsic exciton. From the model explaining the results it becomes clear that BaFBr:Eu²⁺ is an efficient storage material due to energy match between the emission of the self-trapped exciton and a strong absorption band of Eu²⁺.

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