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# Spatial correlation and photostimulability of defect centers in the x-ray-storage phosphor BaFBr:$Eu^{2+}$

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Photostimulable x-ray-storage phosphors in the form of image plates are one of the most important applications of defect centers in ionic crystals. Understanding the underlying mechanism, apart from its practical relevance, creates additional insights into the generation and kinematics of radiation defects in this class of materials. In this paper the commercial storage phosphor BaFBr:$Eu^{2+}$ is investigated. It is shown that x-ray irradiation produces both fluorine and bromine *F* centers, and aggregates thereof. Only the bromine *F* centers were found to contribute to the photostimulability, part of which are spatially correlated with an Eu-hole complex, whereas others are uncorrelated. Apart from the photostimulable centers, the nonphotostimulable centers could be identified via their characteristic infrared emission. Numbers can be deduced on the fraction of photostimulable and nonphotostimulable, correlated and uncorrelated centers. These numbers depend on the sample preparation as well as radiation history. The spectroscopic data and methods presented below should help to control better and improve the properties of storage phosphors.

## I. INTRODUCTION

X-ray-induced photostimulable image plates have gained considerable interest as two-dimensional x-ray detectors in the fields of medicine, physics, and biology.[1] The material commercially employed in these image plates is the rare-earth-doped alkaline-earth halide BaFBr:$Eu^{2+}$. The plates are able to store x-ray information in the form of locally trapped electron-hole pairs as a latent image. This stored information is recovered by optical stimulation, usually with a HeNe laser, which results in the recombination of the electron-hole pair under $Eu^{2+}$ emission at 3.2 eV. Advantages of this system compared to conventional x-ray detectors are a very high dynamic range (about 6 orders of magnitude), a linear dose dependence, and reusability of the plates.[2]

The photostimulation process after x-ray exposure has been studied extensively in the past years, and two mechanisms have been suggested. The mechanism initially proposed by Takahashi *et al.*[3,4] assumes the existence of halide vacancies, so-called $F^+$ centers, which trap electrons, and $Eu^{2+}$ ions which trap holes. During x-ray irradiation the $Eu^{2+}$ ions are partially ionized to their trivalent charge state and the so liberated electrons drift via the conduction band to $F^+$ centers thus forming *F* centers. During the subsequent optical stimulation (photostimulation) the trapped electrons are released into the conduction band and recombine with the $Eu^{3+}$ ions under the characteristic $Eu^{2+}$ emission at 3.2 eV. Due to the band transport no spatial correlation between the *F* center (occupied electron trap) and the $Eu^{3+}$ ion has to be assumed.

In more recent publications von Seggern *et al.* suggested[5-7] a different model in which the *F* center after x-ray irradiation has to be in close proximity to the recombination center which was suggested to be either $Eu^{3+}$ or an $Eu^{2+}$-hole complex. The electron transport was assumed to be optically stimulated tunneling from the relaxed excited state (RES) of the *F* center into the recombination center. In case that the $Eu^{3+}$ ion acts as the recombination center the tunneling results in a higher excited $Eu^{2+}$ ion whereas in case of the $Eu^{2+}$-hole complex picture an excited electron-hole center (trapped exciton) is obtained which upon deexcitation transfers its energy resonantly to the $Eu^{2+}$ thus forming an excited $Eu^{2+}$ ion. The photostimulated luminescence (PSL) is in both cases generated by the radiative deexcitation of the excited $Eu^{2+}$ ion. This model was deduced from the experimental observation of a temperature independent PSL lifetime and efficiency down to liquid-helium temperature (LHeT), which cannot be explained in terms of a band transport. It is known that after *F*-band excitation the excited electron relaxes into the RES of the *F* center. Thermal energy is then required for the escape of the RES electron into the conduction band. Since at low temperatures the thermal energy is lacking, only a tunneling process is able to explain the experimental results. Tunneling, however, requires a spatial correlation between the electron trap and the recombination center. Therefore, a photostimulable luminescence complex (PSLC) was introduced.[5] Recently, Hangleiter and co-workers[8] measured the PSL efficiency with temperature after x-ray irradiation at room temperature (RT) and found a strong efficiency drop during cooling for a crystal of BaFBr:$Eu^{2+}$. They interpreted the low-temperature photostimulable centers as triplet aggregates consisting of weakly bound $Eu^{2+}$-hole *F* complexes which correspond to the PSLC described above. Their interpretation was that excitation into the *F* band causes immediate recombination of the electron-hole center followed by energy transfer to the $Eu^{2+}$ ion. The additional centers responsible for the PSL at higher temperatures were interpreted as *F* centers at intermediate distance from $Eu^{2+}$-hole pairs which recombine after photostimulation via the conduction band.

This paper addresses a number of open questions.

(1) Which of the possible *F* centers—the fluorine or the bromine related ones—are photostimulable?

(2) Which of those are spatially correlated with the Eu ion?

(3) Are other types of electron traps present after x-ray irradiation, apart from *F* centers? And if so, do they contribute to photostimulability after x-ray irradiation?

In the following, apart from identifying the various electronic traps in the material by spectroscopic means in a qualitative way, methods will be presented to evaluate the relative concentrations of these centers [$F(F^-)$ and $F(Br^-)$ centers, correlated and uncorrelated centers, additional centers]. It will be shown that these relative concentrations vary with preparation and radiation history of the samples. In this way more inside is obtained into the mechanism of information storage in x-ray-storage phosphors.

## II. EXPERIMENTAL PARAMETERS

The investigated samples were Czochralski grown crystals of $BaFBr:Eu^{2+}$. Doped and undoped BaFBr single crystals were prepared by Spaeth *et al.* (Paderborn, Germany). The crystals were doped with a concentration of $0.5\times10^{-2}$ mol% $Eu^{2+}$.

The experimental setup is shown schematically in Fig. 1. The sample was mounted in a quartz pocket within a temperature variable cryostat covering a temperature range of 4 to 300 K. X-ray irradiation was carried out in the cryostat utilizing an x-ray voltage of 70 kV and a typical x-ray dose of 15 R.

Stimulation spectra for $Eu^{2+}$ emission after x-ray irradiation were obtained by exciting with a 500-W xenon lamp whose light was chopped and subsequently dispersed and scanned by a 32-cm monochromator. For infrared (IR) light blocking, a 3-mm KG3 filter (Schott Glaswerke) was added. The intensity was calibrated by means of a Si photodiode. To separate the $Eu^{2+}$ emission wavelength from the stimulating wavelength a combination of two 390-nm interference filters and a 3-mm BG3 filter (Schott Glaswerke) was utilized in front of the photomultiplier. The photomultiplier signal was recorded by a lock-in amplifier. Since only a fraction of the total $Eu^{2+}$ emission is measured with this combination of filters, the emission intensity had to be corrected. Therefore the total $Eu^{2+}$ emission was compared with the filtered emission using an optical excitation of the $Eu^{2+}$ ion at 289 nm and an optical multichannel analyzer instead of the photomultiplier covering the total emission spectrum. This comparison was performed over the investigated temperature range.

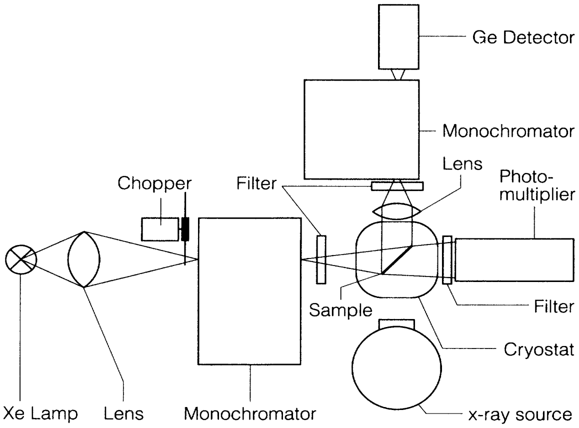

FIG. 1. Schematic diagram of experimental setup.

As discussed later the IR luminescence of the *F* centers and other electron traps produced by x-ray irradiation was also measured. The excitation spectra of the observed IR emission bands were measured with the same excitation setup as in case of the PSL stimulation spectra. The IR emission was detected through a 10-cm monochromator in combination with a liquid-nitrogen (LN) cooled germanium detector (Northcoast) utilizing lock-in techniques. The visible light was additionally filtered out by means of an optical high-band pass filter (3-mm RG 850, Schott Glaswerke). A simultaneous measurement of the IR excitation and the PSL stimulation spectra was also performed in this setup.

The IR emission spectra were measured by exciting through an interference filter whose wavelength was selected according to a characteristic excitation wavelength of the center under investigation.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

### A. Photostimulable centers

It has been generally accepted that *F* centers are the occupied photostimulable electron traps in halide storage phosphors due to an observed similarity with known absorption data.[4,7,9] In BaFBr two types of *F* centers can be thought of, one related to a fluorine vacancy and the other related to a bromine vacancy. To identify if both *F* centers are photostimulable, photostimulation spectra of the $BaFBr:Eu^{2+}$ crystal were measured at various temperatures (see Fig. 2). The sample was irradiated with x rays at 270 K and subsequently cooled in the dark to the respective measuring temperature. The stimulation was performed with small light intensities so that the stored information is detected without erasing it. Therefore the measurement of all spectra can be carried out after one x-ray exposure at room temperature. Two stimulation bands are clearly visible peaking at wavelengths of 495 and 590 nm, respectively. A strong drop in stimulability can be seen between 150 and 50 K whereas above and below this temperature only small changes are observed. This corresponds to the temperature dependence of the PSL described by Hangleiter *et al.*[8] The observed overall narrowing of the stimulation peaks is known for *F* centers and can be explained satisfactorily by the coupling of the ground-state electron with phonons.[10]

To investigate if these two stimulation bands are related to only one ($F^-$ or $Br^-$) or two different *F* centers

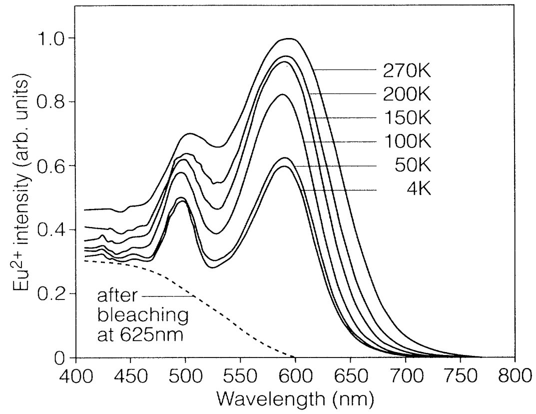

FIG. 2. Photostimulation spectra of the $Eu^{2+}$ emission in a $BaFBr:Eu^{2+}$ single crystal, irradiated with x rays at 270 K, measured at various temperatures. Applied x-ray dose: 15 R.

($F^-$ and $Br^-$) bleaching experiments were performed at 4 K at a stimulation wavelength of 625 nm. Figure 3 shows the spectral components of the bleached information for two experiments. The spectra were obtained as the difference between the stimulation spectrum before and after bleaching. It can be seen that for different bleaching times the information in both peaks erases proportionally. It is interesting to notice that the stimulation spectra after complete bleaching at 625 nm still shows a broad stimulation band slowly increasing from 600 to 400 nm (dotted line in Fig. 2).

The bleaching experiments clearly indicate that both stimulation bands in Fig. 3 have to be assigned to the same *F* center. The splitting of the *F* center stimulation band can be explained in analogy to the observed absorption band splitting in BaFCl and SrFCl which is due to the noncubic ($D_{2d}$ and $C_{4v}$, respectively) symmetry of the $F(F^-)$ and $F(Br^-)$ centers.[11] Whether these stimulation bands are due to the $F(F^-)$ or the $F(Br^-)$ center can be decided on the basis of the following argument: It was shown that in BaFCl and SrFCl both *F*-center types exist and that in both materials the *F* centers based on the halide vacancy with the larger ionic radius [$F(Cl^-)$ center] exhibit their absorption bands at longer wavelength than the respective $F(F^-)$ centers in accordance with the Mollwo relation familiar from *F* centers in alkali halides.[12] The $F(F^-)$ center absorption bands will be shown in the next section and are found at smaller wavelengths compared to the stimulation bands at 495 and 590 nm discussed here. Therefore we ascribe the latter bands to absorption by the $F(Br^-)$ center. The broad background in the stimulation spectrum measured between 400 and 600 nm correspond to the tail of a broad absorption band observed by Hangleiter *et al.*,[8] which peaks at 3.4 eV. The nature of this absorption is not yet understood.

### B. Nonphotostimulable centers

In order to investigate nonphotostimulable centers IR emission bands in the spectral range from 0.85 to 1.65 $\mu$m were measured and are shown in Fig. 4. The Eu doped as well as the undoped crystal were irradiated with x rays at room temperature and subsequently cooled to LHe temperature (4 K) in the dark. In case of the doped crystal an excitation wavelength of 590 nm was used corresponding to an excitation into the $F(Br^-)$ band. An emission peaking at a wavelength of 1.38 $\mu$m was observed and was assigned to the $F(Br^-)$ center IR emission. An excitation at 519 nm delivered two spectrally separated emission bands at 1.1 $\mu$m and at 1.6 $\mu$m. The same bands appear as shoulders in the 1.38-$\mu$m band observed under excitation at 590 nm, see Fig. 4. In the undoped BaFBr crystal only the 1.1-$\mu$m emission is observed for excitation at 519 nm.

In order to correlate these emissions to specific *F*-center types excitation spectra were recorded for all observed emissions. The excitation spectra for the 1.1- and 1.6-$\mu$m emissions are shown in Fig. 5. The 1.1-$\mu$m excitation spectrum exhibits three peaks located at 370, 512, and 712 nm, respectively, whereas the 1.6-$\mu$m excitation

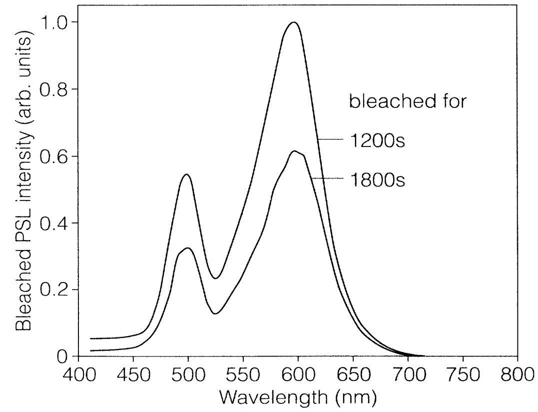

FIG. 3. Spectra of the bleached PSL information for different bleaching conditions as indicated. Bleaching was performed at 4 K after x-ray irradiation at room temperature.

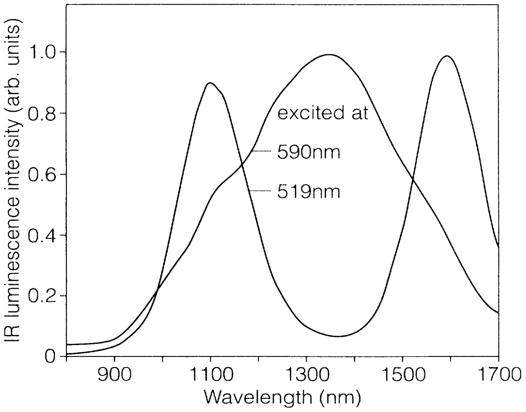

FIG. 4. IR emission spectra of $BaFBr:Eu^{2+}$ single crystals for excitation at indicated wavelengths measured at 4 K after room temperature x-ray irradiation.

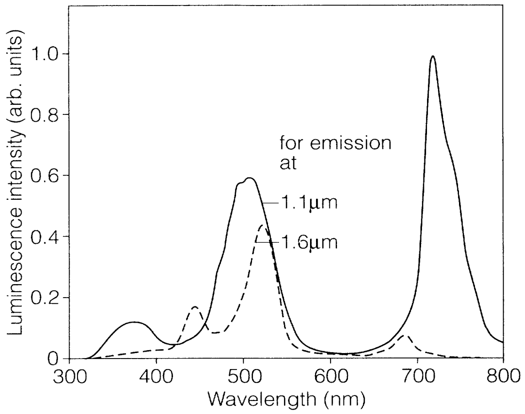

FIG. 5. IR excitation spectra for doped BaFBr single crystals after x-ray irradiation measured at 4 K at indicated emission wavelengths.

spectra shows excitation bands at 445, 520, and a small band at 680 nm. The excitation spectrum of the 1.1-$\mu$m emission of the undoped crystal (not shown) is identical to the 1.1-$\mu$m excitation spectrum of the doped crystal. It is interesting to point out that in the undoped crystal no 1.6-$\mu$m emission was found. The excitation spectrum of the 1.38-$\mu$m emission agrees essentially with the photostimulation excitation spectrum discussed in Sec. III A. Therefore, the 1.38-$\mu$m emission has to be attributed to the $F(\mathrm{Br}^-)$ center.

An interpretation of the above spectra with respect to the Yuste *et al.* results[11] allows the assignment of the 1.1-$\mu$m emission and the related excitation bands at 370 and 512 nm to $F$ centers based on fluorine vacancies. The 1.1-$\mu$m excitation band at 712 nm could be caused by $M(F^-)$ centers (aggregate center of two neighboring fluorine ion vacancies occupied by two electrons). Such centers are known in alkali halides to exhibit an only slightly changed emission band compared to the pure $F$ center but an absorption band at longer wavelength.[10] The 1.6-$\mu$m emission is caused by $\mathrm{Eu}^{2+}$ doping of the pure crystal whereby the smaller $\mathrm{Eu}^{2+}$ ion replaces the bigger $\mathrm{Ba}^{2+}$ ion. As known from the alkali halides doping with a smaller cation produces $F_A$ centers ($F$ centers with an adjacent doping ion) which exhibit emission and absorption bands at higher wavelengths than the pure $F$ centers.[10,13] In the case of an $\mathrm{Eu}^{2+}$ ion adjacent to an $F(F^-)$ center a shift of the absorption and emission wavelength is expected and allows a tentative assignment of the 445- and 520-nm excitation bands of the emission at 1.6 $\mu$m to $F_A(\mathrm{Eu}^{2+},F^-)$-like centers in BaFBr. The 680-nm excitation band might be explained in analogy to the $M(F^-)$ centers as spatially correlated $M_A(\mathrm{Eu}^{2+},F^-)$ centers meaning $M(F^-)$ centers adjacent to $\mathrm{Eu}^{2+}$ ions. The assignments of the various excitation and emission bands are summarized in Table I. It should be made very clear that the above assignments, in particular the $M$ and $M_A(\mathrm{Eu}^{2+},F^-)$ centers, can only be considered to be tentative as long as no microscopic identification has been performed.

TABLE I. Assignments of observed excitation and emission bands. All data were taken at $T=4$ K.

| Excitation peak | Emission peak | Assignment |
|---|---|---|
| $\lambda$ (nm) | $\lambda$ ($\mu$m) | |
| 495 | 1.38 | $F(\mathrm{Br}^-)$ |
| 590 | 1.38 | $F(\mathrm{Br}^-)$ |
| 370 | 1.1 | $F(F^-)$ |
| 512 | 1.1 | $F(F^-)$ |
| 712 | 1.1 | $M(F^-)$ |
| 445 | 1.6 | $F_A(\mathrm{Eu}^{2+},F^-)$ |
| 520 | 1.6 | $F_A(\mathrm{Eu}^{2+},F^-)$ |
| 680 | 1.6 | $M_A(\mathrm{Eu}^{2+},F^-)$ |

The temperature dependence of the integral excitation spectra of BaFBr:$\mathrm{Eu}^{2+}$ was also measured and is shown in Fig. 6. The sample was irradiated with x-rays at 270 K and cooled to 4 K in the dark. During subsequent heating the IR excitation spectra were measured at the indicated temperatures. The total emission was collected between 0.85 and 1.65 $\mu$m. It can be seen that the $F(\mathrm{Br}^-)$ related IR emission, characterized by the excitation band at 590 nm, is only visible at temperatures below 100 K. All the other centers [$F(F^-)$, $F_A(\mathrm{Eu}^{2+},F^-)$, $M(F^-)$, and $M_A(\mathrm{Eu}^{2+},F^-)$ centers] empty proportionally so that the above assignment to various fluorine related $F$ and $M$ centers seems justified. It is interesting to notice that all fluorine related $F$ centers are still excitable at room temperature.

### C. Spatially correlated and uncorrelated photostimulable centers

It has been shown in Sec. III A that the bromine $F$ center, not the fluorine one, takes part in the photostimulation process of x-ray irradiated BaFBr:$\mathrm{Eu}^{2+}$. In Sec.

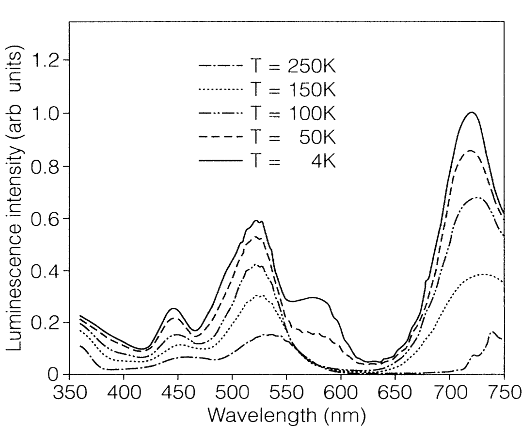

FIG. 6. Excitation spectra for IR emission in the spectral range from $\lambda=0.85$ to 1.65 $\mu$m in BaFBr:$\mathrm{Eu}^{2+}$ single crystals after x-ray irradiation at $T=270$ K at indicated temperatures.

III B it was shown that x-ray irradiation also produces fluorine $F$ centers, some of them as pairs [$M(F^-)$ centers], some of them correlated with $Eu^{2+}$, which do not contribute to the photostimulability. In this section we come back to the photostimulable (bromine) $F$ centers and address the question to what extent they are spatially correlated with the Eu activator. Two experiments have been performed to clarify this situation. In the first experiment PSL and IR efficiency with temperature were measured simultaneously. The result is shown in Fig. 7. The sample was irradiated with x-rays at 270 K and then subsequently cooled to LHeT. The PSL and IR emissions were excited at a wavelength of 590 nm which agrees with the maximum stimulability of the $Br^-$ related $F$ center (see Fig. 2).

The intensity of the exciting light was so small that the whole temperature run could be performed without significant loss of PSL and IR information. The $Eu^{2+}$ emission was measured at 390 nm and corrected for the temperature dependence of the $Eu^{2+}$ emission band. The IR emission was detected at 1.38 $\mu$m which corresponds to the maximum of the $F(Br^-)$ center IR emission band. The PSL intensity was found to be constant up to 40 K and then a thermally activated increase was observed with an activation energy of 35±5 meV. A saturation occurs at temperatures above 120 K. The IR emission intensity shows an opposite behavior meaning that at low temperatures the IR emission is almost constant, declines with temperature above 20 K, and disappears around 100 K.

These observations can be explained in terms of spatially correlated and uncorrelated $F(Br^-)$ centers as follows. A certain fraction of the $F(Br^-)$ centers produced by x-ray irradiation is spatially correlated with the $Eu^{2+}$ activator acting as the hole trap. These $F(Br^-)$ centers, called $F_{\rm corr}(Br^-)$ in the following, are photostimulable even at LHeT, since the $F_{\rm corr}(Br^-)$ center electron can tunnel to the neighboring Eu after optical excitation into its relaxed excited state. All other $F(Br^-)$ centers are isolated from the Eu ion and will be called $F_{\rm uncorr}(Br^-)$ centers. They do not contribute to the photostimulability at low temperatures, because thermal energy in addition to the optical excitation energy is necessary for the transport from the $F$ center RES to the Eu ion. The required energy is the one from the relaxed excited state (RES) to the conduction band. When the temperature is raised beyond 60 K, the isolated $F_{\rm uncorr}(Br^-)$ centers start to contribute to the photostimulation process, because the photoexcited electrons are thermally excited out of the RES into the conduction band, then migrate to the hole trapped at the $Eu^{2+}$ and recombine with the latter under $Eu^{2+}$ emission. Above 120 K the probability for thermal escape out of the RES of the isolated $F_{\rm uncorr}(Br^-)$ center reaches 100% and saturation of the $Eu^{2+}$ intensity (i.e., the PSL) is observed.

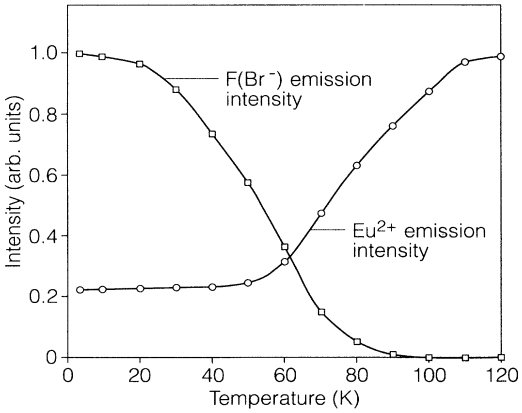

FIG. 7. $Eu^{2+}$ and IR emission (1.38 $\mu$m) as a function of temperature in BaFBr:$Eu^{2+}$ stimulated at $\lambda = 590$ nm [$F(Br^-)$ band] after x-ray irradiation at 270 K.

It follows from these considerations that the IR $F_{\rm uncorr}(Br^-)$ emission must be complementary to the $Eu^{2+}$ emission as a function of temperature. At low temperatures the photoexcited electrons cannot escape from the RES, so they decay back into the ground-state of the $F_{\rm uncorr}(Br^-)$ center under emission of the 1.38-$\mu$m line. When the temperature is raised, the 1.38-$\mu$m-emission intensity decreases because the electrons start to escape into the conduction band, the $Eu^{2+}$ emission intensity correspondingly increases. Above 100 K all electrons escape from the isolated $F_{\rm uncorr}(Br^-)$ centers, so no IR emission out of the RES is observed. The fact that the $F_{\rm uncorr}(Br^-)$ emission starts to decline at temperatures somewhat lower than the one where the $Eu^{2+}$ emission starts to rise can most naturally be ascribed to the onset of radiationless transitions of the electron from the RES to the ground state of the $F_{\rm uncorr}(Br^-)$. It follows from these considerations that the activation energy of 35±5 meV for the rise of the PSL (Fig. 7) corresponds to the escape process RES → conduction band. Furthermore it is seen from Fig. 7 that in the sample under investigation a fraction of about 0.23 of all $F(Br^-)$ centers is spatially correlated with $Eu^{2+}$, corresponding to the ratio of the PSL at LHeT relative to the one above 120 K. As noted in Sec. III D, this fraction depends on sample preparation and irradiation "history." To further support this view bleaching experiments were performed on the same x-ray irradiated BaFBr:$Eu^{2+}$ crystal at 4 and 120 K. The sample was irradiated with x rays at room temperature and subsequently cooled to the bleaching temperature of 4 K. During this cooling cycle the PSL and IR intensities were measured. Subsequently the sample was bleached with 590 nm light at the peak of the low-energy stimulation band of the $F(Br^-)$ center. This wavelength was selected to avoid a possible direct excitation of the $F(Br^-)$ ground-state electron into the conduction band via higher absorption bands ($K$, $L$, etc.) which might occur when exciting into the high-energy stimulation band around 495 nm. Subsequently the sample was heated up to 120 K and again the PSL and IR intensities were detected. The results are shown in Fig. 8. Bleaching at 4 K reduces the overall PSL stimulability by about the same absolute amount whereas bleaching at 120 K results in a proportional drop in the efficiency curve between 4 K and 120

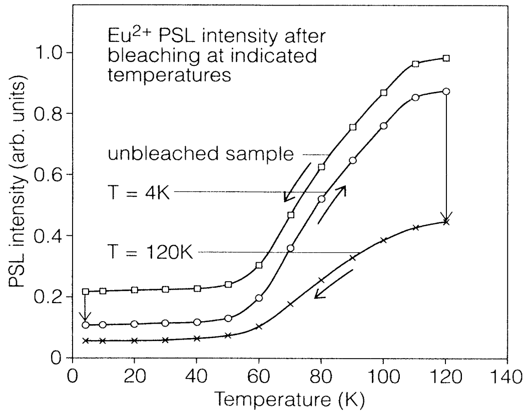

FIG. 8. Influence of 590-nm bleaching at various temperatures on the $Eu^{2+}$ emission with temperature of BaFBr:$Eu^{2+}$ crystal stimulated at $\lambda=590$ nm after x-ray irradiation at $T=270$ K.

K. This experiment demonstrates clearly that in case of the 4 K bleaching only correlated PSL centers are photostimulable whereas at 120 K both the spatially uncorrelated and correlated centers are erased simultaneously. Since in the case of 120 K bleaching both, correlated and uncorrelated centers, bleach by the same amount, the effective optical cross sections for both processes have to be equal.

In the course of the bleaching experiments described above not only the PSL was measured as a function of temperature, but also the IR emission of the $F_{\text{uncorr}}(\text{Br}^-)$ center at 1.38 $\mu$m. According to considerations given above bleaching at 4 K eliminates only the correlated $F_{\text{corr}}(\text{Br}^-)$ centers, which do not contribute to IR emission. So the latter should not be affected by bleaching at 4 K. This is indeed observed, as Fig. 9 shows. The IR emission is reduced, however, by bleaching at 120 K, because at this temperature the uncorrelated $F$ centers responsible for IR emission are affected.

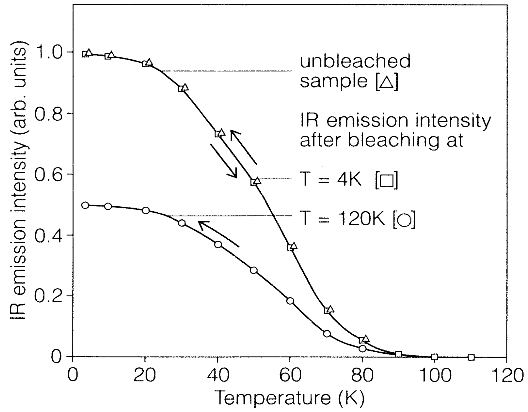

FIG. 9. Influence of 590-nm bleaching at various temperatures on the IR emission measured simultaneously with the $Eu^{2+}$ emission of Fig. 8.

### D. Estimate of the relative center concentrations

By comparing the photoluminescence intensities of the various electron-trap centers (see list of centers in Table I) at LHeT, normalized to equal excitation intensities, an estimate can be given of the relative concentrations of the different species. For lack of better knowledge it is assumed that the absorption cross sections of the different centers are equal, so the estimate can only be a fairly crude one. Results are given in Table II. The Eu correlated $F_{\text{corr}}(\text{Br}^-)$ center does not show IR luminescence, but only PSL. So the number on the $F_{\text{corr}}(\text{Br}^-)$ in Table II is based on the ratio $F_{\text{corr}}(\text{Br}^-)/[F_{\text{corr}}(\text{Br}^-)+F_{\text{uncorr}}(\text{Br}^-)]=0.23$ given in the preceding section. The unknown center giving rise to the broad stimulation band between 400 and 600 nm is not taken into account.

As Table II shows, the dominant center type produced by x-ray irradiation is the $M(F^-)$ center which amounts to about 45% of the total number of color centers. The rest is splitted between $F(F^-)$, $F_A(\text{Eu}^{2+},F^-)$, $F_{\text{uncorr}}(\text{Br}^-)$, $F_{\text{corr}}(\text{Br}^-)$, and $M_A(\text{Eu}^{2+},F^-)$ centers. The smallest group are the correlated $F_{\text{corr}}(\text{Br}^-)$ centers which are only 4.1% of the total center concentration and about 23% of the photostimulable centers. It is remarkable that the photostimulable centers [i.e., $F_{\text{uncorr}}(\text{Br}^-)$ and $F_{\text{corr}}(\text{Br}^-)$] contribute only to a fraction of about 18% to the total content of electron traps produced by the x-rays. The rest of 82% are fluorine related centers (Tables I and II) and do not contribute to PSL. It should be noted that the number of centers vary depending on sample preparation. For example, in the lower doped (0.01 mol%) crystal of Hangleiter *et al.*[8] only 10% of all $F(\text{Br}^-)$ centers are spatially correlated whereas in a powder sample measured and prepared earlier by us[6,7] almost 85% of all bromine related $F$ centers were correlated.

Besides the dependence on preparation, a dependence of the $F$-center creation on the radiation conditions and radiation history was noticed. A distinct difference in the number of correlated $F_{\text{corr}}(\text{Br}^-)$ to the total $F(\text{Br}^-)$ centers was found when x-ray irradiation at 4 K was performed. After x-ray irradiation at 4 K, 70% of the $F(\text{Br}^-)$ centers were correlated, while after x-ray irradiation at room temperature this fraction was 23%. Also prolonged preirradiation with x-rays at RT under continuous $F$-light bleaching was found to reduce consider-

TABLE II. Fraction of x-ray induced defect centers in a particular sample of BaFBr:$Eu^{2+}$, as inferred from the IR excitation spectrum (number for $F_{\text{corr}}(\text{Br}^-)$ is taken from the ratio $F_{\text{corr}}(\text{Br}^-)/[F_{\text{corr}}(\text{Br}^-)+F_{\text{uncorr}}(\text{Br}^-)]=0.23$ given in Sec. III D).

| Type | Fraction (%) |
|---|---|
| $F_{\text{uncorr}}(\text{Br}^-)$ | 13.9 |
| $F_{\text{corr}}(\text{Br}^-)$ | 4.1 |
| $F(F^-)$ | 15.5 |
| $F_A(\text{Eu}^{2+},F^-)$ | 17.5 |
| $M(F^-)$ | 43.7 |
| $M_A(\text{Eu}^{2+},F^-)$ | 5.3 |

ably the fraction of correlated photostimulable centers compared to the value measured without preirradiation. Further studies are necessary to interpret these results. It will be interesting to find out which parameters determine the fraction of photostimulable relative to nonphotostimulable centers.

## IV. SUMMARY

At the end of Sec. I three questions were presented. The answers based on the above results will be summarized and some comments will be added.

*Question 1:* By x-ray irradiation, bromine as well as fluorine $F$ centers are produced. However, only the bromine $F$ centers contribute to the photostimulability. So the photostimulation process is completely described by the band model shown in Fig. 10. As the recombination center we assume an $\mathrm{Eu}^{2+}$-hole center where the hole was assigned by Hangleiter *et al.*[8] to be of $V_k$ center type. The first step of the photostimulation process now consists in excitation of $F(\mathrm{Br}^-)$ centers in its absorption bands at 2.1 and 2.5 eV. The center then transforms into its relaxed excited state (RES) (for details of the optical pumping cycle of the $F$ center we refer to Ref. 10). Once in the RES, the following deexcitation paths are available to the electron: (a) deexcitation into the unrelaxed $F$-center ground state accompanied by IR emission of 0.9-eV energy and subsequent relaxation into the ground state, (b) thermal escape into the conduction band (35 meV) and subsequent recombination at a spatially uncorrelated $\mathrm{Eu}^{2+}$-hole center accompanied by the $\mathrm{Eu}^{2+}$ emission, and (c) tunneling to a neighboring $\mathrm{Eu}^{2+}$-hole center (spatially correlated PSL centers) emitting at the $\mathrm{Eu}^{2+}$ emission band.

Some fraction of the $F(\mathrm{Br}^-)$ centers are spatially correlated with the $\mathrm{Eu}^{2+}$-$V_K$ complex, others are isolated. For the spatially correlated ones, deexcitation via tunneling from the RES to the $\mathrm{Eu}^{2+}$-$V_K$ complex with subsequent emission of the $\mathrm{Eu}^{2+}$ fluorescence is the dominant process at low temperatures, because no thermal activation is required for the tunneling process. Therefore these centers are photostimulable at all temperatures investigated.

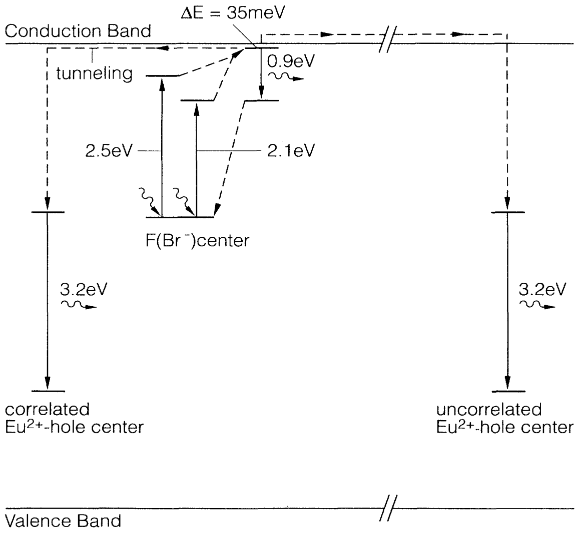

FIG. 10. Band model for the photostimulable luminescence and the related IR emission in $\mathrm{BaFBr:Eu}^{2+}$.

For the isolated $F_{\mathrm{uncorr}}(\mathrm{Br}^-)$ centers an activation energy of 35±5 meV is required for escape of the electron into the conduction band. Hence at low temperatures the only available deexcitation path out of the RES is the transition back into the ground state of the $F$ center (Sec. III A). Above ≈40 K (see Fig. 7) activation from the RES into the conduction band and transport to the $\mathrm{Eu}^{2+}$ can occur, resulting in a rise of $\mathrm{Eu}^{2+}$ emission and a decrease of IR emission in this temperature range.

The fact that the fluorine $F$ center is not photostimulable must be due to the fact that too high an activation energy is required for escape into the conduction band for all temperatures investigated. The electronic level scheme of the $F(F^-)$ center as well as of the other nonphotostimulable centers is given in Fig. 11.

*Question 2:* The answer to this question has already partially been given above as far as bromine centers are concerned. As discussed in Sec. III B we also see fluorine $F$ centers spatially correlated with $\mathrm{Eu}^{2+}$ ("$F_A(\mathrm{Eu}^{2+},F^-)$"), characterized by their excitation bands at 445 nm (2.78 eV) and 520 nm (2.38 eV) and an emission at 1.6 $\mu$m (0.77 eV) (Table I and Fig. 11). Evidently the potential barrier for tunneling from the RES of the $F_A(\mathrm{Eu}^{2+},F^-)$ center to the $\mathrm{Eu}^{2+}$-$V_K$ complex is too high to make this process possible. Therefore no photostimulation is observed.

*Question 3:* In addition to correlated and uncorrelated $F$ centers and $F_A$ centers more complex electronic centers are observed after x-ray irradiation, tentatively identified as $M$ and $M_A$ centers in Sec. III A. They all involve electrons at fluorine vacancies. The level scheme of the $M$ and $M_A$ center is also included in Fig. 11. The $M$ and $M_A$ centers of the fluorine type, like the $F(F^-)$

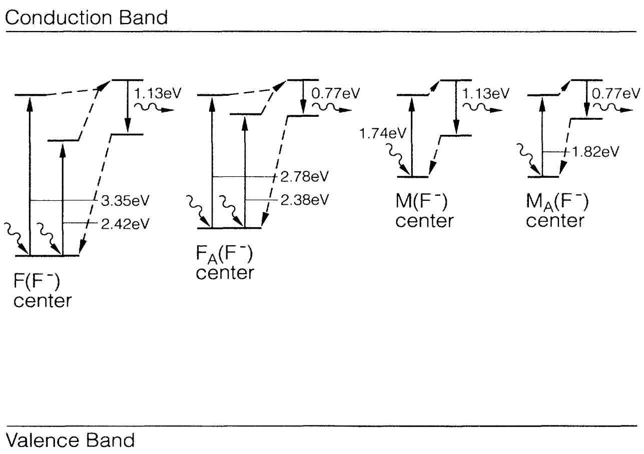

FIG. 11. Band model for nonphotostimulable centers in $\mathrm{BaFBr:Eu}^{2+}$.

centers, do not contribute to PSL, indicating that the activation energy for the transition from the RES to the conduction band is too high, and that the barrier height for the tunneling process is too large in the case of the $M_A$ and $F_A(\mathrm{Eu}^{2+},F^-)$ centers.

It is remarkable that even in the highly efficient commercial x-ray-storage phosphor $\mathrm{BaFBr:Eu}^{2+}$, a considerable fraction of the stored information is not accessible to photostimulation. The data and methods presented in this paper open a way to identify these centers and thus may help to further improve the material.

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