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X-Ray Storage Luminescence of BaFCl:Eu²⁺ Single Crystals

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Temperature behaviors of X-ray luminescence (XL), photoluminescence (PL), photostimulated luminescence, and thermoluminescence (TL) were studied in BaFCl:Eu²⁺ single crystals from room temperature to liquid nitrogen temperature. Six emissions at 275, 315, 365, 385, 435, and 500 nm were observed in the XL spectra and are attributed to Cl excitons, $V_k(\text{Cl}_2^-)$, the $4f^65d^1(^2e_g) \rightarrow 4f^7(^8S_{7/2})$ transition of Eu²⁺, and oxygen vacancies, respectively. Three emission peaks at 315, 365, and 390 nm were observed in the PL and TL measurements. These three emissions are from the transitions of $4f^7(^6I_{7/2}) \rightarrow 4f^7(^8S_{7/2})$, $4f^7(^6P_{7/2}) \rightarrow 4f^7(^8S_{7/2})$, and $4f^65d^1(^2e_g) \rightarrow 4f^7(^8S_{7/2})$ of Eu²⁺, respectively. In our measurements, we observed that the emission of Eu²⁺ increases in intensity upon β -irradiation and did not see any signals related to Eu³⁺ ions, which indicates that Eu²⁺ ions might not be oxidized to Eu³⁺ upon X-ray or β -irradiation. Instead, the color centers, Cl excitons, and oxygen defects are created and are stable at room temperature, and they might play a key role in the storage luminescence.

1. Introduction

Computed radiography (CR) using photostimulable phosphor storage media allows the combination of highly advanced photographic technology with digital computer techniques. This digital X-ray imaging technique is one of the primary candidates to replace the long-established screen-film radiography.¹ Photostimulated luminescence (PSL) is a process where exposure to high-energy (X-ray or UV) photons results in the accumulation of stored charges such as F centers. These stored charges can then be photostimulated to the conduction band using, for example, low-energy visible or near-infrared photons where they may recombine with holes to produce visible photostimulated luminescence.³ X-ray storage phosphors such as BaFX:Eu²⁺ (X = Cl, Br, and I) have been widely discussed.^{1–4}

The luminescence and storage mechanism of the BaFX:Eu²⁺ phosphor has been the subject of several studies. However, the exact mechanism of the PSL process in this material is still not very clear. The PSL mechanism of BaFBr:Eu²⁺ involving X-ray irradiation proposed by Takahashi et al.³ assumes that during X-ray irradiation the Eu²⁺ ions are partly ionized into their trivalent charge state (Eu³⁺) and the liberated electrons drift via the conduction band to form F centers. Upon subsequent photostimulation, the electrons are released from the F centers into the conduction band where they recombine with Eu³⁺ ions to produce the photostimulated luminescence of Eu²⁺ at 390 nm. This model can explain the phenomenon of photostimulated conductivity. It has, however, been criticized by others. Meijerink

and Blasse⁵ reported that they did not see any change in Eu²⁺ fluorescence due to X-ray irradiation in their BaFBr:Eu²⁺ samples. Thus, they questioned the argument that Eu²⁺ is converted into Eu³⁺ during X-ray irradiation. The observations of Su et al.^{6–8} also demonstrate that Eu²⁺ ions did not change their valence state and that the molar ratio of Eu²⁺/Eu³⁺ holds constant during X-ray irradiation or photostimulation. Thus, the interconversion model of $\text{Eu}^{2+} \leftrightarrow \text{Eu}^{3+}$ is questionable. Also, results reported by von Seggern et al.⁹ on the dependence of PSL on temperature during stimulation show nearly complete temperature independence from liquid helium temperature to room temperature. This, according to them, indicates that no thermal activation is involved in the PSL process. In addition, numerical calculation shows that the bimolecular recombination model leads to a quadratic dependence of the PSL intensity on the stimulation intensity⁹ rather than the linear relationship observed.^{2,3} The fact that the PSL decay lifetime is almost the same as the fluorescence lifetime of Eu²⁺ also indicates that the electron transfer from the F center to the recombination center is not via the conduction band. Otherwise, the PSL lifetime should be longer than the fluorescence lifetime of Eu²⁺.

Furthermore, Dong and Su investigated the photoconductivity of BaFBr:Eu²⁺ in more detail.⁷ They observed that, even though the time decay of the photostimulated luminescence is similar to that of the photoconductivity (PC) during photostimulation, the time dependence of the photostimulated luminescence is different from that of the photoconductivity during X-ray irradiation.⁷ In addition, the photostimulated conductivity is temperature-dependent, while photostimulated luminescence is not. These results are different from what Takahashi et al.

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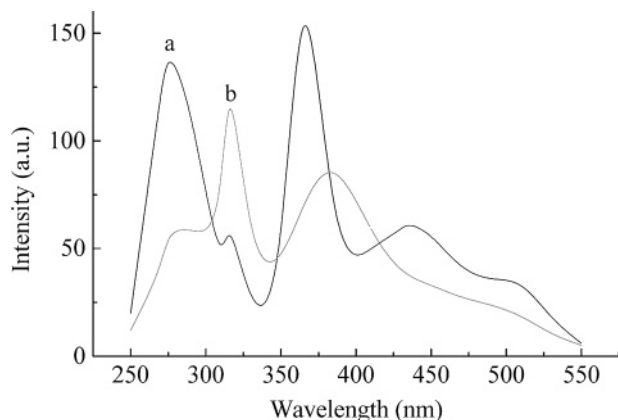


Figure 1. XL Emission Spectra of a BaFCl:Eu²⁺ single crystal recorded at (a) 80 K and (b) 300 K.

reported.^{3,10} Therefore, Dong and Su concluded that the photoconductivity has nothing to do with the photostimulated luminescence. They⁷ attribute photoconductivity to impurities such as O²⁻. Most recently, it was observed by Chen et al.¹¹ that the X-ray luminescence of Eu²⁺ in BaFBr powders and thin films increases in intensity over time. They observed the same phenomenon¹¹ for a commercial imaging plate purchased from Fuji. All these indicate that the storage luminescence processes in BaFX:Eu²⁺ phosphors are not identified yet. The present authors have reported briefly on new results of the storage luminescence of BaFCl:Eu²⁺ and SrFCl:Eu²⁺ crystals.¹² In this paper, we present detailed observations and a discussion on the temperature behaviors of the X-ray luminescence (XL), photoluminescence (PL), photo stimulated luminescence (PSL), and thermoluminescence (TL) of BaFCl:Eu²⁺ single crystals from room temperature (RT) to liquid nitrogen temperature (LNT).

2. Experimental Details

The single crystals of BaFCl:Eu²⁺ were grown by a modified Bridgman method, and their crystal structures were studied by Chen in detail.⁴ The X-ray irradiations were performed between 80 and 300 K with a W tube (40 kV, 15 mA), and the β -irradiations with a Sr⁹⁰ source (~ 13 mCi). For the UV illuminations, a 150 W Xe high-pressure lamp and a 0.25 m grating monochromator were used. The heating rate above RT was 5 °C/s. For the low-temperature TL and phototransfer thermoluminescence (PTTL) measurements, the samples were heated at a rate of 20 °C/min. The emission and excitation spectra were taken with an Aminco-Bowman 2 luminescence spectrometer.

3. Results and Discussion

A. X-Ray Luminescence of BaFCl:Eu²⁺. The XL at room temperature is shown by curve a in Figure 1. The emission consisted of a main narrow band at 315 nm as well as of some broad bands at about 275, 385, 435, and 500 nm. The XL emission at LNT differed markedly from the emission at RT; the main band at LNT was a narrow band at 365 nm (curve b of Figure 1).

The luminescence of the BaFCl:Eu²⁺ phosphor has been reported extensively.⁴ It is well-known that BaFCl:Eu²⁺ has a broad emission peaking around 390 nm that is attributed to the 4f⁶5d¹ (²e_g) \rightarrow 4f⁷ (⁸S_{7/2}) transition of Eu²⁺. Accordingly, the emission at 385 nm of BaFCl:Eu²⁺ single crystals is attributed to the 4f⁶5d¹ (²e_g) \rightarrow 4f⁷ (⁸S_{7/2}) transition of Eu²⁺. Five new emission peaks at 275, 315, 365, 435, and 500 nm are observed from BaFCl:Eu²⁺ single crystals. The temperature dependence

of these emissions excited by X-rays was measured during cooling from RT to LNT. The 385 nm emission decreased sharply below 135 K and disappeared at LNT. This behavior is similar to the temperature behavior of photoluminescence observed for the 4f⁶5d¹ (²e_g) \rightarrow 4f⁷ (⁸S_{7/2}) transition of Eu²⁺ in BaFX.⁴

The 435 and 500 nm bands increase in intensity during cooling from RT to 80 K; however, these two emission peaks are almost invisible at room temperature. Similarly, the 365 nm emission is not seen at room temperature, but it appears at about 190 K and increases in intensity during further cooling and becomes dominant at LNT. These three emissions disappear at room temperature, indicating that they are not emissions from Eu²⁺ ions; they might be from some species created by X-ray irradiation that is only stable at low temperatures.

Under X-ray irradiation, defects are created in the crystals.⁴ These defects may yield luminescence. Of them, color centers are most abundant. In BaFCl crystals, the two common color centers are F(F⁻) and F(Cl⁻) centers with absorption at 440 and 540 nm,¹³ respectively. The luminescence of these color centers has been investigated by Thoms et al.¹⁴ who reported that the emission wavelengths of these color centers are above 1000 nm and the luminescence is only visible at temperatures below 100 K. Obviously, these color centers are not responsible for the two emissions at 435 and 500 nm. These two emissions might be due to oxygen-related defects in these crystals. It has been reported that oxygen cannot be avoided as a contaminant in barium fluorohalide crystals and the oxygen significantly enhances F center generation under X-ray irradiation.¹⁵⁻¹⁷ In BaFCl and BaFBr, oxygen can replace F⁻ sites [O²⁻(F⁻)] and Cl⁻ or Br⁻ [O²⁻(Cl⁻) or O²⁻(Br⁻)] sites. The emission in the BaFBr crystal has been assigned to O²⁻(F⁻), and emissions at 505 nm¹⁵⁻¹⁷ have been assigned to O²⁻(Cl⁻). Through comparison, the two emissions at 435 and 505 nm are assigned to the O²⁻(F⁻) and O²⁻(Cl⁻), respectively.

The 365 nm emission in BaFCl:Eu²⁺ crystals is similar in energy, shape, and temperature behavior to the emission band at around 370 nm observed in BaFCl crystals by Radzhabov and Egranov¹⁸ and Yuste et al.¹⁹ This 370 nm emission disappears at temperatures above 200 K, and it was assigned to the recombination of V_k(Cl₂⁻) centers with electrons by Yuste et al.¹⁹ and off-center self-trapped excitons by Radzhabov and Egranov.¹⁸ We tend to support the assignment by Yuste et al. because the energy of the 370 nm (3.35 eV) emission is too low for the off-center excitons in BaFCl crystals. Theoretically, the emission energy of the off-center excitons in BaFCl is about 4.5 eV or 275 nm in wavelength.¹⁸ Therefore, it is not reasonable to assign the 370 nm emission to the off-center excitons in BaFCl. This emission band was attributed to the off-center excitons by Radzhabov and Egranov¹⁸ because it was the only emission band that they observed in the BaFCl crystal. However, they did point out that *it is rather unexpected that the emission energy of BaFCl excitons is lower than the energy of BaFBr excitons*.¹⁸ All these support the assertion that it is more reasonable to assign the 370 nm emission to the recombination of V_k(Cl₂⁻) centers with electrons in BaFCl crystals.

The two emissions at 275 and 315 nm are new emissions that have never been reported before. The intensity of the 275 nm band increased continuously during cooling, while the 315 nm emission decreased gradually. The possible origins of the 275 nm emission might be from Eu²⁺ ions at different sites, self-trapped excitons, or the higher excited states of Eu²⁺ ions. Eu²⁺ in BaFCl substitutes for the site of Ba²⁺, and BaFCl has only one site for Ba²⁺. The BaFCl:Eu²⁺ single crystals were

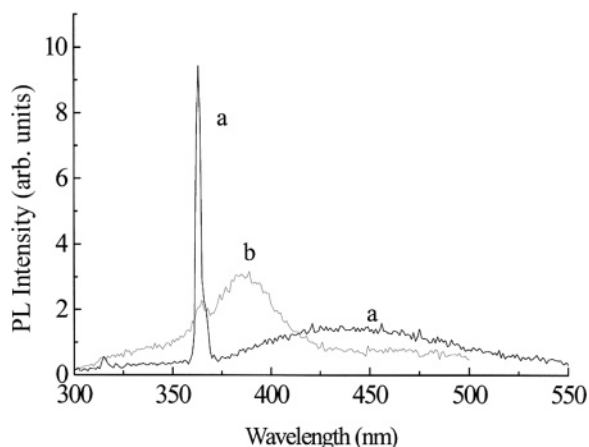


Figure 2. PL Emission Spectra of a BaFCl:Eu²⁺ single crystal recorded after 10 min of X-ray irradiation and stimulation with 260 nm light at (a) LNT and (b) RT.

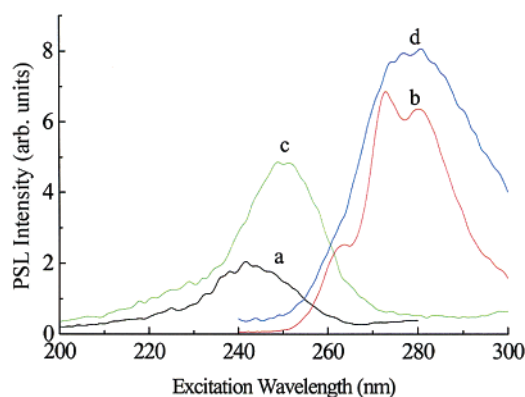


Figure 3. Excitation Spectra of BaFCl:Eu²⁺ for PSL bands: (a) 315 nm, (b) 365 nm, (c) 430 nm, and (d) 385 nm. Curves a–c were measured at LNT and curve d at RT.

grown at temperatures higher than 1200 °C. In this case, it is most unlikely that the 275 nm emission is from Eu²⁺ ions at different sites.

It is well-known that the 5d¹ is split into two levels in the crystal field of BaFCl, ²e_g and ²t_{2g}. The transition of 4f⁶5d¹ (²e_g) → 4f⁷ (⁸S_{7/2}) gives the well-known emission at 385 nm in BaFCl:Eu²⁺. The energy separation between the two emission bands at 275 and 385 nm is about 1.28 eV, which is close to the energy spacing between the ²e_g and ²t_{2g} states.²⁰ It might be possible that the transition of 4f⁶5d¹ (²t_{2g}) → 4f⁷ (⁸S_{7/2}) gives the emission band at 275 nm. However, due to two reasons, the 275 nm emission cannot be attributed to the transition of 4f⁶5d¹ (²t_{2g}) → 4f⁷ (⁸S_{7/2}). First, the transition rate of the 4f⁶5d¹ (²t_{2g}) → 4f⁷ (⁸S_{7/2}) is extremely low because the energy relaxation from the 4f⁶5d¹ (²t_{2g}) excited state to the 4f⁶5d¹ (²e_g) emitting state is very efficient due to the strong coupling of the 5d¹ electron with the lattice phonons. Actually, the emission from the 4f⁶5d¹ (²t_{2g}) excited state of Eu²⁺ ions has never been observed. Second, the 275 nm emission band is in the same position as the absorption band of the 4f⁶5d¹ (²t_{2g}) excited state. Theoretically, the emission and the absorption bands of the state cannot be in the same position because of the strong electron–phonon interaction. All of these indicate that the 275 nm emission is not from the transition of 4f⁶5d¹ (²t_{2g}) → 4f⁷ (⁸S_{7/2}) of Eu²⁺ ions.

Self-trapped excitons in BaFX (X = Cl, Br, and I) can yield luminescence with wavelengths shorter than 300 nm.^{18,21,22} For example, emissions at around 230 and 368 nm have been

observed in BaFCl that were assigned to on- and off-center self-trapped excitons,²² and two emission bands at 5.15 eV (240.6 nm) and 4.2 eV (295 nm) in BaFBr are attributed to the Br excitons.¹⁸ The two emissions are related, and the relation between the two exciton emissions is temperature-dependent. It was observed that there is anticorrelation between the temperature dependence of the 5.15 eV emission and that of the 4.2 eV emission.¹⁸ That is, as temperature decreases, the 5.15 eV emission increases while the 4.2 eV emission decreases in intensity. The temperature behavior shows clearly that the two exciton emissions or configurations can transform into each other.^{18–22} The same temperature behavior was observed for the 275 nm (4.51 eV) and 315 nm (3.93 eV) emissions in BaFCl:Eu²⁺ crystals as shown in Figure 1. Accordingly, the 275 and 315 nm emissions are attributed to the Cl excitons in the BaFCl:Eu²⁺ crystals. The assignments of the six X-ray excited emission bands are summarized in Table 1.

It is noted that all the emissions from the self-trapped excitons in undoped BaFX are not visible at temperatures above 200 K,^{18,21,22} while the 275 and 315 nm emissions in the BaFCl:Eu²⁺ crystals appear at room temperature. This is probably due to the trapping of the excitons to the doped Eu²⁺ ions. In pure crystals, the intrinsic excitons are called free excitons. In doped crystals, the excitons can be trapped at the dopants, thus forming trapped excitons.²³ According to the theory of trapped excitons, the oscillator strength of the trapped excitons is much higher than that of the free excitons. The concept of giant oscillator strength (*f*_{BE}) for bound excitons was introduced by Rashba and Gugenishvili,²³ which implies that

$$f_{\text{BE}} = \left(\frac{a_{\text{ex}}}{a}\right)^3 f \quad (1)$$

where *f* is the oscillator strength for free excitons, *a* is the crystal unit-cell length, and *a*_{ex} is the excitonic Bohr radius. Because the unit-cell length is almost an order of magnitude smaller than the Bohr radius, the oscillator strength of bound excitons is about 3 to 5 orders of magnitude larger than that of free excitons.²⁴ The increase in oscillator strength indicates the increase in the wave function overlap between the electron and the hole of the exciton because the oscillator strength is proportional to the overlap.^{23,25,26} Obviously, the increase in the wave function overlap will enhance the binding energy of the trapped excitons. Therefore, trapped excitons can have higher luminescence efficiencies and are more stable than free excitons.

B. Photoluminescence and Photostimulated Luminescence of BaFCl:Eu²⁺ Single Crystals. The luminescence spectra in Figure 2 were obtained by monochromatic light excitation at 260 nm. The crystal had previously been exposed to X-ray or β-irradiation for 10 min to detect the species created by radiation. The emission spectra show a narrow band at 315 nm, a broad band at 385 nm, and a very broad band centered near 430 nm. These bands showed different temperature dependencies. The 315 nm emission band, which was strong in XL, was relatively weak in PL and appeared mainly at about 140 K. The narrow 365 nm band appeared in the PL as in the XL below 190 K, increased strongly during cooling, and became dominant at LNT. The 385 nm emission was recorded at RT and disappeared near LNT. The 430 nm emission increased near LNT. These emissions are from the transitions of 4f⁷(⁶I_{7/2}) → 4f⁷(⁸S_{7/2}) and 4f⁶5d¹ (²e_g) → 4f⁷(⁸S_{7/2}) of Eu²⁺ ions and oxygen vacancies, respectively.

What we should point out is the emission band at 365 nm. Even though the XL emission and the PL emission bands are peaking at the same wavelength, 365 nm, they are from two

TABLE 1: X-Ray Excited Emissions from BaFCl:Eu²⁺ Single Crystals

emission peak (nm)	275	315	365	385	435	500
assignment	Cl excitons	Clexcitons	$V_k(\text{Cl}_2^-) + e^-$	$^2e_g \rightarrow ^8S_{7/2}$	$\text{O}^{2-}(\text{F}^-)$	$\text{O}^{2-}(\text{Cl}^-)$

TABLE 2: Luminescence Emission and Excitation Bands in BaFCl:Eu²⁺ Single Crystals

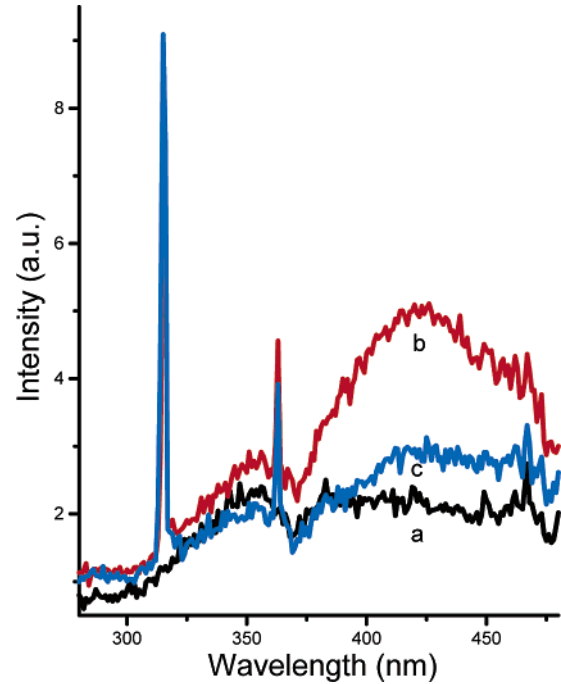
emission (nm)	assignments	excitation (nm)	assignments
315	$4f^7(^6I_{7/2}) \rightarrow 4f^7(^8S_{7/2})$	242	excitons
365	$4f^7(^6P_{7/2}) \rightarrow 4f^7(^8S_{7/2})$	263	$\text{O}^{2-} - h$ centers
		275	$4f^7(^8S_{7/2}) \rightarrow 4f^65d^1(^2t_{2g})$
		285	$4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_6)$
385	$4f^65d^1(^2e_g) \rightarrow 4f^7(^8S_{7/2})$	278	$4f^7(^8S_{7/2}) \rightarrow 4f^65d^1(^2t_{2g})$
430	$(\text{O}^{2-} + h)$ centers	250	$(\text{O}^{2-} + h)$ centers

totally different species. The 365 nm emission in the PL spectra is much narrower in bandwidth than the XL emission band. Furthermore, the PL emission at 365 nm is visible at room temperature, while the 365 nm XL is only visible at temperatures below 190 K. The photoluminescence line emission at 365 nm in Figure 2 is actually from the transition of $4f^7(^6I_{7/2}) \rightarrow 4f^7(^8S_{7/2})$ of Eu²⁺ ions, while the 365 nm XL emission in Figure 1 is from the exciton recombination of $V_k(\text{Cl}_2^-)$ with electrons. They appear to be at the same position in the X-ray emission and photoluminescence emission spectra, but they are from different luminescence centers based on our observations.

Figure 3 shows the excitation spectra of the crystals. As the four emission bands are from different states or species, they have different excitation bands. The 365 nm emission band has excitation maxima at 263, 275, and 285 nm. The 315 and 385 nm emissions and the broad emission band near 430 nm have excitation maxima at 242, 278, and near 250 nm, respectively. The excitation band of the 430 nm emission is consistent with the 252 nm excitation band of oxygen vacancies in undoped BaFCl crystals;¹⁶ therefore, it is due to the absorption of oxygen vacancies. Obviously, the 242 nm excitation band is from the Cl excitons. The broad band peaking at 275 nm is similar to the excitation spectra of the Eu²⁺ emission at 390 nm,⁴ and it is from the $4f^7(^8S_{7/2}) \rightarrow 4f^65d^1(^2t_{2g})$ of Eu²⁺. The origins of the emission and excitation peaks are summarized in Table 2.

It is noted in the comparison of Figures 1 and 3 that the exciton emission of the host overlaps largely with the absorption band of the $4f^7(^8S_{7/2}) \rightarrow 4f^65d^1(^2t_{2g})$ of Eu²⁺, which enables very efficient energy transfer from the host to Eu²⁺ ions and makes Eu²⁺-doped BaFX (X = Cl, Br, and I) highly luminescent phosphors with promising applications in X-ray intensifier screens, X-ray medical imaging, and radiation detection.²⁰

PSL can be divided into electron-stimulated and hole-stimulated luminescence.⁴ Obviously, PSL can result from the optical release of either electrons or holes. There is no correlation, however, between the identity of the active carriers (electrons or holes) and the question of whether the emitted light has a longer or shorter wavelength than the stimulating light. Investigators usually look for cases where the stimulating wavelength is longer than that of the emitted light since in this case they can be sure that it is PSL and not PL. However, higher-energy photons (shorter wavelengths) can easily stimulate lower energy (longer wavelength) emission, which still depends on the prior excitation by β irradiation, for example. The problem here is to distinguish between true PSL and PL, which may occur under the same conditions. Results of annealing and reirradiation may be of great help here. To figure out which peaks are intrinsic emissions from the sample and which are due to the species excited by radiation, the irradiated crystal was heated to 730 °C and then cooled to LNT for the

**Figure 4.** Luminescence emission of a BaFCl:Eu²⁺ crystal recorded during illumination with 250 nm light after β -irradiation (a) at RT, (b) at LNT, and (c) heated to ~ 730 °C and then illuminated at LNT.

luminescence measurement. Figure 4 shows the spectra excited at 250 nm. No strong luminescence signal but just a weak background is observed at room temperature. Two sharp emission peaks at 315 and 365 nm and a broad emission band peaking at around 430 nm were detected at LNT after X-ray irradiation. After being heated to 730 °C and cooled to LNT, the emission at 430 nm was quenched. This indicates that the 430 nm emission is actually a PSL emission generated by radiation. The 250 nm excitation peak and the 430 nm emission are assigned to oxygen defects (vacancies). In the BaFCl crystal, oxygen vacancies are actually hole traps because the divalent oxygen ion (O^{2-}) prefers to capture a hole to balance its charge with the halogen site (Cl^- or F^-) it occupies. So, the 250 nm excitation peak is actually from $(\text{O}^{2-} + h)$ centers. Thus, the 430 nm emission excited at 250 nm is actually a hole-PSL emission.

Figure 5A shows the emission spectra of the β -irradiated crystal measured at LNT with excitation at 285 nm before and after heating to 730 °C. The result shows that before the preheating a sharp emission at 365 nm and a broad emission peaking at 385 nm were observed at LNT. After preheating, the broad emission at 385 nm was quenched by about 60–70%. Furthermore, it was observed that the 385 nm emission is increased after β -irradiation at room temperature as shown in Figure 5B. This is an interesting phenomenon. First, the shape and emission wavelength of the 385 nm band at LNT demonstrate that it is from the $4f^65d^1(^2e_g) \rightarrow 4f^7(^8S_{7/2})$ transition of Eu²⁺ even though it has been reported that the $4f^65d^1(^2e_g) \rightarrow 4f^7(^8S_{7/2})$ emission of Eu²⁺ at 385 nm was quenched at LNT.⁴ Second, the decrease in intensity after heating to 730 °C indicates that the emission is related to some carriers generated by radiation. Most likely, this emission excited at 285 nm is

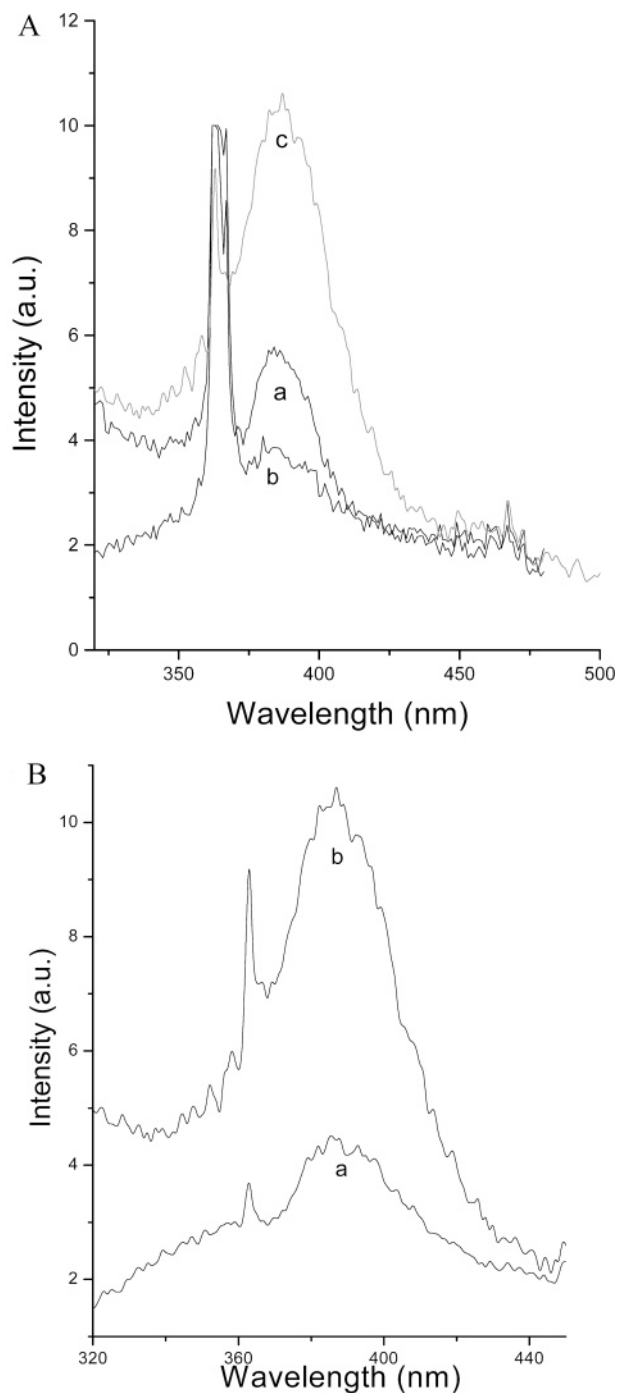


Figure 5. Emission recorded of a BaFCl:Eu²⁺ crystal during illumination at 285 nm. (A) At LNT (a) without preheating and β -irradiation, (b) after heating to 730 °C, and (c) after β -irradiation (~ 2 KGy). (B) At RT (a) without preheating and β -irradiation and (b) after β -irradiation (~ 2 KGy).

mainly contributed from PSL. The increase in the emission intensity after β -irradiation measured at room temperature supports this conclusion further. The increase in the Eu²⁺ emission at 385 nm upon β -irradiation is opposite of the data reported by Takahashi et al.³ Furthermore, in our measurements, we did not see any emission signals from Eu³⁺. All these indicate that the PSL model for the oxidation of Eu²⁺ to Eu³⁺ upon radiation and the reduction of Eu³⁺ to Eu²⁺ upon stimulation are questionable as pointed out by many investigators.^{6–9}

C. Thermoluminescence in BaFCl:Eu²⁺. After X-ray irradiation at LNT, the main glow peak appeared at 170 K, and weaker peaks were observed at approximately 220 and 270 K

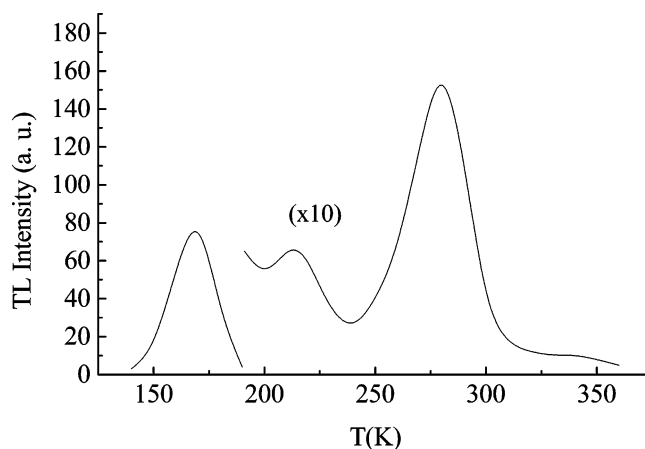


Figure 6. TL of BaFCl:Eu²⁺ recorded after 10 min of X-ray irradiation at LNT.

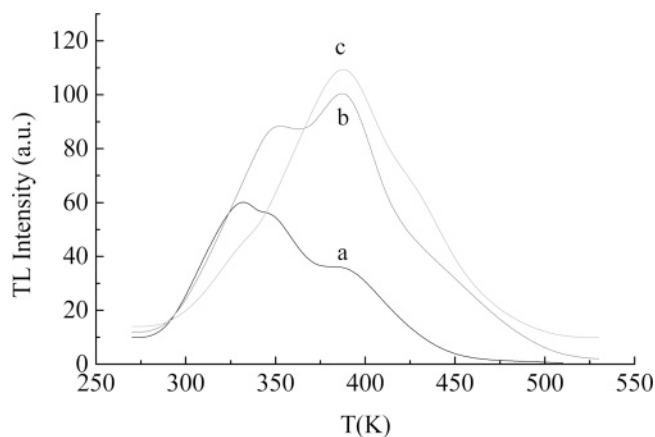


Figure 7. TL of BaFCl:Eu²⁺ recorded after various periods of β -irradiation at RT: (a) 1 min, (b) 10 min (reduced by $1/3$), and (c) 30 min (reduced by $1/10$).

(Figure 6). After low-dose X-ray irradiation at RT, the main peak was recorded at 320 K and additional peaks at approximately 350, 400, and 430 K. With an increased radiation dose, the 350 and 400 K peaks became dominant, indicating a different dose dependence of the various peaks (Figure 7).

It is well-known that the glow peaks at 400 and 430 K are from F(F⁻) and F(Cl⁻) centers, respectively.⁴ As discussed in subsection A, in addition to color centers (F centers), the Cl excitons in BaFCl:Eu²⁺ are stable above room temperature. The Cl exciton has two configurations corresponding to emissions at 275 and 315 nm, respectively. The 315 nm configuration is more stable than the 275 nm configuration. Thus, we assign the two glow peaks at 320 and 350 K to the 275 and 315 nm configurations, respectively. It is noted that at low-dose irradiation (1 min) the 320 K peak is stronger in TL intensity than the 350 K peak, while the 350 K peak is stronger at a higher dose (10 min). This indicates that the two configurations corresponding to the 320 and 350 K peaks can transform into each other. This phenomenon is similar to the temperature behavior of the two XL emissions at 275 and 315 nm and supports the idea that the assignment of the 320 and 350 K glow peaks to the two configurations of the Cl exciton is reasonable.

A glow peak at 270 K in BaFCl has been observed and was attributed to the thermal dissociation of the O²⁻-F(Cl⁻) pair defects.¹⁷ The X-ray luminescence (435 and 500 nm) of the oxygen-related defects in BaFCl:Eu²⁺ crystals is quenched at room temperature as displayed in Figure 1. The quenching

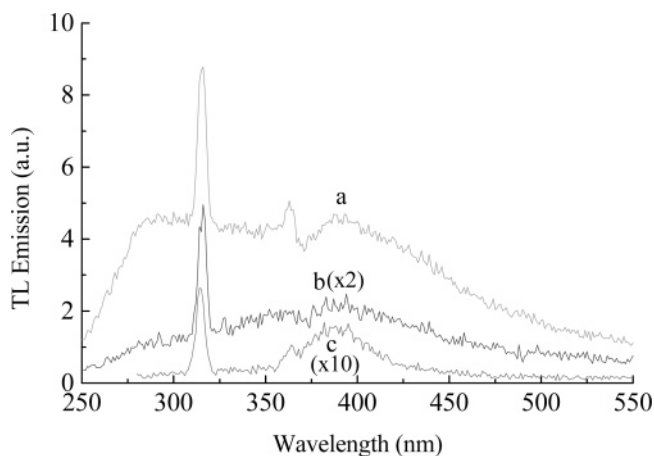
TABLE 3: Thermoluminescence Glow Peaks of BaFCl:Eu²⁺ Single Crystals

peaks (K)	170	220	270	320	350	400	430
assignment	$V_k(F_2^-)$	$V_k(Cl_2^-)$	$O^{2-}(Cl^-)$	Cl exciton (275 nm)	Cl exciton (315 nm)	$F(F^-)$	$F(Cl^-)$

temperature is close to 270 K, which supports the assignment of the 270 K glow peak to oxygen defects.

The recombination emission of the electron with $V_k(Cl_2^-)$ at 370 nm in BaFCl:Eu²⁺ disappears at temperatures above 200 K. This allows us to assign the glow peak at 200 K to the recombination of the electron with $V_k(Cl_2^-)$. Because defects at F⁻ sites are less stable than defects at Cl⁻ sites in BaFCl crystals,⁴ it is reasonable to assign the glow peak at 170 K to the recombination of the electron with $V_k(F_2^-)$. The possible origins of the glow peaks are summarized in Table 3. Figure 7 shows that at a low dose of radiation the excitons are dominant in the crystals, while at a high dose the F centers are dominant. This is quite reasonable because the halogen vacancies, which are necessary for the formation of F centers, can only be created at a high dose of radiation.

The emission spectrum of the main 170 K TL peak consisted of two strong narrow bands at 315 and 365 nm as well as of a strong broad band at 390 nm. The spectra recorded at the other TL glow peaks also showed the strong narrow 315 nm band as well as a broader band at about 390 nm (Figure 8). The

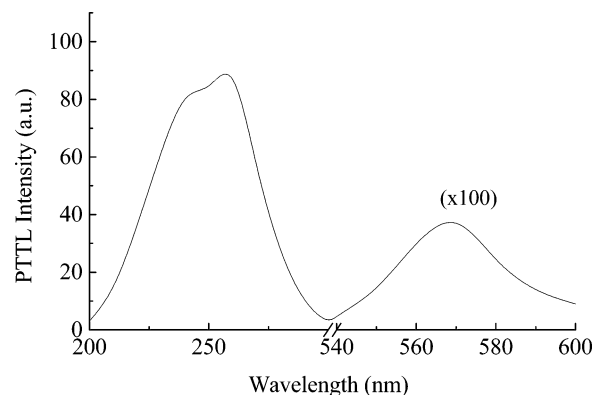
**Figure 8.** BaFCl:Eu²⁺ TL emission spectra recorded after 10 min of X-ray irradiation at the glow peaks: (a) 170, (b) 270, and (c) 320 K.

emissions at 315, 365, and 385 nm are from the transitions of $4f^7(^6I_{7/2}) \rightarrow 4f^7(^8S_{7/2})$, $4f^7(^6P_{7/2}) \rightarrow 4f^7(^8S_{7/2})$, and $4f^65d^1(^2e_g) \rightarrow 4f^7(^8S_{7/2})$ of Eu²⁺, respectively. The TL emission spectra are similar to the PL emission spectra as shown in Figure 2. However, the relative intensities of the two f–f emissions at 315 and 365 nm are totally different in the TL and PL emissions. In the PL spectra, the 365 nm emission is dominant and much stronger than the 315 nm emission, while in the TL spectra, the 315 nm emission is dominant. More interesting is that no f–f emissions are observed in the XL spectra in the same sample. The reason for these differences is not clear yet; however, the phenomenon indicates that the transition processes and probabilities are different in the three types of luminescence.

It has been noticed in our measurements that the f–f emissions at 315 and 365 nm are commonly seen in the photoluminescence and thermostimulated emission spectra. Regarding the probabilities of f–f and d–f transitions from Eu²⁺, certain criteria were described by Blasse.²⁷ One of them is that the equilibrium energy of the excited $4f^65d^1$ state must be higher than that of the lowest excited $4f^7(^6P_{7/2})$ state. Obviously, this criterion is valid for the $4f^7(^6P_{7/2}) \rightarrow 4f^7(^8S_{7/2})$

emission at 365 nm but not for the $4f^7(^6I_{7/2}) \rightarrow 4f^7(^8S_{7/2})$ emission at 315 nm. It is also noted that at room temperature the $4f^65d^1(^2e_g) \rightarrow 4f^7(^8S_{7/2})$ emission at 385 nm is dominant, but this emission decreases in intensity with decreasing temperature; meanwhile, the $4f^7(^6P_{7/2}) \rightarrow 4f^7(^8S_{7/2})$ emission at 365 nm increases in intensity and becomes dominant at LNT. This phenomenon is attributed to the difference in the electron–phonon coupling for the 4f electrons and the 5d electrons and is illustrated very well by Liu et al.²⁸

D. PTTL in BaFCl:Eu²⁺. The PTTL was measured after X-ray or β -irradiation at RT, heating to a certain higher temperature (T_1), and subsequent monochromatic illumination in the 200–600 nm region at LNT. The excitation spectrum of the total PTTL emission has a main maximum at 260 nm with a shoulder at 240 nm and a weaker maximum at 570 nm (Figure 9). It is well-known that the excitation peak at 570 nm is from

**Figure 9.** Excitation spectrum of BaFCl:Eu²⁺ monitored at the 170 K PTTL peak.

$F(Cl^-)$ centers.^{1–4} By comparison with Figure 2 and Table 2, it is known that the excitation peaks at 240 and 260 nm are from Cl excitons and oxygen defects ($O^{2-}(Cl^-)$), respectively. It is assumed that during the X-ray irradiation electron–hole pairs are generated, the electrons are trapped by anion vacancies, forming F centers, and the holes are trapped by Eu²⁺, resulting in Eu³⁺ ions.^{2,3} However, in our measurements we did not see any signal related to Eu³⁺ ions. This might indicate that the conversion of some Eu²⁺ ions to Eu³⁺ ions by radiation does not happen as pointed out by several groups.^{5–8,29} Instead, the creation of color centers, excitons, and oxygen defects play a key role in the storage luminescence.

Our results showed that essentially the same emission bands were emitted in PL, TL, and PTTL after optical and thermal stimulation. PTTL peaks appeared at 170, 220, 270, 320, 350, 400, and 430 K. The finding that the PTTL peaks of BaFCl:Eu²⁺ appeared at the same temperatures and with the same thermal activation energies as the TL peaks indicates that the same trapping levels were filled by the UV-induced transfer from the deeper to the shallower traps as by the β or X-ray irradiation.

Emission spectra recorded at the main 170 K PTTL peak showed a narrow band at 315 nm and a strong broad band at 390 nm. The 365 nm band, which was relatively strong at the 170 K TL peak, did not appear in the PTTL peak at the same temperature. The 320 K PTTL peak consisted mainly of the strong 315 nm band and a broad band at 390 nm. The other

PTTL peaks showed the same spectral composition as the 320 K peak, indicating that the same luminescence centers are responsible for the emission at these peaks. Heating to above 1100 K eliminated the effects of X-ray and β -irradiation, and PTTL could not be recorded, indicating that the deep trap responsible for the phototransfer process is bleachable above this temperature. This is actually beneficial for practical applications because erasable storage materials can be reusable.

4. Summary

In summary, the X-ray luminescence (XL), photoluminescence (PL), photostimulated luminescence (PSL), and thermoluminescence (TL) were studied in BaFCl:Eu²⁺ single crystals from room temperature (RT) to liquid nitrogen temperature (LNT). Six emissions at 275, 315, 365, 385, 435, and 500 nm were observed in the XL spectra and are attributed to Cl excitons, $V_k(\text{Cl}_2^-)$, the $4f^6 5d^1 (^2e_g) \rightarrow 4f^7 (^8S_{7/2})$ transition of Eu²⁺, and oxygen vacancies, respectively. Three emission peaks at 315, 365, and 390 nm were observed in the PL and TL measurements. These three emissions are from the transitions of $4f^7 (^6I_{7/2}) \rightarrow 4f^7 (^8S_{7/2})$, $4f^7 (^6P_{7/2}) \rightarrow 4f^7 (^8S_{7/2})$, and $4f^6 5d^1 (^2e_g) \rightarrow 4f^7 (^8S_{7/2})$ of Eu²⁺, respectively. The f–f emissions of Eu²⁺ were observed in the PL and TL spectra but not in the XL spectra. However, the relative intensities of the two f–f emissions at 315 and 365 nm are totally different in the TL and PL emissions. In the PL spectra, the 365 nm emission is dominant and much stronger than the 315 nm emission, while in the TL spectra, the 315 nm emission is dominant. At room temperature, the $4f^6 5d^1 (^2e_g) \rightarrow 4f^7 (^8S_{7/2})$ emission at 385 nm is dominant, but this emission decreases in intensity with decreasing temperature, whereas the $4f^7 (^6P_{7/2}) \rightarrow 4f^7 (^8S_{7/2})$ emission at 365 nm increases in intensity and becomes dominant at LNT. This phenomenon is considered to be suppressed by phonon coupling. In our measurements, we observed that the emission of Eu²⁺ increases in intensity upon β -irradiation and did not see any signals related to Eu³⁺ ions, which indicates that Eu²⁺ ions might not be oxidized to Eu³⁺ upon X-ray or β -irradiation. Instead, the creation of color centers, excitons, and oxygen defects might play a key role in the storage luminescence.

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