

## MODELING OF A PHOTOSTIMULABLE COMPLEX INDUCED BY X-RAY IRRADIATION OF BaFCl:Eu X-RAY STORAGE PHOSPHOR

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Photostimulated luminescence (PSL) and diffuse reflectance measurements on X-ray irradiated BaFCl:Eu<sup>2+</sup> microcrystalline powders were performed. We have investigated the nature of radiation induced defects involved in the photostimulation effect and its recombination mechanism. The experimental data sustain that X-ray irradiation gives rise to (F(Cl) - O<sub>F</sub><sup>-</sup> - Eu<sup>2+</sup>) photostimulable complexes and we have proposed several geometrical configurations of these complexes.

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### 1. Introduction

Recently, the new detection systems developed for two-dimensional X-ray imaging were proposed, to replace the classic radiography systems, due to their advantages: high sensitivity, processing of digitized images by a computer, reduction of X-ray dose [1, 2]. Among other proposed compounds, europium doped barium fluorohalides show the best performance for using as phosphors in the mentioned systems. The precise mechanism for image production is not yet fully understood, but it is now accepted that the room temperature stable electron and hole centres generated during the irradiation, are involved in the imaging process. Optical excitation of the F centre absorption band during the read-out process determines electron recombination with hole trapped centres, which finally results in the characteristic Eu<sup>2+</sup> luminescence (i.e. photostimulated luminescence or PSL). However, the exact mechanism of photostimulation process is still controversial and not fully understood [3].

The aim of this paper is the investigation of the nature of radiation induced defects involved in photostimulation effect, electron and hole centres, and their recombination mechanism.

### 2. Preparation procedure

Undoped and europium doped BaFCl samples were prepared by coprecipitation method which was described elsewhere [4]. The sintered samples were X-ray irradiated at room temperature with the radiation emitted by a tungstene target of a X-ray tube excited at U=50 kV and I=10 mA for various time intervals.

### 3. Photostimulated luminescence (PSL) measurements

Due to the fact that the samples are opaque, the PSL measurements were performed at the surface of the samples at oblique incidence, the experimental set-up being described elsewhere [4].

The normalised PSL spectra of undoped and europium doped samples, respectively, measured at  $\lambda=390$  nm (3.18 eV) are represented in Fig. 1 - curves "a" and "b". In the undoped samples one can notice two PSL maxima located at 445 nm (2.77 eV) and 545 nm (2.27 eV). In the case of the doped samples, the PSL signal for the same irradiation dose, is about an order of magnitude greater than in the undoped samples and the position of the PSL maximum at 560 nm (2.21 eV) is slightly shifted towards longer wavelengths as compared to the undoped samples.

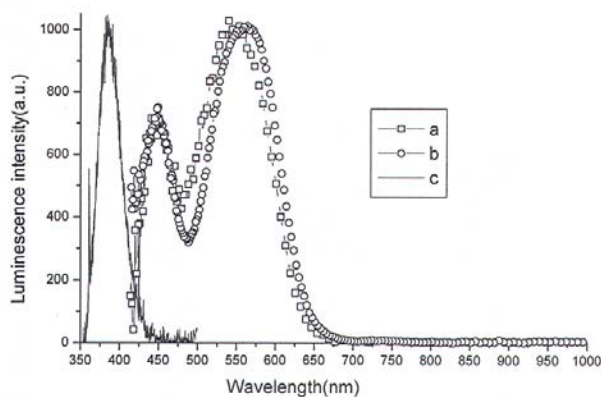


Fig. 1. Normalised PSL spectra of luminescence located at 390 nm recorded at RT: a) BaFCl; b) BaFCl:Eu<sup>2+</sup>; c) radiative emission of Eu<sup>2+</sup>, photostimulated at 560 nm (2.12 eV) and recorded at RT. Both samples have been X-irradiated at RT for 1 min.

#### 4. Diffuse reflectance measurements

The reflectance spectra were performed in the 220-800 nm spectral domain, using a Cary 118 spectrophotometer equipped with an integrating sphere. In the non irradiated samples, several reflection minima located at about 240 nm (5.16 eV), 265 nm (4.68 eV) and 280 nm (4.43 eV) are observed (Fig. 2 - curve "a"), which are growing after the X-irradiation (Fig. 2 - curve "b"). One can notice the presence of two extra reflectance minima at about 445 nm (2.77 eV) and 560 nm (2.21 eV) (Fig. 2 - curve "b"). Optical bleaching of PSL signal with visible light (570 nm) determines an almost total destruction of these two visible bands (Fig. 2 - curve "c") and a partial recovery of the 240 nm band (Fig. 2 - curve "c"). There is no intensity modification of reflectance minima at 265 nm and 280 nm.

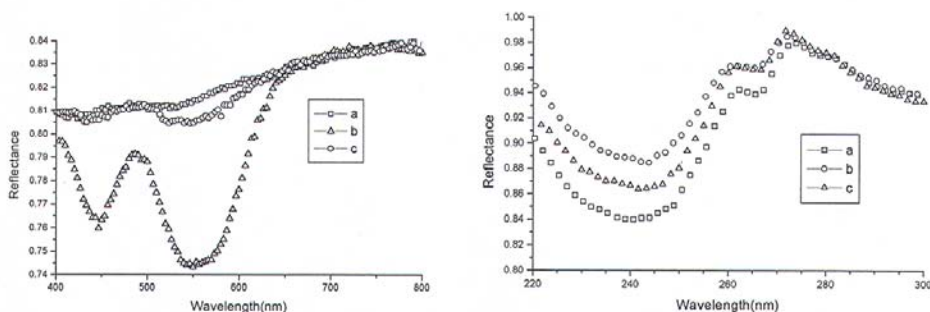


Fig. 2. Diffuse reflectance spectra recorded on BaFCl:Eu<sup>2+</sup> polycrystalline powder: a - before irradiation ; b - after X-ray irradiation for 30 min. at T=300 K; c - after optical bleaching of PSL signal with visible light (570 nm).

## 5. Discussion

In a previous paper we have shown that the model of “triple aggregates” is able to explain the PSL effect observed in BaFCl:Eu<sup>2+</sup> [5]. This model implies that the effect is due to optical recombination inside the “F centre-hole centre-Eu<sup>2+</sup>”, created during the irradiation, which result in europium luminescence [6]. However the model does not explain the nature of radiation induced electron and hole centres involved in PSL effect. In order to investigate the nature of these defects and their recombination mechanism, we compare the results of PSL measurements and their optical bleaching with the reflectance spectral data.

Depending on the location and the nature of the anion vacancy which traps an electron, F<sup>•</sup> or Cl<sup>-</sup> vacancy, in BaFCl lattice it is possible to consider two kinds of F centres, F(F<sup>•</sup>) and F(Cl<sup>-</sup>) [7]. According to the finite, punctual, group theory, they belong to the D<sub>2d</sub> and C<sub>4v</sub> symmetry species, respectively. The F absorption bands are due to an electronic transition from a s-like ground state to a p-like excited state splitted by the crystal field into a singlet and a doublet state. Based on the agreement between spectral position of PSL maxima and the absorption maxima of F(Cl<sup>-</sup>) in pure BaFCl [8] (Table 1), and the constant ratio between intensities maxima, even at high irradiation doses, we found that in X-ray irradiated doped samples the photostimulable centres are F(Cl<sup>-</sup>) centres. Experimentally we do not observe supplementary PSL maxima in the 900 nm-1000 nm spectral domain (even at high irradiation doses or after long storage times), which could be attributed to photostimulable F aggregates like F<sub>2</sub>, F<sub>3</sub> etc. (Fig. 1), which means that the F(Cl<sup>-</sup>) centres are the *only* photostimulable electronic centres. The PSL maxima at 560 nm (2.21 eV) and 445 nm (2.77 eV) are due to A<sub>1</sub>→A<sub>1</sub> and A<sub>1</sub>→E electronic transitions, the last one being splitted by the Jahn-Teller effect with about 0.2 eV [9]. The PSL spectra recorded in undoped and doped samples were decomposed using gaussian function for each individual maximum that is characterized by spectral position and band-width, w. The results of spectral deconvolution are given in Table 1 and Fig. 3. We can associate the slight spectral shift (with 0.05 eV) of the 560 nm (2.21 eV) PSL peak towards the long wavelengths compared to the absorption maxima of F(Cl<sup>-</sup>) centres in BaFCl, which is also observed from reflectance spectra (Fig. 2 b), with a perturbation of F(Cl<sup>-</sup>) centre by an unknown impurity. It is hard to believe that the oxygen impurity found in our samples could be the cause of this perturbation because in this case the same effect should be observed in undoped samples, which is not the case. So, we believe that the europium impurity acts as a perturbation impurity of the F(Cl<sup>-</sup>) centres. The broad luminescent emission at 385 nm (3.22 eV) and the weak emission line at 361 nm (3.43 eV) are due to europium impurity and are ascribed to the 4f<sup>6</sup>5d→<sup>8</sup>S<sub>7/2</sub> and <sup>6</sup>P<sub>7/2</sub>→<sup>8</sup>S<sub>7/2</sub> transitions, respectively [10]. In undoped samples the luminescence emission corresponds to electron-hole recombination [11].

Table 1. The results of spectral deconvolution of PSL spectra recorded with undoped and europium doped X-irradiated BaFCl polycrystalline powder. For comparison, on the right side of the table are presented the experimental results of absorption spectra measurements in BaFCl single crystal.

Sample	PSL Maxima (eV)	Band-width, w (eV)	Absorption maxima (ref.[8])	Spectral transitions
BaFCl	2.17	0.27	A <sub>1</sub> (s)→E (p <sub>x</sub> ;p <sub>y</sub> )	2.25
	2.38	0.32	A <sub>1</sub> (s)→E (p <sub>x</sub> ;p <sub>y</sub> )	
	2.77	0.29	A <sub>1</sub> (s)→A <sub>1</sub> (p <sub>z</sub> )	
BaFCl:Eu <sup>2+</sup>	2.12	0.22	-	-
	2.32	0.25		
	2.77	0.35		

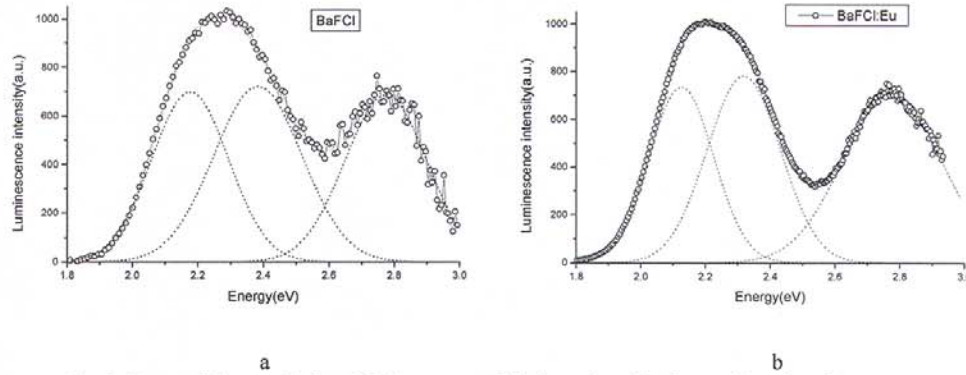
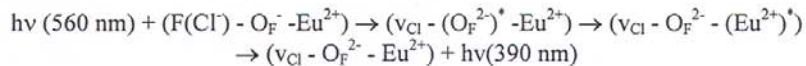


Fig. 3. Spectral deconvolution of PSL spectra of the in undoped and europium doped X-irradiated BaFCl polycrystalline powder.

The effect of the optical bleaching of the PSL signal on reflectance spectra provides valuable information about the nature of the hole centres involved in this effect. Before the irradiation we can observe two reflectance minima at about 240 nm (5.16 eV) and 280 nm (4.43 eV) which are due to  $O_F^{2-} - v_{Cl}$  and respectively  $O_{Cl}^{2-} - v_{Cl}$  oxygen-vacancy complexes, where  $O_X^{2-}$  ( $X=F, Cl$ ) is the substitutional oxygen impurity on X anion site and  $v_{Cl}$  is the compensating charge chloride vacancy [12]. The reflectance minimum at 265 nm (4.68 eV) is due to substitutional hydroxyl ion on chloride site  $OH_{Cl}$  [7]. After X-ray irradiation we observe a growing of the above reflectance minima and the formation of europium perturbed  $F(Cl)$  centres (Fig. 2 a). It was shown from ESR measurements that the free holes and electrons created during the irradiation are trapped by the deep traps hole  $O_X^{2-}$  and  $OH_{Cl}$  and respectively by the  $v_{Cl}$  chloride vacancy giving rise to  $O_X^-$  and  $F(Cl)$  centres [13]. According to “triple aggregates model” for the PSL effect, optical bleaching of the PSL signal in the absorption maxima of  $F(Cl)$  centres at 560 nm determines destruction of photostimulable triple aggregates. However, we can still observe reflectance minima, that we associate with *non-photostimulable* europium perturbed  $F(Cl)$  centres (Fig. 2 a curve “c”). There is a *partial* recovery of the 240 nm reflectance minima which means that a limited number of  $O_F^-$  participate at the PSL mechanism, the remaining oxygen ions behaving as *non-photostimulable hole centres*. Besides, we cannot observe any kind of modification of reflectance minima associated with  $O_{Cl}^{2-} - v_{Cl}$  (oxygen-vacancy) complexes and  $OH_{Cl}$  impurities, which means that  $O_{Cl}^-$  ions didn’t participate at the PSL mechanism and all behaves as *non-photostimulable centres*. So we suppose that the  $O_F^-$  is the only hole which enters in the structure of a triple aggregate and the configuration of such a photostimulable complex is: “ $(F(Cl) - O_F^- - Eu^{2+})$ ”.

The “triple aggregates” model of PSL effect implies that the fast component observed from optical bleaching measurements, is due to the recombination by tunneling of the  $F$  centre’s electron to the hole centre, which results in the europium luminescence, the slow component being due to recombination between the same partners through a diffusion mechanism of the excited electron [6]. Photoluminescence measurements data support the existence of an energy transfer between  $(O_F^{2-})^*$  and  $Eu^{2+}$ , the mechanism being effective only between the mentioned partners and not between  $(O_{Cl}^{2-})^*$  and  $Eu^{2+}$  partners [4]. We suppose that the excited electron of europium perturbed  $F(Cl)$  centre recombines with  $O_F^-$  hole centre, giving rise to excited  $(O_F^{2-})^*$ , which transfers its deexcitation energy to europium impurity followed by its luminescent emission, according to the reaction:



Group theory arguments and RMN measurements data on the oxygen-vacancy complexes provide valuable information about the configurations of such “triple aggregates”. We must take into account the nature of the angular parts of wave-functions which describe the excited states  $A_1$  ( $P_x$ ) and  $E(p_x; p_y)$ , respectively [9] – (see Table 1) and experimental observation of the perturbation effect

only for E state. We suggest that the localization of the europium impurity is in the near neighborhood of the F(Cl) centre, but not on the  $c_4$  symmetry axis, because if so, the  $A_1$  excited state would be perturbed. The RMN data on oxygen doped barium fluorohalides crystals suggest the localization of anion vacancy in the next-neighborhood or the next-near-neighborhood of the  $O_x^{2-}$  substitutional oxygen [14]. The above arguments and the experimental data allow to suggest geometrical models of such "triple aggregates" which are presented in Fig. 4. However, further, measurements are needed to test these models.

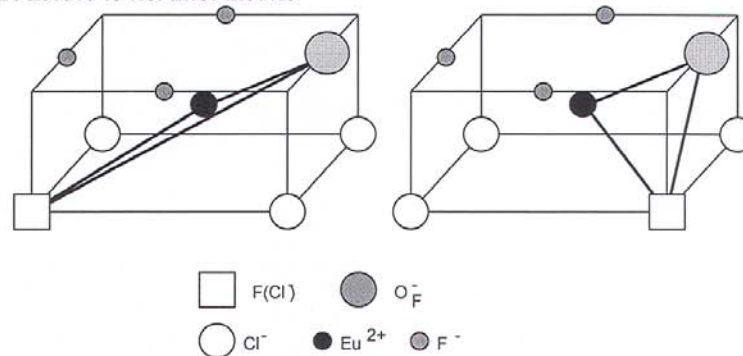


Fig. 4. Geometrical configurations of the "triple aggregates".

## 6. Conclusions

We have improved the triple aggregate model of PSL effect in BaFCl:Eu<sup>2+</sup> polycrystalline powder X-ray storage phosphor in which europium perturbed F(Cl) is the only electronic photostimulable centre and the  $O_F^{2-}$  is the hole centre. We have proposed geometrical configurations of such photostimulable complexes.

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