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Optical storage studies on the trapping states of BaFCl:Eu²⁺

Meng Xian-guo, Wang Yong-sheng, Sun Li, Jin Hui and Zhang Lin

Institute of Optoelectronic Technology, Ministry of Railway Key Lab Laboratory of Materials for Information Storage and Display Northern Jiaotong University, Beijing 100044, China

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Abstract

The optical absorption spectra of BaF_{2-x}Cl_x:Eu in different states of optical storage were measured to clarify the electron trapping mechanism for its optical storage and photo-stimulated luminescence (PSL). Based on the absorption spectra and difference absorption spectra, the electron transfer processes after ultraviolet (UV) light irradiation were investigated. This demonstrates that (1) Eu³⁺ ions are formed upon UV light irradiation at room temperature; (2) the two absorption bands in the visible region (400–600 nm) should be assigned to two different F centres, both of which contribute to the optical storage and PSL, and (3) a third broad difference absorption band around ~650 nm, which matches the common laser better, was observed.

1. Introduction

BaFX:Eu²⁺ (X = Cl, Br), which exhibits photo-stimulated luminescence (PSL) and offers an alternative to conventional x-ray imaging technology, has been studied extensively [1–11, 14, 15]. The PSL mechanism, however, is still in controversy. It was initially proposed by Takahashi *et al* [1] that during x-ray or UV light irradiation, Eu²⁺ ions are ionized into Eu³⁺ and F⁺ centres become F centres; during PSL the opposite process occurs, i.e. Eu²⁺ + e ⇌ Eu³⁺, F⁺ + e ⇌ F. Different models were suggested by others [2, 3]. It was proposed that no Eu³⁺ is formed upon irradiation [2]. Moreover, only the bromine F centres contribute to the photostimulability in BaFBr:Eu²⁺ [3]. It is not clearly known how the energy is transferred to the activator Eu²⁺ which emits at 3.2 eV [4].

In this paper the optical storage and colour centres in europium doped BaFCl are reported and discussed.

2. Experimental details

The samples were prepared from Eu₂O₃, BaCO₃, NH₄Cl and NH₄F intimately mixed according to the desired ratio. The mixture was first fired at 350 °C for 0.5 h, then fired at 800 °C for

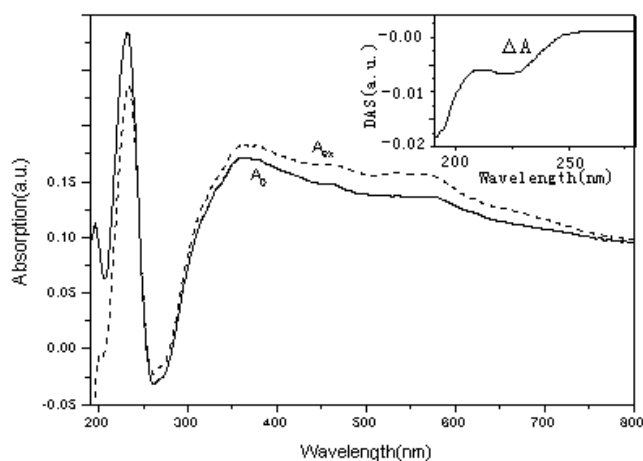


Figure 1. Optical absorption of $\text{BaF}_{1.05}\text{Cl}_{0.95}:\text{Eu}^{2+}$; A_0 , unirradiated by UV.

2 h in carbon and air atmosphere (the concentration of Eu is 0.005 and 0.05 mol) respectively. The resulting powder samples were pressed into pellets (diameter $26 \times 2 \text{ mm}^2$).

A Shimadzu UV-3101 PC spectrophotometer was used to measure the optical absorption spectra. The slit width and scanning speed of the Shimadzu were properly selected so that the signal could be detected with a good resolution and low noise without exciting or stimulating it significantly. For powder samples, the optical absorption spectrum, namely, the wavelength dependence of absorption coefficient $\alpha(\lambda)$, was obtained from the diffused reflection spectrum $R(\lambda)$. In the system we have the relation $\alpha(\lambda) = -\log R(\lambda)$. The BaSO_4 powder was defined as the standard sample with 100% reflection ratio or zero absorption. However, the negative absorption of our samples at some wavelengths in the UV region shows that they have higher reflection ratio than that of BaSO_4 powder. The choice of standard sample will not influence our principal results. A deuterium lamp in a ZF-I UV analyser was used to produce the UV light (245 nm) to write-in. The width of UV light is 7 nm. The x-ray diffraction (XRD) patterns of these samples show that they are substantially single phase. All measurements were carried out at room temperature (RT).

3. Results and discussion

The optical absorption spectra of $\text{BaF}_{1.05}\text{Cl}_{0.95}:\text{Eu}^{2+}$ in different states (A_0 unirradiated by UV light, A_{ex} irradiated by UV light for 300 s) are shown in figure 1. As is shown by curve A_0 , there is a strong absorption band in the UV region (210–250 nm), with a peak at $\sim 235 \text{ nm}$ (5.3 eV). It is known that the Eu^{2+} band is located at 4.6 eV (270 nm) for BaFX ($X = \text{Cl}, \text{Br}$) [1, 4]. The samples produced in the reducing atmosphere are low in oxygen. Oxygen related defects have been investigated in several papers [4–8]. It was reported [7] that O_F^{2-} has a luminescence band excited at 4.95 eV (250 nm). It seems inappropriate whether the above absorption band (5.3 eV) is assumed to be the Eu^{2+} or the O_F^{2-} band since they have very small cross sections. However, some authors [10, 11] studied the optical storage properties of $\text{BaFCl}:\text{Eu}^{2+}$ under UV irradiation (220–320 nm). They pointed out that there is a ‘tunnelling state’ ($\sim 5.2 \text{ eV}$) of Eu^{2+} in the $\text{BaFCl}:\text{Eu}^{2+}$ system, which coincides with the absorption peak at $\sim 5.3 \text{ eV}$ of our sample. The A_0 spectrum shows another absorption band below 210 nm, the peak of which is located at $\sim 195 \text{ nm}$. It was reported [9] that there is an absorption band at 190 nm (6.5 eV) in

BaFBr:Eu²⁺, which was considered to be caused by Eu²⁺ ions. Similarly, the absorption band below 210 nm in BaFCl:Eu²⁺ should be attributed to the excitation of Eu²⁺ ions. In contrast, the A_{ex} spectrum shows decreasing absorption, suggesting that the relative energy band (especially the high energy band below 210 nm) has been suppressed by UV irradiation. The difference absorption spectrum of A_{ex} and $A_0 - \Delta A$ is also shown in figure 1. Therefore, it is very possible that the absorption in the UV region is mainly due to the excitation of Eu²⁺ ions. Some of the excited electrons return to the ground state, which give rise to the broad band emission centred at 386 nm and the sharp line centred at 362.2 nm [10]. Some are captured by electron traps. This indicates that some of the electrons are ionized ($\text{Eu}^{2+} - e \Rightarrow \text{Eu}^{3+}$) by UV light irradiation, which results in the decrease of the number of Eu²⁺ ions. The ionized electrons are captured by the electron traps ($\text{F}^+ + e \Rightarrow \text{F}$) [1, 10], which results in the increase of the number of F centres. The increased region (400–600 nm) corresponds to the absorption of F centres. The energy of 245 nm UV light (~5.0 eV) is not high enough to excite the electron from the valence band to the conduction band as the 8.3 eV bandwidth gap of BaFX (X = Cl, Br). If the Eu²⁺ ions are not ionized to Eu³⁺, it is hard to understand the optical storage caused by UV light. It may be due to the following possibilities:

- (1) there is error in the apparatus and during the process of measuring, or the number of Eu³⁺ caused by UV light is so small, just within the experimental error, that it cannot be observed;
- (2) upon x-ray (or UV light) irradiation, a low concentration of ‘triple aggregates’ between Eu²⁺ and F centres are formed [2] or
- (3) other defects such as O_F²⁻ act as hole traps [4–8]. The above-mentioned suggests that this process is a minor factor at RT.

The difference absorption spectrum (DAS) of BaF_{1.05}Cl_{0.95}:Eu²⁺ is shown in figure 2(a) in order to understand the possible method of electron transition during optical storage. The two difference absorption bands between 400 and 600 nm are formed after UV light irradiation because the F⁺ centres capture some of the electrons caused by the excitation of Eu²⁺ ions. It is interesting to notice that there is a series of sharp difference absorption lines (SDALs) in the region from 350 to 440 nm, which is very like the absorption of divalent europium ions. The experiment was performed time and again, and the SDALs bear good repeatability. This fact indicates that the SDALs do not result from the effect of the noise. From the discussion below, it can be concluded that they are the absorption of Eu³⁺.

The europium ions in BaFCl phosphor prepared in air atmosphere are mainly divalent europium ions as in the absorption spectra shown in figure 2(b). In the region of 350–440 nm, a series of sharp absorption lines with peaks at about 362, 378, 395 and 416 nm respectively is in good agreement with the SDALs of BaF_{1.05}Cl_{0.95}:Eu²⁺ mentioned above. The slight difference between them is that (1) the intensity of the SDALs is weak and not obvious in the region from 400 to 600 nm and (2) the peak at 378 nm in the absorption spectra is split into three peaks in the SDALs which are located at 373, 381 and 386 nm respectively and the SDALs are sharper. The low concentration of Eu³⁺ (<0.01 mol [12]) results in the low absorption ratio. For CaS:Eu, Sm the electron trap and neighbouring Sm³⁺ ion influence each other in absorption [13]. Similarly, the high absorption of F centres may ‘shade’ the absorption of Eu³⁺ to some extent where both F centre absorption and Eu³⁺ absorption occur in the visible region. Figure 2(c) shows the absorption spectrum of free Eu³⁺ ions in water solution where the interaction between ions is very weak [12]. The three sharp peaks (373, 381 and 386 nm) in the DAS are at the same position as those of Eu³⁺ in water solution. The slightly different effect of crystal field induces the slightly different absorption of Eu³⁺. The SDALs of different optical storage states demonstrate the fact that Eu³⁺ ions are formed after the UV light irradiation.

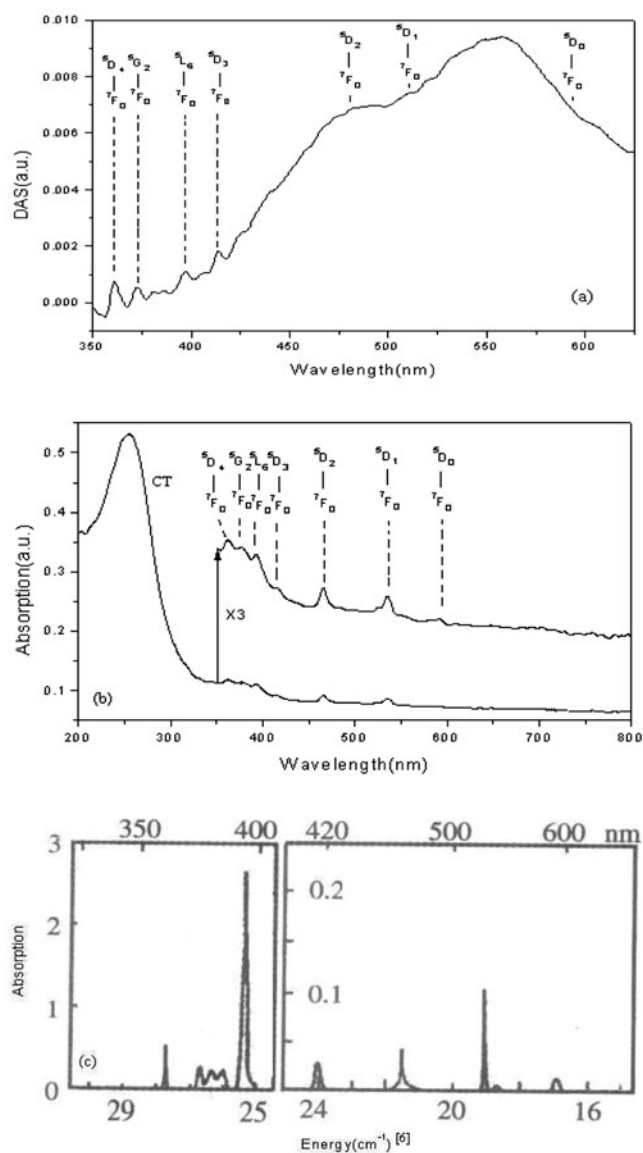


Figure 2. DAS of BaF_{1.05}Cl_{0.95}:Eu²⁺ after 15 s UV light irradiation (a), optical absorption spectra of BaFCl:Eu²⁺ and Eu³⁺ (b) (unirradiated) and (c) absorption.

In order to understand more about the possible method of electron transition during the optical storage and PSL process, DASs of BaF_{1.05}Cl_{0.95} under various UV light doses were investigated as shown in figure 3. The DAS, which is mainly caused by the absorption of F centres, is increased greatly with the increase of irradiation time while the increase of the SDALs is not so obvious. This means that the UV light can only ionize some of the Eu²⁺ ions. Eu³⁺ ions and Eu²⁺-hole complexes may coexist after UV light irradiation. Besides, O_F²⁻ may also act as a hole trap. It has been reported [3] that in BaFBr:Eu²⁺, two peaks in the stimulation spectra are erased proportionally for different bleaching times, which was regarded as the evidence that the two stimulation bands should be assigned to the same F(Br⁻) centre. Only F(Br⁻) centres contribute to photostimulability. However, the DAS information of our

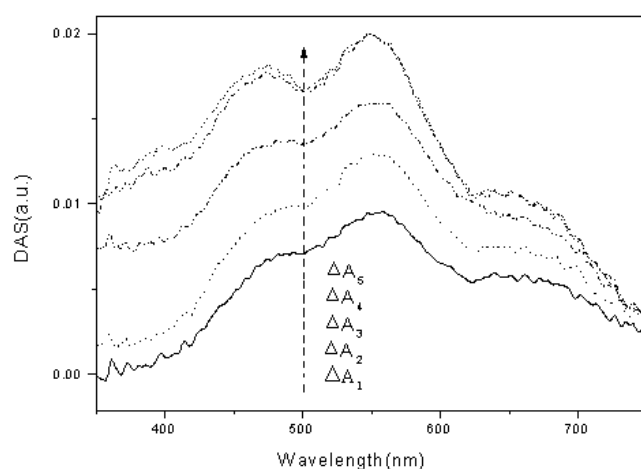


Figure 3. DAS of BaF_{1.05}Cl_{0.95}:Eu²⁺ in different optical storage states, irradiated by UV light for 15 s (ΔA_1), 30 s (ΔA_2), 120 s (ΔA_3), 600 s (ΔA_4) and 900 s (ΔA_5) (DAS increases with increasing illumination time) after 15 s UV light irradiation (ΔA).

sample increases proportionally for different irradiation times. In the previous work [10], the bleaching of 550 nm light to two stimulation bands in BaFCl:Eu²⁺ is not to the same extent. In the DAS, the band with a peak at 550 nm increases faster and saturates first. This means that the two difference absorption bands have to be assigned to different F centres. According to the Mollwo relation [3], the difference absorption band with peaks at about 470 and 550 nm must be caused by F(F⁻) centres and F(Cl⁻) centres respectively, and they both contribute to the PSL. The third interesting point is that there is a broad difference absorption band (with a peak at ~650 nm) in a region from about 550 to 750 nm. However, the third DAS band is hardly observed in BaFCl:Eu²⁺ phosphor. It may have promise in the application of this phosphor because it matches the common lasers such as the He-Ne laser (633 nm) better. Since the vacancies of Cl⁻ ions are increased in BaF_{1.05}Cl_{0.95} compared to that in BaFCl, and its saturation process under UV light irradiation is nearly the same as that of F(Cl⁻) centres, it may be due to the aggregation of F(Cl⁻) centres. Further investigations need to be done on this DAS band.

4. Conclusion

These results suggest that some Eu²⁺ ions can be ionized to form Eu³⁺ upon UV light irradiation. The two difference absorption bands with peaks at about 470 and 550 nm are caused by F(F⁻) centres and F(Cl⁻) centres respectively, and both of them contribute to optical storage and PSL. A third broad difference absorption band (about from 550 to 750 nm) around 650 nm may have promise for application and it is possibly due to the aggregation of F(Cl⁻) centres. We need to study further the nature of this difference absorption band and its behaviour in x-ray (or UV light) storage and PSL processes.

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