X 射线诱导 BaFCl：Eu^{2+}光激励发光过程的新观察

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本文研究了 BaFCl：Eu^{2+}光激励发光(PSL)对 X 射线剂量的响应关系，光激励发光的衰减规律，以及色心的形成与转型．除了简单的 F 心之外，我们还发现了 F 心的缔合中心，它们的吸收带位于 700～950nm．连续光激励 F 心时，光激励发光呈指数型衰减，而光激励 F 缔合中心时，光激励发光呈双曲线型衰减．我们还发现 Eu 激活的 BaFCl 或纯的 BaFCl 基质的热激励发光(TSL)也显现类似的衰减规律．光激励 F 缔合中心时，伴随着光激励或热激励发光还可能有一些无辐射跃迁过程的产生，例如色心的分解、转型和解离电子的再捕获等．我们发现 X 射线辐照前后，Eu^{3+}／Eu^{2+}的相对含量及 Eu^{2+}的 ESR 强度并没有发生明显的改变．在低剂量的 X 射线辐照下光激励发光对 X 射线剂量的响应呈现线性关系，而在高剂量 X 射线辐照下光激励发光对剂量的响应偏离线性关系．这可能是由于色心的转型和电子再捕获的竞争作用而引起的．

关键词： BaFCl：Eu^{2+} X 射线辐照 光激励发光 色心

SOME NEW OBSERVATION ON THE PROCESS OF THE PHOTOSTIMULATED LUMINESCENCE(PSL) OF X-IRRADIATED BaFCl：Eu^{2+}

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X-ray dose dependence of PSL, PSL decay, color centers formation and interconversion of BaFCl：Eu^{2+} have been studied. In addition to the previously known simple F-centers there were found aggregated F centers having absorption bands in the region 700-950nm. Continuously optical stimulation into F-center band and aggregated F centers band would result in logarithmical and hyperbolical decay process of PSL respectively. The thermally stimulated luminescence (TSL) of pure or Eu doped BaFCl show the similar decay trends. There might happen some nonradiative processes accompaning with the PSL and TSL as the crystals are stimulated into aggregated F centers bands, such as decomposition, interconversion and electron-retrapping of ionized color centers. The relative content of Eu^{3+} / Eu^{2+} and the ESR spectra

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of Eu^{2+} in BaFCl : Eu prior and subsequent to X–irradiation practically remain unchanged. The PSL response–dose range of lightly X–irradiated BaFCl : Eu^{2+} exhibits a linear relationship. But for the heavily X–irradiated BaFCl : Eu crystals its PSL–dose response and PSL decay curves of latter period deviate from linearity. That may arise from the interconversion of various F centers and competitive retrapping of electrons by different ionized F centers and other positive centers.

Keywords: BaFCl : Eu^{2+} X–irradiation photostimulated luminescence color center

1. Introduction

Europium–doped BaFX have been studied extensively[1–4] because of their importance for X–ray intersifying screens materials and image storage phosphor. Much work had been done on the formation and ionization of color centers in the process of X–ray irradiation and photostimulated luminescence(PSL). In addition to the previously known $F(F^-)$ and $F(Cl^-)$ centers, we have found the formation of F2, F3 and F4 centers in the X–irradiated BaFCl : Eu^{2+} crystals. They were considered to be aggregates of simple F–centers and denoted as FA[5]. In this paper, we would report more information about their behavior during X–irradiation and PSL process.

Takahashi et al[1] have proposed a mechanism as follows. Preliminary X–irradiation converts Eu^{2+} to Eu^{3+} and creats stable F centers. Photostimulation into the F center absorption band then ionizes electron to the conduction band which subsequently recombine with Eu^{3+} producing the Eu^{2+} luminescence. Another mechanism was postulated by Seggern et al[2]. He considered that the recombination of electron with Eu^{3+} is not through conduction band, but via tunneling. Recently a new model for PSL mechanism was proposed by Hangleiter et al[6] which involves formation of loose triple aggregates of Eu^{2+}, F and hole centers. Koschnick et al[7] have reported their work on the spatial correlation of $F(X^-)$, h^+ and Eu^{2+} ions in the PSL process of BaFBr : Eu^{2+}. All those pushed the research on the PSL mechanism of BaFBr : Eu^{2+}

In this paper the change of color centers and Eu^{2+} ions during X–irradiation and PSL process is studied in detail, and some new observation are reported.

2. Experimental

Single crystals of BaFCl and BaFCl : Eu^{2+} were grown in N_2 atmosphere by programmablly cooling the melt in platinum crucibles. The cooling rate was 1.5K / h in the temperature range 1348 to 1273K. The typical dimension is about $6 \times 8 \times 2mm^3$. The powder samples were synthesized with anhydrous BaF_2, $BaCl_2$ and EuF_2 at 1058K for about 2h in N_2–H_2(5%) atmosphere.

The optical absorption spectra were measured on an UV–365 double beam spectrophotometer. The stimulation spectra, PSL emission spectra and the decay curves of PSL were recorded with a Hitachi M–850 fluorescence spectrophotometer. The glow curves were obtained on a 7185–type thermoluminescence dosimeter with a heating rate 1K / sec. The data and curves were acquired with BBC–B$^+$ computer. EPR spectra were measured at X–band on a Bruker–Analytic EPR Spectrometer. The X–irradiation was carried out by X–rays from an X–ray diffractometer (CuKα, 40kV, 20mA).

3. Results and Discussion

3.1 X–ray dose response of PSL intensity

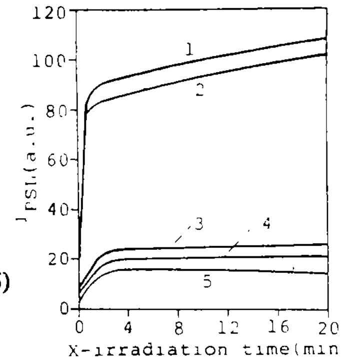

Fig. 1 Dose–PSL response of BaFCl：Eu^{2+} (3×10^{-3} mole) photostimulated into F(F^-) band 540nm(1), F(Cl^-) band 440nm(2), F2 band 870nm(3), F3 band 670nm(4) and F4 band 980nm(5)

It has been reported that the X–ray dose response of PSL BaFCl：Eu^{2+} of phosphers is in linearity[4,8]. Through study in more detail, we found that the X–ray dose dependence of PSL intensity is not in simple linearity but in a rather complicated condition. Fig. 1 shows the dose (expressed as X–irradiation time) response of PSL intensity by stimulation into absorption bands of F(F^-), F(Cl^-), F2, F3 and F4 color centers[5] respectively. It could be seen from Fig. 1 that the increase of PSL intensity with X–irradiation time might be differentiated into two stages. At the first stage, i. e. for lightly (less than one minute) X–irradiation, the PSL intensity increase rapidly with X–irradiation time. At the second stage, i. e. for longer time X–irradiation, the PSL intensity increase slowly. Moreover by stimulation into FA bands of longer time X–irradiated crystals, the PSL intensity dose not increase further. This suggested that there might be a complicated condition for the formation and interconversion of F and FA centers in the process of X–irradiation and photostimulation. Fig. 2 shows that for lightly

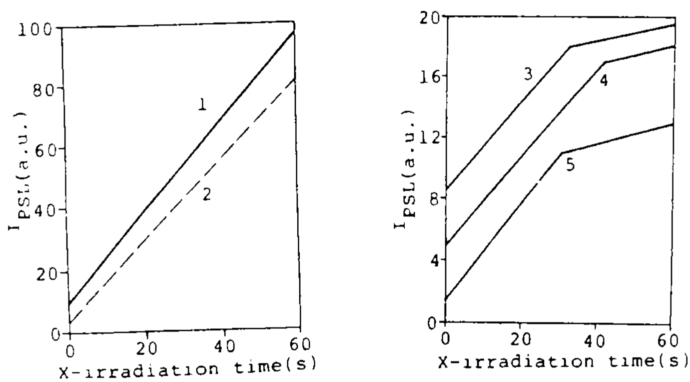

Fig.2 Dose–PSL response of BaFCl：Eu^{2+} preliminaryly X–irradiated within 1 min and then photostimulated into 540(1), 450(2), 870(3), 670(4) and 980nm(5) respectively

X–irradiated BaFCl : Eu, the dose–PSL intensity response is linear.

3.2 Decay of PSL

The PSL decay curves of BaFCl : Eu^{2+} by continuous photostimulation into different color center bands are shown in Fig.3 and Fig. 4. The PSL decay curves can be differentiated into two steps, a fast one and a slow one, which is similar to the result obtained by Hangleiter et al[6]. Moreover there is a difference between the PSL decays by stimulation into F–bands and into FA bands. The former decay logarithmically(Fig.3) and the later decay hyperbolically (Fig.4). The time constants (half–life time) of the former is about 0.1–0.2 min, while that of the later is about 1 min. Similar conclusion were obtained from the PSL decay curves of undoped matrix BaFCl crystal in Fig.5.

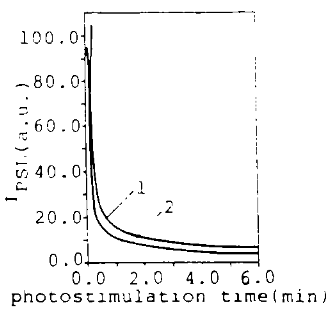

Fig. 3 PSL decay curves of 5min X–rayed BaFCl : Eu^{2+} crystal as being photo–stimulated into its F(F^-) band 540nm(1) and F(Cl^-) band 440nm(2) respectively

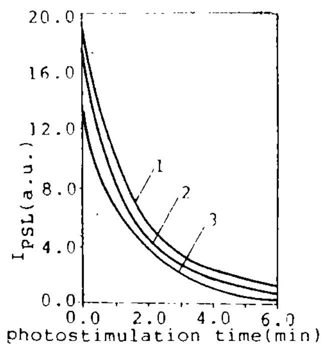

Fig. 4 PSL decay curves of 5min X rayed BaFCl : Eu^{2+} crystal as being photo–stimulated into its F2 band 870nm(1), F3 band 670nm(2) and F4 band 980nm(3) respectively

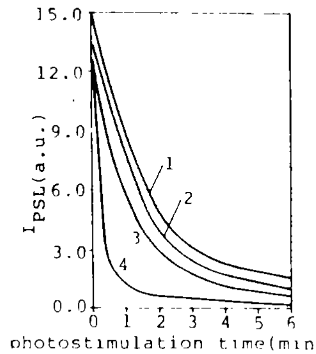

Fig. 5 PSL decay curves of 5min X–rayed undoped BaFCl crystal as being photo–stimulated into its F(F^-) band 546nm(1), F2 band 870nm(2), F3 band 670nm(3) and F4 band 980nm(4) respectively

It is interested to note that thermostimulated luminescence (TSL) decays of these Eu–doped or undoped BaFCl crystals are similar to the of PSL decay, i. e. the TSL associated with F centers decay logarithmically, and the TSL associated with FA centers decay hyperbolically[9]

From the above experimental results we would suppose that there might happen some non–radiative processes accompanying with the PSL as the crystals were photostimulated into FA bands, such as decomposition of FA centers, electron retrapping and interconversion of color centers.

3.3 Interconversion of color centers during PSL process

The optical absorption spectra of X–rayed BaFCl : Eu^{2+} crystal is shown in Fig. 6. The two bands peaking at 440 and 540nm are attributed to the absorptions of F(Cl^-) and F(F^-) centers respectively[5]. It was found that, when the crystal was photostimulated into 540nm, in addition to the appearence of PSL of Eu^{2+}, there occured a decrease of $F(F^-)$ band, and the increase of FA bands. On the other hand, when the crystal was photostimulated into 865nm, the F2 band was decrease, and the F bands increased. As the crystal was thermally stimulated at 393K, the two simple F bands were decreased, and the FA bands increased. The above results indicate that during PSL or TSL process, the F and FA centers are interconvertible.

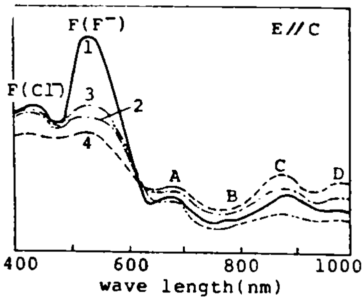

Fig.6 Optical absorption spectra of BaFCl： Eu^{2+} crystal X–rayed for 20min (1), then optically stimulated by 540nm light for 20min(2), then by 865nm light for 20min(3) and finally thermally stimulated at 393K for 5min(4)

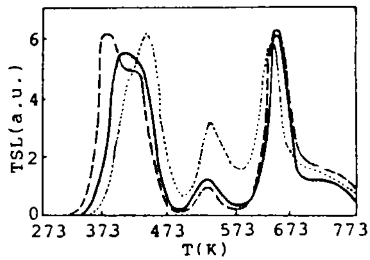

Fig. 7 Glow curves of BaFCl： Eu^{2+} single crystal prior X–irradiated for 5s(▬▬), and then photostimulated by 440nm light (E / / C) for 5min(————); prior X–irradiated for 5s and then photostimulated by 540nm light (E / / C) for 5min(•••••••••)

The interconversion among F and FA centers were also found in the glow curve study. Fig. 7 shows that glow curves of X–rayed BaFCl： Eu^{2+} crystal. There are five glow peaks which are associated with $F(F^-)$, $F(Cl^-)$, F3, F4 and F2 centers respectively[19]. When the crystal was photostimulated into the $F(Cl^-)$ absorption band (440nm), the $F(Cl^-)$ center associated glow peak (422K) decreased, and the $F(F^-)$ and F3 associated glow peaks (396 and 533K) increased. When it was photostimulated into $F(F^-)$ band (540nm), the $F(F^-)$ center associated glow peak decreased, and the $F(Cl^-)$ and F3 center associated glow peaks increased. On the other hand, when the crystal was photostimulated into F2 band (870nm), the F2 center associated glow peaks (705K) decreased, and the $F(Cl^-)$ center associated glow peak (422K) increased slightly

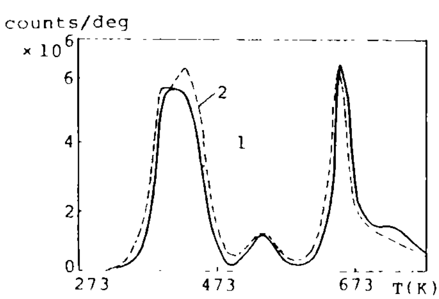

Fig. 8 Glow curves of BaFCl： Eu^{2+} X–rayed for 5s (1) and then photostimulated by 870nm light for 5min (2)

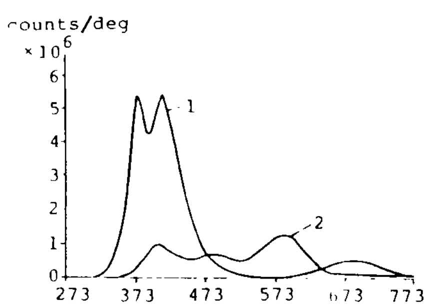

Fig. 9 Glow curves of BaFCl powder X–rayed for 30s(1) and then photostimulated by 440nm light for 5min (2)

(Fig. 8). Therefore it is reasonable to say that during PSL process besides the interconversion among F and FA centers, the $F(F^-)$ and $F(Cl^-)$ centers might interconvert to each other too.

The interconversion among F and FA centers during PSL process might be also observed in undoped BaFCl. Glow curve of BaFCl (curve 1 in Fig. 9) has three peaks which are associated with $F(F^-)$, $F(Cl^-)$ and F2 centers respectively[9]. As this sample was photostimulated with 440nm light, both the two simple F centers and F2 center associated glow peaks were bleached, meanwhile two new glow peaks within 473–653K appeared. These two new peaks were considered to be associated with F3 and F4 centers respectively[9]. From the above results it could be concluded that, by 440nm light stimulation, the F and F2 centers might be converted to F3 and F4 centers, i. e. $F+F2 \longrightarrow F3+F4$.

3.4 Change of Eu^{2+} and Eu^{3+} during X–irradiation and PSL process

Both Takahashi et al[1] and Seggern et al[2] ever proposed that X–irradiation results in the formation of F centers and Eu^{3+} via hole–trapping by Eu^{2+}. Recently a triple aggregate of Eu^{2+}–F hole was proposed to be produced by X–irradiation in BaFBr: Eu^{2+} crystal by Hangleiter et al[6]. Much work had been done in our laboratory in the recent years. As for samples contain only Eu^{2+} and no Eu^{3+} which were synthesized in H_2 atmosphere, no mater how long time they were X–irradiated, we could not find the photoluminescence emission of Eu^{3+}. As for the samples contain both Eu^{2+} and Eu^{3+} which were synthesized in N_2 atmosphere, we really observed the decrease of Eu^{2+} emission and the increase of Eu^{3+} emission during X–irradiation, but the decrease of Eu^{2+} emission is much higher than the increase of Eu^{3+} emission (Fig.10). This suggested that the change of Eu^{2+} to Eu^{3+} by X–irradiation is only a minute.

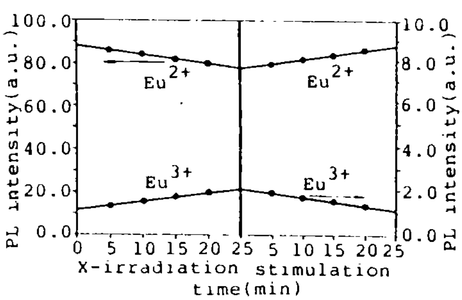

Fig. 10 Concentration change of Eu^{2+} and Eu^{3+} in BaFCl crystal during the processes of prior X–irradiation and subsequent photostimulation

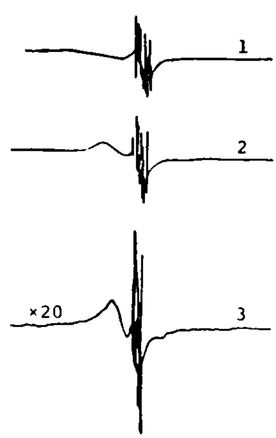

Fig. 11 ESR spectra of BaFCl: Eu^{2+} crystals

1.ESR spectrum before X–irradiation

2.ESR spectrum after X–irradition for 1h

3.ESR spectrum of $BaF_{1.05}Cl_{0.95}$:Eu^{2+}

CF = 3500G, SW = 4000G, frequency = 9.4120GHz

Fig. 11 shows the ESR spectra of BaFCl: Eu^{2+} crystals. It is found that, after

X–irradiation for 1h, the intensity of Eu^{2+} ESR signal is almost unchanged, but a broad ESR signal is appeared at about 3350G. The g values of the broad signal are $g=1.9791$ and $g=1.9850$[9]. The same signal is also found in $BaF_{1.05}Cl_{0.95}$: Eu^{2+} crystal(Fig.11). Compared with the results reported by Takahashi et al[10] and Yuste et al[11], it is believed that this signal is caused by $F(Cl^-)$ center formed[9].

From the above results, we consider that the change of Eu^{2+} in BaFCl

$$Eu^{2+}+O \xrightarrow{\text{X-irradiation}} [Eu^{2+}+h^+]+F(Cl^-)$$

As for BaFCl crystal, doped only with Eu^{3+}, no ESR signal was observed before X–irradiation, but a signal appeared at about 3500G after X–irradiation for 2h (Fig.12). This signal was caused by Eu^{2+}. That means some Eu^{3+} was reduced into Eu^{2+} by X–irradiation:

$$Eu^{3+}+O \xrightarrow{\text{X-irradiation}} Eu^{2+}+Vk$$

Most Vk centers were formed in the matrix along with the creation of F–centers during X–irradiation. But we did not find ESR signal of primary and secondary Vk centers, because it should be observed at low temperature[6].

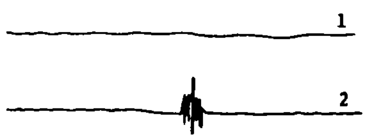

Fig.12 ESR spectra of BaFCl: Eu^{3+} crystal before X–irradiation(1) and after X–irradiation for 2h (2) CF = 3500G; SW = 7000G; frequency = 9.4456GHz

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