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SPECTRAL HOLE BURNING AND PHOTO STIMULATED LUMINESCENCE PROCESSES IN
 $\text{BaF}(\text{Cl},\text{Br}):\text{Sm}^{2+}$

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Before and after X-irradiation, two photon spectral hole burning experiments in $\text{BaF}(\text{Cl},\text{Br}):\text{Sm}^{2+}$ were performed by a 560 nm laser light at liquid nitrogen temperature. The results show that spectral hole burning of Sm^{2+} doped in Alkaline earth metal fluorine halide mixed crystals is accompanied by a photo-stimulated luminescence process. This process causes hole burning efficiency to decrease. Copyright © 1996 Published by Elsevier Science Ltd

1. INTRODUCTION

Since photon gated spectral hole burning in $\text{BaFCl}:\text{Sm}^{2+}$ was reported by Winnaker *et al.* [1] of Sm^{2+} doped in Alkaline earth metal fluorine halide mixed crystals, better materials have been found with useful properties. Especially, they have good properties in high temperature hole burning. Room temperature hole burning has been realized at present [2–4]. These materials have potential use in frequency domain optical storage, therefore they are widely investigated. The host lattice of these compounds belongs to a PbFX system, which is a better host for divalent rare earth ions. Divalent rare earth ions doped PbFX systems have many characteristics. Besides being hole burning materials, they are also photo-stimulated luminescence materials, thermal stimulated luminescence materials, X-ray luminescence materials and UV photo-luminescence materials [5–7]. The studies in this field were performed earlier. Photo-stimulated luminescence processes are similar to spectral hole burning to some extent, and these two processes exist simultaneously in the same sample. Therefore, we studied photo-stimulated luminescence processes so as to increase hole burning

efficiency and to clarify the hole burning mechanism. We found that the hole burning process is accompanied by a photo-stimulated luminescence process, which makes hole burning efficiency decrease. In this paper, hole burning mechanisms are also studied.

2. EXPERIMENTAL

The $\text{BaF}(\text{Cl},\text{Br}):\text{Sm}^{2+}$ powder samples were prepared using the method described in [8]. In experiments of spectral hole burning and photo-stimulated luminescence, the samples were pumped and probed by a dye laser pumped by a Nd:YAG pulsed laser at liquid nitrogen temperature. A D330 monochromator, a Boxcar averager, and a Datamate microcomputer were used to detect and analyse the luminescence of $\text{BaF}(\text{Cl},\text{Br}):\text{Sm}^{2+}$. Before the experiment, a D-max X-ray diffractometer was used to irradiate one of the samples.

3. RESULTS AND DISCUSSION

3.1. Spectral hole burning before and after X-irradiation

On the samples before and after X-irradiation, two photon spectral hole burning experiments were performed by a 560 nm Nd:YAG pulsed laser under the same conditions. Figure 1 shows the dependence of the fluorescence intensity at a burning site on burning time in the samples before (a) and after (b) X-irradiation.

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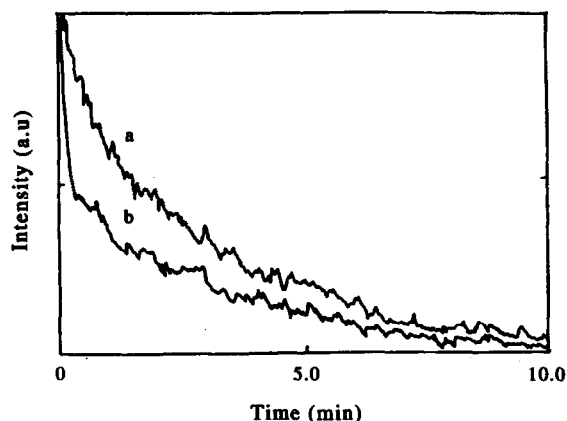


Fig. 1. Dependence of the fluorescence intensity at the burning site on burning time at 77 K performed by a 560 nm pulsed laser in the same condition. (a) Before X-irradiation, (b) After X-irradiation for 20 min (monitoring position: 688 nm).

In the experiments, the samples were excited with the same laser power, and irradiation areas were all 1 cm^2 . The light direction was unchanged. From Fig. 1 we can see that, before and after X-irradiation, the dependence of the fluorescence intensity at the burning site on burning time changed. For the sample after X-irradiation, the fluorescence intensity decreased with time rapidly. This result shows that: (1) By X-irradiation, the electron capturing ability of traps and hole burning efficiency are enhanced so that hole depth is rapidly deepened with burning time. (2) The photo-stimulated luminescence process happens while the sample is excited by a 560 nm laser. The populations of F center increase greatly by X-irradiation so that the photo-stimulated luminescence process is increased. Due to that, photo-stimulated luminescence intensity

decays faster than the burning rate, the fluorescence intensity after X-irradiation decreases with time rapidly.

Figures 2 and 3 show distributions of the excitation spectrum before and after X-irradiation related to Fig. 1, respectively. We can see from Fig. 2 that, compared to the sample before X-irradiation, a hole about 50% of the depth is obtained after burning. From Fig. 3 we can see that, compared to the sample after X-irradiation, no obvious hole is obtained after hole burning. These results show that X-irradiation makes hole burning efficiency decrease greatly. So the change of fluorescence intensity at the burning site in Fig. 3 is mainly attributed to the change of the photo-stimulated luminescence process before and after X-irradiation. We think that, in the samples, a great number of anion vacancies exist, and play the role of electron traps. They can capture electrons in the spectral hole burning process. Due to the energy of the X-ray the photon is larger than the energy gap of the lattice, some electrons in the valence band can be excited into the conduction band, and captured by those anion vacancies to form F center. So the anion vacancies will decrease, the electron capturing ability of anion vacancies becomes weak, and hole burning efficiency of Sm^{2+} decreases. Under X-irradiation, the other type centers are also formed, such as V_K center and F_A center. But 560 nm light cannot be absorbed by these centers to give rise to photo-stimulated luminescence. Some electrons stimulated by the conduction band will be recombined with Sm^{3+} . This process makes the fluorescence intensity increase after X-irradiation, and decay with the increase of stimulation time. In the process of photo-stimulated luminescence, a great number of electrons liberated from the F center will move in the lattice, competing

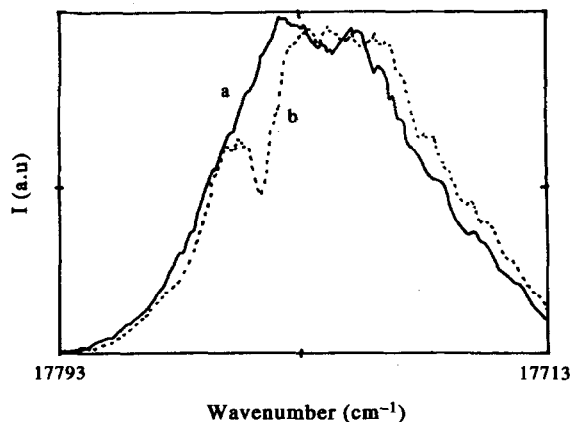


Fig. 2. Excitation spectrum of the sample before X-irradiation before (a) and after (b) hole burning which is related to Fig. 1(a).

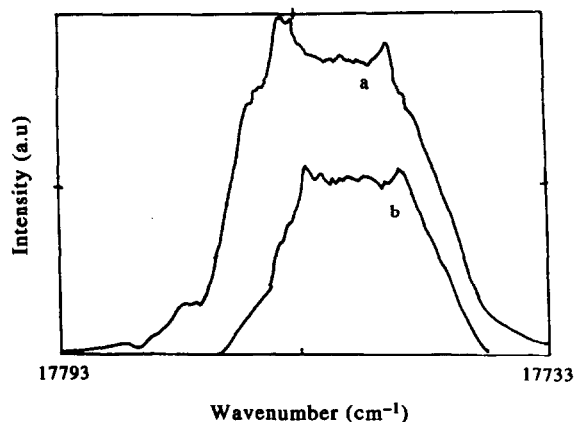


Fig. 3. Excitation spectrum of the sample after X-irradiation before (a) and after (b) hole burning which is related to Fig. 1(b).

for traps with electrons produced by hole burning of Sm^{2+} and therefore affecting hole burning efficiency.

In the processes of X-irradiation and photo-stimulation, the number of Sm^{2+} and Sm^{3+} ions will also change. According to the experimental results of Lin Jianhua *et al.* [9] the concentration of Sm^{2+} ions will increase and the concentration of Sm^{3+} ions will decrease with the increase of X-irradiation. In the photo-stimulated luminescence process there exists an opposite process. In the sample after X-irradiation, the decrease of Sm^{3+} (electron traps) will also make hole burning efficiency decrease. The results above show that the accompanied photo-stimulated luminescence process in spectral hole burning is the main factor to affect hole burning efficiency due to the prior X-irradiation.

3.2. Photo-Stimulated luminescence process and hole burning efficiency of $\text{BaF}(\text{Cl}, \text{Br})\text{:Sm}$

In fact, in the process of sample preparation, some colour centers are formed. The types of these centers are the same as those formed in the sample during X-irradiation [10]. The fluorescence spectrum is observed by the excitation of 566 nm laser light. Since the 566 nm laser light is not a resonance light with 5D_2 level, there are two explanations for the fluorescence produced by 566 nm laser light. (1) The electrons are excited to the tail of the $4f5d$ band by 566 nm light, and then relax from $4f5d$ to $^5D_J (J = 1, 0)$ level from where the emission spectrum occurs. (2) The electrons of F center are stimulated by 566 nm light and recombines with Sm^{3+} to give rise to photo-stimulated luminescence.

In order to prove whether the fluorescence excited by a 566 nm laser includes photo-stimulated

luminescence or not, the emission spectra were measured before and after optical irradiation by a 566 nm laser. Figure 4 shows the emission spectra in $^5D_1-^7F_0$ transition before and after 566 nm optical irradiation. From Fig. 4 we can see that, after 566 nm optical irradiation, the fluorescence intensity decreases. If the fluorescence excited by a 566 nm laser comes entirely from the fluorescence of Sm^{2+} , it cannot change before and after 566 nm optical irradiation. So this result shows that the photo-stimulated luminescence process exists. Comparing the fluorescence of $^5D_1-^7F_0$ excited by a 560 nm resonance laser to that excited by a 566 nm laser, we can find that the fluorescence intensity excited by resonance light is about 100 times of that excited by a 566 nm laser (with the same laser power). 566 nm and 560 nm lights all locate at the position of the absorption band of F center, and the absorption ability of F center to 566 nm and 560 nm laser light has almost no change. Therefore, we can claim that the photo-stimulated luminescence is only a small part of the total fluorescence excited by resonance light.

In the sample before X-irradiation, the photo-stimulated luminescence process is also a factor to hole burning efficiency. In the experiment, holes were burnt by a 560 nm light with weak laser power. We did not observe any holes at the burning site, but observed that the inhomogeneous line area becomes small. The decrement is much less than that in the sample after X-irradiation. We think that photo-stimulated luminescence is an easier process than spectral hole burning, and causes hole burning efficiency to decrease, so no obvious hole was observed. In multi-spectral hole burning, we also observed this fact. Figure 5 shows the excitation spectrum distributions before

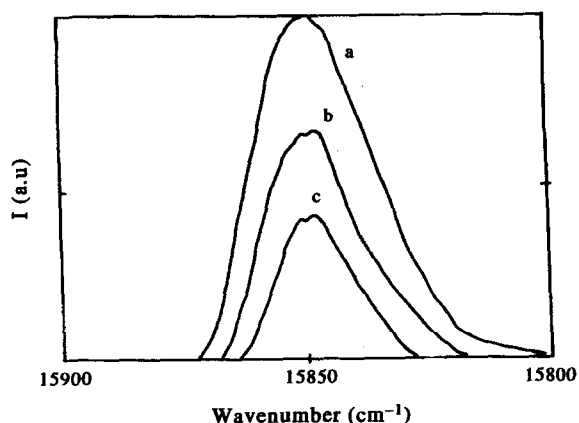


Fig. 4. Emission spectra of $^5D_1-^7F_0$ transition excited by a 566 nm laser before and after a 566 nm laser irradiation. (a) Without irradiation, (b) after X-irradiation for 5 min, (c) after X-irradiation for 10 min.

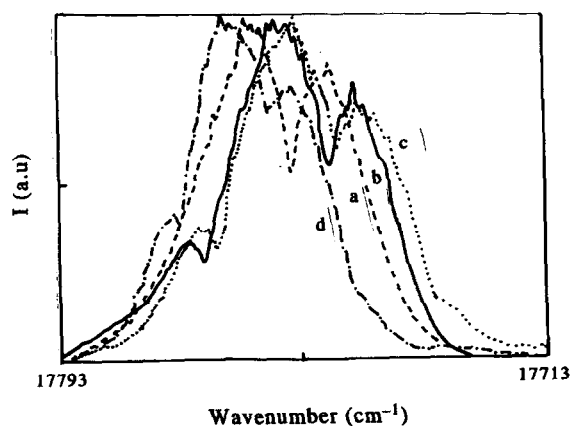


Fig. 5. Excitation spectra after multi hole burning at 77 K with the same burning time and the same laser power. (a) burning at 17819 cm^{-1} , (b) at 17811 cm^{-1} , (c) at 17825 cm^{-1} , (d) at 17830 cm^{-1} .

and after hole burning. The multi-holes were burnt with the same burning time and the same laser power at 17819, 17811, 17825, and 17830 cm^{-1} respectively. From Fig. 5 we can observe that, after burning the first hole (17819 cm^{-1}), a hole about half depth was obtained. After burning the second hole (17811 cm^{-1}), only a shallow hole was obtained, and the first hole became shallow. After burning at 17825 and 17830 cm^{-1} , we did not observe any obvious hole except bleaching of the fluorescence. We also attributed it to the influence of the photo-stimulated luminescence process. Due to being stimulated by laser burning, the electrons captured by traps in advanced hole burning will be ionized and move in the lattice. So the electron capturing ability of traps from Sm^{2+} will become weak. The traps being mostly filled in advanced hole burning, it is another reason causing hole burning efficiency to decrease. We can also observe from Fig. 5 that, in multi-hole burning, the position of the excitation spectrum shifts. It is because of the transfer between Sm^{2+} and Sm^{3+} ions in spectral hole burning.

4. CONCLUSIONS

In two-photon spectral hole burning, due to the burning laser wavelength at the position of the absorption band of F center, the F centers will be ionized by stimulation. The ionized electrons

recombine with Sm^{3+} to give rise to photo-stimulated luminescence. The photo-stimulated luminescence process occurs more readily than spectral hole burning. The electrons ionized by stimulation will compete for traps with electrons ionized from Sm^{2+} . This process makes hole burning efficiency decrease. In the sample after X-irradiation, the photo-stimulated luminescence process is more obvious.

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