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The mechanism of photobleaching in Sm^{2+}-doped alkaline-earth fluorohalides

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Abstract

The fluorescence intensity of divalent samarium (Sm^{2+}) ions doped in alkaline-earth fluorohalides were found to decrease under the optical excitation from a blue laser, a green laser or even a red laser. This photobleaching effect has a mysterious and unknown mechanism. After the bleaching effect happened, no Sm^{3+} ions generation, no relative spectral change in Sm^{2+} emissions and no lifetime decrease for the levels of Sm^{2+} ions could be observed. Under blue- or green-laser irradiation, the decrease of Sm^{2+} fluorescence showed a perfect biexponential function; however, when the exciting photon energy was lower than that of $^5D_0 \rightarrow {}^7F_0$ transition, the photobleaching effect could not be observed anymore. An identical mechanism in the photobleaching with that in the spectral hole burning was proposed.

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Keywords: Photobleaching; Irradiation; Photoluminescence

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1. Introduction

Divalent samarium (Sm^{2+}) ion has played an important role as a function material in frequency domain optical storage and information processing since the persistent spectral hole burning (SHB) in CaF_2:Sm^{2+} and the photon-gated SHB in BaFCl:Sm^{2+} were reported by Macfarlane [1] and Winnacker [2]. Some materials doped with Sm^{2+}, such as alkaline-earth fluorohalides with the PbFCl-type structure, borate glasses [3–6], fluoride [7–8] glasses, Al_2O_3–SiO_2 glass [9–17] and ZnS nanocrystals [18], etc., have been investigated

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for applications of the frequency domain optical storage. In the investigation of room temperature hole burning, much attention has been paid on getting a broad inhomogeneous emission band [3,19–21]. However, intense and stable fluorescent emission should be another important character for frequency storage materials, especially for those aiming at practical applications. The investigation on it will also help researchers to understand the mechanism of the frequency domain optical storage and to design applicable materials.

Photobleaching in Sm^{2+}-doped material was observed and reported firstly by Krebs et al. in 1997 [22]. They found that the fluorescence intensity of Sm^{2+} selectively doped epitaxial CaF_2 film decreased nonexponentially with time under an optical excitation. They also found that the bleaching rate depended linearly on the intensity of the optical excitation and that the shape of the emission line was not altered during the bleaching process. In 2001, more materials doped with Sm^{2+} were found to have the bleaching effect by Mikhail et al. [23]. They studied single crystals of CaF_2, SrF_2, BaFCl, SrFCl, $SrFCl_{0.85}Br_{0.15}$, SrB_4O_7 and ceramic samples of $BaCl_2$, $SrSO_4$ for the bleaching effect. To explain the bleaching phenomenon, they assumed a nonradiative decay mechanism that resulted in a decrease of the Sm^{2+} fluorescence. An important thing declared in that paper was the reversible bleaching of the Sm^{2+} luminescence; however, the reversible bleaching in their work was only available for the broadband transition $4f^55d$–$4f^6$ of Sm^{2+} in the crystal sample of CaF_2:Sm^{2+}. Additionally, all the decrease processes of the bleaching were treated exponentially by the authors, which maybe a mistake based on the experimental observations of other researchers [22,24]. Tanaka et al. reported a reversible photochromic process they observed in BaClF:Sm^{2+} in 2001 [25]. They found that the fluorescence intensity of Sm^{2+} in BaClF decreased under the excitation of 325-nm light from a He–Cd laser and recovered with the 488-nm light from an Ar^+ ion laser at room temperature. The reversible bleaching was interpreted as follows: Sm^{2+} was photoionized to Sm^{3+} by 325-nm light and the excited electrons were captured by halogen vacancies of BaClF, while the trapped electrons were released under the 488-nm light and Sm^{3+} was reduced to Sm^{2+}. Recently, we investigated the photobleaching with Sm^{2+} doped in alkaline-earth fluorohalides and found that the deepest decrease reached 96% under an excitation of 488-nm line of an argon laser in 30 min. A biexponential bleaching mode was found by fitting the decrease curves [24].

Here, we report our novel investigation on photobleaching of fluorescence intensity of the Sm^{2+} ions doped in alkaline-earth fluorohalides $MFCl_{0.5}Br_{0.5}$ (M = Ba or Mg + Sr). It is that, under an optical excitation (blue, green or red light), the intensities of Sm^{2+} fluorescence in the alkaline-earth fluorohalides decreased with the exposure time. This investigation on the decrease of Sm^{2+} fluorescence intensity relates directly to the mechanism of the Sm^{2+} f–f transition as well as to the mechanism of SHB in the alkaline-earth fluorohalides.

2. Experimental

The samples we used in the experiment are alkaline-earth fluorohalides multi-crystal $MFCl_{0.5}Br_{0.5}$ (M = Ba or $Mg_{0.5}+Sr_{0.5}$): 1 mol% Sm^{2+}, which were prepared by high-temperature solid reaction and reduced in H_2 atmosphere or by X-ray irradiation. For H_2-reduced samples, the raw materials with the stoichiometric compositions were sintered at 1100 °C for 1 h in H_2; for X-ray-reduced samples, the raw materials with the stoichiometric compositions were sintered at 1100 °C in air for 1 h and then the resultants were irradiated by X-ray for 8 h using the Cu Kα line at 45 kV and 300 mA. To measure the emission spectra of samarium ions (Sm^{2+} and Sm^{3+}), the samples were excited with 488-nm line of an argon ion laser at room temperature and the luminescence from 550 to 750 nm was then detected with a PMT (R928) mounted on a spectrometer (SPEX 1702). An OG-530 cut-off filter was placed in front of the spectrometer to block off the scattered laser lines. Almost no Sm^{3+} emission could be detected within H_2-reduced samples, which indicates that the Sm^{3+} ions in them were well reduced to Sm^{2+} ions by firing in a H_2 atmosphere. The red laser employed here is a dye laser operating with DCM and was pumped by the 514.5-nm line of the argon ion laser. The line width of the tunable dye laser is about 1.4 cm^{-1} full-width at half-maximum. A pulsed YAG laser (SLII-10, 10 ns pulse width) with a third-harmonic generator was used as the excitation source in the measurement of lifetime. Decay curves were recorded using a LeCroy 9350A 500 MHz digital oscilloscope and computer-controlled data acquisition system. A laser power controller (LPC) was used in our experiments to stabilize the excitation power.

3. Results and discussion

The emission spectra of the Sm-doped alkaline-earth fluorohalides excited at room temperature by 488-nm laser light were recorded, and the results are shown in Fig. 1. H_2-reduced samples presented only the luminescence characteristics of Sm^{2+} ions. The fluorescence from $^5D_0 \rightarrow {}^7F_{0,1,2}$ and $^5D_1 \rightarrow {}^7F_{0,1,2}$ transitions could be observed easily, as shown in Fig. 1(a). The dot line is an amplified spectrum in Fig. 1(a), in which, the broad emission band centered at 560 nm is due to 5d–4f transition of Sm^{2+} ions in a crystalloid sample ($BaFCl_{0.5}Br_{0.5}$:Sm^{2+}, reduced in H_2). Fig. 1(b) is the spectrum of an X-ray-reduced sample ($Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$:$Sm^{2+}$, Sm^{3+}). The emissions of Sm^{3+} were contained besides the emissions of Sm^{2+}. These spectra indicate that almost all the Sm^{3+} ions were reduced into Sm^{2+} ions in the H_2-reduced samples and that only a part of the Sm^{3+} ions had been reduced to Sm^{2+} ions in the X-ray-reduced sample.

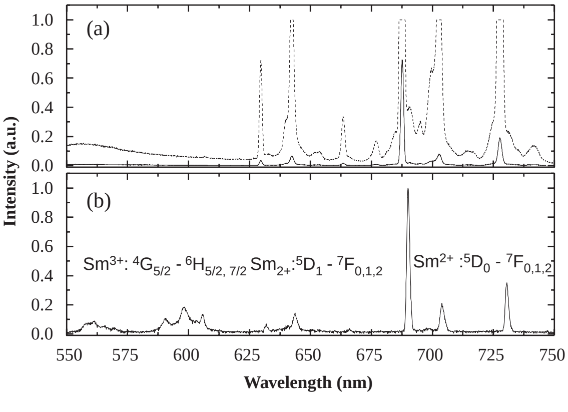

Fig. 1. Spectra of alkaline-earth fluorohalides doped with Sm^{2+} ions under an excitation with 488-nm laser light (Ar^+ ion laser). (a) is the spectrum of the crystalline samples ($BaFCl_{0.5}Br_{0.5}$:Sm^{2+}) reduced in a H_2 atmosphere; the dot line in (a) is an amplified spectrum. (b) is the spectrum of the multi-crystal sample reduced by X-ray irradiation ($Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$).

Under 488-nm blue laser light, the fluorescence intensity of Sm^{2+} ions decreased nonexponentially with the exposure time for all samples; however, these decreases were same for all emissions of Sm^{2+}, i.e. absolute intensities decreased and relative intensities did not change, as shown in Fig. 2. Under the same excitation conditions, the emissions of Sm^{2+} in the H_2-reduced sample ($Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$:$Sm^{2+}$) were recorded before and after a 1-h irradiation at 488 nm (5 mW), as shown in Fig. 2(a). The two spectra are identical after normalized at the fluorescence peak of $^5D_0 \rightarrow {}^7F_0$. This relative unchanged spectral property suggests that no structural change occurs in the sample's matrix when the photobleaching effect happens.

To check the reversible bleaching phenomenon reported by Mikhail et al. [23], we monitored the intensity of $4f^55d \rightarrow 4f^6$ broad emission band of Sm^{2+} in the crystalloid sample; however, a similar nonexponential decrease was obtained, as shown

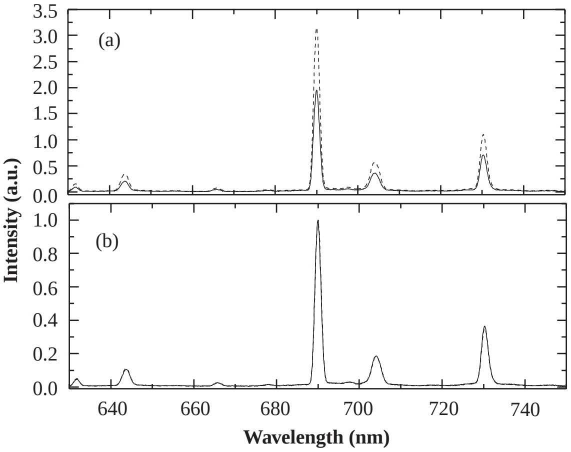

Fig. 2. Photoluminescence spectra (a) recorded before (dash line) and after (solid line) 1-h irradiation at 488 nm. These two spectra are same after normalization at the peak of 690 nm (b).

in Fig. 3. No recovery could be observed with the $4f^55d \rightarrow 4f^6$ emission as well as with the other emission peaks of Sm^{2+} when the irradiation had, for a while, a break.

The spectra of the X-ray-reduced sample were recorded under the excitation of 488-nm laser, as shown in Fig. 4(a). These spectra were gotten one after another and each scan took about 5 min. Only the emissions of $^5D_0 \rightarrow {}^7F_{1,2}$ (Sm^{2+}) and $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (Sm^{3+}) are drawn in Fig. 4(a) for clarity. While the intensity of Sm^{2+} fluorescence decreased with the exposure time, a stable intensity of Sm^{3+} fluorescence was recorded. No evidence of increased Sm^{3+} ions was observed when the intensity of Sm^{2+} fluorescence decreased much after longtime strong irradiation, as shown in Fig. 4(b). The intensities of $^5D_0 \rightarrow {}^7F_2$ emission in all scans are lined in Fig. 4(b), which shows a nonexponential decay. Similarly, when the analogous experiment was practiced with H_2-reduced samples, also no Sm^{3+} emission could be found after the photobleaching happened even after heavy irradiation. Based on these experimental facts, we believe that the mechanism of the photobleaching of Sm^{2+} ions in our mixed crystal alkaline-earth fluorohalides is not a photoionization process in which the Sm^{2+} ions were photoionized into Sm^{3+} ions. In other words, the fluorescence decrease of Sm^{2+} ions in alkaline-earth fluorohalides did not result in the generation of Sm^{3+} ions by the photobleaching process.

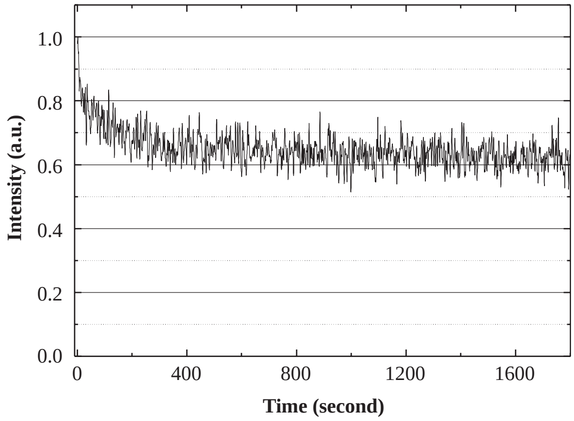

Fig. 3. 5d–4f fluorescence of Sm^{2+} in the crystal sample ($BaFCl_{0.5}Br_{0.5}$:Sm^{2+}, reduced in H_2) shows a photobleaching effect under 488-nm irradiation.

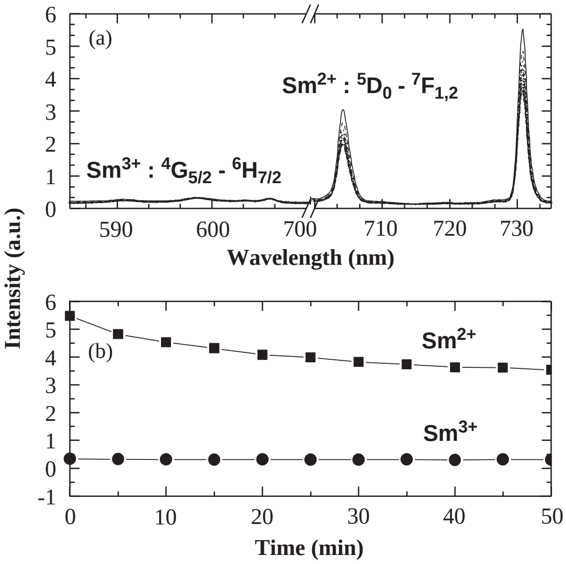

Fig. 4. Spectra of the X-ray-reduced sample ($Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$:$Sm^{2+}$, Sm^{3+}) obtained under the excitation at 488 nm (a). They were recorded one after another and each scan took about 5 min. The intensities of $^5D_0 \rightarrow {}^7F_2$ (Sm^{2+}, ■) and $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (Sm^{3+}, ●) emission for all scans are lined in (b), respectively.

In Ref. [23], Mikhail et al. assumed a nonradiative decay mechanism in explaining the photobleaching of Sm^{2+} fluorescence, because their experiment did not show any increase of the Sm^{3+} photoluminescence with a decrease of Sm^{2+} luminescence. To check their assumption, we measured the lifetimes of $^5D_0$ level (Sm^{2+}) with the H_2-reduced sample and the X-ray-reduced sample, respectively. In Fig. 5, we give two decay curves of $^5D_0$ level (Sm^{2+}) measured before and after the irradiation of intense blue laser with the X-ray-reduced sample. When the two decay curves were normalized, we found that they were identical and the lifetimes of $^5D_0$ level (Sm^{2+}) before and after the irradiation were almost the same, ~1.20 ms, as shown in the inset of Fig. 5. This experimental result does not support Mikhail and Hulliger's assumption on the increased nonradiative process inducing the photobleaching.

It is necessary to investigate the dependence of the photobleaching on excitation photon energy in

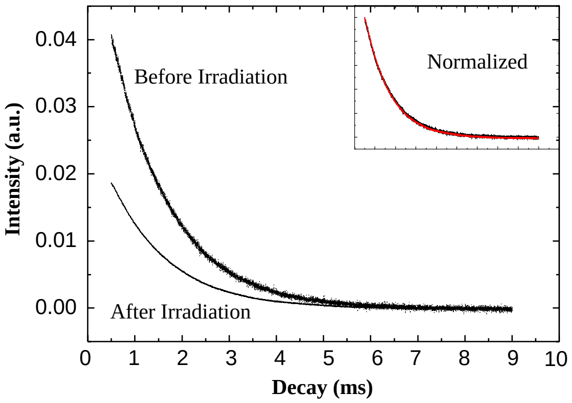

Fig. 5. Decay curves of $^5D_0$ level (Sm^{2+} doped in $Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$, X-ray-reduced sample) recorded with an oscilloscope before and after blue laser irradiation at 488 nm. When they were normalized, the two decay curves were identical (inset).

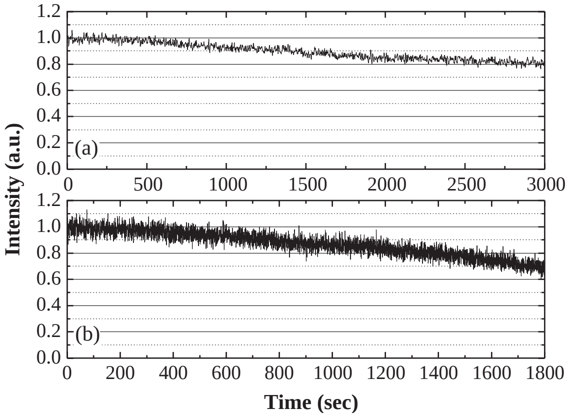

Fig. 6. Photobleaching induced by red lasers. The $^5D_0\rightarrow{}^7F_0$ fluorescence of the X-ray-reduced sample ($Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$:$Sm^{2+}$, Sm^{3+}) decreased ~20% in 50 min under 38-mW laser irradiation at 678 nm (a) and ~30% in 30 min under 70-mW laser irradiation at 650 nm (b).

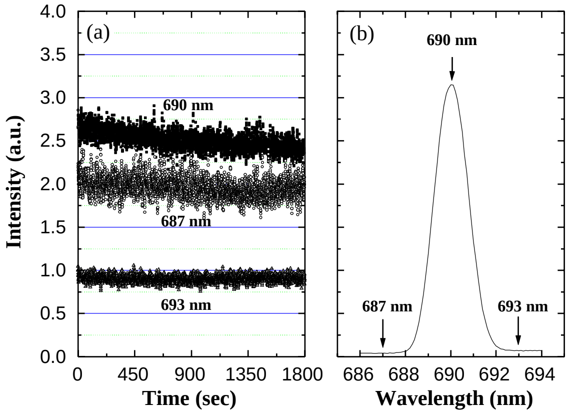

Fig. 7. (a) $^5D_0\rightarrow{}^7F_2$ fluorescence of the X-ray-reduced sample ($Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$:$Sm^{2+}$, Sm^{3+}) was detected under three excitations, 687, 690, and 693 nm, respectively. The three excitation wavelengths were marked in the $^5D_0\rightarrow{}^7F_0$ spectrum (b). The power of each laser was 10 mW.

order to explore the bleaching mechanism. In our former investigation on the photobleaching [24], we have reported that both the 488-nm blue laser (5 mW) and 514.5-nm green laser (5 mW) could induce a rapid decrease of the fluorescence in Sm^{2+}-doped alkaline-earth fluorohalides. Here, we checked the photobleaching effect with low-energy photons as excitations. We irradiated the X-ray-reduced sample with several red lasers (650, 678, 687, 690, and 693 nm) and found that the photobleaching happened as long as the excitation photon energy was higher than the energy of $^5D_0\rightarrow{}^7F_0$ transition, as shown in Figs. 6 and 7(a). In Fig. 6, under the excitations at 650 nm (70 mW) and 678 nm (38 mW), the intensity of $^5D_0\rightarrow{}^7F_0$ emission decreased by about 30% in 50 min and 20% in 30 min, respectively. Furthermore, a similar experiment was done with respect to the transition of $^5D_0\rightarrow{}^7F_0$. Three pump wavelengths, 687, 690, and 693 nm, were employed in it. The photon energy of 690-nm light corresponds resonantly to the transition energy of $^7F_0\rightarrow{}^5D_0$, and the photon energies of 687- and 693-nm lights are a little higher and a little lower than the resonant energy, respectively, as shown in Fig. 7(b). Under these three excitations, three intensity evolutive curves of the $^5D_0\rightarrow{}^7F_2$ emission on the exposure time were recorded, as shown in Fig. 7(a). The resonant excitation of 690-nm light induced an obvious photobleaching and the excitation of 687-nm light also induced a weak decrease of the $^5D_0\rightarrow{}^7F_2$ fluorescence; however, the low-energy photon of 693-nm light did not induce any decrease of Sm^{2+} emission. This result indicates that there is an energy threshold in the photobleaching of Sm^{2+}, the energy of $^5D_0\rightarrow{}^7F_0$ transition.

Sm^{2+}-doped alkaline-earth fluorohalides have been studied as SHB materials for a long time. A 690-nm laser can burn a spectral hole within our mixed crystal materials. It is well known that SHB is a selective photobleaching effect. In the research of SHB, researchers have found that the depth of the spectral hole had a nonexponential dependence on the exposure time [7,26–29]. They attributed the nonexponential dependence to a dispersive distribution of the environments around hole-burning centers. Especially, Zha et al. reported that the decay curve of the hole area was composed of a fast component and a slow component under a laser irradiation in laser-induced filling and temperature cycling experiments with the sample of $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ [30]. They concluded that there are two kinds of traps which govern hole burning and filling processes in the sample. One is related to some impurities or defects, and the other is related to Sm^{3+} ions. Similarly, we found that the photobleaching effect also contained two processes, one fast process and one slow process [24]. In Fig. 8, the time parameters of these photobleaching processes were given under different excitation powers. These time parameters were obtained by fitting the decrease curves (as shown in the inset of Fig. 8) with a biexponential function,

$$I(t) = I(\infty) + I_1 e^{-t/\tau_1} + I_2 e^{-t/\tau_2},$$

where $I(t)$ is the fluorescence intensity of Sm^{2+} at t time, $I(\infty)$ the fluorescence intensity when the exposure time t goes to infinite, $I_1 + I_2 = I(0) - I(\infty)$, and τ_1 and τ_2 the two time parameters for the fast bleaching and the slow bleaching, respectively. Therefore, it is reasonable for us to believe that the mechanism of photobleaching is the same as that of SHB in Sm^{2+}-doped alkaline-earth fluorohalides. Furthermore, from Fig. 8 we can see that, for both fast process and slow process, these time parameters decreased with increasing irradiation power. In the 1990s, Jiaqi Yu and Shihua Huang's research group had studied the mechanism of SHB within Sm^{2+}-doped alkaline-earth fluorohalides [30–32]. They concluded that the hole-burning mechanism in this system was the electron transfer from Sm^{2+} ions to electron traps. They thought that Sm^{3+} ions were generated in the hole-burning process as effective traps to recombine with electrons. However, in the research on SHB, the area of a burnt hole is too small compared with the area of whole spectral profile to figure out whether Sm^{3+} ions generated or not. It is easy to figure out whether Sm^{3+} ions generated or not in photobleaching experiments for the Sm^{2+} fluorescence can be quenched as deep as 96% of its initial intensity [24]. However, even when the photobleaching happened for a 96% quenching degree, we did not find any evidence of Sm^{3+} generating in the sample. Based on the above experimental results and discussions, we strongly propose that the mechanism of photobleaching, as well as the mechanism of SHB, in Sm-doped alkaline-earth fluorohalides should be attributed to the recombination of the electrons released from Sm^{2+} ions with the defect traps in the matrix. To prove this idea, we checked the photobleaching effect in the below experiments. Firstly, we ground the crystal sample into powder and found that the ground powder sample had a more rapid and deeper photobleaching process than that in the crystal sample under the same irradiation conditions, as shown in Fig. 9(a). Secondly, we irradiated the H_2-reduced sample with X-ray and found that the photobleaching

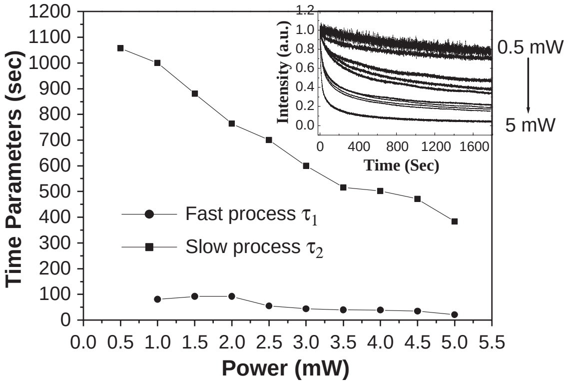

Fig. 8. Photobleaching processes in the X-ray-reduced sample ($Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}:Sm^{2+}$, Sm^{3+}) were recorded under laser irradiation at 488 nm with different powers (from 0.5 to 5 mW with 0.5-mW power intervals, as shown in the inset). These bleaching curves can be fitted with a biexponential function. There are two decrease processes in the photobleaching in terms of time parameters, a fast process (●) and a slow process (■).

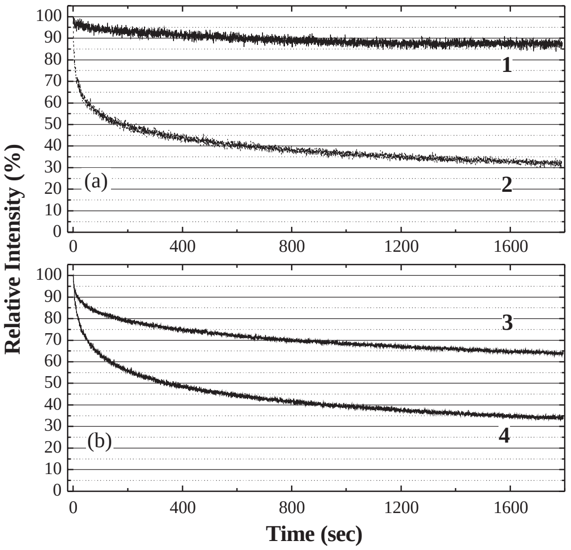

Fig. 9. (a) Under laser irradiation at 488 nm, the intensity of the $^5D_0 \rightarrow {}^7F_0$ emission of Sm^{2+} ions was monitored both with the crystalline (1) and powder (2) samples of $BaFCl_{0.5}Br_{0.5}$:Sm^{2+}(1%). (b) Photobleaching in the H_2-reduced block sample of $Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$:$Sm^{2+}$ (3) and the X-ray-irradiated H_2-reduced block sample of $Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$:$Sm^{2+}$ (4).

happened more drastically in the X-ray-treated sample, as shown in Fig. 9(b). Compared with a block sample, a ground powder sample has much more surface area and many more surface states (defect centers), and, it is generally known that X-rays produce color centers (e.g. F or F-aggregated centers) in samarium-doped alkaline-earth fluorohalides. A color center is a lattice defect in a crystalline solid consisting of a vacant negative ion site and an electron bound to the site. Such defects will absorb light and make certain normally transparent crystals appear colored. In our experiment, the X-ray-reduced block samples appeared green on their surfaces after X-ray irradiation, which means the X-ray irradiation had produced many color centers in the samples, especially on their surfaces. According to our observation, the green color disappeared when the photobleaching happened under 488-nm laser irradiation; thus, it is reasonable to say that the defects induced by X-ray irradiation had played an important role in the photobleaching of X-ray-treated sample. Based on the above experimental observations, we propose the mechanism of the photobleaching in Sm^{2+}-doped alkaline-earth fluorohalides to be the process as given below:

$$Sm^{2+} + (\mathrm{trap}) \xrightarrow{h\nu} [Sm^{3+}(\mathrm{trap})^-]$$

or

$$Sm^{2+} + (\mathrm{trap}) \xrightarrow{h\nu} [Sm^{2+*}(\mathrm{trap})].$$

In the first reaction, the electron released from a Sm^{2+} ion recombines with a defect center under the optical excitation, and the electronegative trap, $(\mathrm{trap})^-$, bounds strongly with the samarium ion to form a $[Sm^{3+}(\mathrm{trap})^-]$. In the second reaction, the excited Sm^{2+*} is trapped by a defect center and loses its ability of luminescence. Both the reactions mean that no Sm^{3+} ions generated in the photobleaching process of Sm^{2+} (as well as in the SHB of Sm^{2+}), thus we could not observe any evidence of generated Sm^{3+} ion in luminescence or in absorption spectra [24]. However, until now, we could not give a more clear picture about the $[Sm^{3+}(\mathrm{trap})^-]$ or the $[Sm^{2+*}(\mathrm{trap})]$, but, at least, we know that the existence of defect centers makes the photobleaching effect more considerable.

Furthermore, a SHB experiment was done before and after photobleaching in order to check the photobleaching effect on SHB efficiency. We found that the SHB efficiency decreased a lot for a bleached sample, as shown in Fig. 10, which indicates that the same factor dominates in photobleaching and SHB. On the other hand, this observation also suggests that the photobleaching effect should play an important role in erasing a burnt hole in SHB.

4. Conclusion

The fluorescence of Sm^{2+} ions doped in alkaline-earth fluorohalides can be bleached by optical irradiation of a blue laser, a green laser or even a red laser. When the bleaching effect occurred, no generated Sm^{3+} ions, no relative spectral change in Sm^{2+} emissions and no lifetime decrease for the excited states of Sm^{2+} ions could be observed. Under a blue or green laser irradiation, the photobleaching is rather obvious and the decrease

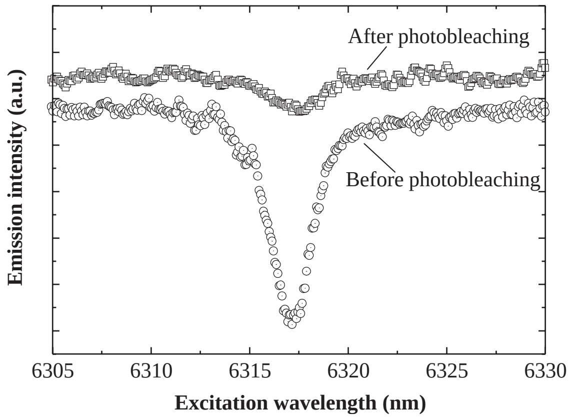

Fig. 10. Spectral hole burnt near the peak of the $^7F_0 \to {}^5D_1$ excitation line before and after photobleaching at room temperature in the H_2-reduced block sample of $Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}:Sm^{2+}$. The spectra are offset for clarity, but the vertical scales are the same.

curves of Sm^{2+} fluorescence can be fitted well with a biexponential function. However, when the excitation photon energy was lower than that of $^5D_0 \to {}^7F_0$ transition, the photobleaching effect could not be observed anymore. An identical mechanism, the recombination of the electrons released from Sm^{2+} ions with the defect traps in the matrix, was proposed for explaining the photobleaching as well as for explaining the SHB in Sm^{2+}-doped alkaline-earth fluorohalides.

Acknowledgments

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