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Photo-Bleaching Effect in Divalent Samarium-Doped Alkaline-Earth Fluorohalides

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When a CW laser was focused on a sample of divalent samarium-doped alkaline-earth fluorohalides ($Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5} : Sm^{2+}$ or $BaFCl_{0.5}Br_{0.5} : Sm^{2+}$), the fluorescence intensity of Sm^{2+} ions decreased rapidly. Under irradiation from a 488-nm laser with a power density of 10 W/cm^2, the intensity of the $^5D_0 \rightarrow {}^7F_0$ (Sm^{2+}) emission decreased as much as 96 % of its initial intensity in 30 minutes (for an X-ray-reduced sample). The so-called photo-bleaching effect can be influenced by the processes used for sample synthesis, such as the reduction method, the grinding process or X-ray irradiation. The decreasing curves obtained in the photo-bleaching experiments were fitted, a biexponential decreasing mode was found, which included a fast decrease (time constant ∼ tens of seconds) and a slow decrease (time constant ∼ hundreds of seconds). There was no evidence to support the divalent samarium ions being photo-ionized into trivalent samarium ions in the photo-bleaching process. The most probable mechanism for the photo-bleaching effect involves structural defects and color centers in the samples.

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I. INTRODUCTION

The alkaline-earth fluorohalides with the PbFCl-type structure are an important class of materials because of their wide range of applications. For examples, alkaline-earth fluorohalides doped with divalent europium ions are used as X-ray phosphors for medical imaging via a photostimulated luminescence process [1, 2]. Also, $SrFCl:Sm^{2+}$ was found to have a special function in pressure measurements [3]. Especially, since persistent spectral hole burning in $CaF_2:Sm^{2+}$ and photon-gated spectral hole burning in $BaFCl:Sm^{2+}$ were reported by Macfarlane and Shelby [4] and Winnacker *et al.* [5], divalent samarium-doped alkaline-earth fluorohalides have been widely investigated, because they have potential applications in frequency domain optical storage [6] and information processing [7]. In the investigation of room-temperature hole burning, much attention was paid to getting a broad inhomogeneous emission band [8–10]. However, an intense fluorescence and high stability should be other important properties for frequency storage materials, especially for those aiming at practice applications. Investigations of those materials will also help researchers to understand the mechanism of frequency domain optical storage and to design applicable materials.

Photo-bleaching in Sm^{2+}-doped material was observed and reported firstly by Krebs *et al.* in 1997 [11]. They

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found that the fluorescence intensity of Sm^{2+} selectively doped epitaxial CaF_2 films decreased non-exponentially with time under an optical excitation. In 2001, more materials doped with Sm^{2+} were found to have the bleaching effect by Mikhail *et al.* [12]. To explain the bleaching phenomenon, they assumed a nonradiative decay mechanism that produced a decrease in the Sm^{2+} fluorescence. An important observation in that paper is the reversible bleaching of the Sm^{2+} luminescence; however, the reversible bleaching in their work was only available for the broad-band transition $4f^5 5d$-$4f^6$ of Sm^{2+} in the crystal sample of CaF_2:Sm^{2+}. Additionally, they treated all the decreasing processes of bleaching exponentially. In 2001, Tanaka *et al.* reported a reversible photochromic process in BaClF:Sm^{2+} [13]. 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 at room temperature under the 488-nm light from an Ar^+ ion laser. The reversible bleaching was interpreted in terms of Sm^{2+} being photoionized to Sm^{3+} by the 325-nm light and the excited electrons being captured by halogen vacancies of BaClF, with trapped electrons being released under the 488-nm light and Sm^{3+} being reduced to Sm^{2+}.

Here, we present a study on the photo-bleaching of divalent samarium ions doped in alkaline-earth fluorohalides $MFCl_{0.5}Br_{0.5}$ (M = Ba or Mg0.5+Sr0.5). Under irradiation with 488-nm blue laser light, the intensity of the Sm^{2+} fluorescence in the alkaline-earth fluorohalides decreases biexponentially with exposure time. This investigation on the decreasing Sm^{2+} fluorescence intensity relates directly to the mechanism of the Sm^{2+} f-f transition, as well as to the mechanism of spectral hole burning in the divalent samarium-doped alkaline-earth fluorohalides

II. EXPERIMENT

Seven samples (1-7) were employed in this investigation to check the so-called photo-bleaching effect. Sample 1 is a crystalline sample of $BaFCl_{0.5}Br_{0.5}$:Sm^{2+}(1 %); 2 is a powder sample of $BaFCl_{0.5}Br_{0.5}$:Sm^{2+}(1 %) ground from crystalline sample 1; 3 is a block sample of $Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$:$Sm^{2+}$(1 %) reduced in a hydrogen atmosphere; 4 is a powder sample ground from sample 3; 5 is a block sample of $Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$:Sm(1 %) fired in air and then reduced by X-ray irradiation; 6 is a powder sample ground from sample 5; 7 is a powder sample of $Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$:$Sm^{2+}$(1 %) reduced in a hydrogen atmosphere and then irradiated by X-rays for 8 hours. All the samples are listed in Table 1.

Two different compositions, $BaFCl_{0.5}Br_{0.5}$ and $Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$, were used in the synthesis of the samples; the dopant was 1 % mol Sm_2O_3. All the samples were prepared by using a high-temperature solid reaction in the first stage. Two methods were employed in reducing the trivalent samarium ions into divalent ions: firing in a flowing hydrogen gas atmosphere or reduction by X-ray irradiation after the raw material had been sintered in air. In the first method, the raw materials with stoichiometric compositions were sintered at 1,100 °C for 1 hour in a strong reducing atmosphere (H_2); we call this kind of samples as H_2-reduced samples in this paper. In the second method, raw materials with the same compositions were sintered at 1,100 °C for 1 hour in air; then, the resulting materials were irradiated with X-ray for 8 hours using the Cu K α line at 45 kV and 300 mA. We call this kind of samples as X-ray-reduced samples. The crystalline sample, which had a composition of $BaFCl_{0.5}Br_{0.5}$:Sm^{2+}(1 %), was prepared by firing in a flowing hydrogen gas atmosphere, but a long annealing time was needed in order to get bigger crystal sizes.

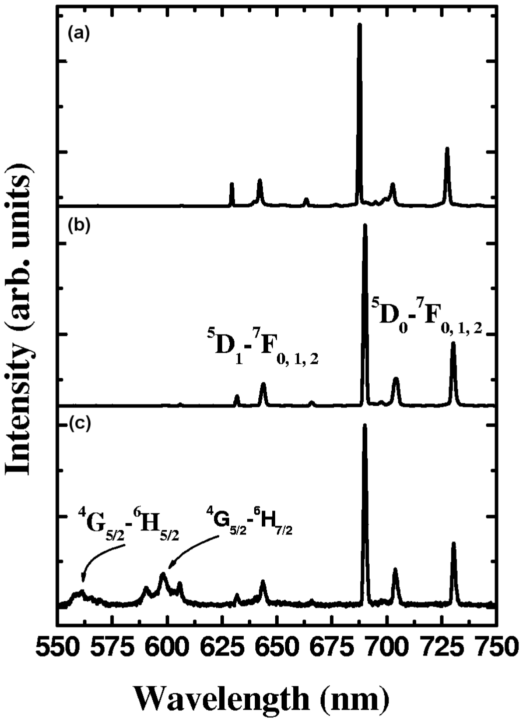

Fig. 1. Spectra of samarium ions (Sm^{2+}, Sm^{3+}) under laser excitation at 488 nm: (a) the spectrum of the crystalline samples (1 and 2) reduced in a H_2 atmosphere, (b) the spectrum of the multi-crystal samples (3, 4 and 7) reduced in a H_2 atmosphere, and (c) the spectrum of the multi-crystal samples reduced by X-ray irradiation (5 and 6).

To measure the emission spectra of samarium ions (Sm^{2+} and Sm^{3+}), we excited the samples at room temperature by using the 488-nm line of an argon-ion laser and the luminescence from 550 nm to 750 nm was then detected with a photomultiplier tube (PMT) (Hamamatsu, R928) mounted on a spectrometer (SPEX 1702). An OG-530 cut-off filter was placed in front of the spectrometer to block off laser lines. For the H_2-reduced samples, almost no Sm^{3+} emission could be detected, as shown in Fig. 1(a) and Fig. 1(b), which means that

Table 1. Samples employed in our experiment.

Sample	State	Stoichiometry	Reduction	Grinding	τ_1 (sec)	τ_2 (sec)
1	Crystal	$BaFCl_{0.5}Br_{0.5}$	H_2	No	557.7	-
2	Powder	$BaFCl_{0.5}Br_{0.5}$	H_2	Yes	607.1	32.29
3	Block	$Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$	H_2	No	544.9	46.4
4	Powder	$Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$	H_2	Yes	477	24.9
5	Block	$Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$	X-ray	No	307.4	16.8
6	Powder	$Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$	X-ray	Yes	473.4	33.9
7	Block	$Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}$	H_2 + X-ray	No	640.6	47.8

Sm^{3+} ions were well reduced to Sm^{2+} ions by firing in a H_2 atmosphere.

III. 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. The H_2-reduced samples (1-4) present mainly the luminescence characteristics of Sm^{2+} ions, and $^5D_0 \rightarrow {}^7F_{0,1,2}$ and $^5D_1 \rightarrow {}^7F_{0,1,2}$ transitions could be observed easily at room temperature, as shown in Fig. 1(a) and Fig. 1(b). Figure 1(c) is the spectrum of an X-ray-reduced sample; in it, the emissions of Sm^{3+}, as well as the emissions of Sm^{2+}, are observed. These spectra indicate that almost all the Sm^{3+} ions had been reduced to 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 samples. Under 488-nm blue laser light, we found that the fluorescence intensity of divalent samarium ions decreased with the exposure time for all samples. This phenomenon is called photo-bleaching effect [11]. These decreases were the same for all emissions of Sm^{2+}; *i.e.*, the absolute intensities decreased and their relative intensities did not change.

When we irradiated crystalline sample 1 with 488-nm laser light at a power density of ~10 W/cm^2 and monitored the fluorescence intensity of the $^5D_0 \rightarrow {}^7F_0$ transition (687.8 nm), the decrease in the fluorescence was only about 13 % of its initial intensity in 30 minutes, shown in Fig. 2(a). The decreasing curve could be fitted well with a single exponential function, $I(t)=I(\infty)+I_1\exp(-t/\tau)$, where I(t) is the intensity at time=t, $I(\infty)$ is the fluorescence intensity when the exposure time t goes to infinite, $I_1=I(0)-I(\infty)$, and τ is a time constant. Through fitting the curve, a 557.7-s time constant was found for the photo-bleaching of Sm^{2+} in the crystal sample. For the H_2-reduced multi-crystal sample (3, block sample), the decrease was about 37 % in 30 minutes, shown in Fig. 2(b); for the X-ray-reduced multi-crystal sample (5, block sample), the decrease reached as much as 96 %, shown in Fig. 2(c). Both of the above decreasing curves, Figs. 2(b) and 2(c) could be fitted with a biexponential function, $I(t)=I(\infty)+I_1\exp(-t/\tau_1)+ I_2\exp(-t/\tau_2)$, where $I_2=I(0)-I(\infty)-I_1$. The time constants from our fitting processes are listed in Table 1. Through analyzing τ_1 and τ_2 in Table 1, we found that there were two decreasing processes in the photo-bleaching effect, a slow one (τ_1 ~ hundreds of seconds) and a fast one (τ_2 ~ tens of seconds).

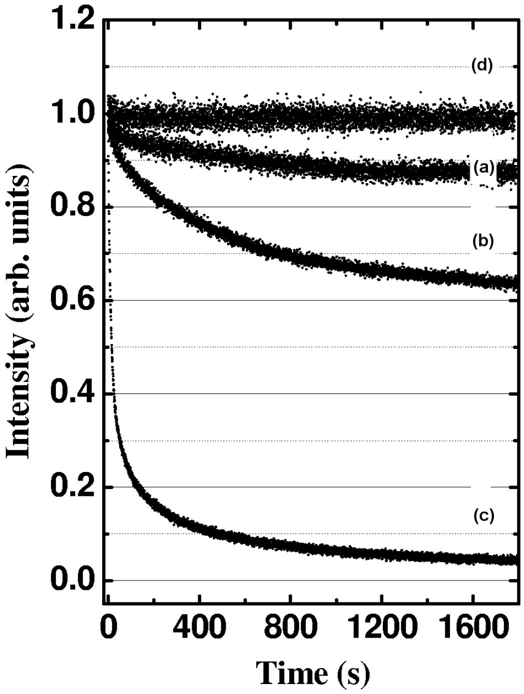

Fig. 2. Photo-bleaching effect in different samples. Under laser irradiation at 488 nm with a power density of ~ 10 W/cm^2, the intensity of the $^5D_0 \rightarrow {}^7F_0$ emission of Sm^{2+} ions was monitored, for (a) the H_2-reduced crystal sample (1), (b) the H_2-reduced block sample (3), and (c) the X-ray-reduced block sample (5). (d) Result of monitoring the 598 nm fluorescence (Sm^{3+}, $^4G_{5/2} \rightarrow {}^6H_{7/2}$) in the X-ray-reduced block sample (5).

Furthermore, we found that the photo-bleaching effect could be influenced by grinding and by X-ray irradiation. After the crystalline sample (1) had been ground into a powder (2), the photo-bleaching went deeper and the fluorescence decreased as much as 67 %, shown in

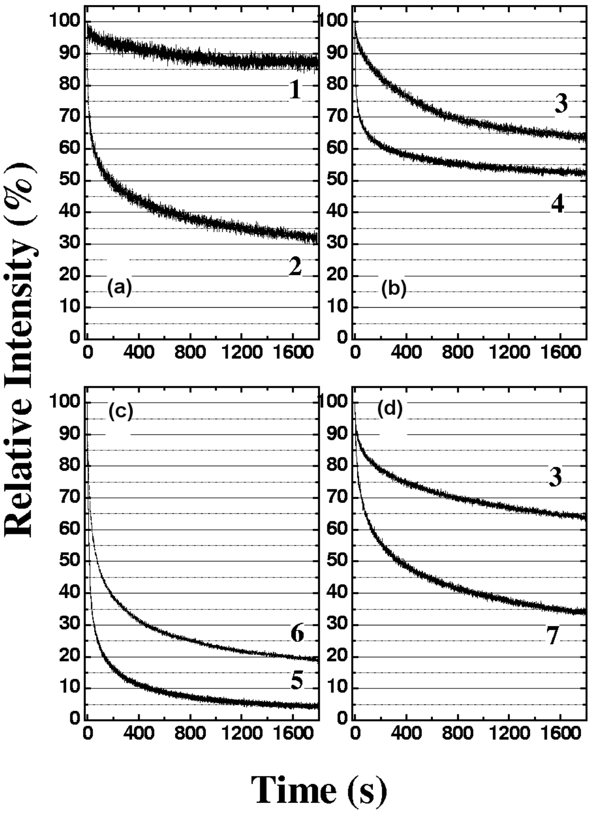

Fig. 3. (a) Under laser irradiation at 488 nm (~ 10 W/cm^2), the intensity of the $^5D_0 \rightarrow {}^7F_0$ emission of Sm^{2+} ions was monitored both with the crystalline (1) and powder (2) samples of BaFCl$_{0.5}$Br$_{0.5}$:Sm^{2+}(1 %). (b) Photo-bleaching in H$_2$-reduced block (3) and powder (4) samples. (c) Photo-bleaching in X-ray-reduced block (5) and powder (6) samples. (d) Photo-bleaching in the H$_2$-reduced block sample (3) and the X-ray irradiated H$_2$-reduced block sample (7).

Fig. 3(a). Similarly, as shown in Fig. 3(b), after the H$_2$-reduced sample (3) had been ground to a powder form (4), the fluorescence intensity under blue laser irradiation decreased more rapidly in its initial stage. However, grinding had a different effect on the photo-bleaching of the X-ray-reduced sample (6), as shown in Fig. 3(c). Under the same irradiation conditions, the decrease in the Sm^{2+} fluorescence intensity in powder sample 6 was not as much as that in block sample 5, which means the photo-bleaching effect was lowered by grinding the X-ray-reduced sample to a powder form. The difference in the degree of photo-bleaching between the two samples (5 and 6) should come from the nonuniformity of divalent samarium ions in the X-ray-reduced sample (5) because the reduction induced by X-ray irradiation only affected the samarium ions on the sample's surface. If the X-ray penetration depth is taken into consideration, the concentration of reduced Sm^{2+} ions on the surface of the block X-ray-reduced sample is surely higher than the average Sm^{2+} concentration in the ground X-ray-reduced sample. The irradiation density on the sample's surface was higher than that inside the sample, so that the high distribution of Sm^{2+} ions on the sample's surface meant that more Sm^{2+} ions received strong laser irradiation, which induced a rapid decrease in the Sm^{2+} fluorescence during the initial stage of photo-bleaching. The decreasing curves in Fig. 3(c) were fitted with a biexponential function and a smaller time constant was obtained for the block sample, as listed in Table 1.

In order to check the effect of X-ray irradiation on photo-bleaching, we irradiated the block H$_2$-reduced sample (3) with X-rays for 8 hours and obtained sample 7. We did the same experiment with sample 7 and found that X-ray irradiation increased the photo-bleaching more considerable, as shown in Fig. 3(d). Since there were no Sm^{3+} ions in the H$_2$-reduced sample (3), the irradiation with X-ray could not change the concentration of Sm^{2+}. However, the X-ray irradiation could produce defects, such as color centers, in the H$_2$-reduced sample. Thus, the defects (the color centers) produced by the X-ray irradiation in the sample must play an important role in inducing photo-bleaching of Sm^{2+}. Combining the grinding effect on photo-bleaching and the low bleaching rate in the crystalline sample (1), we deduce that the defects in our samples, produced in the sintering process or produced by X-ray irradiation and grinding, should logically be the electron traps that quenching the Sm^{2+} fluorescence.

On the other hand, we also checked the Sm^{3+} fluorescence from the X-ray-reduced samples and found no obvious photo-bleaching effect on the luminescence of trivalent samarium, as shown in Fig. 2(d). Additionally, no Sm^{3+} fluorescence was detected in the H$_2$-reduced samples (1-4 and 7), even after very intense blue laser irradiation, which indicates that the decrease in the Sm^{2+} fluorescence is not due to the photoionization of Sm^{2+} to Sm^{3+}; *i.e.*, there was no evidence to support a photochemical process existing in the photo-bleaching process.

To investigate the mechanism of the photo-bleaching effect further, we measured the absorption spectra of these samples before and after blue laser irradiation. It was interesting for us to find that the absorption spectra of the H$_2$-reduced samples did not change, as shown in Fig. 4(a), but the absorption of the X-ray-reduced sample decreased in the short-wavelength region (< 500 nm), as shown in Fig. 4(b). The reduced absorption revealed another possible mechanism for the rapid bleaching of Sm^{2+} in the X-ray-reduced samples. It is generally known that X-rays produce color centers (F-centers), besides reducing Sm^{3+} to Sm^{2+}, 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 our sam-

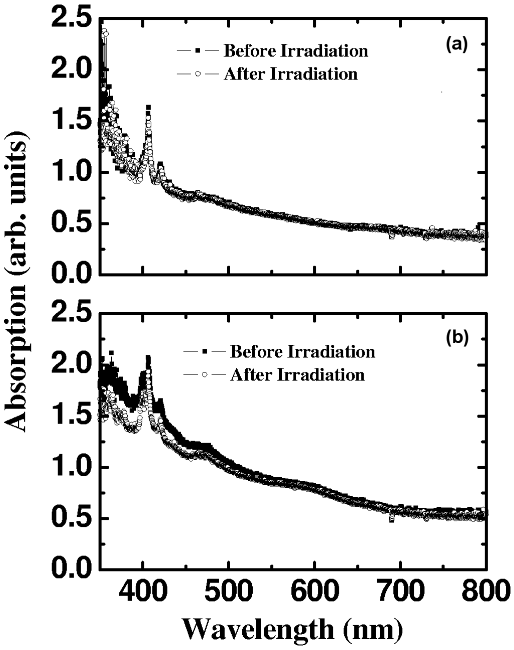

Fig. 4. Absorption spectra measured before and after laser irradiation at 488 nm (~2 × 10 W/cm^2 and 30 min); (a) H_2-reduced sample and (b) X-ray-reduced sample.

ples, and these color centers were concentrated mainly on the surfaces of samples. According to our observation, the green color disappeared after an extended period of 488-nm laser irradiation, thus, it is reasonable to say that blue light can destroy the color centers in X-ray-reduced samples. Based on the above analysis, we deduced that the color centers might play two possible roles in exciting Sm^{2+} ions and bleaching them. A) In exciting Sm^{2+} ions, the color centers absorb photon energy first and then transfer the photon energy to Sm^{2+} ions to make them excited. Under blue laser irradiation, the color centers were used up at a fast rate and then the energy transfer from color centers to Sm^{2+} no longer occurred. Thus, a fast photo-bleaching process could occur in X-ray-reduced samples. However, so far, we have not found any proof to support this energy transfer mechanism. Even if this energy transfer mechanism existed, it would only function in X-ray-reduced samples; however, the photo-bleaching also occurred in H_2-reduced samples without reduced absorption. B) In the bleaching process, as electronic traps that quench Sm^{2+} fluorescence, color centers trap electrons of excited Sm^{2+} ions, which leads to photo-bleaching of Sm^{2+} ions; at the same time, the color centers are destroyed by trapping, and the absorption induced by them is decreased. According to mechanism B, the photo-bleaching rate in an X-ray-reduced sample should be proportional to the concentration of color centers. With B, we can understand Fig. 3(d) better. Whatever mechanism, A or B, is at work here, the photo-bleaching effect in X-ray-reduced samples should be partly because of the decrease in the absorption induced by laser irradiation.

Similarly, structural defects produced in the grinding process also can function as electron traps to quench Sm^{2+} fluorescence. Compared with a block sample, a ground powder sample has much more surface area and many more surface states (defect centers). More surface area means more luminescence centers and defect centers can be excited (irradiated) under the same excitation conditions, which should be one reason for photo-bleaching happening more drastically in a powder sample than in a block sample. However, until now, we cannot figure out the exact role of the defects centers in exciting Sm^{2+} ions and in inducing the photo-bleaching effect, but, at least, we know that the existence of defect centers makes the photo-bleaching effect more considerable.

IV. CONCLUSION

When a sample of divalent samarium-doped alkaline-earth fluorohalides was irradiated with CW blue laser light, the fluorescence intensity of Sm^{2+} ions in the sample decreased with the exposure time. This phenomenon is called the photo-bleaching effect. For an X-ray-reduced sample, photo-bleaching can decrease fluorescence intensities of Sm^{2+} ions by as much as 96 %. The degree of photo-bleaching is influenced by the processes used for sample preparation, such as reduction, grinding, or X-ray irradiation. The photo-bleaching effect is weakest (~13 %) in crystal samples (1) and strongest (~96 %) in X-ray-reduced block samples (5) under irradiation with 488-nm laser light with a power density of ~ 10 W/cm^2. On the other hand, there was no spectral evidence to support divalent samarium ions being photo-ionized into trivalent samarium ions in the photo-bleaching process. By fitting the photo-bleaching curves, a biexponential decreasing mode was found, which include a fast mode (time constant ~ tens of seconds) and a slow mode (time constant ~ hundreds of seconds). In explaining the photo-bleaching phenomenon, the function of defect centers and color centers were discussed.

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