

Photobleaching of Sm^{2+} doped in $\text{Al}_3\text{O}_2\text{-SiO}_2$ glass

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Abstract

The fluorescence intensity of Sm^{2+} ions doped in $10\text{Al}_2\text{O}_3\text{-}90\text{SiO}_2$ glass decreased biexponentially under 488-nm irradiation. The irradiation induced a decrease of optical absorption in the glassy sample, which should be a factor for the photobleaching. An identical mechanism in the photobleaching with that in the spectral hole burning was proposed.

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Krebs et al. reported photobleaching in Sm^{2+} -doped material firstly in 1997 [1]. They found that the fluorescence intensity of Sm^{2+} selectively doped epitaxial CaF_2 film decreased non-exponentially with time under an optical excitation. In their observations, the bleaching rate depended linearly on the intensity of the optical excitation and the emission lineshapes were not altered. In 2001, Mikhail et al. [2] reported further about the bleaching effect with more Sm^{2+} -doped materials. 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 $4f^55d \rightarrow 4f^6$ of Sm^{2+} in the crystal sample of $\text{CaF}_2:\text{Sm}^{2+}$. Additionally, they treated all the decrease processes of bleaching exponentially, which maybe was a mistake based on the experimental observations of other researchers [1,3]. In 2001, Tanaka et al. reported a reversible photochromic process in $\text{BaClF}:\text{Sm}^{2+}$ [4]. They found that the fluorescence intensity of Sm^{2+} in BaClF decreased under 325-nm irradiation and recovered under 488-nm excitation.

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+} . Recently, we investigated the photobleaching with Sm^{2+} doped in alkaline-earth fluorohalides and found the deepest decrease reached 96% under excitation of 488-nm laser in 30 min. A biexponential bleaching mode was found by fitting the decreasing curves [3,5].

Here, we report our investigation of the photobleaching of Sm^{2+} doped in $10\text{Al}_2\text{O}_3\text{-}90\text{SiO}_2$ glasses. Under 488-nm irradiation, the intensity of the Sm^{2+} fluorescence in the aluminosilicate glass decreases biexponentially with exposure time.

$10\text{Al}_2\text{O}_3\text{-}90\text{SiO}_2:\text{Sm}^{2+}$ glassy specimens were synthesized by using a sol-gel process and then a hydrogen reduction at 800 °C. To record the luminescence of samarium ions (Sm^{2+} and Sm^{3+}), we excited the samples by using the 488-nm line of an argon-ion laser. At room temperature, the fluorescence from 550 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

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to block off the scattered laser lines. No obvious Sm^{3+} emission could be detected in the glassy specimens, which indicates that most Sm^{3+} ions have been well reduced to Sm^{2+} ions. A laser power controller (LPC) was used in our experiments to stabilize the excitation power. A tungsten lamp was employed for obtaining transmission and absorption spectra in the experiment.

The emission spectra were recorded under 488-nm excitation at room temperature, as shown in Fig. 1. The glassy sample presented mainly the luminescence characteristics of Sm^{2+} ions, and the strongest fluorescent peak (683 nm) is from the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition. In the spectral region of 550–650 nm, there are three weak emissions (564, 602, and 649 nm) due to the remnant unreduced Sm^{3+} ions ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2, 7/2, 9/2}$). There are seven spectra in Fig. 1; they were recorded one after another with a 5-min interval by using a monochromator combined with a fiber and a CCD detector. Under 488-nm and $\sim 10 \text{ W/cm}^2$ irradiation the fluorescence intensity of the Sm^{2+} ions decreased with exposure time, which indicates that the photobleaching effect happened in the specimen. The inset of Fig. 1 shows the amplified $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission peaks recorded in all scans for clarity. Although the remnant unreduced Sm^{3+} ions emitted weak fluorescence, with them in the glassy sample, strong and sharp Sm^{3+} absorption peaks (360, 375, and 406 nm) could be observed, as shown in Fig. 2. We recorded the absorption spectra before and after laser irradiation at 488 nm. It was interesting for us to find that the absorption decreased in almost whole visual spectral range after laser irradiation. The inset of Fig. 2 shows the difference of absorption coefficients before and after laser irradiation, which indicates that laser irradiation induced an absorption decrease in the aluminosilicate glass. To investigate the photobleaching phenomenon, we plotted the fluorescence intensities of three peaks, 562, 683, and 726 nm, in Fig. 3. After normalization, as shown in Fig. 3b, we can see that two Sm^{2+} emissions decreased at the same rate, i.e., the absolute intensities decreased but the relative intensities did not change. However, the decrease in

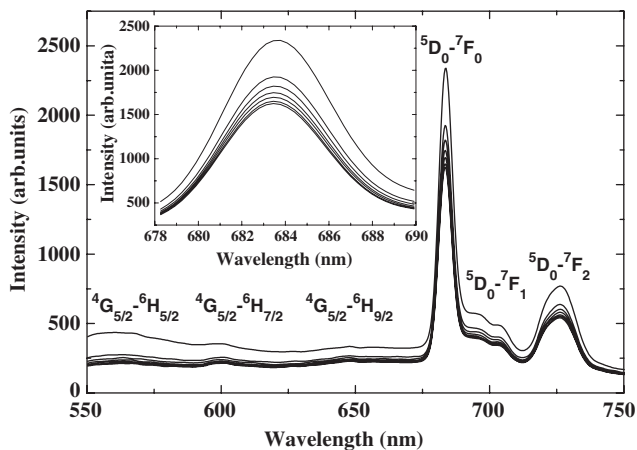


Fig. 1. Photo luminescence spectra of $10\text{Al}_2\text{O}_3\text{-}90\text{SiO}_2$ glass doped with samarium ions.

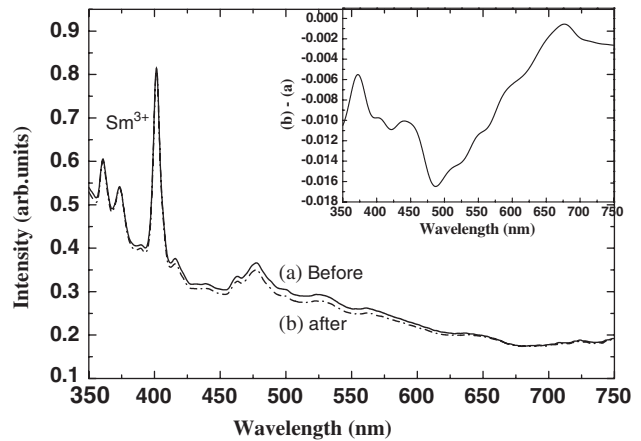


Fig. 2. Absorption spectra measured before and after laser irradiation at 488 nm ($\sim 10 \text{ W/cm}^2$ and 30 min). The inset is the difference between (a) and (b).

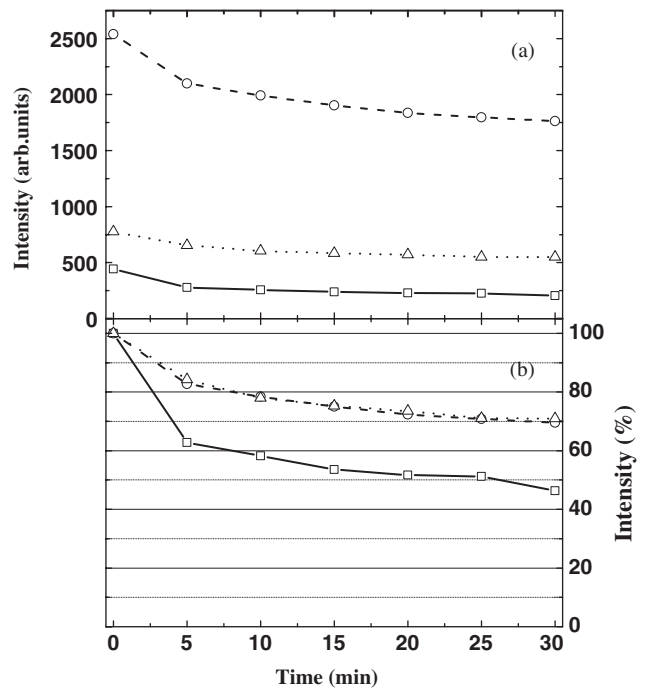


Fig. 3. Photobleaching effect in samarium-doped aluminosilicate glass under laser irradiation at 488 nm. Three emissions, 562 nm (\square), 683 nm (\circ), and 726 nm (\triangle), decreased with exposure time before (a) and after normalization (b).

the 562-nm fluorescence had a faster rate and a deeper bleaching than that in the 683 or 726-nm fluorescence. In Ref. [6], Song observed a wideband-shape emission in the wavelength range of 400–650 nm in his time-resolved fluorescence spectrum (delay time = $1 \mu\text{s}$) and suggested that the wideband emission came from the emission of $4f5d$ band to the ground state of Sm^{2+} ions. From Fig. 3b, we know that the wideband emission could not be the emission of divalent samarium ions because it had a different photobleaching rate compared with the fluorescence decrease of $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transitions (683 or 726 nm). On the other hand, although the position of 562-nm emission

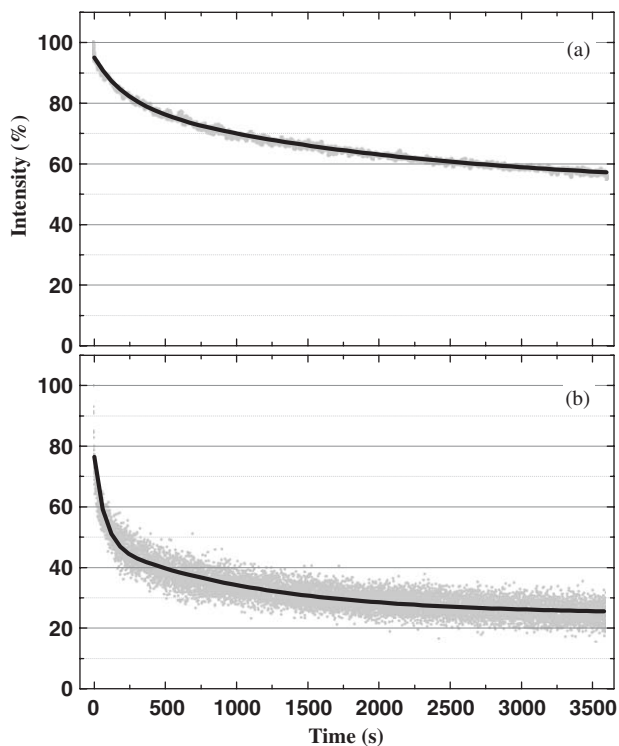


Fig. 4. Decrease of intensity of the ${}^5D_0\text{--}{}^7F_0$ emission (683 nm) of Sm^{2+} ions with time when under irradiation at 488 nm. (a) A biexponential decreasing mode was found by fitting this photobleaching process. Similarly, (b) is the photobleaching curve of 562-nm fluorescence obtained in the same conditions.

is at the same wavelength of the ${}^4G_{5/2}\text{--}{}^6H_{5/2}$ transition (Sm^{3+}), we do not think the decrease of the emission comes from quenching Sm^{3+} fluorescence according to our former investigation [3]. The most possibility for the source of this wideband is from the remnant impurities or defects in the aluminosilicate glass. Under the same irradiation conditions, 683-nm fluorescence (${}^5D_0\text{--}{}^7F_0$) and 562-nm wideband were monitored, as shown in Fig. 4. The photobleaching was about 40% for Sm^{2+} fluorescence and more than 70% for 562-nm emission in 1 h. Both of them can be fitted well with a biexponential function (black curves in Fig. 4), just like that in Ref. [4].

Sm^{2+} -doped aluminosilicate glass prepared by a sol-gel process has been studied as persistent spectral hole burning (SHB) material for some years, however until now, the mechanism of SHB in the glass is not clear. As we know, SHB is a selective photobleaching effect and has the same mechanism of photobleaching [4]. In the investigation of SHB researchers have found that the depth of spectral hole had a non-exponential dependence on burning time [7–9].

They attributed the non-exponential 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 laser irradiation in laser-induced filling and temperature cycling experiments with the sample of $\text{BaFCl}_{0.5}\text{Br}_{0.5}\text{Sm}^{2+}$ [10]. They concluded that there are two kinds of traps governing hole burning and filling processes in their samples. One is related to some impurities or defects, and another is related to Sm^{3+} ions. Nogami et al. observed similar phenomenon within Sm^{2+} -doped aluminosilicate glass [11]; additionally, they also reported the decrease of Sm^{2+} fluorescence with irradiation time. Both of the decay curves, hole depth burned as a function of burning time and Sm^{2+} fluorescence intensity as a function of irradiation time, were non-exponential according to their investigations. Though we have not known the mechanism of the biexponential decrease mode until now, it is reasonable for us to believe that the mechanism of the photobleaching is the same with that of SHB in Sm^{2+} -doped materials.

Based on above experimental results and discussions, we strongly propose that the mechanism of the photobleaching, as well as the mechanism of SHB in the same material system, should be attributed to the recombination of the electrons released from Sm^{2+} ions with the defect traps in the matrix.

Acknowledgements

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