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Room-temperature persistent spectral hole burning of x-ray-irradiated Sm³⁺-doped glass

Jianrong Qiu†§, Kentarou Nouchi†, Kiyotaka Miura†, Tsuneco Mitsuyu† and Kazuyuki Hirao‡

† Hirao Active Glass Project, ERATO, JST, Keihanna Plaza, Hikaridai, Seika-cho, Kyoto 619-0237, Japan

‡ Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

E-mail: jrqi@mail.goo.ne.jp

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Abstract. We report on persistent spectral hole burning in the x-ray-irradiated Sm³⁺-doped fluoroaluminate glasses at room temperature. 0.1SmF₃ · 14.9YF₃ · 10MgF₂ · 20CaF₂ · 10SrF₂ · 10BaF₂ · 35AlF₃ (mol%) glass was prepared under an Ar + NF₃ (5 vol.%) atmosphere. Absorption and photoluminescence spectra showed that some of the Sm³⁺ ions in the glass sample were reduced to Sm²⁺ ions after the x-ray irradiation. The hole was burned in the ⁷F_{0–5}D₀ line of the Sm²⁺ ions by means of a DCM dye laser. No antihole or increased excitation (absorption) peak was observed around the burned hole. It was concluded that the persistent spectral hole burning was formed by the optically activated recombination of the electrons trapped by the Sm³⁺ ions with the trapped holes.

1. Introduction

Conventional optical storage techniques, such as magneto-optic disks and CD-ROMs, record a single bit of information at each particular substrate location. They can only register information at 10⁹ bits cm⁻² using visible wavelengths at the diffraction limit [1]. Many efforts [3–9] have been made to realize an optical memory with a high storage density in order to satisfy the requirements of high performance computers in the last decade. Some approaches have been done to record data information in time [2], space [3] and wavelength [4, 5] domains. Novel techniques such as swept-carrier time-domain optical storage [2], three-dimensional optical storage [3, 6–9] and photochemical hole burning [4, 5] were proposed and have been studied extensively.

Persistent spectral hole burning (PSHB) in rare-earth-doped materials has attracted much attention because multiple bits can be recorded at a single storage material location by multiplexing the bits spectrally using different optical frequencies to record data bits [4, 5]. PSHB phenomena were first found in the Pr³⁺-doped LaF₃ crystal at 2 K [10]. Since then, PSHB has been observed in many rare-earth-doped crystals e.g. Sm²⁺-doped BaClF [11], Pr³⁺-doped Y₂SiO₅ [4] and Eu³⁺-doped Y₂SiO₅ [12] at temperatures below 10 K.

From the viewpoint of practical applications, high-temperature especially room-temperature PSHB and permanent holes are expected. In 1991, Jaaniso and Bull and Wei *et al*

§ To whom all correspondence should be addressed.

reported room-temperature PSHB in Sm^{2+} -doped $\text{SrFCl}_{1/2}\text{Br}_{1/2}$ crystals [13, 14], respectively. In 1993, Hirao *et al* observed PSHB in Sm^{2+} -doped borate glasses [15]. Glasses are considered to be more favourable than crystals because almost every element in the periodic table can be stuffed into glasses, which makes it easier to control the quantities and energy levels of electron and hole traps in glasses than in crystals. Moreover, glass can be easily fabricated into various forms such as a fibre and a large size plate. Therefore, there were a lot of investigations on PSHB in Sm^{2+} -doped glasses [15–17].

When the glasses are melted under ambient or oxidation atmosphere, Sm ions are present in trivalent state in the glasses. To obtain glasses doped with Sm^{2+} ions, glasses must be prepared under a strong reducing atmosphere [15–17]. Usually, hydrogen gas is used as a reducing atmosphere and a furnace with a well closed structure is needed when one wants to fabricate Sm^{2+} -doped glasses.

On the other hand, Calvert and Danby reported that Eu^{3+} and Sm^{3+} in CaSO_4 were reduced to Eu^{2+} and Sm^{2+} after x-ray irradiation in 1984 [18]. But, there were few reports on the x-ray-induced reduction of rare-earth ions in the glasses to the best knowledge of the present authors. Recently, we have observed that Sm^{3+} ions doped in some oxide, fluoride and chloride glasses can be reduced to Sm^{2+} ions after the irradiation of x-rays, γ -rays and focused femtosecond infrared lasers [19]. In this paper, we report on the x-ray-induced reduction of Sm^{3+} ions to Sm^{2+} ions in a fluoroaluminate glass. PSHB has also been observed in the x-ray-irradiated glass at room temperature. The mechanisms of the x-ray-induced reduction of Sm^{3+} ions to Sm^{2+} ions and PSHB are also discussed.

2. Experiment

The composition of the Sm^{3+} -doped fluoroaluminate glass sample used in this study was $0.1\text{SmF}_3 \cdot 14.9\text{YF}_3 \cdot 10\text{MgF}_2 \cdot 20\text{CaF}_2 \cdot 10\text{SrF}_2 \cdot 10\text{BaF}_2 \cdot 35\text{AlF}_3$ (mol%). 5 N purity-grade SmF_3 , YF_3 , MgF_2 , CaF_2 , SrF_2 , BaF_2 and AlF_3 were used as starting materials. A mixed 30 g batch of glass was melted in a glassy carbon crucible at 800°C for 60 min in an Ar + NF_3 (5 vol.%) atmosphere. NF_3 gas was used to convert residual oxides into fluorides. The melt was taken out of the furnace and kept at room temperature in a glove box filled with Ar gas and a transparent and colourless glass sample was obtained. After the glass sample was annealed at the glass transition temperature for 1 h, it was cut and polished for the measurement of optical properties.

The glass samples with 3.0 mm thickness were irradiated by 40 kV/30 mA x-rays from a Cu target for 600 s. Absorption spectra of the glass samples were measured by a spectrophotometer (JASCO V570). Photoluminescence spectra of the glass samples were measured by a fluorescence spectrophotometer (Spex 270M) using a 532 nm light from a frequency-doubled diode-pumped Nd^{3+} -YAG laser as the excitation source. Electron spin resonance (ESR) spectra of the glass samples were measured at X-band frequency by an ESR spectrophotometer (JEOL-FE3X).

Hole burning experiments were made for the $^5\text{D}_0$ – $^7\text{F}_0$ transition of Sm^{2+} ions by using a 4-dicyanmethelene-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM) dye laser with a linewidth of about 1.3 cm^{-1} pumped by all lines of an Ar^+ laser. The dye laser beam was focused on the x-ray-irradiated glass sample, and the laser power density was 50 mW mm^{-2} . After the burning process, the hole burning spectrum was measured by fluorescence excitation spectroscopy with a beam whose intensity was about 0.5 mW mm^{-2} . For the excitation spectroscopy, the fluorescence of the $^5\text{D}_0$ – $^7\text{F}_2$ transition of Sm^{2+} ions at 725 nm was detected by a photomultiplier through a 25 cm monochromator.

All of the experiments were carried out at room temperature.

3. Results and discussion

After the x-ray irradiation for 600 s, the part from the surface to about 1 mm inside the glass sample became orange. Figure 1 shows the absorption spectra of the Sm^{3+} -doped glass before and after the x-ray irradiation. A small absorption peak is observed at 400 nm in the spectrum of the x-ray-unirradiated glass sample. It can be attributed to the 4f–4f transition of Sm^{3+} ions [19]. Several peaks are observed in the absorption spectrum of the glass sample after the x-ray irradiation. A shoulder peak at about 280 nm can be assigned to the absorption due to 5d–4f transitions of Sm^{2+} ions [19]. The origins of the peak at 220 nm and the shoulder peak at about 500 nm are unclear. We suggest that they are due to the hole and electron trapped defect centres induced by the x-ray irradiation as observed in radiation-irradiated fluoride glasses [21].

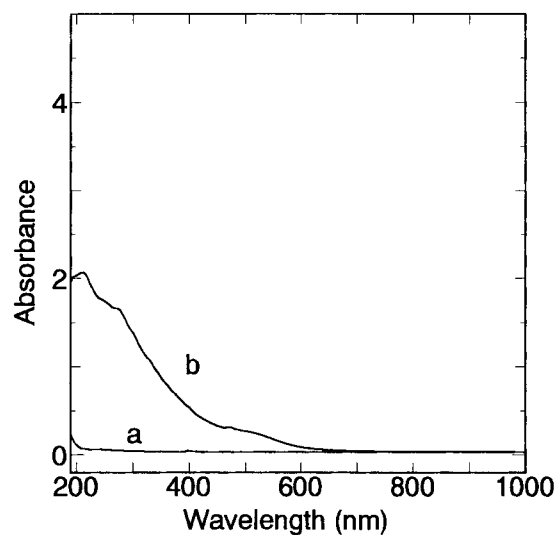


Figure 1. Absorption spectra of Sm^{3+} -doped fluoroaluminate glass sample before (a) and after (b) the x-ray irradiation.

Figure 2(a) shows the photoluminescence spectra of the Sm^{3+} -doped glass sample before and after the x-ray irradiation excited by the 532 nm laser light. The emissions at 560, 595, 640 and a weak peak at 705 nm in the unirradiated glass sample can be attributed to the 4f–4f transitions of Sm^{3+} ions [19]. New emission peaks can be observed at around 680 and 740 nm in the photoluminescence spectrum of the glass sample irradiated by the x-rays. Figure 2(b) shows the enlarged photoluminescence spectra at the wavelength region from 670 to 750 nm. The emissions at 680, 695 and 720 nm can be attributed to the 4f–4f transitions of Sm^{2+} ions [19]. Therefore, some of the Sm^{3+} ions were reduced to Sm^{2+} ions after the x-ray irradiation.

Figure 3 shows the electron spin resonance spectra of the Sm^{3+} -doped glass sample before and after the x-ray irradiation at room temperature. No apparent signals were observed in the spectrum of the non-irradiated glass sample, while a broad signal was observed in the spectrum of the glass sample irradiated by the x-rays. The signal is caused by intrinsic defect centres formed by x-ray irradiation, as in radiation-irradiated fluoride glasses [20].

Usually, samarium ions are present in trivalent state in glasses. Because of its electron configuration ($4f^5$), Sm^{3+} ions tends to capture electrons to form an electronic configuration which is near the stable half-filled 4f shell when sufficient electrons are provided. Therefore,

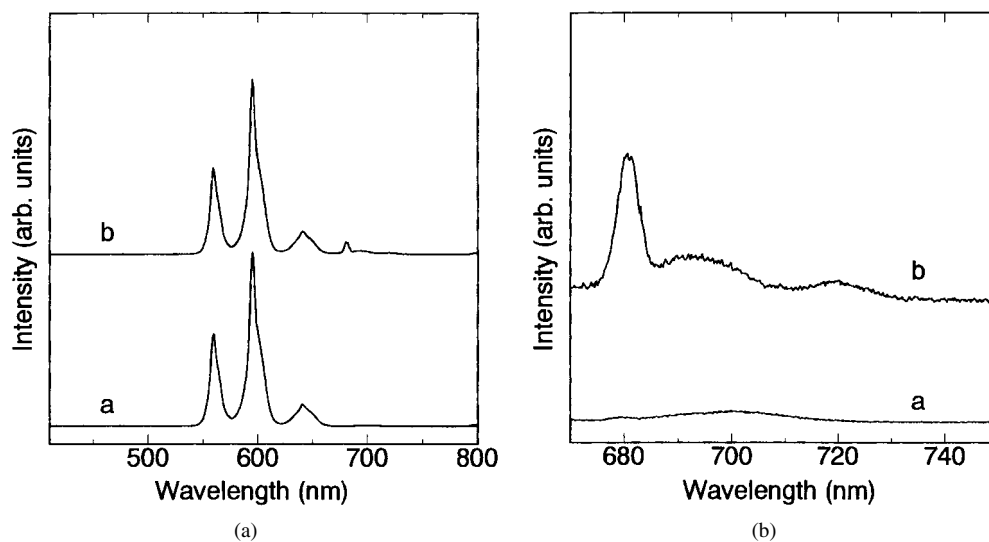


Figure 2. (a) Photoluminescence spectra of Sm^{3+} -doped fluoroaluminate glass sample before (a) and after (b) the x-ray irradiation excited with 532 nm laser light. (b) Enlarged photoluminescence spectra of Sm^{3+} -doped fluoroaluminate glass sample: before (a) and after (b) the x-ray irradiation excited with 532 nm laser light.

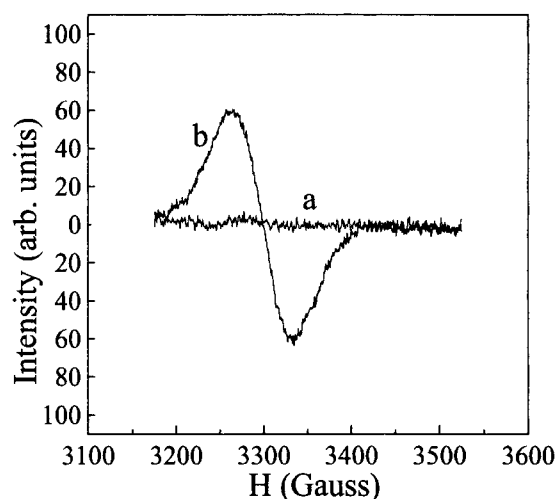


Figure 3. Electron spin resonance spectra of Sm^{3+} -doped glass sample before (a) and after (b) the x-ray irradiation.

samarium can also exist in the Sm^{2+} state in some crystals and glasses under a certain condition. We suggest that the mechanism of the x-ray-induced reduction of Sm^{3+} ions to Sm^{2+} ions is as follows. After the x-ray irradiation, free electrons and holes are induced in the glass sample. Some of the holes are trapped by active sites in the glass matrix and some of the electrons are trapped by the Sm^{3+} ions, leading to the formation of Sm^{2+} ions. We have examined the stability of the x-ray-induced Sm^{2+} ions by means of absorption and photoluminescence spectra, and have observed that the x-ray-induced Sm^{2+} ions were stable at room temperature.

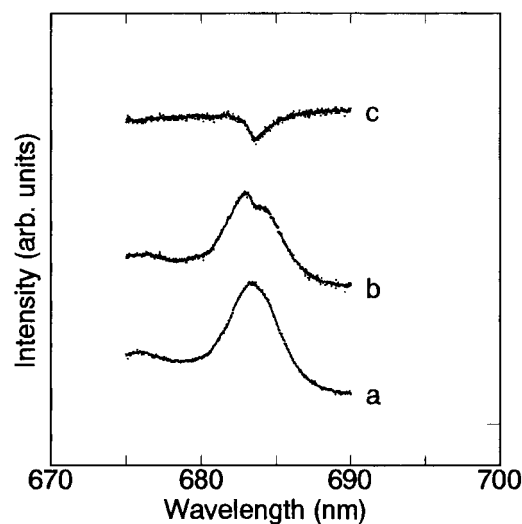


Figure 4. Excitation spectra of x-ray-irradiated Sm^{3+} -doped glass sample before (a) and after (b) irradiation with a DCM dye laser at 683.5 nm by monitoring the ${}^5\text{D}_0$ - ${}^7\text{F}_2$ transition of Sm^{2+} ions. c is the difference spectrum of the excitation spectra before and after the DCM dye laser irradiation.

This results exhibited that the activation barrier of the x-ray-induced hole-trapped centres as well as electron-trapped centres e.g. Sm^{2+} ($= \text{Sm}^{3+} + \text{an electron}$) are large and cannot be excited by thermal energy at room temperature to the conduction band and return to their previous state at room temperature.

Hole burning experiments were done on the excitation spectrum of the ${}^7\text{F}_0$ - ${}^5\text{D}_0$ transition of Sm^{2+} ions. The x-ray-irradiated glass sample was irradiated with the DCM dye laser at 683.5 nm operating at 50 mW mm^{-2} . Figure 4 shows the excitation spectra of the x-ray-irradiated Sm^{3+} -doped glass sample by monitoring the ${}^5\text{D}_0$ - ${}^7\text{F}_2$ emission of Sm^{2+} ions before (a) and after (b) the irradiation with the dye laser for 600 min. A shallow hole was observed at 683.5 nm in the spectrum after the dye laser irradiation.

Several physical models have been proposed to explain the spectral hole burning phenomena in the rare-earth-doped materials [21, 22]. They are two-level hole burning, metastable trap state, hyperfine hole burning and gated photoexcitation into a conduction band [21, 22]. We have observed that the spectral hole can still be detected 1 hour after the hole burning at room temperature. Therefore, the mechanism of the hole burning in the present glass is not due to the two-level hole burning and the metastable trap state, considering the lifetime of the $4f$ - $4f$ transition is shorter than ms.

The curve c in figure 4 is the difference spectrum of the excitation spectra before and after the DCM dye laser irradiation at 683.5 nm by monitoring the ${}^5\text{D}_0$ - ${}^7\text{F}_2$ transition of Sm^{2+} ions. There was no antihole or increased excitation (absorption) peak observed around the burned hole. Therefore, the mechanism of PSHB is also not due to the hyperfine hole burning because usually regions of enhanced absorption, or antiholes can be observed in the case of hyperfine hole burning due to the shifted absorptions from the hole-burned ions inside the inhomogeneous distribution. We assume that after the DCM dye laser irradiation, electrons were released from the electron-trapped Sm^{2+} ($= \text{Sm}^{3+} + \text{an electron}$) ions which have absorptions at around 683.5 nm, and recombined with the holes captured by the active sites in the glass matrix via a tunnelling process or multiphoton process through the conduction band.

We suspected that the hole burning rate in the x-ray-irradiated glass could be higher than that of Sm^{2+} -doped glass fabricated under a strong reducing atmosphere, since hole-trapped centres which can easily capture electrons were actively introduced near the Sm^{2+} (= Sm^{3+} + an electron) ions. However, at present, we have not observed any apparent difference in the hole burning rate between the x-ray-irradiated glass and Sm^{2+} -doped glass fabricated under a reducing atmosphere. One reason may be that some active sites which also easily capture electrons are introduced in the glass when fabricated under the strong reducing atmosphere. Further study is needed to clarify the detailed mechanism of the hole burning in the x-ray-irradiated glass.

4. Conclusions

We have observed persistent spectral hole burning in the x-ray-irradiated Sm^{3+} -doped fluoroaluminate glasses at room temperature. Samarium ions were present in trivalent state in the glass prepared under an Ar + NF_3 (5 vol.%) atmosphere. Some of the Sm^{3+} ions in the glass sample were reduced to Sm^{2+} ions after the x-ray irradiation. Persistent spectral hole burning was observed in the ${}^7\text{F}_0$ - ${}^5\text{D}_0$ line of Sm^{2+} ions by means of the 4-dicyanmethelene-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran dye laser. No antihole or increased excitation (absorption) peak was observed around the burned hole. The persistent spectral hole burning is suggested to be due to the optically activated recombination of the electrons trapped by Sm^{3+} ions with the trapped holes.

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