Formation of Sm^{2+} Ions and Spectral Hole Burning in X-ray Irradiated Glasses

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Al$_2$O$_3$−SiO$_2$ glasses were prepared for doping with Sm^{3+} ions using a sol−gel method, followed by X-ray irradiation, in which formation of the Sm^{2+} ions and persistent spectral hole burning (PSHB) were investigated. The X-ray irradiation brought about hole centers in the oxygen ions bound with Al^{3+} ions. And the released electrons are captured in the Sm^{3+} ions to form Sm^{2+} ions. The X-ray reduced Sm^{2+} ions are not so stable that they change into Sm^{3+} by heating at 200 to 300 °C. The spectral holes were burned in the $^7F_0\rightarrow{}^5D_0$ line of the Sm^{2+} ions, in which deep holes could be burned within a short laser-irradiation period compared with that of the H$_2$-gas heated glass. Hole spectra were stable up to room temperature, at which the hole depth was ∼20% of the total fluorescence intensity. Bleaching at the low energy sites of the $^7F_0\rightarrow{}^5D_0$ transition was observed during irradiation with the laser. The results definitely reveal that the PSHB is formed by the electron transfer between the Sm^{2+} ions and the hole centers formed in oxygen ions bound through the excited $^5D_0$ state.

Introduction

Since the first observation of room-temperature persistent spectral hole burning (PSHB) phenomena in Sm^{2+}-doped BaFCl crystal was reported by Jaaniso and Bill,[1] many studies have been carried out to develop the Sm^{2+}-doped PSHB crystals[2,3] and glasses[4−6] because of their potential use in high-density frequency-domain optical memories. As a host material, glasses are thought to be more favorable than crystals, because of their wide inhomogeneous line-width, compositional variety, and easy mass production. In the Sm^{2+}-doped glasses, Hirao et al.[4] and Izumitani and Payne[5] produced Sm^{2+}-doped borate and fluoride glasses by a melting method and observed room temperature PSHB. The samarium ions are generally incorporated as the trivalent state in glasses, and must be reduced into the Sm^{2+} by heating at high temperature under a strong reducing atmosphere. Recently, room-temperature PSHB was also observed in Eu^{3+}-doped glasses.[7−9]

In contrast, using a sol−gel method, we successfully prepared Sm^{2+}- and Eu^{3+}-ion-doped silicate glasses exhibiting PSHB up to room temperature.[10,11] Silicate glasses are more favorable as the host material for practical application than borate and fluoride glasses, because they have excellent chemical durability and high mechanical strength. In the sol−gel method, glasses are prepared through the hydrolysis of the alkoxy-derived solution, in which a large amount of hydroxyl groups remain. We found that the hole depth proportionally increased as the hydroxyl content increased and the PSHB with ∼40% depth could be burned at 77 K.[12] The proposed hole-burning mechanism for the sol−gel-derived rare-earth ions-doped glasses is the optically activated rearrangement of the hydroxyl bonds surrounding the rare-earth ions in glasses.[13] In this viewpoint, the sol−gel method is appropriate for preparing the PSHB glasses with high hole-burning efficiency. More recently, we observed room-temperature PSHB in the sol−gel-derived Eu^{3+}

ions-doped glasses that were irradiated with X-rays or heated in a H$_2$ gas atmosphere.[14]

In the sol−gel-derived Sm^{2+}-doped PSHB glasses, the glasses are prepared to incorporate the Sm^{3+} ions and then heated in a hydrogen gas atmosphere to reduce into Sm^{2+}.[15] The hole-burning mechanism is thought to be photoionization of the Sm^{2+} ions, though the question where the electrons are captured is not clearly understood. On the other hand, there are a few reports on the reduction of Sm^{3+} ions by X-ray irradiation. Recently, we have observed that Al$_2$O$_3$−SiO$_2$ glasses are liable to form the defect centers in Al−O polyhedra by the X-ray irradiation, resulting in the reduction of the Sm^{3+} ions into Sm^{2+}. In this paper, we study the reduction of the Sm^{3+} ions in Al$_2$O$_3$−SiO$_2$ glasses by X-ray irradiation and compare the reduction process of the Sm^{3+} ions in the H$_2$-gas-treated glasses. The PSHB properties are also discussed to relate with the chemical states of the Sm^{2+} ions.

Experiments

Using a sol−gel method, 10Al$_2$O$_3$·90SiO$_2$ (mol %) glasses were prepared to contain nominally 5 wt % Sm$_2$O$_3$. The materials were commercially available and were used as received: Si(OC$_2$H$_5$)$_4$ (Colcoat), Al(OC$_4$H$_9$^{sec})$_3$ (Kanto Chemical), and SmCl$_3$·6H$_2$O (Nacalai Tesque). Gels were synthesized through hydrolysis of the mixed materials in ethanol, a detailed explanation of which is given elsewhere.[10,15] The gels were heated in air at 50 °C/h to 700 °C and held at that temperature for 2 h. Some of the glasses were irradiated with X-rays. The X-ray irradiation was performed using the Cu Kα line with 40 kV and 20 mA for 14 h at room temperature. Others were heated at 800 °C under a flowing H$_2$ gas in a fused silica tube previously under vacuum.

The optical absorption spectra of glasses were measured with a Jasco, V-570 spectrometer in the range from 200 to 2000 nm. The fluorescence spectra were recorded at right angles using a Hamamatsu, R955 photomultiplier. A xenon lamp passed through a monochromator was used for excitation. Electron spin
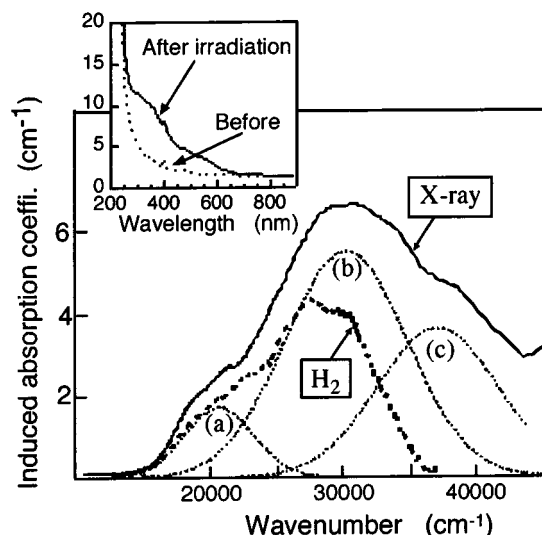
Figure 1. Optical absorption spectra induced by X-ray irradiation or H_2-gas heat-treatment. The Sm-doped $10Al_2O_3 \cdot 90SiO_2$ glasses were irradiated with X-rays for 14 h at room temperature or heated in H_2-gas at 800 °C for 15 h. The inset is the spectra before and after X-ray irradiation.

resonance (ESR) measurement was performed using a Jasco, JES-FE ME3X spectrometer at room temperature. The *g*-values of the obtained ESR signals were calibrated by the utilization of diphenyl−picrylhydrazal (DPPH).

The PSHB was observed on the excitation spectra of the $^7F_0 \rightarrow ^5D_0$ line of the Sm^{2+} ions. Holes were burned by irradiating a cw Ar^+-ion laser-pumped dicyanoimidazole (DCM) dye laser with a line width of ~1 cm^{-1} full width at half-maximum (fwhm). The excitation spectra before and after hole burning were recorded by scanning the dye laser from 14700 to 14450 cm^{-1} while monitoring the fluorescence of the $^5D_0 \rightarrow ^7F_2$ transition at 13800 cm^{-1}. The laser power for scanning was reduced by neutral-density filters so that the hole burning during the measurement was negligible.

Results and Discussion

Formation of the Sm^{2+} Ion in Glasses. The glasses heated in air are transparent, colorless, and show optical properties characteristic of the f−f transition of Sm^{3+} ions. When the glasses were irradiated with X-rays, they became faintly brown, while the H_2-gas heated glasses appeared very faintly pink. Figure 1 shows absorptivity change induced by the X-ray irradiation or H_2-gas treatment. The optical absorption spectra before and after X-ray irradiation are also illustrated in the inset of Figure 1. Heating in H_2 gas causes broad absorption bands peaking at ~22000 and ~28000 cm^{-1}, which can be assigned to the $4f^6 \rightarrow 4f^5 5d$ transition of the Sm^{2+} ions.[10] The 5d orbital of $4f^5 5d$ configuration is affected by a crystal field into two degenerate levels of e_g and t_{2g} components and the ~22000 and ~28000 cm^{-1} bands could be assigned to these components, respectively. The reduction of the Sm^{3+} into Sm^{2+} in glass is apparent from the fluorescence (FL) spectrum shown in Figure 2. In the H_2-gas heated glass, the fluorescence bands peaking at 683, 700, and 725 nm are observed in addition to the FL lines from the Sm^{3+} ions (560, 600, and 650 nm), which are attributed to the $^5D_0 \rightarrow ^7F_{0,1,2}$ transitions, respectively, of the Sm^{2+} ions. On the other hand, the glass irradiated with X-rays exhibits similar change in the FL spectra, although the FL intensities are a little small compared with those for the H_2-gas heated glass. These results strongly indicate that the Sm^{3+} ions are reduced into Sm^{2+} by X-ray irradiation.
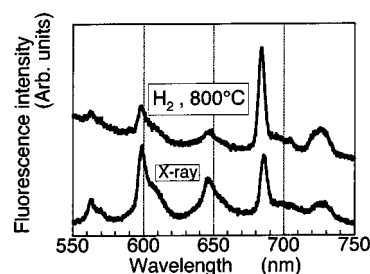

Figure 2. Fluorescence spectra for Sm-doped glasses irradiated with X-ray for 14 h at room temperature or heated in H_2-gas at 800 °C for 15 h. The fluorescence spectra were obtained using Xe lamp irradiation at 400 nm.
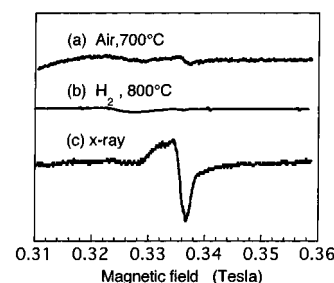

Figure 3. ESR spectra for Sm^{3+}-doped glasses heated in air at 700 °C (a), followed by heating in H_2-gas (b) or irradiating with X-ray (c)

Generally known is that X-rays act to ionize the rare-earth ions in oxide glasses. There are few reports on the reduction of the Sm^{3+} into Sm^{2+} by X-ray irradiation. Qiu et al. used fluoroaluminate glass as the matrix for the reduction of the Sm^{3+} ions to Sm^{2+}.[16] To study the effect of the glass composition on the X-ray reduction of the Sm^{3+} ions, some silicate glasses were prepared to contain metal oxides such as Na_2O, B_2O_3, and TiO_2 using the sol−gel method, followed by irradiation with X-rays. However, no change in the Sm^{2+} ions was observed in these glasses. Al_2O_3-containing glasses were only effective in reducing the Sm^{3+} ions into Sm^{2+}. In contrast to the FL spectra, the absorption spectrum of the X-ray irradiated glass was different from that of the H_2-gas heated glass, i.e., broad but strong absorption was induced in high energy sites above ~35000 cm^{-1}. The X-ray induced absorption bands were fitted with three Gaussian curves peaking at 20500, 30000, and 37000 cm^{-1} (see Figure 1), the former two bands of which are due to the $4f^6 \rightarrow 4f^5 5d$ transition of the Sm^{2+} ions. Appearance of a new absorption band at 37000 cm^{-1} suggests the formation of some defect centers and breaking of the glass structure by the X-ray irradiation.

ESR spectra were recorded to investigate the defect centers in glass. The samples treated in the same way were used to measure the ESR spectra at 77 K, which are shown in Figure 3. No apparent signals were detected in glasses heated in air and followed by heating in H_2-gas. The Sm^{2+} ions are nonmagnetic and do not contribute to the ESR spectra. On the other hand, the glass after X-ray irradiation showed the strong signals at around 0.32 to 0.33 T. It is reported that the γ-ray irradiated silicate glasses containing Al_2O_3 are induced the optical absorption and ESR signals, which are assigned to the hole centers in oxygen ions bound with Al^{3+} ions.[17] From this and the obtained ESR signals with the *g*-value higher than the free electron ($g = 2.0023$), it is concluded that the hole centers are trapped at oxygen ions by the X-ray irradiation. The released electrons can be captured in the Sm^{3+} ions to form the Sm^{2+} ions. The Sm^{3+} ions tend to capture electrons to form a stable half-filled $4f^6$ electron configuration, if sufficient electrons are

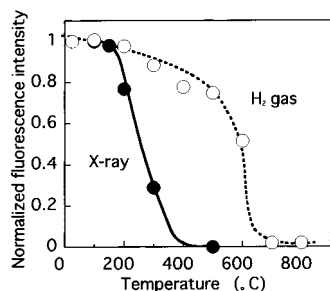**Figure 4.** Relation between FL intensity of the $^5D_0 \rightarrow {}^7F_0$ transitions of Sm²⁺ at 685 nm and heat-treatment temperature in air. FL intensities were normalized to the intensities after the X-ray irradiation and H₂-gas heating.
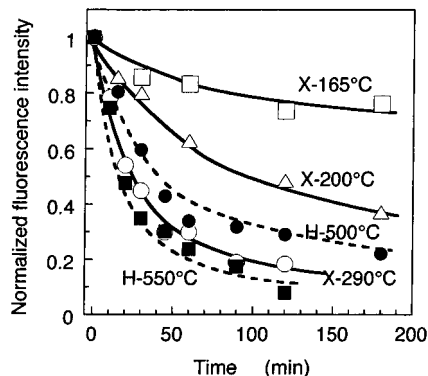

Figure 5. Dependence of the FL intensity of the $^5D_0 \rightarrow {}^7F_0$ transitions of Sm²⁺ ions on heating time in air for the Sm²⁺-doped glasses irradiated with X-ray (X-Temperatures) or heated in H₂ gas (H-Temperatures).
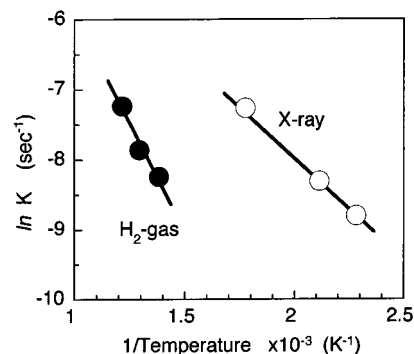

Figure 6. Relation between the rate constant of the oxidation of Sm²⁺-doped glasses irradiated with X-ray or heated in H₂-gas and the reciprocal temperature in Kelvin.
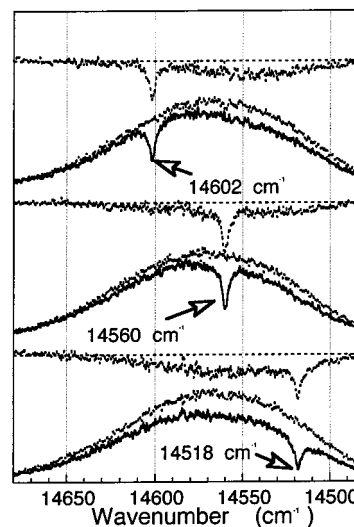

Figure 7. PSHB spectra for the X-ray irradiated glass before and after hole burning and their difference spectra. The holes were burned with a laser power of 300 mW for 15 min at 7 K.

provided. Therefore, the absorption band at 37000 cm⁻¹ induced in the X-ray irradiated glass can be attributed to the hole centers in the oxygen ions bound with Al³⁺ ions. Glass structure, particularly, the coordination of oxygen surrounding the Sm²⁺ ions, might not be changed after X-ray irradiation. On the other hand, when the glass is heated in H₂ gas, the H₂ molecules react with oxygen ions to form H₂O. Removal of the generated H₂O causes the number of oxygen ions surrounding Sm³⁺ to decrease, resulting in the reduction of the Sm³⁺ ions. Thus, the reduction behavior of Sm³⁺ ions is different between the X-ray irradiated and the H₂-gas treated glasses.

The Sm²⁺ ions in the X-ray irradiated and H₂-gas heated glasses were further investigated from their thermal relaxation into the Sm³⁺. Samples were heated in air at various temperatures for 30 min, the FL spectra of which were measured. The FL intensities of the $^5D_0 \rightarrow {}^7F_0$ transition of Sm²⁺ ions are shown in Figure 4 as a function of the heating temperature. The FL intensities are normalized to the intensities after the X-ray irradiation and H₂-gas heating. It is evident that the intensities decrease as the heat-treatment temperature increases, but the dependence of the intensity on temperature is quite different. The FL intensity for the X-ray irradiated glass rapidly decreases from ∼200 °C and disappears above 400 °C. On the other hand, for the H₂-gas heated glass, the FL intensity is only ∼80% of its initial value at 400 °C. Further heating is necessary to diminish the intensity and it completely disappears at 700 °C. This result also indicates that the bonding features of the Sm²⁺ ions are quite different between the X-ray irradiated and H₂-gas heated glasses. Figure 5 shows dependence of the FL intensities on the heating time. The FL intensities decrease with increasing time and approach saturated levels. Assuming that the FL intensity corresponds to the concentration of the Sm²⁺ ions, the rate equation of oxidation of the Sm²⁺ into Sm³⁺ can

be written using the FL intensity, I_t, as $I_t = I_0\{1 - \exp(-Kt)\}$, where I_0 is the saturated intensity after an infinite period and K is a rate constant. The experimental data were fitted using this equation to determine the rate constant by the least-squares fitting. The determined rate constant values are plotted in Figure 6 as a function of reciprocal temperature. The lines are the fit of these data to the Arrhenius equation; $K = K_0 \exp(-E/RT)$, where E, R, and T are the activation energy, gas constant, and temperature, respectively. The slope of this function gives the activation energy for the oxidation of Sm²⁺ ions, which are calculated as 25 and 50 kJ/mol for the X-ray irradiated and H₂-gas heated glasses, respectively. Note that the activation energy for the X-ray irradiated glass is only half the value of the H₂-gas heated glass, indicating that the Sm²⁺ ions in the X-ray irradiated glass are unstable and easily oxidized into Sm³⁺ compared with those in the H₂-gas heated glass.

Persistent Spectral Hole Burning. PSHB was observed on the excitation spectrum of the $^7F_0 \rightarrow {}^5D_0$ transition of the Sm²⁺ ions. Figure 7 shows typical excitation spectra before and after hole burning and its difference signals. Holes are clearly observed at the burning points of 14602, 14560, and 14518 cm⁻¹. The hole depth and width are ∼60% of the total fluorescence intensity at the burning position and ∼4 cm⁻¹ fwhm, respectively, which are almost independent of the burning position. The hole depth decreased and the hole width increased as the burning temperature increased. Of further interest in Figure 7 is that after burning, the intensities decrease at low
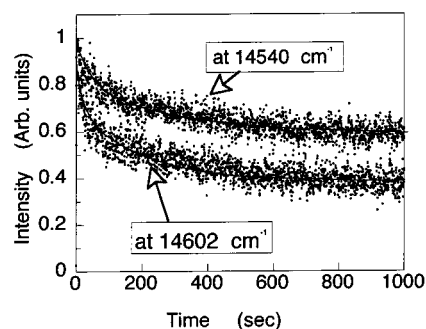
Figure 8. FL intensities at 14602 and 14540 cm^{-1} as a function of burning time. The hole was burned using 14602 cm^{-1} excitation energy of the DCM dye laser.

energy sites of the excitation spectra. Bleached intensities consist of a broad band with a peak at 14540 cm^{-1} and width of ∼50 cm^{-1} fwhm. Although the origin of this bleaching by laser irradiation is not clear, we consider at present that the electrons excited by the burning laser relax into low energy sites of the $^7F_0 \rightarrow ^5D_0$ transition, followed by exciting the electrons, which causes the FL intensity decrease. Further investigations are necessary to study the bleaching mechanism for the X-ray irradiated Sm^{2+} ions.

To further investigate the hole burning and FL bleaching of the X-ray irradiated glass, the dynamics of both the burning and bleaching were measured. The FL intensities at 14602 and 14540 cm^{-1} were monitored under laser irradiation at 14602 cm^{-1}, which are shown in Figure 8 as a function of time during burning. It is evident that the intensities, normalized to the intensities before burning at 14602 and 14540 cm^{-1}, decrease to constant values within a few hundred seconds. True hole-depth at 14602 cm^{-1} can be determined by subtracting the bleached intensity from the measured hole depth, because the bleaching band is spread to the hole burning position. Assuming the bleaching band has a Gaussian distribution, the bleaching intensities at the burning position are calculated and subtracted from the measured hole depth, giving the true hole depth, which are illustrated in Figure 9 together with the bleaching intensities. It is evident that the hole depth decreases as the burning temperature increases, while the bleaching intensity increases with increasing temperatue. The hole-growth data are well-fitted to the first equation; $D_t = D_0\{1 - \exp(-Kt)\}$, where D_t and D_0 is the hole depth at burning time, t, and after an infinite period, respectively, and K is a rate constant. The estimated rate constant, K, is ∼1.0 × 10^{-2} s^{-1} at 7 K for the X-ray irradiated glass, and almost independent of the burning temperature. Compared with the burning rate for the H$_2$-treated glass (see Figure 9), which is estimated as ∼1.3 × 10^{-3} s^{-1}, the X-ray irradiated glass exhibits hole burning rate by about 10 times faster than the H$_2$-treated glass. These different hole-burning dynamics for two glasses should be based on different Sm^{2+} ions in both glasses.

A possible hole-burning mechanism for the H$_2$-treated glass is the photoionization of the Sm^{2+} ions and capture of the released electrons in the neighboring Sm^{3+} ions: Sm$_I^{2+} \rightarrow$ Sm$_I^{3+}$ + e$^-$, and Sm$_{II}^{3+}$ + e$^- \rightarrow$ Sm$_{II}^{2+}$, where the Sm$_I^{2+}$ and Sm$_{II}^{3+}$ are separately coordinated in glass network structure.[18] In this reaction, the electron transfer between the Sm$_I^{2+}$ and Sm$_{II}^{3+}$ determines the hole burning dynamics. On the other hand, in the X-ray irradiated glass, the Sm^{3+} ions are reduced into Sm^{2+} by capturing the electron from the neighboring oxygen. The oxygen ions surrounding the Sm^{2+} ions are not changed in their numbers but have hole centers. On laser irradiation for hole burning, the Sm^{2+} ions are photoionized and the released
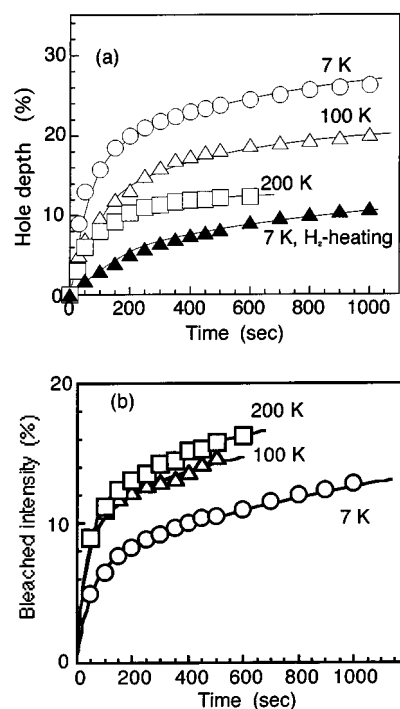

Figure 9. Dependence of the hole depth (a) and bleaching intensity (b) on burning time. The holes were burned at 7, 100, and 200 K for the X-ray irradiated glasses and at 7 K for the H$_2$-gas heated glass.
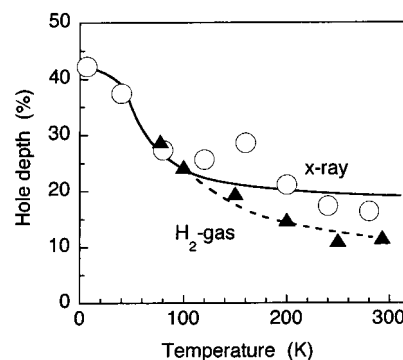

Figure 10. Relation between the hole depth and the excursion temperature for the X-ray irradiated or H$_2$-gas heated glass.

electrons can be captured in hole-centers in the oxygen ions. In other words, spectral holes are formed by the electron transfer between the Sm^{2+} ions and the defect centers in oxygen ions.

To study the stability of PSHB burned in the X-ray irradiated glass, the thermal stability of the burned holes was examined from the temperature excursion measurement of the holes. A hole was burned at 7 K, after cycling through a temperature higher than 7 K, the hole depth was again measured at the hole-burning temperature. During this process, the hole is partially filled. Figure 10 shows the relation between the hole-depth and the excursion temperature. It is evident that the hole with ∼20% depth is clearly observed after excursion to room temperature, though it decreases at temperatures below ∼150 K. In Figure 10, the result of the excursion measurement for the H$_2$-gas treated glass is also shown for comparison. It is evident that the stable and deep holes can be observed in the X-ray irradiated glasses compared with the H$_2$-gas treated one.

Conclusions

We found that the Sm^{3+} ions doped in the sol−gel-derived Al$_2$O$_3$−SiO$_2$ glasses were reduced into Sm^{2+} by X-ray irradia-

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tion. The X-ray reduced Sm^{2+} ions were unstable compared with the H$_2$-gas reduced Sm^{2+} ions, which were oxidized into Sm^{3+} by heating in air at 200 to 300 °C. The proposed reduction mechanism of the Sm^{3+} ions was the formation of the hole centers in the oxygen ions bound with Al^{3+} ions and the capturing of the electrons in the Sm^{3+}. The X-ray irradiated glass exhibited deep PSHB spectra compared with that of the H$_2$-gas heated glass, the hole burning rate of which was faster by 10 times than the H$_2$-gas heated glass. Bleaching at the low energy sites of the $^7F_0 \rightarrow {}^5D_0$ transition was observed during irradiation with laser. The results definitely reveal that the PSHB is formed by the electron transfer between the Sm^{2+} ions and the hole centers formed in oxygen ions bound with Al^{3+} ions through the excited $^5D_0$ state. These fast and high efficient hole burning glasses are makes it an attractive candidate for high-density memories.

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