Photochemical Hole Burning of Sm^{2+} in Sodium Borate Glasses Induced by Near-Infrared Femtosecond-Laser Irradiation

Koji FUJITA, Chikafumi YASUMOTO and Kazuyuki HIRAO

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto-shi 606-8501

近赤外フェムト秒レーザー照射により誘起されたナトリウムホウ酸塩ガラスにおける Sm^{2+} の光化学ホールバーニング

藤田晃司・安本親文・平尾一之

京都大学大学院工学研究科材料化学専攻, 606-8501 京都市左京区吉田本町

We report on photochemical hole burning of Sm^{2+} in sodium borate glasses irradiated with femtosecond-laser pulses of 800 nm wavelength. The irradiation of Sm^{3+} -doped sodium borate glasses with femtosecond-laser pulses causes electron-trapped Sm^{3+} , i.e., Sm^{2+} and point defects such as an oxygen hole center and an electron trapped near Na^+ . The measurements of spectral hole burning were carried out for the 5D_0 – 7F_0 transition of Sm^{2+} using a DCM dye laser. Photoionization hole burning is observed at 77 K to room temperature for the glasses exposed to femtosecond-laser pulses, and also for the glasses prepared by melting under reducing conditions. The hole-burning efficiency of Sm^{2+} produced by the photoinduced process is about twice higher than that by the thermal process. It is thought that the metastable Sm^{2+} ions and oxygen hole centers induced by femtosecond-laser irradiation are responsible for the observed phenomenon. We propose that the efficient photoionization hole burning is caused by the photostimulated recombination of the electron trapped by Sm^{3+} with the oxygen hole center.

[Received September 21, 2000; Accepted February 16, 2001]

Key-words : Near-infrared femtosecond-laser pulses, Sodium borate glasses, Samarium ions, Persistent spectral hole burning

1. Introduction

Interaction of radiation with matter attracts considerable attention in many areas of science since the discovery of the laser. In particular, vigorous investigations have been carried out into the interaction of laser radiation with glass, which is a key material in modern optical technology. The recent development of femtosecond-laser pulses with high-energy density has provided us with the unexplored potential for inducing photophysical and photochemical reactions in glass. The femtosecond-laser pulses can be used to rapidly and precisely deposit energy in solids. For instance, the light is absorbed by electrons, and the optical excitation is completed before the lattice is upset; the electrons transfer their excess energy to the lattice on a time scale of picoseconds, and micrometer-scale atomic displacement occurs on a time scale of nanoseconds. Besides, the strength of electric field of tightly focused 100 fs pulses, the energy of which is 1 μJ , can reach $\sim 100 \text{ TW}/\text{cm}^2$, which is sufficient for inducing nonlinear optical effects in materials. Consequently, femtosecond pulses have an additional unique advantage in laser processing of transparent materials.

Recent observation that photoinduced permanent and metastable structural changes can be produced only near the beam focusing area inside transparent glasses with femtosecond-laser pulses^{1)–4)} has attracted great attention, because they can be applied to the fabrication of integrated circuits, photonic band gap materials, patterned grating in fibers, and three-dimensional optical memory. Of particular interest is internal microstructuring of transparent glasses, which is not accompanied by crack as observed with nanosecond laser pulses. One-photon excitation that is resonant with the intrinsic absorption of glass leads to the reaction in all the exposed areas adjacent to the glass surface, since the energy is deposited beneath the surface. In the case of the

near-infrared femtosecond laser beam, on the other hand, the multiphoton excitation can induce the space-selective reaction in the vicinity of the focal point of the laser beam, where the pulse energy is sufficiently high.

In the present investigation, we examine photoinduced valence changes of samarium ions inside sodium borate glasses exposed to near-infrared femtosecond-laser pulses. Qiu et al.^{5),6)} reported the reduction of Sm^{3+} to Sm^{2+} and the creation of point defects in a fluoroaluminate glass and a sodium aluminoborate glass using near-infrared femtosecond-laser pulses, and proposed that the multiphoton process of near-infrared radiation is responsible for the observed phenomenon. Our interest here is whether the glass structure around the photoreduced Sm^{3+} (Sm^{2+}) is experiencing a combination of defect formation and structural relaxation. For this purpose, photoionization of Sm^{2+} is measured by means of spectral hole burning both for the glasses exposed to femtosecond-laser pulses and the glasses prepared by melting in reducing conditions. The sodium borate glasses were chosen as hosts because Sm^{3+} is reduced to Sm^{2+} during melting under reducing conditions.^{7)–9)} This makes it possible to compare the optical properties of Sm^{2+} created by the photoinduced process with those of Sm^{2+} formed by the thermal process.

2. Experimental procedures

Reagent-grade Na_2CO_3 , B_2O_3 , and Sm_2O_3 powders were used to prepare glasses with $15\text{Na}_2\text{O} \cdot 85\text{B}_2\text{O}_3 \cdot 1.0\text{Sm}_2\text{O}_3$ and $25\text{Na}_2\text{O} \cdot 75\text{B}_2\text{O}_3 \cdot 1.0\text{Sm}_2\text{O}_3$ compositions in molar ratio. A 10 g batch composed of the raw materials was mixed thoroughly, and melted in a platinum crucible at 1100°C for 30 min in air. The melt was poured onto a stainless steel plate and cooled to room temperature in air. For comparison, we prepared the sodium borate glass with the identical composition by melting in a glassy carbon crucible at 1350°C .

°C for 30 min under a 95%Ar–5%H₂ atmosphere, which we will refer to in the following often as thermally reduced glass. The glass sample thus obtained was cut into a rectangular parallelepiped using a saw pasted with diamond powder, and the surfaces of the resultant glass sample were polished. The size of the glass sample was about 3 mm × 3 mm × 3 mm. The compositions of 15Na₂O·85B₂O₃ and 25Na₂O·75B₂O₃ were selected because Sm²⁺ ions can be easily incorporated into the sodium borate glasses with low sodium contents compared with those with high sodium contents such as 30Na₂O·70B₂O₃ and 35Na₂O·65B₂O₃.⁷⁾

A laser system that generates and amplifies 800 nm wavelength pulses at a repetition rate of 200 kHz with a pulse width of approximately 120 fs was employed in our study. The laser beam with an average power of 400 mW was focused on the glass sample through an objective lens (Nikon, ×10 magnification, numerical aperture NA=0.30) of the microscope (Nikon, Optiphot 2). After the irradiation for 1 s, a colored spot was formed in the focal point. The diameter of the colored spot was nearly 5 μm when transmitted light optical microscope was used. Because of its small size, it was difficult to directly measure the optical properties. Instead, with the help of an XYZ stage, the glass sample was translated at a rate of 10000 μm/s perpendicular to the incident laser beam to produce a colored line with 3 mm length. Subsequently, 3 mm × 3 mm arrays of the colored lines at intervals of 10 μm were created within the glass sample so that the optical properties were examined.

Optical absorption and photoluminescence spectra were obtained using a spectrophotometer (Hitachi 330) and a fluorescence spectrometer (Hitachi 850), respectively. The photoluminescence spectra were measured using a 514.5 nm light of an Ar⁺ laser (Spectra Physics, Stabilite 2017) as a light source. For these measurements, we took scans before and after the femtosecond-laser irradiation. All the experiments were carried out at room temperature.

Spectral holes were burned into ⁵D₀–⁷F₀ transition of Sm²⁺ using a Rhodamine 6G dye laser (Spectra Physics 375B, linewidth ~1.3 cm⁻¹) pumped by an Ar⁺ laser (Spectra Physics, Beamlok 2060, all lines). A typical laser intensity under the burning was 10 W/cm², and the burning time was 300 s. For hole detection, the laser wavelength was scanned, while the fluorescence of ⁵D₀–⁷F₂ transition of Sm²⁺, selected with a monochromator combined with a glass filter, was detected with a photomultiplier tube (Hamamatsu Photonics, R928). The laser power for reading was ~0.25% of that for burning. For the measurements below the room temperature, the sample was fixed in a cryogenic refrigerator (Iwatani Plantech, Model CRT-006-2000) equipped with a compressor (Iwatani Plantech, Model CA101). In this apparatus, low temperatures can be accomplished by the adiabatic expansion of helium gas supplied by the compressor.

3. Results and discussion

Variation in optical absorption spectra of Sm³⁺-doped 25Na₂O·75B₂O₃ glasses with femtosecond-laser irradiation is shown in Fig. 1(a). The broken and solid curves represent the optical absorption spectra before and after femtosecond-laser irradiation, respectively. The sharp peaks due to 4f–4f transitions of Sm³⁺ are observed at 350 to 500 nm for the unirradiated glass. In addition to these peaks, the irradiation of the glass with femtosecond-laser pulses induces the broad absorption band over the wavelength range of 250 to 800 nm. Color of the glass is colorless and red brown before and after laser irradiation, respectively. The solid curve of Fig. 1(b) shows the absorption effectively induced by laser irradiation. The optical absorption spectrum of thermally reduced glass is shown in

Fig. 1. (a) Variation in optical absorption spectra of Sm³⁺-doped 25Na₂O·75B₂O₃ glasses with femtosecond-laser irradiation. The solid and broken curves represent before and after femtosecond-laser irradiation, respectively. The measurement was carried out at room temperature. (b) Femtosecond-laser-induced absorption band of Sm³⁺-doped 25Na₂O·75B₂O₃ glasses (solid curve), which was obtained by subtracting the spectrum of the sample before laser irradiation from that after laser irradiation. The broken curve is optical absorption spectrum of Sm²⁺-doped 25Na₂O·75B₂O₃ glass prepared by melting in a reducing condition.

the broken curve of Fig. 1(b) for comparison. The broad absorption band at around 350 nm observed for the thermally reduced glass is attributable to 4f⁶→4f⁵5d transition of Sm²⁺.⁷⁾ The spectral shape of induced absorption is similar to the absorption band due to Sm²⁺. A close look at Fig. 1 (b) also reveals that the induced absorption extends to longer wavelength regions compared with the thermally reduced glass. This discrepancy may be ascribed to the creation of point defects by femtosecond-laser irradiation as mentioned below.

Figure 2 shows the variation in emission spectra of Sm³⁺-doped 25Na₂O·75B₂O₃ glass with femtosecond-laser irradiation. The curves (a) and (b) correspond to the emission spectra before and after femtosecond-laser irradiation, respectively. For the laser-unirradiated glass, the emission peaks due to ⁴G_{5/2}→⁶H_J (J=5/2, 7/2, 9/2) transitions of

Fig. 4. (a) Hole burning at 77 K for the 5D_0 - 7F_0 transition of Sm^{2+} in $25\text{Na}_2\text{O} \cdot 75\text{B}_2\text{O}_3$ glass irradiated with femtosecond-laser pulses. The burning of hole was carried out at the wavelength of 686.8 nm for 300 s using a DCM dye laser. (b) Hole burning at 77 K for the 5D_0 - 7F_0 transition of Sm^{2+} in $25\text{Na}_2\text{O} \cdot 75\text{B}_2\text{O}_3$ glass prepared by melting in a reducing condition. The hole was burned under the same condition as in (a). Both the hole spectra were obtained by monitoring the emission due to the 5D_0 - 7F_2 transition of Sm^{2+} before and after laser irradiation.

Fig. 4(b). The comparison between Figs. 4(a) and 4(b) reveals that the spectral hole burning of $(\text{Sm}^{3+})^-$ is more efficient than that of Sm^{2+} ; in the photoreduced glass, a fairly large fraction of the absorption line corresponding to the selected $(\text{Sm}^{3+})^-$ ions ($\sim 70\%$ compared with $\sim 40\%$ in the thermally reduced glass) is lost from the line profile. Similar result was obtained at room temperature for the $15\text{Na}_2\text{O} \cdot 85\text{B}_2\text{O}_3$ glasses, which is shown in Fig. 5. The curves (a) and (b) correspond to the photoreduced and thermally reduced glasses, respectively. Spectral holes are clearly burned at room temperature. The depth of hole is about twice larger in the photoreduced glass than in the thermally reduced glass.

Hole burning of thermally reduced glasses involves photoionization of Sm^{2+} :⁷⁾

It is known that the photoionization hole burning is significantly affected by local environment around Sm^{2+} .^{7),13)}

Fig. 5. Room-temperature hole spectra for the 5D_0 - 7F_0 transition of Sm^{2+} in $15\text{Na}_2\text{O} \cdot 85\text{B}_2\text{O}_3$ glass exposed to femtosecond-laser pulses (a) and $15\text{Na}_2\text{O} \cdot 85\text{B}_2\text{O}_3$ glass prepared by melting in a reducing condition (b). The burning of hole was carried out at the wavelength of 686.8 nm for 300 s using a DCM dye laser. Both the hole spectra were obtained by subtracting the excitation spectrum of the sample before laser irradiation from that after laser irradiation.

For instance, in different alkali borate glasses, the depth of hole increases with an increase in the local basicity around Sm^{2+} .⁷⁾ This is because the higher valence state is favorable for valence alternative ions in the glasses with higher basicity. In such a situation, the photoionization of Sm^{2+} to Sm^{3+} takes place more readily. Also, it was found that the irradiation of Sm^{2+} -doped sodium borate glasses with X-rays enhances the hole-burning rate at the Sm^{2+} sites perturbed by defects such as oxygen hole centers.¹³⁾ In the present case, the photoreduced Sm^{3+} , i.e., $(\text{Sm}^{3+})^-$ is metastable compared with Sm^{2+} formed by the thermal process, since the local structural rearrangement following femtosecond-laser irradiation is not plausible in the rigid state near room temperature. In other words, $(\text{Sm}^{3+})^-$ in Reaction (3) can be regarded as the higher energy state, owing to its excess negative charge. This state is partly relaxed by photoionization of $(\text{Sm}^{3+})^-$ to Sm^{3+} according to Reaction (4), which contributes to more efficient hole burning. Electrons generated by the ionization transfer to nearby traps with spectral holes being formed. The predominant centers that act as the electron traps are oxygen hole centers as described in Reactions (1) and (2). In photoreduced glasses, thus, the hole burning may occur by the optically activated recombination of the electron released from $(\text{Sm}^{3+})^-$ with the oxygen hole center. We propose that the incomplete structural relaxation around photoreduced Sm^{3+} , i.e., $(\text{Sm}^{3+})^-$ and the formation of oxygen hole centers are responsible for the efficient photoionization hole burning.

Sm^{2+} -doped borate glasses show photon-gated hole burning, i.e., hole burning that occurs only in the presence of both wavelength-selective and gating-light beams;⁷⁾ two-step photoionization of Sm^{2+} occurs only in the part where the two light beams overlap with each other. By use of focused femtosecond-laser pulses, on the other hand, it is possible to induce the photoreduction of Sm^{3+} to Sm^{2+} with micrometer precision inside a transparent glass. The combination of both effects thus offers interesting possibilities from a practical viewpoint, one being wavelength- and space-selective optical memory.⁶⁾

4. Conclusions

Photoinduced valence changes of samarium ions were examined for binary sodium borate glasses. Electron-trapped Sm^{3+} , i.e., Sm^{2+} , oxygen hole centers, and electrons trapped near Na^+ are formed by the irradiation of Sm^{3+} -doped sodium borate glasses with 800 nm femtosecond-laser pulses. Photoionization hole burning on the 5D_0 – 7F_0 transition of Sm^{2+} was observed at 77 K to room temperature using a DCM dye laser for the glasses exposed to femtosecond-laser pulses and the glasses prepared by melting in reducing conditions. The efficiency of hole burning is about twice higher for Sm^{2+} produced by the photoinduced process than for Sm^{2+} formed by the thermal process. The observed phenomenon can be related to the metastable Sm^{2+} ions and oxygen hole centers induced by femtosecond-laser pulses. It is suggested that the efficient photoionization hole burning takes place as a result of photostimulated recombination of the electrons trapped by Sm^{3+} with the oxygen hole centers.

Acknowledgment This work is financially supported by the Nippon Sheet Glass Foundation. The authors would like to thank Dr. J. Qiu and Dr. J. Si of Photon Craft Project, Japan Science and Technology Corporation, for experiments of the femtosecond-laser irradiation.

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