Formation of Sm^{2+} ions in femtosecond laser excited $Al_2O_3 - SiO_2$ glasses

2003 J. Phys.: Condens. Matter 15 1259

(http://iopscience.iop.org/0953-8984/15/8/310)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 1259–1265 PII: S0953-8984(03)56354-8

Formation of Sm^{2+} ions in femtosecond laser excited Al_2O_3–SiO_2 glasses

Gil Jae Park, Tomokatsu Hayakawa and Masayuki Nogami[1]

Department of Materials Science and Engineering, Nagoya Institute of Technology, Showa Nagoya, 466-8555, Japan

E-mail: nogami@mse.nitech.ac.jp

Received 20 November 2002
Published 17 February 2003
Online at stacks.iop.org/JPhysCM/15/1259

Abstract

Al_2O_3–SiO_2 glasses doped with Sm^{3+} ions were irradiated with an 800 nm wavelength femtosecond laser pulse and the formation of Sm^{2+} ions was investigated. The Sm^{3+} ions were reduced to Sm^{2+} within a few minutes of laser irradiation. Electron spin resonance spectra indicated that the hole was trapped in non-bridging oxygen bound to Al^{3+}, while the electron was captured in the Sm^{3+}, leading to the Sm^{2+} formation. The thermal stability of the photoinduced Sm^{2+} ions was also investigated by fluorescence spectroscopy. The Sm^{2+} ions were converted to Sm^{3+} ions by heating the glasses in air at 300–400 °C.

1. Introduction

Rare-earth ion-doped glasses have stimulated much interest because of their potential use in various areas such as optoelectronic devices, sensors and lasers. Our research interest focuses on the preparation of new functional glasses containing rare-earth ions using a sol–gel method. Recently, using this technique, we succeeded in the preparation of silicate glasses doped with Eu^{3+} and Sm^{2+} ions exhibiting persistent spectral hole burning up to room temperature [1, 2]. Spectral holes are considered to be burned by photoinduced chemical reactions within the rare-earth ions or between the rare-earth and matrix glass structure. The sol–gel process is appropriate for preparing these hole-burning glasses because of its ability to modify glass composition at temperatures lower than those required for the conventional melting method. More recently, we demonstrated the reduction of Sm^{3+} ions into Sm^{2+} by x-ray irradiation and fast hole-burning phenomena [3]. With respect to the microscopic modifications of the glass, x-ray or laser irradiation is of greater advantage than the heating process.

Femtosecond lasers have been recognized as outstanding tools for accurate and effective material processing especially for microscopic modifications, enabling internal micro fabrication of the glass structure without serious thermal bulk damage which often occurs

[1] Author to whom any correspondence should be addressed.

when using nanosecond lasers. For these reasons, some glasses have been processed using femtosecond lasers [4–7]. There are only a few reports concerning the reduction of Sm^{3+} ions by femtosecond laser and these are limited to borate, fluoride and $ZnCl_2$ based glasses prepared using melting methods [8–10] and aluminosilicate glasses prepared by vapour deposition methods [11]. Although these recent pioneering works showed the modification of Sm^{3+} ions, the photochemical reaction process by the femtosecond laser irradiation is still not yet clear. Here, we report the formation of Sm^{2+} ions in doped Al_2O_3–SiO_2 glasses irradiated by a femtosecond laser, using measurements of the optical absorption and fluorescence (FL) properties. The mechanism for the photoreduction of the Sm^{3+} ions into Sm^{2+} and the stability of the Sm^{2+} ions are also discussed.

2. Experimental details

The $10Al_2O_3{\cdot}90SiO_2$ (mol%) glasses, doped with 10 wt% Sm_2O_3, were prepared by a typical sol–gel method. All the raw materials and reagents are commercially available and were used as received. A detailed explanation of the gel preparation is given elsewhere [12, 13]. The gels obtained were heated at 500 °C in air for two hours, polished and then heated at 800 °C in air for a further two hours.

The femtosecond pulse laser irradiation of the glass was performed by a Ti:sapphire regenerative amplifier laser system (Spectra Physics, Hurricane) operating at a wavelength of 800 nm with a 1 kHz repetition rate and 130 fs pulse duration. The laser beam, with an average power of 780 mW, was tightly focused on the sample through an objective lens.

The optical absorption spectra were measured with a spectrometer (Jasco, V-570) in the range from 200 to 900 nm wavelength. The FL spectra were recorded using an N_2 laser with a 337 nm wavelength for excitation. A monochrometer (Jobin Yvon, HR 320) combined with CCD camera was used for recording. Electron spin resonance (ESR) spectra were obtained at 123 K by applying X-band microwave frequencies (Jasco, JES-RE1X). The quoted g-values were referenced to the value for diphenyl-picrylhydrazal (DPPH).

3. Results and discussion

3.1. Optical absorption spectra

When the glass was exposed to the 800 nm femtosecond laser, the colour of the glass was changed from colourless to pale yellow. No collateral damage was found in the glasses during laser irradiation. The optical absorption spectra, measured before and after irradiation by the femtosecond laser, are given in figure 1. The distinct absorption bands peaking at 345, 360, 375 and 402 nm before the irradiation are assigned to the $4f \rightarrow 4f$ inner shell transition of the Sm^{3+} ions. After irradiation by the laser for 20 s, a large broad absorption appeared in the 200–800 nm wavelength region. The differential optical absorption spectrum is shown in the inset of figure 1. It is evident that the laser irradiation causes broad bands peaking around 320 and 500 nm. These spectral characteristics are similar to those reported previously for Sm^{2+} ions in x-ray irradiated glasses, where the included absorption bands were ascribed to the $4f^6 \rightarrow 4f^5 5d$ transition of the Sm^{2+} ions [3]. The 5d orbital of the $4f^5 5d$ configuration is changed by the crystal field into two degenerate levels of t_{2g} and e_g components and the two bands at 320 and 500 nm can be assigned to these components, respectively. The absorption intensities measured at 320 and 500 nm are plotted as a function of the laser irradiation time in figure 2. Clearly, the absorption intensities of both bands increase as the time of the laser irradiation increases and approach constant levels within a few minutes. However, detailed

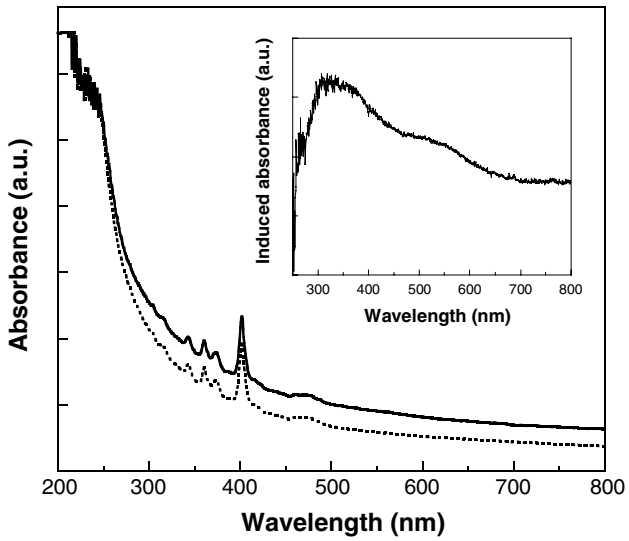

Figure 1. Optical absorption spectra of Sm^{3+}-doped Al_2O_3–SiO_2 glass before (dotted curve) and after (solid curve) femtosecond laser irradiation for 20 s at room temperature. Inset shows the differential absorption spectrum.

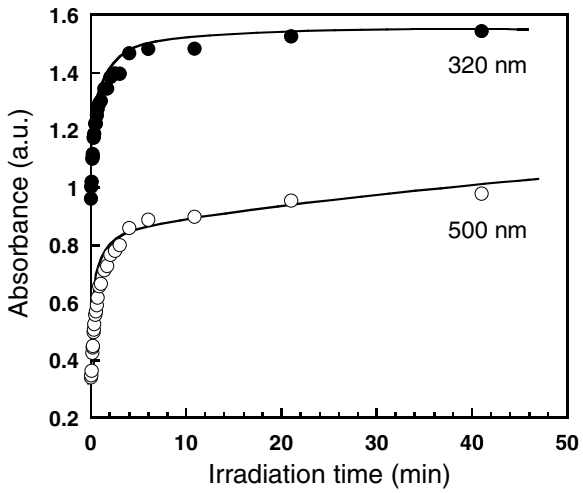

Figure 2. Relation between the optical absorbance changes monitored at 320 and 500 nm and the femtosecond laser irradiation time.

observation of figure 2 shows that the intensity of the 500 nm band continues to increase after the 320 nm band has reached a constant value. This prolonged intensity of the 500 nm band strongly suggests the existence of defect centres formed in the glass structure, which is discussed later.

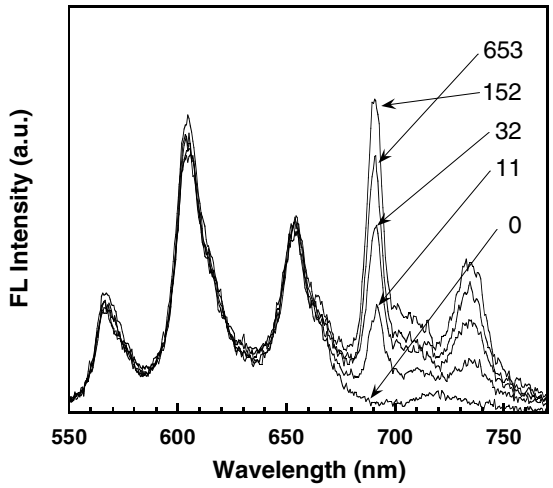

Figure 3. FL spectra of Sm^{3+}-doped Al_2O_3–SiO_2 glass during femtosecond laser irradiation from 0 to 653 s.

3.2. Fluorescence spectra

The reduction of Sm^{3+} ions into Sm^{2+} can be seen from measurements of the FL spectra. The FL spectra were taken in the visible wavelength region using the 337 nm excitation wavelength of a N_2 laser and are shown in figure 3. Before laser irradiation, the glass exhibited strong FL peaks at 567, 604 and 654 nm, which were all assigned to the $^4G_{5/2} \rightarrow {}^6H_{5/2,7/2,9/2}$ transitions, respectively, of the Sm^{3+} ions. After irradiation, new FL lines have noticeably emerged around 690, 710 and 735 nm. These bands are characteristic of Sm^{2+} ions arising from the $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions, respectively. Thus, it is concluded that the femtosecond pulse laser is effectively being used to reduce the Sm^{3+} ions into Sm^{2+} in the glass matrix. In figure 3, Sm^{2+} FL intensities clearly rise abruptly up to some constant level within a few minutes and then decrease gradually. The partial decay of the Sm^{2+} FL intensity after prolonged irradiation might be due to photo-oxidation of the Sm^{2+} ion to Sm^{3+} or thermal oxidation during the irradiation. Although this decay process is not fully understood, it is interesting to note that the photo-oxidation of Sm^{2+} ion can be achieved even with a 800 nm femtosecond laser. We also measured the incident laser power dependence of the photoreduction. The incident power was varied using neutral density (ND) filters and we monitored the growth of FL intensities of the $^5D_0 \rightarrow {}^7F_1$ transition of the Sm^{2+}. We found that the FL intensities increase nonlinearly with the increase of the laser power, which will be discussed in detail in future papers.

In a previous paper, we discussed the reduction of Sm^{3+} ions in doped glasses when heated in a hydrogen atmosphere or irradiated with x-ray, and showed the first-order kinetics of the reaction between the samarium ions [14]. The FL intensities of the Sm^{2+} ions are plotted in figure 4 using the first-order equation, $I_t = I_0\{1 - \exp(-Kt)\}$, where I_t is the FL intensity at time t, I_0 is the temporal saturated intensity and K is a rate constant. The FL intensity of the Sm^{2+} ions is determined as the ratio of the FL intensity of the Sm^{2+} ions (band at 685 nm) to the total intensities of the Sm^{2+} (at 685 nm) and Sm^{3+} ions (at 600 nm). In this figure, the experimental data for glasses irradiated with x-rays are compared [14]. The estimated rate constant, K, is $3.3 \times 10^{-2}\ s^{-1}$ for the laser irradiation, which is two orders of magnitude larger than that of the x-ray irradiation ($K = 2.4 \times 10^{-4}\ s^{-1}$). Thus, the femtosecond laser surpasses the x-ray with regard to the reduction rate of samarium ions. The reason for this rate difference

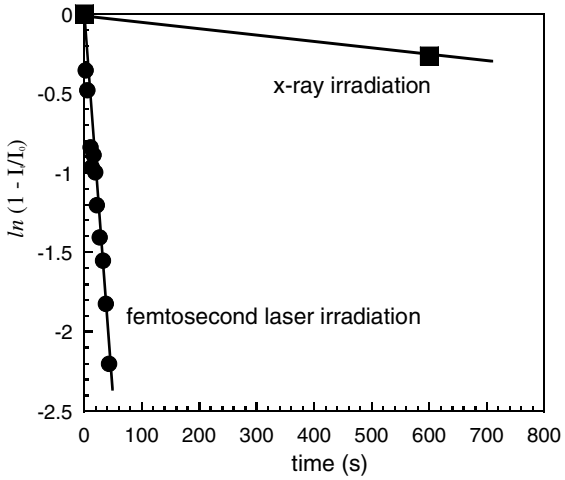

Figure 4. Dependence of the FL intensity of Sm^{2+} ions on femtosecond laser irradiation time (●) and x-ray irradiation time (■) [14].

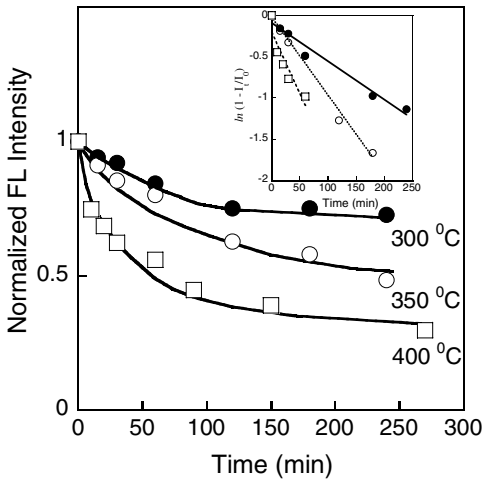

Figure 5. Dependence of the FL intensity of the $^5D_0 \rightarrow {}^7F_0$ transition of Sm^{2+} ions on heating time in air for femtosecond laser induced Sm^{2+}-doped Al_2O_3–SiO_2 glasses. The inset shows the first-order kinetic plot for FL intensity data.

is as follows. The x-ray irradiation can excite all kinds of possible effects in the glasses, while femtosecond laser irradiation excites only a small number of well-defined defects which may facilitate the reduction of the Sm^{3+} ions. Moreover, most of x-ray quanta pass through the glasses which means the probability of interaction is very much lower than the laser case.

The redox equilibrium of the samarium from the thermal oxidation of the Sm^{2+} into Sm^{3+} was also investigated. The glasses were heated in air from 300 to 400 °C, the FL intensities of which were shown in figure 5. The FL intensities of the $^5D_0 \rightarrow {}^7F_1$ transition of Sm^{2+} ions were normalized to the intensities after the laser irradiation. It is apparent that the FL intensities decrease with increasing time and approach saturated levels. The oxidation data, according to the first-order rate equation, were plotted in the inset of figure 5 and show good linearity. Thus, it is evident that the Sm^{2+} ions formed by the laser irradiation are relaxed by

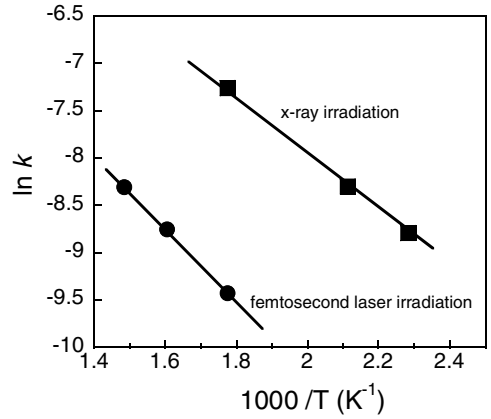

Figure 6. Arrhenius plots of the rate constants of the oxidation of Sm^{2+} ions in the femtosecond irradiated (●) and x-ray irradiated glasses (■) [14].

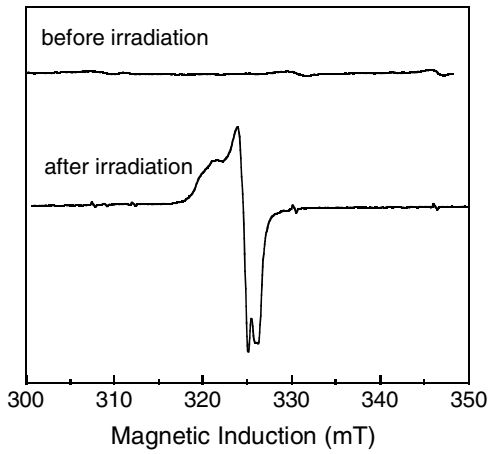

Figure 7. ESR spectra of Sm^{3+}-doped Al_2O_3–SiO_2 glass before and after femtosecond laser irradiation.

the thermal energies corresponding to temperatures of 300–400 °C. The rate constant values are plotted in figure 6 as a function of reciprocal temperature together with those for the x-ray irradiated glasses [14]. Note that the Sm^{2+} ions formed by laser irradiation exhibit a larger rate constant than those irradiated by x-ray. The lines show 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 reduction of the Sm^{3+} ions, which is calculated as 32 and 25 kJ mol^{-1} for the laser and x-ray irradiated glasses, respectively. It is interesting to notice that the Sm^{2+} ions in the laser-irradiated glass are stable compared with those in the x-ray-irradiated glass.

3.3. Formation process of the Sm^{2+} ions

Femtosecond laser pulses with high intensity are known to produce free electrons in glasses via multiphoton absorption and avalanche ionization leading to plasma generation [15]. As a result, the bond cleavage in the glass network and trapped electrons give rise to colour-centre

defect formation. The defect centre of the femtosecond laser irradiated glasses was investigated by ESR measurement. Figure 7 shows the ESR signals, observed at 123 K, for the glasses before and after laser irradiation. No significant signals were observed before the irradiation, while strong signals appeared after the irradiation of around 325 mT with $g = 2.009$. Since Sm^{2+} ions are usually ESR inactive, the observed signals are due to the intrinsic defect centres formed during the laser irradiation. The entire spectral shape and the determined g-value are analogous to those of x-ray irradiated glasses [3]. Thus, it is reasonable to identify the defect as hole centres in the oxygen ions bound to Al^{3+} ions. These defect centres might be mainly responsible for the induced absorption in the visible region. From these results, we can propose the mechanism of the Sm^{2+} formation as follows. The non-bridging Al–O bonds are cleaved during the laser irradiation, resulting in the formation of hole centres. Since the Sm^{3+} ion is a very good electron acceptor, the electrons liberated from the oxygen ions are transferred to nearby Sm^{3+} ions to form Sm^{2+}.

4. Conclusion

In summary, we demonstrated the formation of Sm^{2+} from Sm^{3+} in sol–gel derived Al_2O_3–SiO_2 glasses by irradiation with a femtosecond laser. The formation of Sm^{2+} was completed within the irradiation time of 2 min. The hole centre was induced in non-bridging oxygen bound to Al^{3+}, and the released electron was captured in Sm^{3+} ions causing the Sm^{2+} formation. The thermal relaxation rate of the Sm^{2+} ions into Sm^{3+} was determined by first-order kinetics in the temperature range of 300–400 °C and the deduced activation energy was 32 kJ mol^{-1}. Considering the fast formation of the Sm^{2+} ions and their stability, the present technique has great potential for developing new optical glassy materials.

Acknowledgments

This research was partly supported by a Grant-in-Aid for Scientific Research (No 13305048) from the Ministry of Education, Science, and Culture of Japan and the NIT-21st century COE Program for Environmental Friendly Ceramics.

References

[1] Nogami M, Abe Y, Hirao K and Cho D H 1995 *Appl. Phys. Lett.* **66** 2952
[2] Nogami M, Hayakawa T and Ishikawa T 1999 *Appl. Phys. Lett.* **75** 3072
[3] Nogami M and Suzuki K 2002 *Adv. Mater.* **14** 923
[4] Davis K M, Miura K, Sugimoto N and Hirao K 1996 *Opt. Lett.* **21** 1729
[5] Glezer E N, Milosavlijevic M, Huang L, Finley R J, Her T-H, Callan J P and Mauzer E 1996 *Opt. Lett.* **21** 2023
[6] Schaffer C B, Brodeur A, Garcia J F and Mazur E 2001 *Opt. Lett.* **26** 93
[7] Watanabe M, Juodkazis S, Sun H-B, Matsuo S and Misawa H 1999 *Appl. Phys. Lett.* **74** 3957
[8] Qiu J, Miura K, Suzuki T, Mitsuyu T and Hirao K 1999 *Appl. Phys. Lett.* **74** 10
[9] Qiu J, Miura K, Nouchi K, Suzuki T, Kondo K, Mitsuyu T and Hirao K 2000 *Solid State Commun.* **113** 341
[10] Qiu J, Kojima K, Kubo A, Yamashita M and Hirao K 2000 *Phys. Chem. Glasses* **41** 150
[11] Fujita K and Hirao K 2001 *Japan. J. Appl. Phys.* **40** 1651
[12] Nogami M, Hiraga T and Hayakawa T 1998 *J. Non-Cryst. Solids* **241** 98
[13] Nogami M, Hayakawa N, Sugioka N and Abe Y 1996 *J. Am. Ceram. Soc.* **79** 1257
[14] Nogami M, Eto T, Suzuki K and Hayakawa T 2002 *J. Mater. Res.* **17** 2053
[15] Stuart B C, Feit M D, Herman S, Rubenchik A M, Shore B W and Perry M D 1995 *Phys. Rev. Lett.* **74** 2281