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Room-temperature persistent spectral hole burning of Eu^{3+} coupling with Al^{3+} in glass

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Room-temperature persistent spectral hole burning was observed in Eu^{3+}-doped Al_2O_3-SiO_2 glasses. The sol-gel-derived Eu^{3+}-doped glasses were heated in hydrogen gas and irradiated with x ray, in which the oxygen deficient centers were induced in Al-O bonds and some Eu^{3+} ions were reduced into Eu^{2+} by heating in hydrogen gas. The spectral holes were burned in the excitation spectra of the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+}. The maximum depth of the hole burned at room temperature was found to be ~10% of the total excitation intensity for both the glasses and independent of the treatment conditions of glasses. A proposed model for hole burning is the excitation of the Eu^{3+} ion and subsequent hole trapping in the oxygen-defect centers in the Al-O bonds. The burnt holes were easily erased by laser irradiation with the energy different from burning one.

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I. INTRODUCTION

Persistent spectral hole burning (PSHB) phenomenon has attracted much attention because of its potential use in high-density frequency-selective optical memories.[1,2] The primary object of this strategy involves the fabrication of stable materials exhibiting highly efficient hole burning at room temperature. Many materials doped with organic dye molecules and rare-earth ions display the PSHB property, however, in most of them, PSHB cannot be observed near room temperature. Sm^{2+} and Eu^{3+} ions are special cases, where the PSHB can be observed at room temperature.[3–13] Room temperature PSHB materials with high efficiency, if easily prepared, have a high potential for use in high-density memory devices. As a host material for these rare earth ions, glass is more favorable than crystals because of its wide distribution of the rare-earth ions and high transparency.[9–13] When the glass is melted, the Sm^{3+} ions are incorporated as the trivalent state. To reduce the Sm^{3+} ions, it is necessary to melt the glass at high temperature under a strong reducing atmosphere.[9–11] Recently, we succeeded in preparing the Sm^{2+} and Eu^{3+} ions-doped glasses by a sol-gel method and observed room temperature PSHB.[14–17] The sol-gel process is appropriate for preparing a glass at moderately lower temperatures than required for the conventional melting method.

Sm^{2+} and Eu^{3+} ions have the same $4f^6$ electron configuration the lowest and first excited states of which are $^7F_0$ and $^5D_0$, respectively. The hole spectra are observed on the excitation spectra of the $^7F_0 \rightarrow {}^5D_0$ transition of the Sm^{2+} and Eu^{3+} ions, though the hole burning mechanism is still unknown. A possible mechanism for the hole burning of these ions is the photoinduced charge transfer between the rare earth ions by the laser irradiation. The photoionization of the Sm^{2+} ions into Sm^{3+} has been observed in the Sm^{2+}-doped BaClF crystals.[3,6,8] The released electrons are captured by Sm^{3+} ions to form the Sm^{2+}. On the other hand, Fujita *et al.* considered that in the Eu^{3+}-doped glasses, the hole is burned by the reduction of the Eu^{3+} ions and the released holes are captured by the Eu^{2+}.[12,13]

In contrast, we found that the Eu^{2+} ions do not necessarily act as the main trap for holes. In the sol-gel derived glasses, the room temperature PSHB of the Eu^{3+} ions is observed only in the Al^{3+} ion-containing silicate glasses, and not in the SiO_2 glass.[17] We postulated that the electron transfer takes place between the Eu^{3+} ions and the matrix structure. Further investigations are necessary to clarify the PSHB mechanism of the Eu^{3+} ions doped in glasses.

The aim of this work is to study how the glass structure relates to the room-temperature PSHB of the Eu^{3+} ions doped in Al_2O_3-SiO_2 glasses. Some of the glasses were heated in a hydrogen gas atmosphere, while others were irradiated using an x ray. The effect of the Eu^{2+} ions and the defect structure in the Al-O polyhedra is discussed in relation to the hole-burning efficiency. This report is very significant when considering the hole-burning mechanism and the application of PSHB glasses to memory devices.

II. EXPERIMENT

$1Al_2O_3 \cdot 9SiO_2$ (mole ratio) glasses containing nominally 10 wt. % Eu_2O_3 were prepared by the sol-gel method using commercially available $Si(OC_2H_5)_4$, $Al(OC_4H_9^{\mathrm{sec}})_3$, and $EuCl_3 \cdot 6H_2O$. A detailed explanation of the gel preparation is given elsewhere.[16,17] The gels were heated in air at 500 °C for 2 h. The ~1 mm thick glasses were polished with fine CeO_2 powders, followed by heating in air at 800 °C for 2 h. The obtained glasses showed optical properties characteristic of the Eu^{3+} ions, i.e., absorption bands at 465 and 395 nm and fluorescence bands around 580, 590, 615, and 645 nm in the visible region, all of which are assigned to the f-f transitions of the Eu^{3+} ions.

As previously reported, when the glasses are heated in air, a large amount of hydroxyl bonds remain in the glass and the spectral holes are burned by the rearrangement of the hydroxyl bonds surrounding the Eu^{3+} ions.[15,16] To eliminate the effect of the hydroxyl bonds on the hole burning, the glasses were heated in a vacuum at 800 °C for 2 h, followed by heating under a flowing mixed gas with $20\%H_2-80\%N_2$ at 500 to 800 °C. The x-ray irradiation was performed using the Cu$K\alpha$ line with 40 kV and 20 mA at room temperature for 1, 7, and 14 h. The PSHB was observed on the excitation spectra of the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} by scanning a

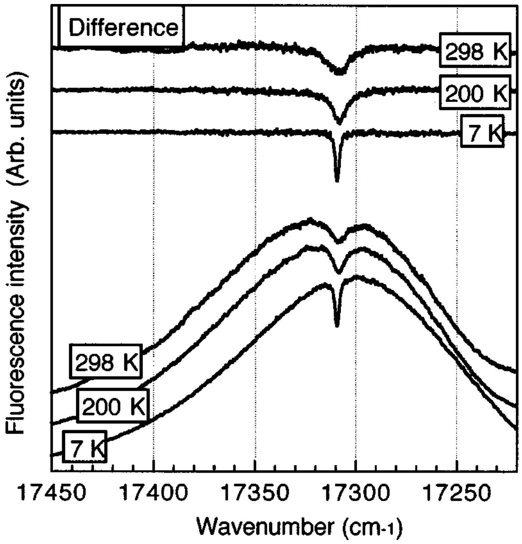

FIG. 1. PSHB spectra, burned and measured at 7, 200, and 298 K, of Eu^{3+}-doped $1Al_2O_3 \cdot 9SiO_2$ glass heated in H_2 gas at 600 °C for 1 h. At the top is shown the difference between the fluorescence intensities before and after burning.

Rhodamine 6*G* dye laser over the $^7F_0 \rightarrow {}^5D_0$ transition while monitoring the fluorescence of the $^5D_0 \rightarrow {}^7F_2$ transition at 619 nm.

III. RESULTS AND DISCUSSION

A. Room temperature hole burning for glass heated in H_2 gas

The sol-gel-derived glasses typically contain a large amount of hydroxyl bonds in glass, because water is used in the hydrolysis reaction of raw materials. We already reported that the PSHB is observed in these sol-gel-derived Eu^{3+}-doped glasses and the hole depth increases proportionally with the increasing OH content.[15,16] On the other hand, the present glasses were heated in a vacuum prior to the heat treatment in H_2 gas, resulting in a lower OH content. We confirmed that no PSHB is observed in these glasses at any temperature prior to heat treatment.

When the glasses are heated in H_2 gas, they become faintly yellow. The hole was burned by irradiating with a laser with a power of ~300 mW at a ~2 mm diameter spot at the wavelength around the peak position of the $^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+} ions for 30 min. Typical hole spectra, burned and measured at 7, 200, and 298 K, are shown in Fig. 1. The holes are clearly observed at the burning position of 17 310 cm^{-1}. The hole width (FWHM) is 1.9, 8.1, and 12.6 cm^{-1} at 7, 200, and 298 K, respectively. The hole depth, defined as the depth to the total fluorescence intensity at the burning wave number, is 21, 17, and 13 %, respectively. This room-temperature PSHB discovery for the Eu^{3+} ions is of significant importance in basic and practical investigations of the PSHB materials.

Figure 2 shows the optical absorption and fluorescence spectra of the glass before and after heating in H_2 gas at 600 °C for 1 h. The glass heated in air has optical properties characteristic of the Eu^{3+} ions, i.e., small and sharp absorption bands peaking at 394 and 465 nm in the absorption spectrum and fluorescence bands ranging from 570 to 660 nm in the visible wavelength region, all of which are assigned to the *f*-*f* transitions of the Eu^{3+} ions. On the other hand, the absorption spectrum of glass after heating in H_2 gas shows the increase in absorption below 400 nm in addition to the sharp lines of the Eu^{3+} ions. The absorbance in the violet wavelength region suggests the existence of the Eu^{2+} ions.[18] The Eu^{2+} ion has a $4f^7$ configuration, the excited ^6P levels of which may lie close to the first excited level of the $4f^65d$ configuration and the optical bands are determined by the relative position of the lowest level of the $4f^7$ and $4f^65d$ excited states. Since the $5d$ orbital has a large spatial extension and two e_g and t_{2g} components, the optical spectra due to the *f*-*d* transitions are usually broadened and dependent on the surroundings of the Eu^{2+} ions. However, the observed absorption band could not be resolved into its components due to the limited resolution of the spectroscopy used. On the other hand, the broad and asymmetric fluorescence band peaking at a 440-nm wavelength is observed in the H_2 gas-treated glass. The broad fluorescence around 440 nm can be assigned to the $4f^65d \rightarrow f^7(^8S_{7/2})$ transition of the Eu^{2+} ions.[19] The relaxation pathway of the excited electrons is associated with the nonradiative relaxation of the electrons to the lowest energy level of the $4f^65d$ configuration and the radiative transition into the ground $^8S_{7/2}$ level.

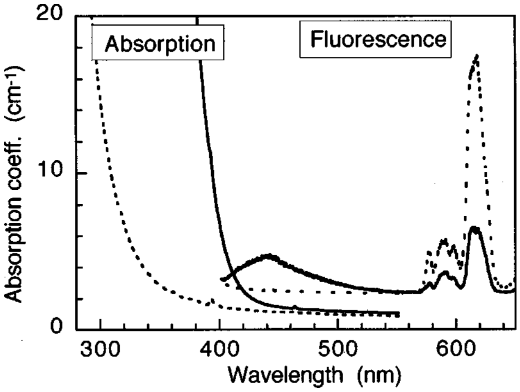

FIG. 2. Optical absorption and fluorescence spectra of Eu^{3+}-doped $1Al_2O_3 \cdot 9SiO_2$ glass before (dotted lines) and after (solid lines) heating in H_2 gas at 600 °C for 1 h. The fluorescence was obtained using a xenon 395-nm excitation wavelength.

It was found that the fluorescence intensity of the 440-nm band increases with increased heating time, whereas the intensity of the Eu^{3+} ions decreased. Contrary to the absorption intensity, which is linearly related to the concentration of the rare earth ions, the fluorescence intensity is not initially determined by the concentration of the rare-earth ions. Therefore, the ratio of the fluorescence intensity of Eu^{2+} and Eu^{3+} can be determined. Shown in Fig. 3 is the ratio of the intensity of the bands at 440 nm ($4f^65d \rightarrow {}^8S_{7/2}$ transition of Eu^{2+}) and 619 nm ($^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}) as a function of the heating time. It is evident that the ratio of Eu^{2+}/Eu^{3+} increases as the heating time increases. We should point out that the Eu^{3+} ions are completely changed

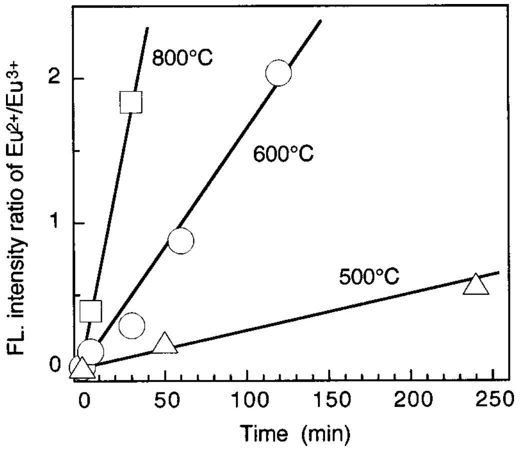

FIG. 3. Fluorescence intensity ratio of $4f^{6}5d\rightarrow{}^{8}S_{7/2}$ (Eu^{2+}) to ${}^{5}D_{0}\rightarrow{}^{7}F_{2}$ (Eu^{3+}) transition for Eu^{3+}-doped $1Al_2O_3\cdot9SiO_2$ glass as a function of the heat treatment time in H_2 gas at 500, 600, and 800 °C. The fluorescence intensities for the Eu^{3+} and Eu^{2+} ions were measured at 619 and 440 nm, respectively.

into the Eu^{2+} ions after heating for a long time. The total time required is shorter for the glass heated at high temperature.

The efficiency of the hole burning was measured for the glasses heated at 500 to 800 °C in H_2 gas. The holes were burned by laser irradiation at a power of 300 mW for 30 min at 200 K. The hole depth, defined as the ratio of the depth to the total fluorescence intensity at the burning wave number, is plotted in Fig. 4 as a function of the heating time and temperature. The hole depth increases as the heat-treatment time increases and approaches a maximum depth of about 18%. It is evident, however, that a prolonged heat-treatment results in a decreased hole depth.

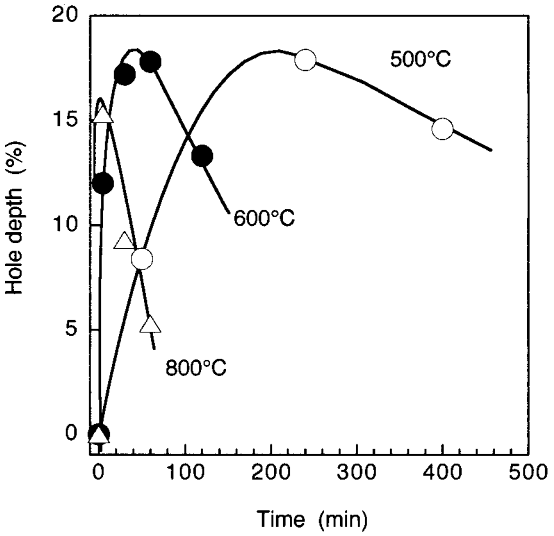

FIG. 4. Hole depth as a function of H_2 gas heat-treatment time and temperature of Eu^{3+}-doped $1Al_2O_3\cdot9SiO_2$ glass. Holes were burned at 200 K and hole depth was defined as the depth to total fluorescence intensity.

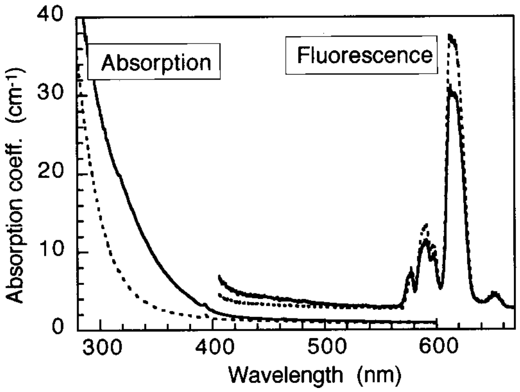

FIG. 5. Optical absorption and fluorescence spectra of Eu^{3+}-doped $1Al_2O_3\cdot9SiO_2$ glass before (dotted lines) and after (solid lines) x-ray irradiation for 14 h at room temperature. The fluorescence was obtained using a xenon 395-nm excitation wavelength.

B. Room temperature hole burning for glass irradiated by x ray

The glasses were irradiated by Cu-$K\alpha$ x ray, the optical absorption and fluorescence spectra of which are shown in Fig. 5. There is no change in the fluorescence spectra before and after the x-ray irradiation except for a slight decrease in the intensities of the Eu^{3+} ions. No fluorescence band of the Eu^{2+} ions is observed at around 440 nm. However, the x-ray-irradiated glass shows an induced-absorbance in the ultraviolet wavelength range below 400 nm. This absorbance should be assigned to optical sites other than the Eu^{2+} ions.

The hole was burned on the ${}^{7}F_{0}\rightarrow{}^{5}D_{0}$ transition of the Eu^{3+} ions. The PSHB spectra, burned and measured at 7, 200, and 298 K, are shown in Fig. 6. The width (FWHM) and depth (defined as the depth to the total fluorescence in-

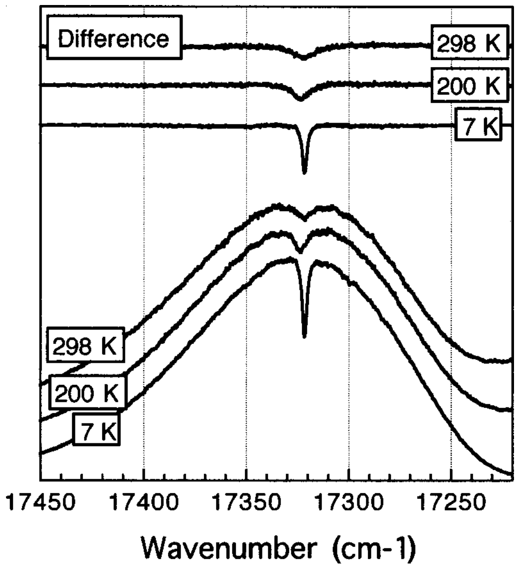

FIG. 6. PSHB spectra, burned and measured at 7, 200, and 298 K, of Eu^{3+}-doped $1Al_2O_3\cdot9SiO_2$ glass irradiated with x ray for 14 h at room temperature. At the top is shown the difference between the fluorescence intensities before and after burning.

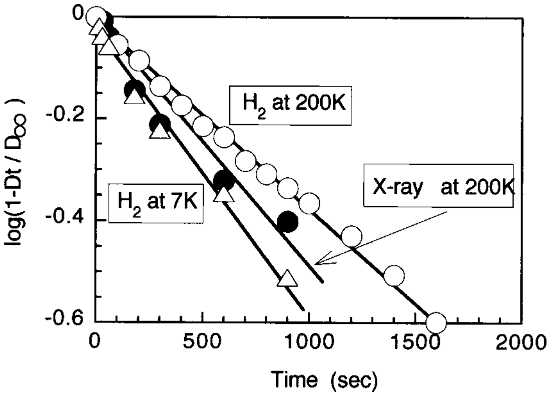

FIG. 7. Logarithmic plots of the dependence of hole depth on the burning time for Eu^{3+}-doped $1Al_2O_3 \cdot 9SiO_2$ glass heated in H_2 gas or irradiated with x ray. Holes were burned at 7 and 200 K.

tensity) of the holes burned at 7, 200, and 298 K are 2.5, 8.1, and 12.5 cm^{-1}, and 40, 12, and 9 %, respectively. This behavior is comparable to those of the holes burned in the glasses heated in H_2 gas. It was also found that the hole depth increased with the increased x-ray-irradiation time. Compared to the H_2 gas-heated glasses, the x-ray-irradiated glasses show strong fluorescence intensities from the Eu^{3+} ions. This greatly simplifies the observation of the hole spectra, which is a valuable quality for PSHB materials.

The dependence of the hole-burning efficiency on the burning time was studied for the H_2-gas-treated and the x-ray-irradiated glasses. We found that the hole depth increases with burning time and approaches a saturated level. If the hole is formed by the charge transfer between the burnt and unburnt states of the Eu^{3+} ions, the conversion rate of the Eu^{3+} ions is determined by the first-order kinetics. Assuming that the hole depth corresponds to the concentration of the burned Eu^{3+} ions, the hole depth D_t can be written as[20,21]

$$D_t = D_\infty[1 - \exp(-Kt)], \tag{1}$$

where D_∞ is the hole depth after an infinite period and K is a rate constant. The hole-growth data are plotted according to Eq. (1) in Fig. 7, where the D_∞ value was determined by the least-squares fit of the equation. The data follow Eq. (1), indicating that the hole burning is controlled by the rate equation and the rate constant increased with the decreased burning temperature. These seems to be no difference in the samples between these heated in H_2 gas and irradiated by x ray. These results strongly suggest that the PSHB is formed by the same process in the H_2-gas heated and the x-ray-irradiated glasses.

C. Effect of the glass composition on the hole burning

The observation of the room temperature PSHB is a special case. In a previous paper, we reported that the SiO_2 glass does not demonstrate PSHB at room temperature, even though heating in H_2 gas.[17] The SiO_2 glass was prepared for doping the Eu^{3+} ions, followed by x-ray irradiation for 14 h at room temperature. An attempt was made to burn a hole using a laser with power of ~300 mW for 30 min at the wavelength around the peak position of the ${}^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+} ions at 298 K, but no hole was observed. Thus, we should point out that the formation of the room temperature PSHB is strongly affected by the glass composition doped with Eu^{3+} ions.

D. Room-temperature hole burning for Eu^{3+} coupling with Al^{3+} in glass

In the sol-gel-derived Eu^{3+}-doped glasses, we already reported that the spectral hole is burned by the optically activated rearrangement of the OH bonds surrounding the Eu^{3+} ions and the hole-depth linearly increases with the increasing OH content.[15,16] Based on these results, the sol-gel technique is a successful method for preparing PSHB glasses with a high hole burning efficiency. However, the formed holes decrease their depth with increasing temperature and are erased above ~150 K. The present glasses contain few OH bonds that affect the hole burning. An important feature of the sol-gel-derived glasses is that the room temperature PSHB becomes observable by heating in H_2 gas or by x-ray irradiation.

With respect to the room temperature PSHB of the Eu^{3+} ions, Fujita *et al.* measured the room temperature PSHB of the Eu^{3+} ions-doped Na_2O-Al_2O_3-SiO_2 glasses melted in hydrogen gas and found that the hole depth increases as the Eu^{2+} ion content increases.[12,13] They considered that the hole is formed by the photoinduced reduction of the Eu^{3+} ions and the released holes are captured in the Eu^{2+} ions. This indicates that the deep holes should be formed as the content of the Eu^{2+} ions acting as the hole-trap increases. However, our results indicate no direct evidence for the existence of such a relationship (see Figs. 3 and 4). Furthermore, we observed the room temperature PSHB in the x-ray-irradiated glasses, where the Eu^{3+} ions are not changed in Eu^{2+} (see Figs. 5 and 6). We also found that the SiO_2 glass is not appropriate as the matrix glass for the room-temperature PSHB materials, even though it contains the Eu^{2+} ions. These results strongly exclude the possibility of the Eu^{2+} ions acting as hole traps. At present, we should point out that the room temperature PSHB is only observed in the sol-gel-derived glasses doped with both Eu^{3+} and Al^{3+}.

In our glass system, the Al^{3+} ions are coordinated with the four and/or six oxygens, forming the network structure together with Si^{4+} ions. The excess negative charge of the Al-O polyhedra, partly compensated by the Eu^{3+} ions, sometimes causes oxygen vacancies in the glass structure. Recently, Jin *et al.* analyzed the glass structure in the Sm_2O_3-Al_2O_3-SiO_2 system using the nuclear magnetic resonant spectroscopy and x-ray radial distribution method.[22] The AlO_4 tetrahedra adjacent to the Sm^{2+} ions change into a large size AlO_6 octahedra and this structure change leads to an enlargement of the vacancies. These structural features would be similar to the Eu_2O_3-Al_2O_3-SiO_2 glasses. The sol-gel process is known to bring about many kinds of defects in a glass during its chemical and thermal treatments, which are investigated using optical spectroscopy in the ultraviolet wavelength region.

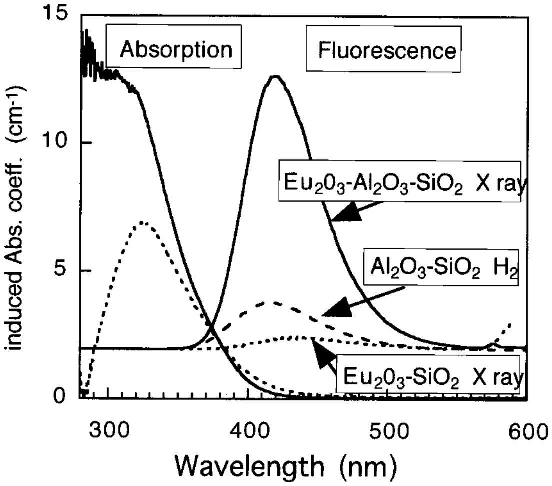

FIG. 8. Difference optical absorption and fluorescence spectra induced in the Eu^{3+}-doped $1Al_2O_3 \cdot 9SiO_2$ (solid lines) and SiO_2 (dotted lines) glasses irradiated with x ray for 14 h. The fluorescence spectrum for the no Eu_2O_3-containing $1Al_2O_3 \cdot 9SiO_2$ glass heated in H_2 gas is also shown (broken line). Fluorescence spectra were measured by exciting using N_2 laser at 337 nm.

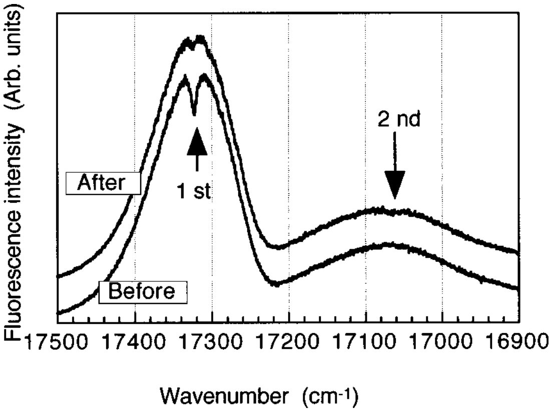

FIG. 9. PSHB spectra, measured at 77 K, burned firstly at 17 323 cm^{-1}, followed by irradiating laser with 17 065 cm^{-1}. The hole was filled by irradiating the laser with different energy.

The difference in the optical absorption and fluorescence spectra induced by irradiating the x ray are shown in Fig. 8. In the absorption spectra, the Eu_2O_3-Al_2O_3-SiO_2 glass shows a broad absorption band peaking at around 300 nm or below and a shoulder around 320 nm wavelength, while the Eu_2O_3-SiO_2 glass has a relatively sharp band at 320 nm. It is evident that this absorption band should not be assigned to the Eu^{2+} ions, because there is no fluorescence from the Eu^{2+} ions at 440 nm (see Figs. 2 and 5). Mackey *et al.* measured the optical absorption spectra of the Eu^{3+}-doped silicate glasses irradiated with x ray and attributed the induced band at ~330 nm to the electron-trapped Eu^{3+} ions.[23] This center, designated as an $[Eu^{3+}]^-$ state, is considered to be different from the Eu^{2+} ions. According to their results, the induced absorption band at around 320 nm in the x-ray-irradiated glass can be attributed to the activated state of the Eu^{3+} ions. On the other hand, the induced band at ~300 nm or below may be attributed to the defect centers in the glass structure. The most remarkable change in the glass structure is observed in the fluorescence spectra; the Eu_2O_3-Al_2O_3-SiO_2 glass has an intense fluorescence band at 420 nm, but the $Eu_2O_3SiO_2$ glass has no fluorescence. Previously, we reported the formation of defect centers in the Al_2O_3-SiO_2 glasses. When heated in H_2 gas, the Al_2O_3-SiO_2 glass containing no Eu_2O_3 shows an absorption band at around 220 nm, which is attributed to structure imperfections such as oxygen-deficiency defects in the Al-O polyhedra.[17] This Al_2O_3-SiO_2 glass shows the fluorescence band at 420 nm by x-ray irradiation (see Fig. 8). The optical emission from the glasses heated in H_2 gas has been extensively investigated for the GeO_2-SiO_2 or SiO_2 glasses for use as optical fibers.[24,25] These glasses have a strong fluorescence around 400 nm, which is attributed to the structure imperfections such as oxygen deficiency, electron, and hole-trap centers. By comparing these glasses, the fluorescence band at 420 nm in the present Al_2O_3-SiO_2 and Eu_2O_3-Al_2O_3-SiO_2 glasses can be attributed to the oxygen-deficiency defects such as Al-Al bonds or hole-trapping centers. The formation of these defect centers is enhanced by codoping the Eu^{3+}. The oxygen deficiency centers are photosensitive. From these results and the hole burning experiments, the formation of a hole can be considered as follows: A narrow burning laser-beam selectively excites electrons from the ground state of the Eu^{3+} ions, and, at same time, the laser resonant with the oxygen-defect centers in the Al-O bonds. This double coupling would make the electron transfer between the excited-Eu^{3+} ion and defect centers easy, resulting in the formation of a hole. The proposed mechanism of hole burning was examined using a hole-bleaching experiment. The glass in which the hole was first burned on the ${}^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+} ions, was irradiated by the laser at a wavelength different from the burning one. A typical result is shown in Fig. 9, where the glass is irradiated at a 17 065 cm^{-1} wave number after the first burning at 17 323 cm^{-1}. It is evident that the hole burned first is filled upon light irradiation. The finding that the burned holes are stable to temperature and easily erased by a laser with a different energy from that for burning is significant for practical applications as a memory device.

IV. CONCLUSIONS

In this paper, we demonstrated that room-temperature persistent spectral hole burning was observed in Eu^{3+}-doped Al_2O_3-SiO_2 glasses by heating in H_2 gas or irradiating the x ray. The treatment of a glass under these conditions brings about many oxygen deficient centers in the glass structure and some Eu^{3+} ions were reduced to Eu^{2+} in the glass heated in H_2 gas. The maximum depth of the hole burned at room temperature was found to be ~10% for both the glasses and independent of the glass treatment conditions. The burnt holes were easily erased by irradiating the laser with an energy different from the burning one. The hole formation could be explained by a model of the excitation of the Eu^{3+} ion and subsequent hole trapping in the oxygen-defect centers in the Al-O bonds.

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[1] W. E. Moerner, *Persistent Spectral Hole-burning: Science and Applications*, in Current Physics Vol. 44 (Springer-Verlag, Berlin, 1988).

[2] J. Friedrich and D. Haarer, Angew. Chem. Int. Ed. Engl. **23**, 113 (1984).

[3] R. Jaaniso and H. Bill, Europhys. Lett. **16**, 569 (1991).

[4] R. M. Macfarlane and R. M. Shelby, Opt. Lett. **9**, 533 (1984).

[5] R. M. Macfarlane and R. S. Meltzer, Opt. Commun. **52**, 320 (1985).

[6] A. Winnacker, R. M. Shelby, and R. M. Macfarlane, Opt. Lett. **10**, 350 (1985).

[7] A. Oppenlander, F. Madeore, J. Vial, and J. Chaminade, J. Lumin. **50**, 1 (1991).

[8] J. Zhang, S. Huang, and J. Yu, Opt. Lett. **17**, 1146 (1992).

[9] K. Hirao, S. Todoroki, D. H. Cho, and N. Soga, Opt. Lett. **18**, 1586 (1993).

[10] D. H. Cho, K. Hirao, and N. Soga, J. Non-Cryst. Solids **189**, 181 (1995).

[11] A. Kurita and T. Kushida, Opt. Lett. **19**, 314 (1994).

[12] K. Fujita, K. Hirao, and N. Soga, Opt. Lett. **23**, 543 (1998).

[13] K. Fujita, K. Tanaka, K. Hirao, and N. Soga, J. Opt. Soc. Am. B **15**, 2700 (1998).

[14] M. Nogami, Y. Abe, K. Hirao, and D. H. Cho, Appl. Phys. Lett. **66**, 2952 (1995).

[15] M. Nogami and Y. Abe, Appl. Phys. Lett. **71**, 3465 (1997).

[16] M. Nogami and T. Hayakawa, Phys. Rev. B **56**, R14 235 (1997).

[17] M. Nogami, T. Hayakawa, and T. Ishikawa, Appl. Phys. Lett. **75**, 3072 (1999).

[18] J. Lubio, J. Phys. Chem. Solids **52**, 101 (1991).

[19] M. Nogami, T. Yamazaki, and Y. Abe, J. Lumin. **78**, 63 (1998).

[20] R. Jankowiak, R. Richert, and H. Bassler, J. Phys. Chem. **89**, 4569 (1985).

[21] T. Okuno and T. Suemoto, Phys. Rev. B **59**, 9078 (1999).

[22] J. Jin, S. Sakida, T. Yoko, and M. Nogami, J. Non-Cryst. Solids **262**, 183 (2000).

[23] J. H. Mackey, H. L. Smith, and J. Nahum, J. Phys. Chem. Solids **27**, 1773 (1966).

[24] H. Hosono, Y. Abe, D. L. Kinser, R. A. Weeks, K. Muta, and H. Kawazoe, Phys. Rev. B **46**, 11 445 (1992).

[25] J. Nishi, K. Fukumi, H. Yamanaka, K. Kawamura, H. Hosono, and H. Kawazoe, Phys. Rev. B **52**, 1661 (1995).