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Spectral hole burning and excited electrons in Sm^{2+}-doped Al_2O_3-SiO_2 glasses

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Persistent spectral hole burning in the $f \rightarrow f$ transition and changes in the $f \rightarrow d$ transition spectra upon laser irradiation were investigated in Sm^{2+}-doped Al_2O_3-SiO_2 glasses prepared by a sol-gel process. The hole was burned in the ${}^7F_0 \rightarrow {}^5D_0$ line of Sm^{2+} ions using a DCM dye laser at 77 K and the dependence of the burning efficiency on laser power and burning time was measured. The hole depth increased with increasing laser irradiation time, reaching up to ~12% of the total intensity within a few hundred seconds. Neither an antihole around the burned hole nor a change in the fluorescence line narrowing spectrum were observed after hole burning. The hole depth linearly increased with increasing the incident laser power up to ~1 W/mm², indicating a single-photon hole-burning process. On the other hand, laser irradiation with a wavelength corresponding to the energy of the $4f^6 \rightarrow 4f^55d$ transition resulted in a decrease of both the absorption and fluorescence intensities but no formation of a hole. It was concluded that the electrons excited in the $4f^55d$ level were further excited into the conduction band of the host matrix by a two-photon absorption process and then captured in the trapping center. [S0163-1829(97)02025-0]

I. INTRODUCTION

Recently, persistent spectral hole burning (PSHB) has been observed at room temperature for the f-f transitions of Sm^{2+} ion-doped fluoride single crystals.[1–6] This room-temperature PSHB is a significant scientific breakthrough for the development of new optical memory devices. Many host materials have been prepared to develop materials doped with Sm^{2+} ions. Among them, glasses are considered to be more favorable than single crystals, because of their wide inhomogeneous width and easy mass production. So far, Sm^{2+} ion-doped fluoride glasses have been prepared by melting the raw material under a reducing atmosphere.[7–9] Hirao *et al.* produced borate glasses doped with Sm^{2+}.[10–13] In contrast, recently, we have successfully prepared Sm^{2+} ion-doped silicate glasses by a sol-gel method.[14–17] Since the silicate glasses surpass fluoride and borate glasses in chemical durability, it thus becomes possible to extend the study beyond the limitations of these fluoride and borate glasses.

Room-temperature PSHB is observed in the excitation spectra when detecting the fluorescence of the ${}^5D_0 \rightarrow {}^7F_0$ transition of Sm^{2+}. A possible mechanism for hole burning in this system is the photoionization of Sm^{2+} into Sm^{3+} by laser irradiation, although experimental evidence for this is lacking. The question where the electrons produced by the ionization are captured still remains unknown. Winnacker *et al.* asserted that the electrons are trapped in the Sm^{3+} ions based on an experiment involving photon-gated hole burning in a Sm^{2+}:BaClF crystal.[4] On the other hand, it has been reported that hole burning occurs without gating light.[9,12] Hirao *et al.*[9] and Kurita *et al.*[12] measured hole burning using fluoride and borate glasses doped with Sm^{2+} and considered that Sm^{3+} is not the main trap for electrons. The search for hole burning in Sm^{2+}-doped glasses is necessary for both the understanding of the mechanism of hole burning and the development of new materials with the properties required for optical memory devices. To date, experimental studies have been limited to the fluoride and borate glasses. New glass compositions, if available, are expected to elucidate the mechanism of hole burning. We doped the Sm^{2+} ions in aluminosilicate glasses using the sol-gel process. The sol-gel technique can be used to advantage in preparing glasses with high purity and high homogeneity at lower temperatures than that required in the melting method. The obtained glasses, faintly pink colored, exhibit high transparency compared with fluoride and borate glasses, which is favorable for studying the optical properties involving hole burning.

In this paper, we report hole-burning measurements in the ${}^7F_0 \rightarrow {}^5D_0$ line of Sm^{2+} ions at 77 K and changes in the spectra upon laser irradiation to the $f \rightarrow d$ transition in Al_2O_3-SiO_2 glasses. Fluorescence line narrowing spectra are compared before and after hole burning to find Sm^{2+} ions responsible for the hole formation. The behavior of electrons excited in the $4f^55d$ level is also investigated using absorption, fluorescence, and photoconductivity measurements.

II. EXPERIMENT

Sm^{3+}-containing aluminosilicate glasses were prepared by the sol-gel method using $Si(OC_2H_5)_4$, $Al(OC_4H_9)_3$, and $SmCl_3 \cdot 6H_2O$. $Si(OC_2H_5)_4$ was first hydrolyzed with a solution of H_2O, C_2H_5OH, and HCl, followed by a reaction with $Al(OC_4H_9)_3$ to form an alkoxide complex of Si and Al ions. After adding $SmCl_3 \cdot 6H_2O$ dissolved in C_2H_5OH, the alkoxide solution was further hydrolyzed with a mixture of H_2O, C_2H_5OH, and HCl, and then kept at room temperature for 2 weeks to form a stiff gel. The gel was heated in air at 500 °C for 1 h. The glass was cut into a 10×10×2 mm block and the 10×10 mm surfaces were polished with fine CeO_2 powders. The glass composition is $10Al_2O_3 \cdot 90SiO_2$ (in mol %) containing nominally 5 wt % Sm_2O_3. The glass heated in air showed optical properties characteristic of the Sm^{3+} ions, i.e., sharp absorption peaks at 345, 360, 375, and 406 nm and broad fluorescence bands around 550, 600, and 650 nm, all of which are assigned to the f-f transitions of the Sm^{3+} ions.

To reduce the Sm^{3+} ions to Sm^{2+}, the glass was heated at 800 °C under flowing H_2 gas. A detailed explanation of the glass preparation is given elsewhere.[14–17] When heated in H_2, the glass became faintly pink, indicating the formation of the Sm^{2+} ions.

The optical absorption spectra were measured with a spectrometer (Jasco, U-best 50). A hole was burned in the $^7F_0 \rightarrow {}^5D_0$ line near $14\,640\ \mathrm{cm}^{-1}$ by a cw Ar^+-laser-pumped DCM dye laser [Coherent CR599, bandwidth of $\sim 1\ \mathrm{cm}^{-1}$ full width at half maximum (FWHM)]. The burning-fluence density was changed from 0.15 to $8\ \mathrm{W/mm}^2$. The hole spectra were recorded by scanning the laser from 14 380 to 14 810 cm^{-1} while monitoring the fluorescence of the $^5D_0 \rightarrow {}^7F_2$ transition at $13\,790\ \mathrm{cm}^{-1}$. The laser power for reading the hole was attenuated by ND filters to less than 0.1% of that for burning.

A fluorescence line narrowing (FLN) spectral measurement was performed using the Ar^+-laser-pumped DCM dye laser. The fluorescence intensity was measured at 77 K with a chopper that alternately opened the optical paths before and after the sample. The chopping frequency was 150 Hz. The fluorescence wavelength was selected using a Jobin Yvon 32 cm monochromator.

Photoconductivity measurements were made using blocking electrodes. The transparent ITO electrodes were coated on the 10×10 mm surfaces, where the Ar^+-ion laser was passed through the water filter to avoid any heat effect on the sample. The current was measured at an applied 5-V dc with a vibrating reed electrometer which was sensitive to 10^{-16} A.

III. RESULTS

A. $f \rightarrow f$ transition of the Sm^{2+} ions

Heating the glass in H_2 gas reduces the Sm^{3+} ions to Sm^{2+}. The obtained glass exhibited a broad absorption spectrum ranging from 620 to 300 nm with a peak at 350 nm and a shoulder around 500 nm. The Sm^{2+} ion has a $4f^6$ configuration, which is the same as that of the Eu^{3+} ion. The lowest and first excited states of the $4f^6$ configuration are ^7F and ^5D, respectively. In view of this configuration, the absorption spectrum of the Sm^{2+} ions is expected to resemble that of the Eu^{3+} ion. However, no absorption from the f-f transition of the $4f^6$ configuration was observed. The broadband can be assigned to the $4f^6 \rightarrow 4f^5 5d$ transition of the Sm^{2+} ions and its separation into the 350 and ~ 500 nm bands is due to the degeneration of the $5d$ orbital. The $5d$ orbital of the excited-state configuration is crystal-field-split into two degenerate e_g and t_{2g} components. The magnitude of the crystal-field splitting of the two levels in our glass was calculated to be $\sim 8500\ \mathrm{cm}^{-1}$ based on the position of the two separate peaks.

In the fluorescence spectrum using the 406-nm excitation wavelength of a Xe lamp, three lines were observed at 683, ~ 700, and 725 nm in the visible region, which are attributed to the $^5D_0 \rightarrow {}^7F_{j\ (j=0,1,2)}$ transitions, respectively, of the Sm^{2+} ions. No radiative transition from the $4f^5 5d$ level was observed. These results indicate that the fluorescence of the Sm^{2+} ions is associated with the non-radiative $4f^5 5d \rightarrow {}^5D_0$ relaxation and the radiative transition from the $^5D_0$ level into the ground ^7F_j states. Based on these experimental results, the energy-level diagram of the Sm^{2+} ions doped in Al_2O_3-SiO_2 glasses is schematically drawn in Fig. 1. The $4f^5 5d$ has a broadband originating at $\sim 16\,100\ \mathrm{cm}^{-1}$ (620 nm), which is higher by about $1460\ \mathrm{cm}^{-1}$ than the $^5D_0$ level at $14\,640\ \mathrm{cm}^{-1}$ (683 nm). The lower energy of the $^7F_0 \rightarrow {}^5D_0$ transition is appropriate for observing the hole burning.

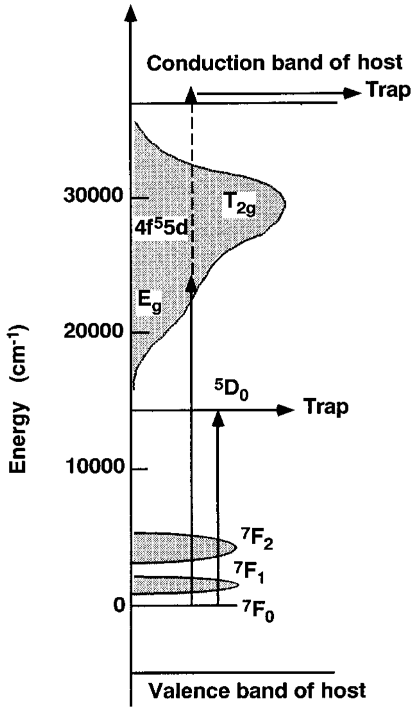

FIG. 1. Energy-level diagram of the Sm^{2+} ion doped in $10Al_2O_3 \cdot 90SiO_2$ glass. The energy gap of the host glass is estimated from the optical absorption spectrum. The trapping of electrons via the conduction band proceeds through a two-photon absorption process.

B. Hole burning

Hole burning was observed on the excitation spectrum of the $^7F_0 \rightarrow {}^5D_0$ transition. Figure 2 shows typical excitation and FLN spectra of the glass before and after hole burning at 77 K. A hole was burned by irradiating with a DCM dye laser with a power of $1\ \mathrm{W/mm}^2$ at $14\,640\ \mathrm{cm}^{-1}$ for 10 min. A hole is clearly observed in the excitation spectrum after burning. The hole width (FWHM) and depth are $5\ \mathrm{cm}^{-1}$ and $\sim 12\%$, respectively. We found that the hole width increased with increasing burning temperature; it was $\sim 15\ \mathrm{cm}^{-1}$ at room temperature. The excitation profile represents an inhomogeneous line shape with a width of $80\ \mathrm{cm}^{-1}$ FWHM. This large width is due to the random structure of the glass and is much broader than that observed in crystals[6] and fluoride glasses,[9] but is comparable to borate glasses.[11] The inhomogeneous width did not change after burning, and was almost independent of temperature up to room temperature.

The FLN spectra, measured at 77 K under the $14\,640$-cm^{-1} excitation energy of the DCM dye laser, show two groups of bands in the wave-number ranges 14 500–14 100 cm^{-1} and 14 000–13 600 cm^{-1} due to the

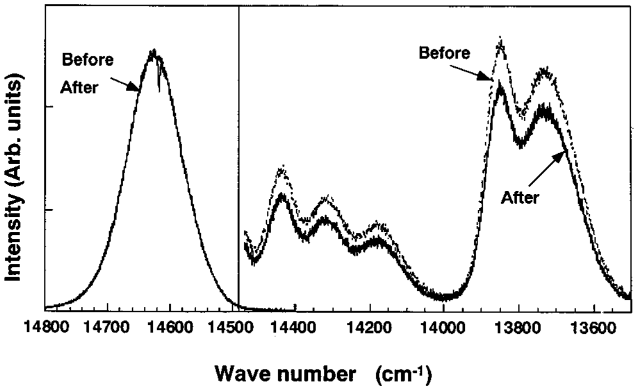

FIG. 2. Excitation and fluorescence spectra, measured at 77 K, of Sm^{2+}-doped glass before (dotted line) and after (solid line) hole burning with a DCM dye laser at 14 640 cm^{-1}. Burning power and time are 1 W/mm^2 and 10 min, respectively. The excitation spectrum was obtained by monitoring the $^5D_0 \rightarrow {}^7F_2$ fluorescence at 13 790 cm^{-1}. The fluorescence spectrum was obtained using 14 640 cm^{-1} excitation energy of the DCM dye laser.

$^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively. In the wave-number range of the $^5D_0 \rightarrow {}^7F_2$ transition, which theoretically consists of five Stark components, only two broad incompletely resolved bands are seen. On the other hand, three distinct peaks due to the Stark splitting of the $^7F_1$ state appear in the wave-number range from 14 500 to 14 100 cm^{-1}. Compared with the FLN spectrum before burning, it is evident that the fluorescence intensity decreases, but no change in the shape of the spectrum is observed after burning. Figure 3 shows the hole depth dependence on time during burning at 77 K. The hole depth, which is normalized to the excitation intensity before burning at the burning wavelength, increases with burning time up to about 12% within a few hundred seconds.

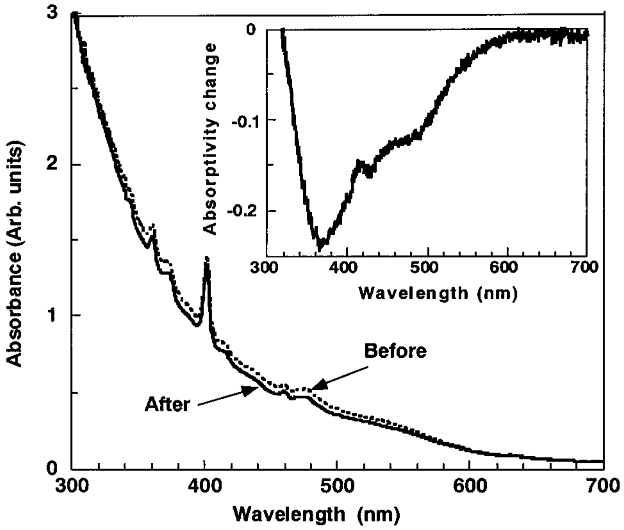

FIG. 4. Optical absorption spectra, measured at 77 K, of Sm^{2+}-doped glass before (dotted line) and after (solid line) irradiation using the 488-nm line of an Ar^+ laser for 10 min. The inset shows the difference before and after irradiation.

C. $4f^6 \rightarrow 4f^5 5d$ transition of the Sm^{2+} ions

The glass was irradiated using the Ar^+-ion laser at 488-nm wavelength corresponding to the energy of the $4f^6 \rightarrow 4f^5 5d$ transition of Sm^{2+}. Figure 4 shows the optical absorption spectra before and after irradiation. The sharp bands peaking at 360, 375, and 406 nm are due to the existence of the Sm^{3+} ions which remain unreduced. The difference spectrum before and after irradiation, shown in the inset of Fig. 4, indicates that the laser irradiation causes a decrease in the intensities of the e_g and t_{2g} components of the $5d$ levels of the $4f^5 5d$ configuration. The decrease in intensity at a selective position such as 488 nm was not observed.

Figure 5 shows the fluorescence spectra change before and after laser irradiation. The 337 nm of a N_2 laser was used for excitation. It is evident that the intensities of the lines due to the $^5D_0 \rightarrow {}^7F_j$ transitions decreased after irradiation. In contrast, a small but positive fluorescence change was observed from 18 000 to 23 000 cm^{-1} upon irradiation. The origin of this fluorescence is unknown at the present time. Instead of the N_2 laser, which is not effective for the excitation of Sm^{3+}, the 406-nm wavelength of a Xe lamp was used

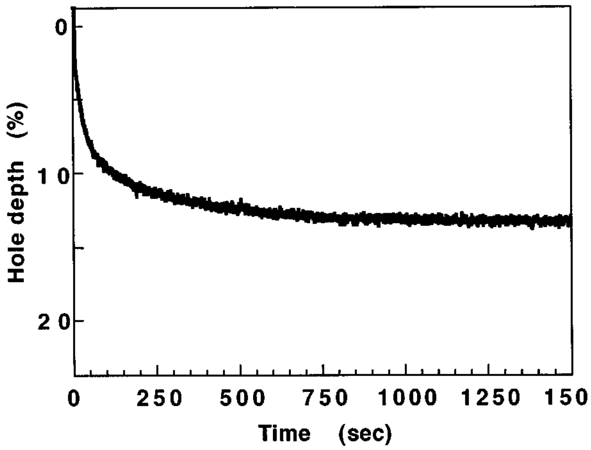

FIG. 3. Hole depth burned as a function of burning time. The hole was burned using 14 640 cm^{-1} excitation energy of the DCM dye laser with a power of 1 W/mm^2. The depth was normalized to the excitation intensity before burning.

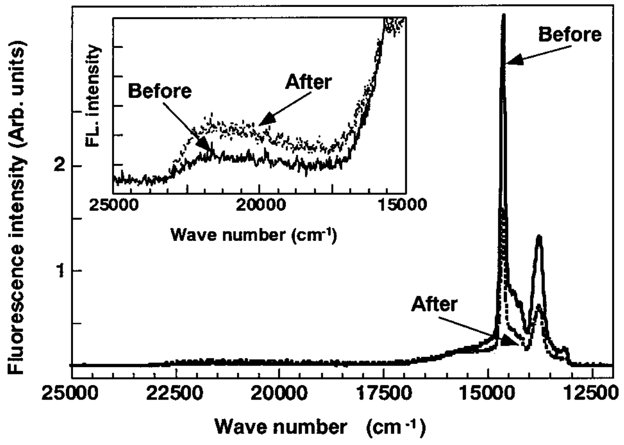

FIG. 5. Change in fluorescence, measured at 77 K upon irradiation with the 488-nm line of an Ar^+ ion laser with a power of 1 W/mm^2 for 3 min. The inset shows an enlargement of this change for clarity.

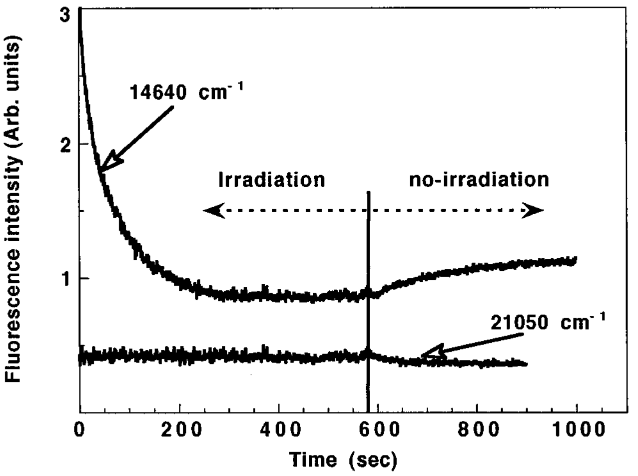

FIG. 6. Fluorescence intensities at 14 640 and 21 050 cm^{-1} as a function of time during irradiation and after stopping the irradiation.

for the excitation to examine the changes in the fluorescence spectra of the Sm^{3+} ions. However, even under excitation with a 406-nm wavelength, the intensities of the fluorescence bands due to the Sm^{3+} ions did not change following irradiation.

The fluorescence intensities in the two wavelength regions of 18 000–23 000 and 13 000–15 000 cm^{-1} were measured under the Ar laser irradiation. Figure 6 shows the fluorescence intensities at 14 640 and 21 050 cm^{-1} as a function of time under irradiation and after stopping the irradiation. The intensity at 14 640 cm^{-1} decreased to a constant value within a few hundred seconds. After stopping the irradiation, the intensity increased but did not reach the initial intensity, even after a long period. On the other hand, the behavior of the fluorescence at 21 050 cm^{-1} was reversed.

IV. DISCUSSION

A. *f-f* transition of Sm^{2+} and spectral hole burning

As shown in Fig. 2, the hole of the Sm^{2+} ions is observed in the excitation spectrum of the $^7F_0 \rightarrow {}^5D_0$ transition, the depth of which is saturated at about 12% after about 10-min irradiation. This hole-burning behavior is similar to that observed in crystals and other fluoride and borate glasses containing Sm^{2+} ions. One possible mechanism of hole burning is the photoionization of the Sm^{2+}; $Sm^{2+} \rightarrow Sm^{3+} + e^-$. However, at the present time, it is unknown where the released electrons are captured. Winnacker *et al.* observed photon-gated hole burning in a Sm^{2+}:BaClF crystal and claimed that the electrons are trapped by the Sm^{3+} ions.[4] In this system, the pumping electrons move back and forth between Sm^{3+} and Sm^{2+} in the hole-burning and erasing process. The question whether the Sm^{3+} ions act as a trap for electrons still remains unanswered. In the glass structure, Sm^{2+} and Sm^{3+} ions are located in more random sites than in crystals. According to this idea, when the released electrons are captured on Sm^{3+} located at different sites than the burned Sm^{2+} ions, a change due to the reduction of Sm^{3+} ions should be detected in the optical spectra, because each Sm ion has a different environment. However, as shown in Fig. 2, we found no significant change in intensity at the selected wavelength in the FLN spectrum but only a decrease in the whole line after burning. No anti-hole was observed around the burned hole. These results imply that the Sm^{3+} ions are not the main trap for the released electrons.

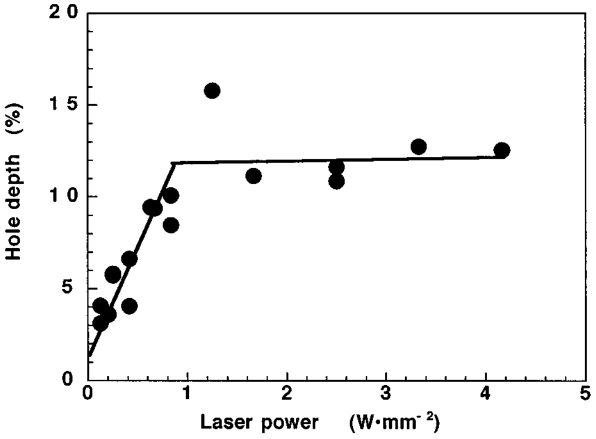

FIG. 7. Hole depth burned as a function of burning power. A line is drawn as a guide for the eye.

The hole depth is related to the number of electrons captured in the trap. The hole was burned using the DCM dye laser with a power of 0.15–5 W/mm^2 at 77 K, the depth of which is plotted in Fig. 7 as a function of burning power. It is evident that the hole depth linearly increases with the power of the laser, and reaches about 12% at 1 W/mm^2. This linear dependence of the depth on power strongly suggests that hole burning in this system is a single-photon process but not a two-photon process as shown in the Sm^{2+}-doped halide single crystals. In this one-photon process, the electrons, which are excited into the $^5D_0$ level, nonradiatively move into the trapping center without being excited into upper levels. The hole-burning time shown in Fig. 3 is considered to correspond to the time required for trapping the electrons through the nonradiative decay pathway. This time is as long as a few hundred seconds for the present glass. However, the driving force for pumping the electrons into the trapping center is still unknown at the present time.

B. Electron transition in the $4f^55d$ level

At energies higher than the $^5D_0$ level there are broad absorption bands arising from transitions to the $4f^55d$ states (see Fig. 1). The $4f^55d$ configuration has a wide distribution in energy and overlaps with the $4f^6$ levels and the conduction band of the host. Therefore, although this level is not directly related with hole burning, it is important to study the behavior of electrons excited into the $4f^55d$ configuration for a better understanding of the hole-burning mechanism. In this section, the behavior of electrons excited into the $4f^55d$ level is investigated based on measurements of the absorption, fluorescence, and photoconductivity.

Upon irradiation using the 488-nm line of an Ar^+ laser, a decrease was observed in both the absorption intensities of the E_g and T_{2g} components in the $4f^55d$ configuration (see Fig. 4) and the fluorescence intensities of the $^5D_0 \rightarrow {}^7F_j$ transitions (see Fig. 5). The fluorescence in the wavelength region of 15 000–12 500 cm^{-1} shown in Fig. 5 is due to the transition from the $^5D_0$ level, in which electrons excited into

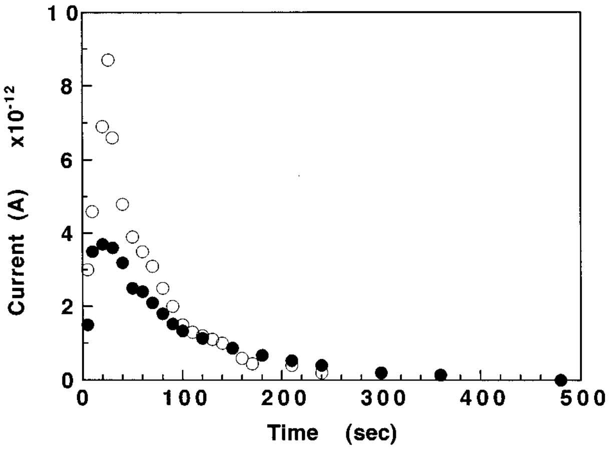

FIG. 8. Change in photocurrent under irradiation using the 488-nm line of an Ar$^+$ ion laser with a power of 0.5 (solid circles) and 1 (open circles) W/mm^2.

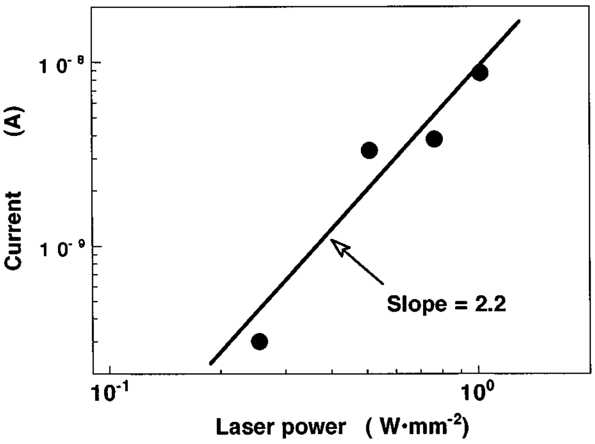

FIG. 9. Photocurrent at the maximum value as a function of laser power. The line drawn has a slope of about 2.2.

the $4f^55d$ level are nonradiatively relaxed, and the decrease in intensity is associated with the decrease in the relaxation probability of the $4f^55d\rightarrow{}^5D_0$ transition. This means that the electrons which are not relaxed into the $^5D_0$ level are captured by some trapping center. One possible pathway for the released electrons is the conduction band. The broad $4f^55d$ band may overlap with the conduction band of the host matrix. A photoconductivity measurement is useful to detect the interaction of electrons between the $4f^55d$ level, the conduction band, and the other $4f^6$ levels. Figure 8 shows a typical experimental result indicating the photocurrent dependence on laser irradiation time. The photocurrent rapidly increases within a few seconds, and then gradually decreases over a few hundred seconds. The appearance of photoconductivity means that the electrons are excited into the conduction band of the host matrix. Furthermore, the gradual decrease in the photocurrent after approaching the maximum value strongly suggests that the electrons in the conduction band are captured in a trapping center. The time required for the completion of the photocurrent is almost the same as that for the decrease in fluorescence intensity at 14 640 cm^{-1} (Fig. 6).

Figure 9 shows the relationship between the maximum photocurrent, I, and the incident laser power, P, at 488 nm. This result can be fitted to a power-law behavior, $I=P^n$, with $n=2.2$. The experimental value $n=2.2$ is close to an $n=2$ exponent in the power-law behavior, indicating that the pumping of electrons to the conduction band proceeds through a two-photon absorption process. As shown in Fig. 1, we concluded that this two-photon process could happen from the E_g level of the $4f^55d$ configuration. Excitation by the Ar laser pumps electrons from the ground state to the $4f^55d$ level, followed by promoting them to the conduction band by absorbing one more photon, and electrons are then captured in the trap. However, pumping of these electrons does not result in formation of hole burning such as observed in the $f\rightarrow f$ transition. Hole vacancies produced by the removal of electrons are compensated by other electrons in the broad $4f^55d$ configuration.

V. CONCLUSIONS

In this paper, the behavior of electrons excited into the $f\rightarrow f$ and $f\rightarrow d$ transitions of Sm^{2+} ions doped in Al_2O_3-SiO_2 glasses prepared by the sol-gel process was discussed as a consequence of PSHB, FLN, and photoconductivity measurements. We concluded that spectral hole burning proceeds as a single-photon process, and electrons excited into the $^5D_0$ level move nonradiatively into the trapping center within a few hundred seconds without being excited into upper levels. On the other hand, electrons excited into the $4f^55d$ level are captured in the trapping center via the conduction band by absorbing a second photon.

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