

Room-temperature photochemical hole burning in Eu^{3+} -doped Al_2O_3 - SiO_2 glass

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Persistent spectral hole burning was observed at room temperature in Eu^{3+} -doped Al_2O_3 - SiO_2 glass. The glass was obtained by heating in hydrogen gas to reduce some Eu^{3+} ions to Eu^{2+} and the spectral hole was burned in the excitation spectrum of the ${}^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} . The depth of the hole burned at 200 K was $\sim 7\%$ of the total excitation intensity and independent of temperature up to 350 K. A possible mechanism for hole burning is the electron transfer between the Eu^{3+} ions and the Al-related defect centers. © 1999 American Institute of Physics. [S0003-6951(99)04046-2]

The persistent spectral hole-burning (PSHB) phenomenon of rare-earth ions has attracted significant attention, because of its high potential use in high-density frequency-domain optical memories.¹ For this purpose, high hole-burning efficiency at high temperature is required, but in most rare-earth ion, PSHB is limited to low temperature using liquid helium. Sm^{2+} and Eu^{3+} ions are special cases favorable to high temperature PSHB. Room-temperature PSHB was first observed in a $\text{Sm}^{2+}:\text{BaClF}$ crystal.² Recently, we succeeded in preparing Sm^{2+} -doped silicate glasses by a sol-gel method and observed PSHB at room temperature.³ As a host material, glasses are thought to be more favorable than crystals because of their wide inhomogeneous linewidth, high transparency, and easy mass production. In addition, we prepared the Eu^{3+} -doped silicate glasses exhibiting holes with a depth of $\sim 40\%$ at 77 K.^{4,5} The depth of the holes burned in the Eu^{3+} -doped glass decreased as the temperature increased and was erased above ~ 200 K.

The Eu^{3+} ion has a $4f^6$ electron configuration, which is the same as that of the Sm^{2+} . In view of this configuration, we can expect room-temperature PSHB in the Eu^{3+} ions. In this letter, we demonstrate the preparation of the Eu^{3+} -doped glass exhibiting PSHB at room temperature and discuss the hole burning mechanism. Recently, Fujita *et al.* reported a persistent spectral hole burning at room temperature in the Eu^{3+} -doped glass melted under a reducing atmosphere.⁶ In our experiment, the Eu^{3+} ions are doped in the Al_2O_3 - SiO_2 glass, the same as that of the Sm^{2+} ions, which is appropriate for discussing the hole-burning mechanism.

$1\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ (mole ratio) glass containing 10 wt % Eu_2O_3 was prepared by the sol-gel method. A detailed explanation of gel preparation is given elsewhere.^{4,5} The gel was heated in air at 800 °C, followed by heating in air at 800 °C for 1 h, then heated at 800 °C for 30 min under a flowing mixed gas with 20% H_2 -80% N_2 . The resultant glass has optical properties characteristic of both the Eu^{3+} and Eu^{2+} ions, i.e., sharp f - f transition-bands of the Eu^{3+} ions and broad f - d transitions bands of the Eu^{2+} ions. The fluorescence intensity of the Eu^{3+} ions was reduced to about one-

third its initial intensity before heating in the H_2 - N_2 gas. Eu^{3+} -doped SiO_2 glass was also heated in H_2 - N_2 gas to partially reduce the Eu^{3+} ions into Eu^{2+} . Holes were burned in the ${}^7F_0 \rightarrow {}^5D_0$ line of the Eu^{3+} ion by continuous wave Ar^+ -ion-laser pumped Rhodamine 6G dye laser with a line width of $\sim 1 \text{ cm}^{-1}$ full width at half maximum (FWHM) and a power of 300 mW for 30 min. Hole spectra were recorded by scanning the dye laser from 17 500 to 17 200 cm^{-1} while monitoring the fluorescence of the ${}^5D_0 \rightarrow {}^7F_2$ transition at 17 307 cm^{-1} . The laser power for scanning was attenuated by neutral-density filters to less than 0.2% of that for burning.

A typical PSHB spectrum burned at 7 K is shown as curve (a) in Fig. 1. The width and depth of the burned hole are 2.7 cm^{-1} FWHM and 28% of the total fluorescence intensity at the burning wave number, respectively. The thermal stability of the burned hole is examined from the temperature-dependent hole-erasure measurement. A hole was burned at 7 K, and the PSHB spectrum was measured. After cycling through a temperature higher than 7 K, the spectrum was again measured at 7 K. During this process, the hole is partially filled. Shown in Fig. 1 are the PSHB spectra after cycling up to 300 K. Note that the hole is clearly observed after cycling through 300 K. The hole depths are plotted in Fig. 2 as a function of the cycling temperature. It is evident that the hole depth is almost independent of temperature above 150 K and $\sim 5\%$ at 300 K, though it decreases rapidly at temperatures below 150 K. We reported previously that the hole is formed by the rearrangement of OH bonds surrounding the Eu^{3+} ions in the sol-gel derived glasses.^{4,5} The burned hole is thermally filled and erased at ~ 150 K. The optical activated rearrangement of these OH bonds contribute to the hole formation at 7 K. The thermally filling data in the temperature below 150 K were fitted using a Gaussian distribution equation to be ~ 0.3 eV as the barrier height, which is compared to that for the hole burned in the glass heated in air. This result again indicates that the barrier height for the rearrangement of the OH bonds is too low for holes to persistently exist at room temperature. The hole was burned at 200 K to avoid the effect of the OH bonds on the hole formation, the depth of which is also plot-

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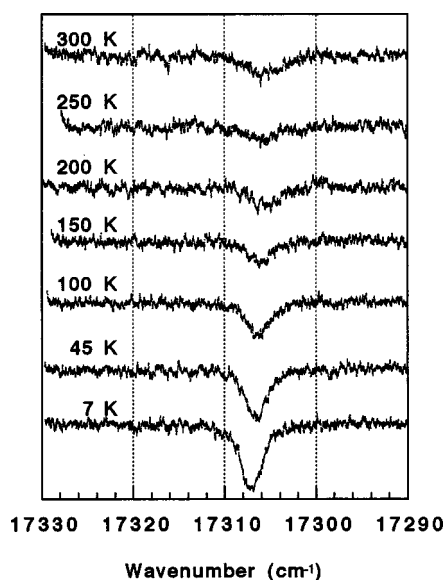


FIG. 1. PSHB spectra, burned and measured at 7 K, of Eu^{3+} -doped $\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ glass heated in H_2 glass at 800 °C. PSHB spectra are measured at 7 K after cycling through the temperature shown in the figure.

ted in the figure as a function of the cycling temperature. No decrease is observed in the hole depth up to 300 K.

We next consider the formation of the hole observable up to room temperature. The present glass is prepared by heating in hydrogen gas to reduce some Eu^{3+} ions to Eu^{2+} . For the other method, Fujita *et al.* melted the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses using a carbon crucible and hydrogen gas and observed the long-lived hole spectra of the Eu^{3+} at room temperature.⁶ They considered that the hole is formed by the photoinduced reduction of Eu^{3+} ions and the released holes are captured in Eu^{2+} ions, although no experimental evidence for this is given. To study whether the Eu^{2+} ions act as the positive hole center, SiO_2 glass was prepared for doping the Eu^{3+} ions, followed by heating in H_2 to reduce the Eu^{3+} into Eu^{2+} . The ratio of the fluorescence intensities of the Eu^{3+} and Eu^{2+} is almost the same as that in the earlier-mentioned $\text{Al}_2\text{O}_3-\text{SiO}_2$ glass. The dependence of hole depth, burned at 7 K, on the cycling temperature is also shown in Fig. 2. It is evident that the depth of the hole

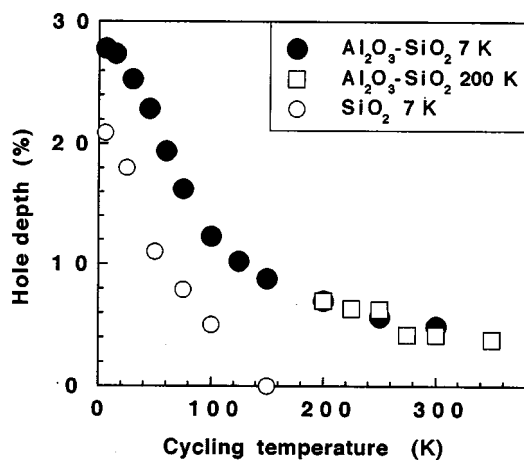


FIG. 2. Relation between the hole depth and the cycling temperature of Eu^{3+} -doped $\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ and SiO_2 glasses heated in H_2 gas at 800 °C. Holes are burned at 7 and 200 K for Eu^{3+} -doped $\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ and 7 K for Eu^{3+} -doped SiO_2 glass, respectively.

burned at 7 K decreases and disappears above 150 K. If the Eu^{2+} ions act as the positive hole-trap centers, the PSHB should be observed above 150 K. We also point out that no antihole is observed in the sides of the burned hole (see Fig. 1). These results strongly exclude the possibility of Eu^{2+} ions acting as hole traps. Another possibility for the hole burning is the two-step photoionization from the first excited 5D_0 level to the conduction band of the host. A two-photon hole burning experiment was carried by using an Ar laser and 532 nm Nd:yttrium-aluminum-garnet laser in addition to the burning light. No difference was observed in the hole burning efficiency before and after the laser irradiation, meaning that the hole is formed by a one-step excitation. In contrast, we noticed that the hole burning is related with the glass structure, especially the existence of Al^{3+} ions. In $\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses, 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 sometimes causes defects in the glass structure and might be compensated by the other cations such as alkali ions.

Generally, the sol-gel process is known to bring about many kinds of defects in a glass during its chemical and thermal treatments.^{7,8} Strong luminescence around the 450 nm wavelength is attributed to chemical bond breakage and/or nonstoichiometry created during sol-gel processing, though the nature of which is still not completely understood. This luminescence is more prominent in the $\text{Al}_2\text{O}_3-\text{SiO}_2$ system,⁷ which can be used in high temperature phosphors. These photosensitive centers should be created in the present Eu^{3+} -doped $\text{Al}_2\text{O}_3-\text{SiO}_2$ glass during heating in H_2 gas. The SiO_2 and $\text{Al}_2\text{O}_3-\text{SiO}_2$ binary glasses were prepared without Eu_2O_3 by the sol-gel process in order to eliminate the overlapping of the optical adsorption and fluorescence of the Eu^{2+} ions in the range from 200 to 500 nm. Figure 3 (inset) shows the optical absorption spectra of the $\text{Al}_2\text{O}_3-\text{SiO}_2$ and SiO_2 glasses heated in air at 800 °C. Note that the $\text{Al}_2\text{O}_3-\text{SiO}_2$ glass has a strong absorption above $30\,000\text{ cm}^{-1}$ compared with the SiO_2 glass. Furthermore, the $\text{Al}_2\text{O}_3-\text{SiO}_2$ glass exhibited a large change in the absorption spectrum by heating in H_2 gas. Shown in the figure is the difference spectrum before and after H_2 gas treatment. The curve fitting technique implies that the absorbance is composed of three component bands peaking at $48\,000$, $41\,000$, and $37\,000\text{ cm}^{-1}$ and the former band increases while the latter two bands decrease upon heating in H_2 gas. A spectroscopic study of the defects induced in a glass heated in H_2 gas has been extensively carried out for the $\text{GeO}_2-\text{SiO}_2$ or SiO_2 glasses for use as optical fibers.^{9,10} The absorption in the ultraviolet region is attributed to the structure imperfections such as oxygen deficiency, electron, and hole-trap centers. By comparing these glasses, the absorption observed in the $\text{Al}_2\text{O}_3-\text{SiO}_2$ glass can be attributed to the oxygen-deficiency defects such as Al-Al bonds. The $\text{Al}_2\text{O}_3-\text{SiO}_2$ glass was then irradiated with a laser beam having the same energy as that used for hole burning. Also shown in the figure is the induced absorption spectrum which is obtained by subtracting the absorption before irradiation from that after irradiation. It is evident that the absorption band at $48\,000\text{ cm}^{-1}$ bleaches, indicating that the oxygen-deficiency defects

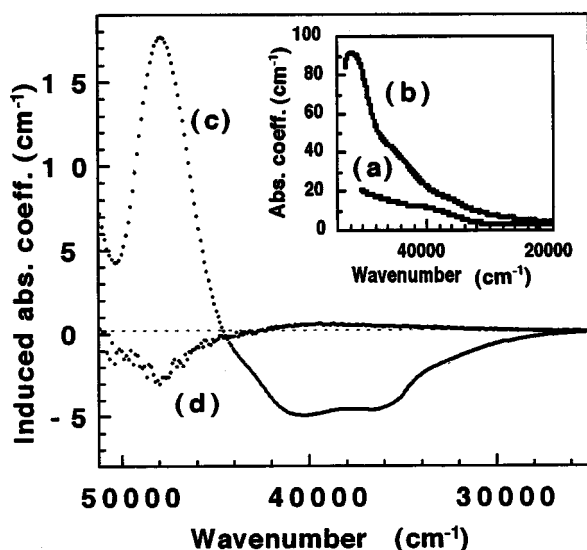


FIG. 3. Difference optical absorption spectra induced by heating the $\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ glass in H_2 gas (800 °C for 1 h) (c) and by irradiation with the 578 nm dye laser (300 mW for 30 min). (d). The inset shows the absorption spectra of SiO_2 glass (a) and $\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ glass (b) heated in air at 800 °C.

couple to the laser beam. The formation of these oxygen-deficiency defects was confirmed from the electron spin resonance spectrum exhibiting the absorption at a g value of ~ 2.00 . From these results and the hole burning experiments, we would postulate the formation of a hole as follows: A narrow burning laser beam selectively excites electrons from the ground state of Eu^{3+} ions, and, at the same time, the laser resonates with the oxygen-defect centers in the Al–Al 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. This is also revealed from the experimental result that the hole depth increased with an increase in the Al_2O_3 concentration.

The holes are formed by the tunneling of an electron between the excited- Eu^{3+} ions and the Al–Al defect centers. The hole-burning dynamics should be dependent on the length between two centers. The rate equation of conversion of the Eu^{3+} ions into the burnt state of Eu^{3+} ions can be written as^{11,12}

$$dM_t/dt = K(M_0 - M_t), \quad (1)$$

where M_0 and M_t denote the concentration of Eu^{3+} ions at the initial and time t , respectively. K is a rate constant proportional to $\exp(-\lambda)$ where λ is the tunneling parameter. The dependence of the hole depth on the burning time at 200 K is shown in Fig. 4. The hole depth increases with burning time and approaches a saturate level of about 7%, not 100%, suggesting that there are centers which can easily be burned and those which are hardly burned. Assuming that the hole depth corresponds to the concentration of the burned Eu^{3+} ions and K is independent of the burning time, the hole depth D_t is given by integrating Eq. (1)

$$D_t = D_0[1 - \exp(-Kt)], \quad (2)$$

where D_0 is the hole depth after an infinite period, $\sim 7\%$ in this case. The hole-growth data are plotted according to Eq.

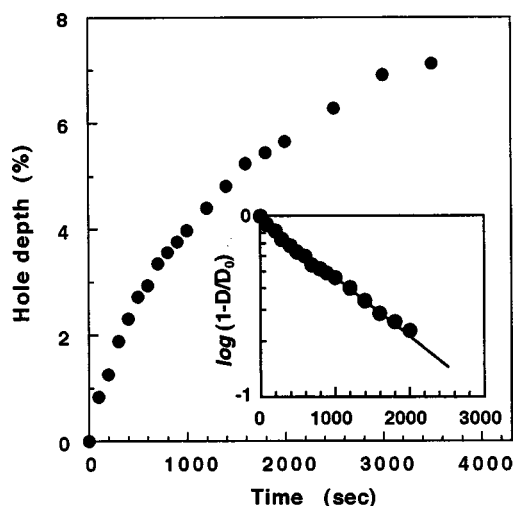


FIG. 4. Depth of the hole burned as a function of burning time. The inset shows logarithmic plot of the hole depth.

(2) in the inset in Fig. 4, where the value of D_0 was determined to be 7% by the least-squares fit of the equation. Note that good linearity was obtained, indicating that the hole burning is controlled by the rate equation with a constant rate of 8.2×10^{-4} 1/s. A small burning rate suggests a long distance between the two centers. In the present glass, the concentration ratio of Al ion to Eu ion is about five. The Eu^{3+} ions are preferentially coordinated with Al–O polyhedra to compensate for the excess negative charge of the Al–O polyhedra. Thus, the Al–O bonds far from the Eu^{3+} ions are not neutralized forming the defect centers. The interaction over a long distance between the Eu^{3+} ions and the Al–Al defect centers should result in a low hole-burning efficiency.

In conclusion, we successfully prepared the Eu^{3+} ion-doped Al_2O_3 – SiO_2 glass exhibiting a persistent spectral hole burning at room temperature. It is concluded that the hole burning proceeds as the electron transfer between the excited Eu^{3+} ions and the Al-related defect centers. The room-temperature PSHB-exhibiting glass makes it an attractive candidate for high density memories.

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