Persistent spectral hole burning of sol-gel-derived Eu^{3+}-doped SiO_2 glass

Masayuki Nogami* and Tomokatsu Hayakawa

Nagoya Institute of Technology, Showa, Nagoya, 466-8555 Japan

Persistent spectral hole burning (PSHB) was observed at temperatures higher than 77 K in the sol-gel-derived Eu^{3+}-doped SiO_2 glasses. $1Eu_2O_3 \cdot 99SiO_2$ (mole ratio) glass was prepared by heating gel synthesized from metal alkoxides at 400 to 1000 °C. The hole was burned in the $^7F_0 \rightarrow {}^5D_0$ line of Eu^{3+} ions by means of a Rhodamine 6G dye laser at 77 K and the burnt hole depth was measured as a function of temperature. The hole depth increased with increasing OH content in the glass. It was found that the hole burnt at 77 K was thermally filled and an average thermal barrier height for the hole filling was ~0.3 eV, which was higher for the glass heated at high temperature, indicating that the stable hole is burned with the increased heat-treatment temperature. It was concluded that the PSHB was formed by the optically activated rearrangement of proton in the first coordinating sphere of the Eu^{3+} ions.

[S0163-1829(97)52046-7]

Persistent spectral hole burning (PSHB) glasses doped with organic dye molecules and rare-earth ions have attracted significant attention, because they have a large potential for a high-density frequency-domain optical data storage.[1–5] For this purpose, high-temperature PSHB and a stable hole are expected. Room-temperature PSHB has been observed in Sm^{2+}-doped crystals[6,7] and glasses.[8] Among them, glasses are considered to be more favorable than single crystals, because of their wide inhomogeneous width and easy mass production. 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 under a strong reducing atmosphere.[8–10] The residue of the Sm^{3+} ions lowers the efficiency of hole burning. For the Eu^{3+}-doped glasses long-lived holes have been observed at liquid helium temperature.[11–13] To date, however, no one has succeeded in the preparation of the Eu^{3+}-doped glasses exhibiting PSHB at high temperature. We have been conducting a study of the preparation of the PSHB glasses by use of a sol-gel method,[14–16] and recently succeeded in preparing Eu^{3+} ion-doped silica glass exhibiting PSHB up to 130 K.[17] Since the Eu^{3+}-doped glasses are obtained without heating in reducing atmosphere, it thus becomes possible to extend the study beyond the limitation of the Sm^{2+}-doped glasses. Further, the Eu^{3+}-doped silica glasses have proven useful for a practical system in connection with the optical silica glass fibers.

Our Eu^{3+}-doped silica glasses, prepared by heating the gels up to 900 °C, exhibited the hole with the width and depth of ~2 cm^{-1} and ~15%, respectively, at 77 K.[17] The mechanism for hole burning was not clear at that time, though it suggested that the residual water in glass affects the hole burning. The search for hole burning in the Eu^{3+}-doped glasses is necessary for both the understanding of the mechanism of hole burning and the development of glasses exhibiting PSHB at high temperature.

In this paper, we demonstrate how the hydroxyl groups surrounding the Eu^{3+} ions contribute to the hole burning, and discuss the thermal stability of the burnt hole from the hole refilling experiments. $1Eu_2O_3 \cdot 99SiO_2$ (mole ratio) glass was prepared by the hydrolysis of $Si(OC_2H_5)_4$ and $EuCl_3 \cdot 6H_2O$.

A detailed explanation of gel preparation is given elsewhere.[17] The gel was heated in air at 50 °C/h to a given temperature of 400–1000 °C, where it was held for 2 h. The synthesized gel is porous, containing a large amount of water incorporated during synthesis. When heated, the gel transforms into glass according to a dehydration and polycondensation reaction. In the fluorescence spectra of glasses using a 463-nm excitation wavelength of a Xe lamp, four lines are observed a 580, 590, 615, and 650 nm in the visible wavelength region, all of which are attributed to the $^5D_0 \rightarrow {}^7F_{j\ (j=0,1,2,3)}$ transitions, respectively, of the Eu^{3+} ions. The fluorescence spectrum of glass heated at 500 °C had weak intensity, which increased with the increased temperature and at 1000 °C reached an intensity higher than four times that at 500 °C (as will be shown in Fig. 2). This weakened fluorescence at low temperatures is due to the OH concentration quenching.[18,19] The presence of OH groups in the first coordination sphere of Eu^{3+} ions provides an effective pathway for the radiationless dexcitation via energy transfer to OH vibration, which results in quenching the fluorescence. Heating causes the glass to lose the OH groups in response to a dehydration-condensation reaction, resulting in the formation of the Eu^{3+} ions embedded in the glass network.

Hole-burning experiments were done on the excitation spectrum of the $^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+} ions. Holes were burned by irradiating a tunable cw Ar^+-ion-laser-pumped Rhodamine 6G dye laser with a linewidth of ~1.0 cm^{-1} full width at half maximum (FWHM) and a power of 20–300 mW/mm^2 for 30 min. Hole spectra were recorded by scanning the dye laser from 17 150 to 17 550 cm^{-1} while monitoring the fluorescence of the $^5D_0 \rightarrow {}^7F_2$ transition at 16 230 cm^{-1}. The laser power for scanning was already attenuated by neutral-density filters to less than 0.2% of that for burning. Figure 1 shows a typical hole spectrum of glass heated at 800 °C. A hole is clearly seen at the wave number of 17 287 cm^{-1}. The hole width and depth are ~2 cm^{-1} and ~10%, respectively. The hole depth, which is defined as the intensity ratio to the total fluorescence intensity and is normalized to the intensity before burning at the burning wave number, increases with burning time up to about 10% within
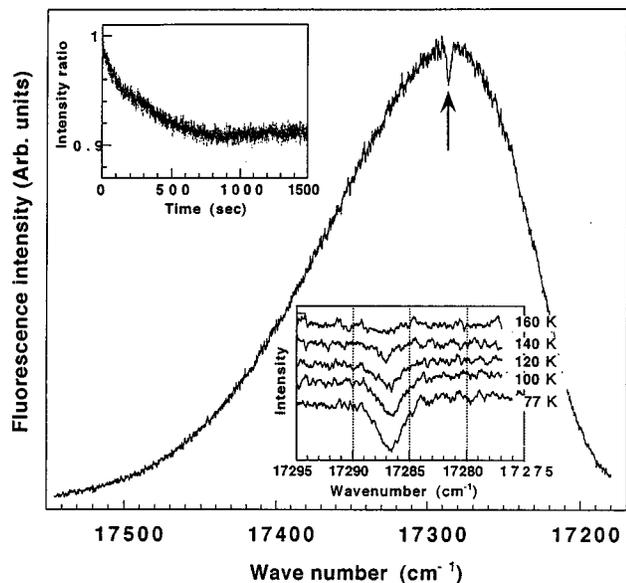
FIG. 1. Hole spectrum, measured at 77 K, of Eu^{3+}-doped SiO_2 glass prepared by the sol-gel method after burning with a Rhodamine 6G dye laser with a power of 100 mW/mm^2 at 17 287 cm^{-1}. The inset shows the hole depth burned as a function of burning time, where the depth was normalized to the excitation intensity before burning. Another inset shows the hole spectra, measured at 77 K, after cycling through the temperature shown in the figure.

a few hundred seconds (inset of Fig. 1). The hole depth linearly increased with the power of the laser and reached $\sim$10% at 150 mW/mm^2. Antiholes were not observed near the holes. The hole burning experiments were done for glasses heated at 400–1000 °C with a power of 100 mW/mm^2 at 77 K, the depths of which are plotted in Fig. 2 as a function of heat-treatment temperature. It is evident that the hole depth decreased with increasing temperature and
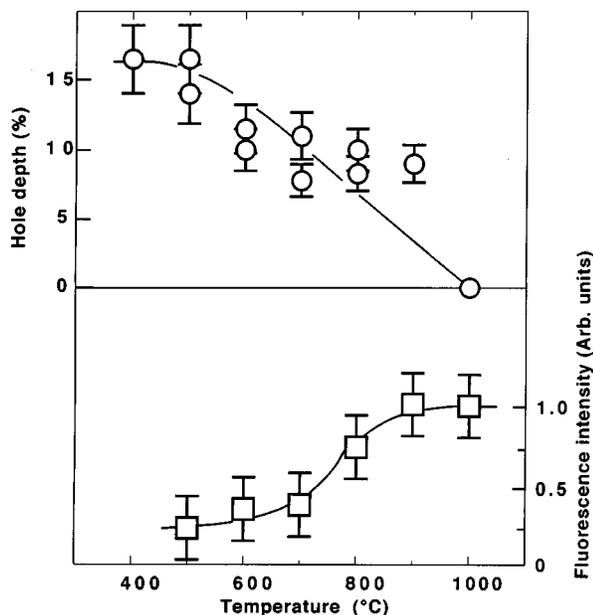
FIG. 2. Hole depth and fluorescence intensity as a function of heat-treatment temperature of glass. The fluorescence intensity is of the $^5D_0 \rightarrow {}^7F_2$ transition and normalized to unity for glass heated at 1000 °C.
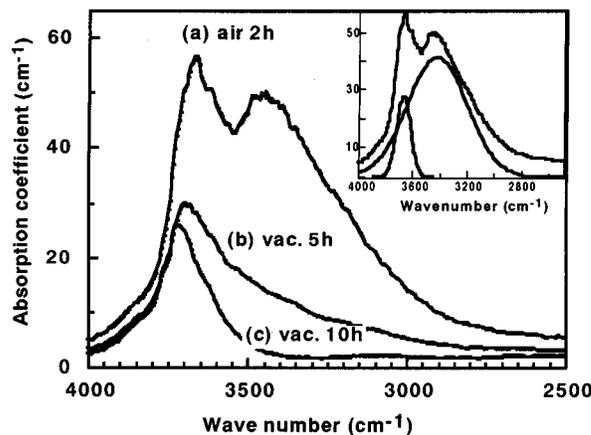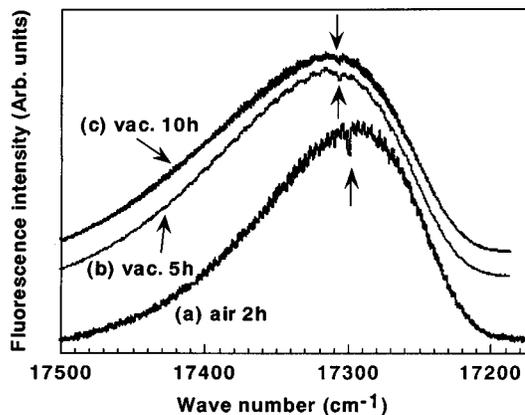
FIG. 3. Hole and infrared absorption spectra of glass heated at 800 °C for 2 h in air, followed by heating for 5 and 10 h in vacuum. The inset shows the deconvolution of the spectrum (a).

was not burned for the glass heated above 1000 °C. In Fig. 2, the fluorescence intensities of the $^5D_0 \rightarrow {}^7F_2$ transition are also plotted as a function of heat-treatment temperature: the dependence of the fluorescence intensity on temperature is in contrast to that of the hole depth. The increase in the fluorescence intensity with the increased temperature is due to the reduction of the OH groups around the Eu^{3+} ions. Thus, these experimental results indicate that the hole burning is related with the residual OH groups in the glass.

To study the effect of OH groups on the hole burning, the glasses were heated at 800 °C in air and vacuum, the PSHB and infrared (IR) absorption spectra of which are shown in Fig. 3. It is apparent that the hole burnt in glass heated for a long time decreases in depth and no hole is burned after 10 h. The IR spectrum of glass heated at 800 °C in air has two absorption bands at 3650 and 3400 cm^{-1}, which are both assigned to the fundamental OH stretching. The position of the OH-absorption bands depends on the degree of association to neighboring oxygen through hydrogen bonding. The bands shift to low wave numbers with increasing strength of hydrogen bonding.[20] The IR spectrum for SiO_2 glass containing no Eu_2O_3, measured for comparison, had a sharp absorption band at 3650 cm^{-1}. This band is assigned to the hydrogen-bonding free OH groups in the rigid silica network structure.[21] Compared with the SiO_2 glass, the presence of modifier ions such as alkali and alkaline earth in silicate glasses leads to the formation of broad bands at low wave number regions.[22] The broad band at 3400 cm^{-1} shown in
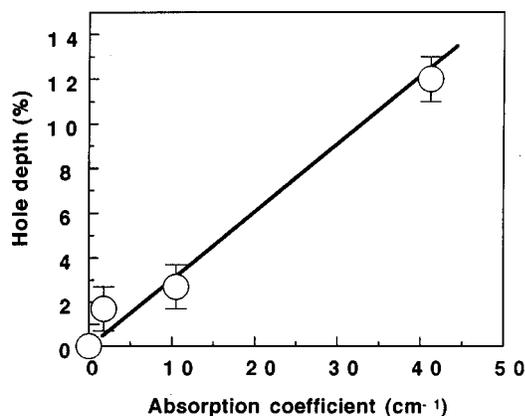
FIG. 4. Hole depth as a function of absorption coefficient of 3400 cm^{-1} band.

the Eu^{3+}-doped glass, therefore, can be attributed to the OH groups bound with the Eu^{3+} ions through hydrogen bonding. As shown in Fig. 3, the IR spectra preferentially decreased in the intensity of the 3400 cm^{-1} band during heating in vacuum, which were deconvoluted into two bands at 3650 and 3400 cm^{-1} using a Gaussian function and the result for glass heated in air was shown in the inset of Fig. 3. Among the deconvoluted bands, the absorption coefficient of the 3400 cm^{-1} band decreases with increasing the heat-treatment time, that is, 41, 11, and 2 cm^{-1} for 0, 5, and 10 h, respectively. On the other hand, the absorption coefficient of the 3650 cm^{-1} band is insensitive to the time and constant at 20–28 cm^{-1}. These experimental results indicate that the OH groups bound with Eu^{3+} ions are preferentially liberated during heating. The absorption coefficient of these bands is a measure of the concentration of OH groups, although the extinction coefficient of these OH bonds is not determined in this study. Figure 4 shows the relation between the hole depth and the absorption coefficient of the 3400 cm^{-1} band, satisfying the linear relation between two values. This indicates that the presence of OH groups bound with the Eu^{3+} ions is essential for the hole burning of the sol-gel-derived Eu^{3+}-doped glasses. We propose that the hole is formed by the concerted action of OH bonds in the first coordination sphere surrounding the Eu^{3+} ion. When the sample is irradiated with the high power laser, a proton in the EuOH bonds changes its position to form a different bonding feature. The rearrangement of proton in the EuOH bonds results in the hole burning. This burning mechanism is considered to be different from that of the Sm^{2+} ions, where the photoionization of Sm^{2+} into Sm^{3+} by laser irradiation is the main reaction.[8,23]

The stability of the holes depends on the recovery of the proton configuration from the burnt state to the unburnt state. Assuming a thermally activated recovery process, the optically activated state relaxes across the activation barrier to the unburnt configuration state. To investigate the thermal stability of the hole, the thermal hole-erasure measurements were performed for the glasses obtained by heating at 500 and 800 °C. A hole was formed at 77 K, at which the hole area was measured. After cycling through a certain temperature higher than 77 K, the area was again measured at 77 K. During this process, all the products with barriers lower than the activation barrier corresponding to that temperature re-
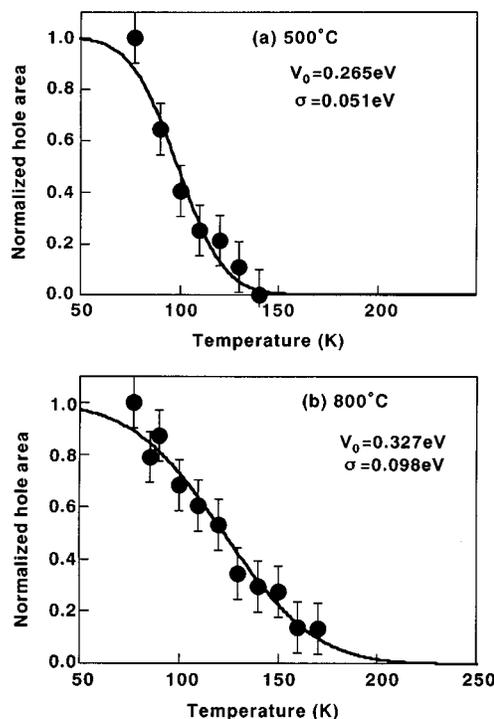
FIG. 5. Hole area as a function of cycling temperature of glass obtained by heating at 500 and 800 °C. The solid curves indicate a fit to data based on a Gaussian distribution function.

cover to the unburnt state. The PSHB spectra, recorded after cycling up to 160 K, of glass heated at 800 °C are shown in the inset of Fig. 1. The hole area that remains after this thermal cycle is normalized to unity at 77 K and plotted in Fig. 5 as a function of temperature. It is obvious that the hole area decreases as the temperature increases. The fraction of the remaining hole, F, is a measure of the fraction of the photoproducts whose activation barriers are greater than a critical barrier height, V, and given by[24–26]

$$FF = 1 - \int_0^{kT_{max}\ln(R_0 t)} g(V) dV, \qquad (1)$$

where R_0 is the attempt frequency of protons and t is the holding time at a certain cycling temperature T_{max}. Assuming that the barrier height follows a Gaussian distribution, $g(V)$ is written as

$$g(V) = (2\pi\sigma^2)^{-1/2} \exp[-(V-V_0)^2/2\sigma^2], \qquad (2)$$

with a central barrier height V_0 and the width σ. A fit of the data using Eq. (1) for both glasses is shown by solid curves in Fig. 5, where the fitting parameters are $V_0 = 0.27$ eV, $\sigma = 0.051$ eV and $V_0 = 0.33$ eV, $\sigma = 0.098$ eV for glasses heated at 500 and 800 °C, respectively. The obtained V_0 values are smaller than that required for the dissociation of proton from the EuOH bonds which is estimated as ~1 eV or larger from the measurement of proton conductivity of glasses.[21] Therefore it is considered that the hole burning is caused not by the dissociation of proton but by the optically activated rearrangement of position of protons in the Eu-O polyhedral. It is worth stressing that the V_0 value for glass heated at high temperature is larger than that heated at low temperature. This finding is good guidance for the develop-

ment of the glasses exhibiting PSHB at high temperature. However, it should be noted that the hole depth declines with this increased heat-treatment temperature.

We conclude that the hole burning in the Eu^{3+}-doped glass is caused by the photoactivated rearrangement of protons in the first coordinating sphere of Eu^{3+} ions. The burnt state has an activation barrier height of ~0.3 eV higher than that of the unburnt state. The hole depth proportionally in-

creases with the increase of OH content. The sol-gel method is appropriate to prepare the PSHB glasses because of its possibility to contain a large amount of OH bonds.

---

*Corresponding author; Fax: +81 52 735 5285; electronic address: nogami@mse.nitech.ac.jp

[1] G. Castro, D. Haarer, R. M. Macfarlane, and H. P. Trommsdorff, U.S. Patent No. 4 101 976 (1978).

[2] *Persistent Spectral Hole-Burning: Science and Applications*, edited by W. E. Moerner (Springer, Berlin, 1988).

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

[4] R. Yano, M. Mitsunaga, and N. Uesugi, J. Opt. Soc. Am. B **9**, 992 (1992).

[5] N. Peyghambarian, Nature (London) **378**, 339 (1995).

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

[7] J. Jhang, S. Huang, and J. Yu, J. Lumin. **56**, 51 (1993).

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

[9] T. Izumitani and S. A. Payne, J. Lumin. **54**, 337 (1993).

[10] K. Hirao, S. Todoroki, K. Tanaka, N. Soga, T. Izumitani, A. Kurita, and T. Kushida, J. Non-Cryst. Solids **152**, 267 (1993).

[11] R. M. Macfarlane and R. M. Shelby, Opt. Commun. **45**, 46 (1983).

[12] Th. Schmidt, R. M. Macfarlane, and S. Volker, Phys. Rev. B **50**, 15 707 (1994).

[13] D. M. Boye, R. M. Macfarlane, Y. Sun, and R. S. Meltzer, Phys. Rev. B **54**, 6263 (1996).

[14] M. Nogami and Y. Abe, Appl. Phys. Lett. **64**, 1227 (1994).

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

[16] M. Nogami and Y. Abe, Phys. Rev. B **56**, 182 (1997).

[17] M. Nogami and Y. Abe, Appl. Phys. Lett. (to be published).

[18] R. Campostrini, G. Carturan, M. Ferrari, M. Montagna, and O. Pilla, J. Mater. Res. **7**, 745 (1992).

[19] M. J. Lochhead and K. L. Bray, J. Non-Cryst. Solids **170**, 143 (1994).

[20] Y. Abe, H. Hosono, Y. Ohta, and L. L. Hench, Phys. Rev. B **38**, 10 166 (1988).

[21] M. Nogami and Y. Abe, Phys. Rev. B **55**, 12 108 (1997).

[22] H. Scholze, Glastech. Ber. **32**, 142 (1959).

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

[24] S. P. Love, C. E. Mungan, A. J. Sievers, and J. A. Campbell, J. Opt. Soc. Am. B **9**, 794 (1992).

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

[26] H. Yugami, R. Yagi, S. Matsuo, and M. Ishigame, Phys. Rev. B **53**, 8283 (1996).