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Persistent Spectral Hole Burning in Eu^{3+}-Doped Silicate Glasses Codoping Al^{3+} and P^{5+} Ions

Masayuki Nogami,* Takehito Nagakura, Tomokatsu Hayakawa, and Tomokazu Sakai

Nagoya Institute of Technology Showa Nagoya, 466-8555 Japan

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Eu^{3+}-doped SiO_2, $Al_2O_3-SiO_2$, and $P_2O_5-SiO_2$ glasses were prepared by a sol−gel method from metal alkoxides, and their persistent spectral hole burning (PSHB) properties were investigated in relation to the local environment of the Eu^{3+} ions in glass. Fluorescence line narrowing spectra indicated that Eu^{3+} clustering occurred in SiO_2 glass. The addition of Al_2O_3 or P_2O_5 promoted better dispersion of Eu^{3+} in the glass matrix, though two sites for Eu^{3+} ions seemed to exist in $Al_2O_3-SiO_2$ glass. The holes were burned in the $^7F_0 \rightarrow {}^5D_0$ line of the Eu^{3+} ions using a Rhodamine 6G dye laser, the hole area of which increased proportionally with the content of hydroxyl groups. The holes that were burned by the photoinduced rearrangement of the OH bonds were thermally refilled and the barrier height of the burnt-state was determined as 0.14, 0.30, and 0.40 eV for $P_2O_5-SiO_2$, SiO_2, and $Al_2O_3-SiO_2$ glass, respectively.

Introduction

Rare-earth-doped glasses have attracted significant attention because of their potential abilities for various applications, such as laser, upconversion and stimulated phosphor, and hole-burning high-density memory.[1,2] Among them, our research interest focuses on the persistent spectral hole burning (PSHB) glasses. Generally, PSHB, observed in many materials, is limited at extremely low temperature using liquid helium. For practical use in high-density frequency-domain optical data memory, high-temperature PSHB is required. Recently we succeeded in preparing Eu^{3+}- and Sm^{2+}-doped glasses with a sol−gel method, exhibiting PSHB above 200 and 300 K, respectively.[11−14] The samarium ions, incorporated in the trivalent state in glasses, are reduced into Sm^{2+} during melting the glasses in H_2 gas atmosphere. On the other hand, the Eu^{3+}-doped glasses are obtained without heating in reducing atmosphere; it thus becomes possible to extend the study beyond the limitations of the Sm^{2+}-doped glasses, though the temperature for PSHB is lower. So far, we have reported the PSHB spectra in Eu^{3+}-doped silica[13] and Eu^{3+}-doped aluminosilicate[14] glasses. It was suggested that the presence of water in glass is essential for hole burning and the stability of the burnt holes is related to the glass composition.[15] Further research on the hole burning of the Eu^{3+} ions doped into various glass compositions is necessary to both understand the mechanism of hole burning and to develop glasses exhibiting PSHB at high temperature.

Eu^{3+} ions have been investigated most frequently because of their unique fluorescence properties.[16−18] When doped in a silica glass, the Eu^{3+} ions cluster, resulting in quenching of the fluorescence.[19,20] This fluorescence quenching is significantly improved by codoping of a third cation in the silica matrix. Several researchers have noted that codoping with Al^{3+} and/or P^{5+} ions is effective at dispersing Eu^{3+} ions in silica and silicate glasses.[21] However it is not clear how these codoped cations contribute to the hole burning and the fluorescence properties.

In this paper, we compare for the first time the PSHB of Eu^{3+}-doped silicate glasses codoped with P^{5+} and Al^{3+} ions, and discuss the effect of glass composition on the stability of PSHB from thermal refilling experiments of the burnt holes. The local structure around the Eu^{3+} ions is studied by the fluorescence line narrowing technique.

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* Corresponding author. Telephone and Fax: 81 52 735 5285. E-mail: nogami@mse.nitech.ac.jp.

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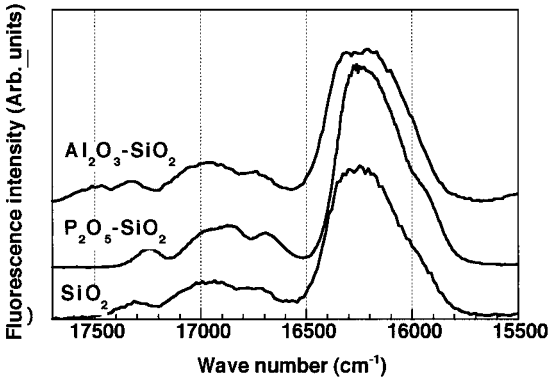

Figure 1. Fluorescence spectra, measured at room temperature, of Eu^{3+}-doped SiO_2, $Al_2O_3-SiO_2$, and $P_2O_5-SiO_2$ glasses using a Xe lamp at 394 nm wavelength as pumping source.

Experiments

Sample Preparation. First, $100SiO_2$, $10Al_2O_3{\cdot}90SiO_2$ and $5P_2O_5{\cdot}95SiO_2$ (mole ratios) glasses containing nominally 2 wt % Eu_2O_3 were prepared by the hydrolysis of $Si(OC_2H_5)_4$, $Al(OC_4H_9^{sec})_3$, $PO(OCH_3)_3$, and $Eu(NO_3)_3{\cdot}6H_2O$. The starting materials were commercially available and used as received. The $Si(OC_2H_5)_4$ was first hydrolyzed with a mixed solution of H_2O, C_2H_5OH, and HCl as a catalyst. Then, $Al(OC_4H_9^{sec})_3$ or $PO(OCH_3)_3$ was reacted with this partially hydrolyzed $Si(OC_2H_5)_4$ to form a Al−O−Si or P−O−Si alkoxide complex. After adding $Eu(NO_3)_3{\cdot}6H_2O$ dissolved in C_2H_5OH, the solution was further hydrolyzed with H_2O and then dried to form a stiff gel. A detailed explanation of gel preparation is given elsewhere.[13−15] The dried gel was heated to 150 °C in a tightly sealed vessel together with water and held for 15 h to completely hydrolyze the alkoxides. The resulting gel was heated in air at 50 °C/h to 600−800 °C and held at that temperature for 2 h.

Measurements of Fluorescence Spectra and Hole Burning. Broadband fluorescence spectra were recorded at room temperature using a Xe lamp at 394 nm wavelength as the pumping source. The energy of the 394 nm wavelength matches the $^7F_0 \rightarrow {}^5L_6$ transition of the Eu^{3+}. The fluorescence line-narrowing measurement was conducted under excitation with a wavelength within the $^7F_0 \rightarrow {}^5D_0$ transition using Rhodamine 6G dye laser. The FL intensity was measured with a chopper that alternately opened the optical paths before and after the sample. The chopping frequency was 150 Hz. All spectra were recorded at 77 or 6 K with the Jobin Yvon HR 320 monochromator.

The PSHB was observed on the excitation (EX) spectrum of the $^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+}. The EX spectrum was obtained by scanning the output of a cw Ar^+ ion laser-pumped Rhodamine 6G dye laser with a line width of ~1.0 cm^{-1} full width at half-maximum (fwhm) from 17 100 to 17 500 cm^{-1} while monitoring the fluorescence of the $^5D_0 \rightarrow {}^7F_2$ transition band. The glass was then irradiated for 30 min using Rhodamine 6G dye laser operating at 300 mW with the spot size of about 1 mm diameter. After irradiation, the EX spectrum was recorded in the same way. The laser power for scanning was attenuated by ND filters to <0.2% of that for burning.

Results and Discussion

Fluorescence Spectra. Figure 1 shows the room-temperature broadband fluorescence spectra for Eu^{3+} doped in SiO_2, $P_2O_5-SiO_2$, and $Al_2O_3-SiO_2$ glasses. All the spectra consist of three broadened bands peaking at around 17 300, 16 900, and 16 300 cm^{-1}, which are assigned to the transitions from $^5D_0$ to $^7F_0$, $^7F_1$, and $^7F_2$ states, respectively. Among them, the $^5D_0 \rightarrow {}^7F_0$ transition is nondegenerate and not subject to crystal field splitting changes in the vicinity of the Eu^{3+} ion. Therefore, the position and line width (fwhm) of this 0−0 transition provide a measure of the local bonding environment of the Eu^{3+} ion. It is evident that $Al_2O_3-SiO_2$ glass exhibits a broadened (130 cm^{-1} fwhm) band with high energy (17 340 cm^{-1}) compared with those in SiO_2 glass (120 and 17 320 cm^{-1}). In contrast, the $^5D_0 \rightarrow {}^7F_0$ band for $P_2O_5-SiO_2$ glass shifts to lower energy (17 250 cm^{-1}) and it becomes much narrower (60 cm^{-1}) in comparison with those for SiO_2 and $Al_2O_3-SiO_2$ glasses. These fluorescence properties suggest that the Eu^{3+} ions doped in $P_2O_5-SiO_2$ glass are more covalently bound with the surrounding oxygens. The two broad bands of the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole and the $^5D_0 \rightarrow {}^7F_2$ electric dipole transitions consist of multiple peaks due to their Stark splittings, but they are not well resolved.

The local environment around the Eu^{3+} ions has been widely studied by fluorescence line narrowing (FLN) spectroscopy.[16−18] The spectra were obtained by selective excitation across the inhomogeneously broadened $^7F_0 \rightarrow {}^5D_0$ absorption band, and are shown in Figure 2. For Eu^{3+}-doped SiO_2 glass (Figure 2a), no line-narrowing effect was observed in the shape and the peak positions of the components of the $^7F_1$ and $^7F_2$ states, and the spectra for the individual excitation energy are similar to the broad-band spectrum (see Figure 1). This behavior is similar to that observed in Eu^{3+}-doped SiO_2 glasses prepared by sol−gel and another methods.[16−20] The absence of the line-narrowing effect is explained by phonon-assisted energy transfer between adjacent Eu^{3+} ions in Eu^{3+} clusters. Clustering of Eu^{3+} leads to short distances between the Eu^{3+} ions. Because of this proximity, the Eu^{3+} ions resonant with the laser can transfer the energy to the adjacent nonresonant Eu^{3+} ions, resulting in spectral broadening. In addition, there is a appearance of $^5D_0 \rightarrow {}^7F_0$ fluorescence intensity adjacent to the excitation energy, providing direct evidence for the energy transfer between Eu^{3+} ions.

In contrast to the Eu^{3+}-doped SiO_2 glass, as seen in Figures 2b and 2c, P^{5+}- and Al^{3+}-codoped glasses exhibit a line-narrowing effect, which is extremely strong in Al^{3+}-codoped glass. This fact indicates that the Eu^{3+} ions do not cluster under codoping with the P^{5+} and Al^{3+} ions. Because the $^7F_0 \rightarrow {}^5D_0$ excitation energy is a measure of the strength of the crystal field acting on the central Eu^{3+} ions, such a spectral shift can be attributed to the variation of the local crystal field strength of the Eu^{3+} ions in glass. The $^5D_0 \rightarrow {}^7F_1$ band appears to consist of three peaks due to Stark splitting of the $^7F_1$ state, suggesting that the Eu^{3+} ions are located in a site with C_{2v} or lower symmetry. On the other hand, five components of the $^5D_0 \rightarrow {}^7F_2$ transition were not distinguished owing to experimental limitations. The splitting behavior of the Stark components is strongly dependent on the glass composition. In the $P_2O_5-SiO_2$ glasses, of the three lines of the $^5D_0 \rightarrow {}^7F_1$ band, the highest-energy line shifts to the higher-energy side with increasing excitation energy, whereas the two low-energy lines are almost independent of the excitation energy. This continuous change in the three components with the excitation energy indicates that the Eu^{3+} ions in the glass matrix have C_{2v} symmetry of ligand environment and are located in similar sites. Unlike the $P_2O_5-SiO_2$ glass, the $Al_2O_3-SiO_2$ glass shows a peculiar line-

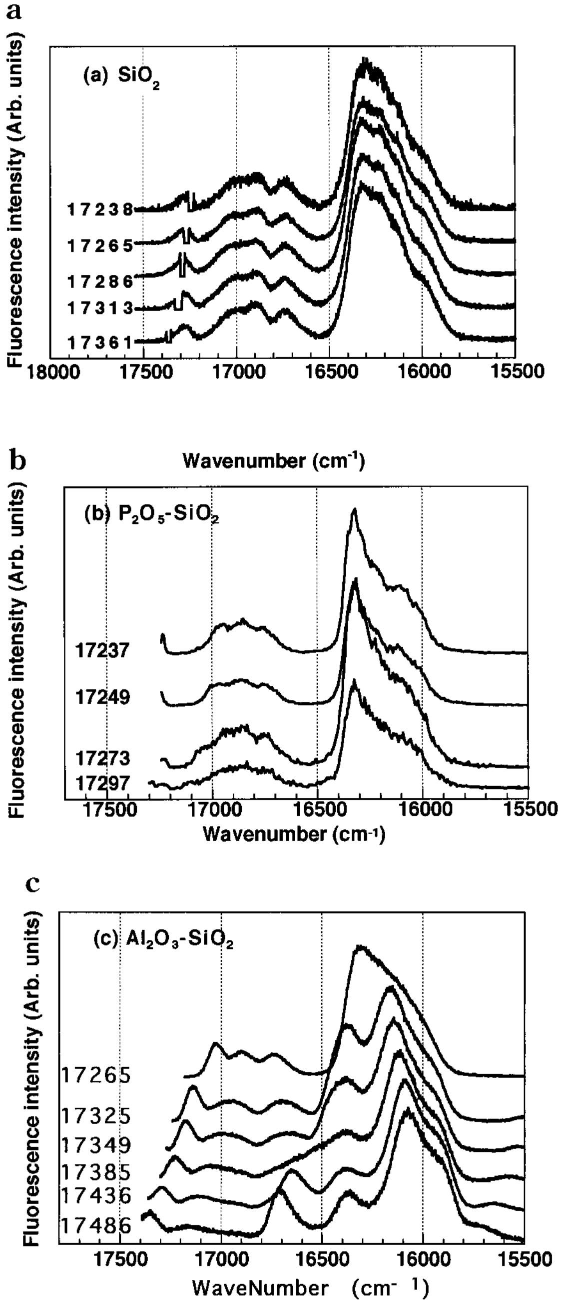

Figure 2. Fluorescence line-narrowing spectra of the $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+}-doped SiO$_2$, (b), P$_2$O$_5$−SiO$_2$, and (c) Al$_2$O$_3$−SiO$_2$ glasses. Spectra were measured under dye-laser excitation into the $^7F_0 \rightarrow {}^5D_0$ transition line at 6 K (P$_2$O$_5$−SiO$_2$) and 77 K (SiO$_2$, Al$_2$O$_3$−SiO$_2$). Numbers indicate the wavenumber of the excitation laser beam.

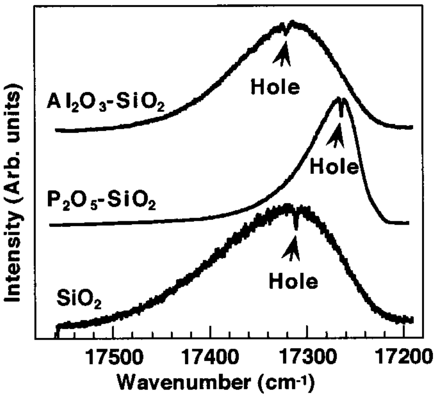

Figure 3. Hole-burning spectra of Eu^{3+}-doped SiO$_2$, Al$_2$O$_3$−SiO$_2$, and P$_2$O$_5$−SiO$_2$ glasses. Holes were burned and measured at 15 K (P$_2$O$_5$−SiO$_2$) and 77 K (SiO$_2$, Al$_2$O$_3$−SiO$_2$).

narrowing effect with the fluorescence peak shifting and intensity changing as the excitation energy is varied. In the lower excitation energy range, the three Stark components tend to converge to a triply degenerate point at around 16 800 cm^{-1} and disperse with increasing excitation energy. This behavior is similar to that observed in P$_2$O$_5$−SiO$_2$ glass. On the other hand, at excitation energy >17 350 cm^{-1}, the spectrum becomes increasingly asymmetric and has more than three components. In particular, a new band appears at around 16 700 cm^{-1}, the intensity of which increases with increasing excitation energy. These spectral changes with the excitation energy are also observed in the $^5D_0 \rightarrow {}^7F_2$ transition bands. The fluorescence of $^5D_0 \rightarrow {}^7F_2$ transition is divided into two main bands peaking at 16 300 and 16 000 cm^{-1} with the width of about 300 cm^{-1} fwhm. It is evident that the excitation at high energy leads to increased relative intensity of the band at 16 000 cm^{-1}. These results suggest that the Eu^{3+} ions are in two different site distributions. Further details will be discussed in a future paper.

PSHB Spectra. PSHB spectra were recorded on the excitation spectra of the $^7F_0 \rightarrow {}^5D_0$ transition by monitoring the fluorescence of the $^5D_0 \rightarrow {}^7F_2$ transition. Figure 3 shows the excitation spectra after hole burning with a laser with a power of 300 mW for 30 min. It is evident that holes are clearly observed at the burning-wavenumber, shown as arrows, for three different glasses. Furthermore the Eu^{3+}-doped P$_2$O$_5$−SiO$_2$ glass exhibits the lowest energy of the $^7F_0 \rightarrow {}^5D_0$ transition at 17 260 cm^{-1} with 63 cm^{-1} fwhm. Compared with the P$_2$O$_5$−SiO$_2$ glass, the Al$_2$O$_3$−SiO$_2$ and SiO$_2$ glasses exhibit broadened inhomogeneous bandwidths of 123 and 150 cm^{-1} fwhm, respectively, which are around twice that for the P$_2$O$_5$−SiO$_2$ glass. On the other hand, the widths of the burnt holes are ~2 (at 15 K), ~3 (77 K), and ~2 (77 K) cm^{-1} for the P$_2$O$_5$−SiO$_2$, Al$_2$O$_3$−SiO$_2$, and SiO$_2$ glasses, respectively. A capacity of the data storage of the memory devices is proportional to the ratio of width of the inhomogeneous band to that of the hole width. From this point of view, the wide inhomogeneous bandwidth in the SiO$_2$ and Al$_2$O$_3$−SiO$_2$ glasses may be promising material for memory devices with high-density data storage.

In our previous paper, we reported that the hole depth of the sol−gel-derived Eu^{3+}-doped glasses increased proportionally as the residual water content increased.[14,15] Water in glass is bound to the glass-network-forming cations, such as Si^{4+} and P^{5+} ions, in the form of hydroxyl groups, such as SiOH and POH, where the bonding strength of hydroxyl groups is dependent on the bond strength between oxygen and the cation. The Eu^{3+} ions are bound with oxygens and hydroxyl groups with a wide distribution of bond strength, resulting in the broadened fluorescence bands. When these Eu^{3+}-doped glasses are irradiated by a laser beam, the hydroxyl groups surrounding Eu^{3+} ions resonant with the laser energy change their bonding environment such as bond angles and distances. This rearrangement of the proton bonding can be considered to result in hole burning.[15]

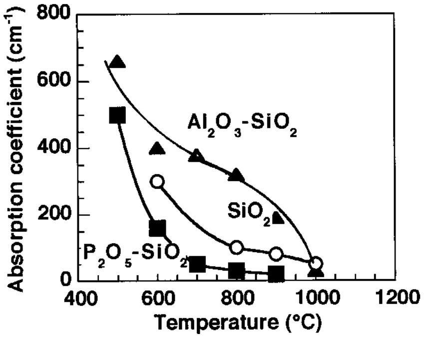

Figure 4. Infrared absorption coefficient of hydroxyl groups at around 3300 cm^{-1} as a function of the heat-treatment temperature of glasses.

Sol−gel-derived glasses are characterized by a large number of hydroxyl groups compared with glasses prepared by the conventional melt-quenching method. The gels synthesized through the hydrolysis of metal alkoxides are porous and contain a large amount of water incorporated during gel synthesis. Upon heating, these gels transform into glasses according to the dehydration−condensation of the hydroxyl groups and sintering. The dehydration−condensation reaction is strongly dependent on the gel composition and synthesis conditions, as established by infrared spectroscopic experiments. The IR absorption band position of the OH bonds can range from 3700 to 2500 cm^{-1}, depending on the degree of association to neighboring oxygen through hydrogen bonding, and is shifted to low wavenumber with increasing strength of hydrogen bonding.[22] The presence of modifier ions in silicate glasses leads to the appearance of bands at low wavenumber regions. It was found that the present glasses had the broad absorption band peaking at around 3300 cm^{-1}, and the absorption intensity was dependent on the glass composition and the heat-treatment temperature. Figure 4 shows the change in the absorption coefficient at peak wavenumber as a function of the heat-treatment temperature. It is evident that the absorption coefficient decreases with increasing the heat-treatment temperature and in the temperature range of 600 to 900 °C, the extent of hydroxyl group relation follows the order $Al_2O_3-SiO_2 > SiO_2 > P_2O_5-SiO_2$.

Holes were burned in the different three glasses obtained by heating at various temperatures, and the areas of these holes are plotted in Figure 5 as a function of the absorption coefficient at peak wavenumber. In this figure, the hole area is defined as the ratio of hole area to the total area of the $^7F_0 \rightarrow {}^5D_0$ excitation band. A linear dependence is observed between these two quantities, suggesting that the existence of the hydroxyl group is important for the hole burning.

Thermal Stability of Burnt Holes. A proposed mechanism for the hole burning is the laser-induced rearrangement of the hydroxyl groups surrounding the Eu^{3+} ions. When the sample is irradiated with a laser beam, the protons in the hydroxyl groups surrounding Eu^{3+} ions change their positions to form a different ligand environment, thereby producing holes. The stability of the hole-burnt state can be discussed from the temperature-dependent hole-erasure experiments. The hydroxyl groups in the hole-burnt state should have energies higher than those of the unburnt state and relax into the unburnt state. Thermal relaxation of the high-energy state is given by the following rate equation:[23]

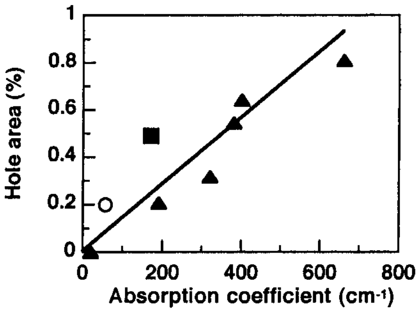

Figure 5. Hole area as a function of absorption coefficient of hydroxyl groups at around 3300 cm^{-1} of (○) Eu^{3+}-doped SiO_2, (▲), $Al_2O_3-SiO_2$, (■), and $P_2O_5-SiO_2$ (Å°) glasses.

$$R = R_0 \exp (V/kT) \tag{1}$$

where R_0 is the attempt frequency, V is the barrier height, k is the Boltzmann constant, and T is the temperature in K. Assuming that the barrier height follows a Gaussian distribution, $g(V)$, and the fraction of the remaining holes, F, is proportional to the number of photoproducts of the burnt state, the value of F is given by[23]

$$F(T) = 1 - \int_0^{kT\ln(R_0t_0)} g(V)\, \mathrm{d}V \tag{2}$$

where t_0 is the holding time at the holding temperature, T, which is higher than the burning temperature. The dependence of hole area on temperature was investigated from the temperature-cycling experiment of the hole spectra. A hole was burned at 15 K ($P_2O_5-SiO_2$) and 77 K (SiO_2 and $Al_2O_3-SiO_2$), the area of which was determined at the burning temperature. After cycling through a certain temperature higher than the burning temperature, the spectra were again measured at the burning temperature. During this process, the hole might be partially filled. The dependence of the hole area on the cycling temperature is presented in Figure 6 for $P_2O_5-SiO_2$, SiO_2, and $Al_2O_3-SiO_2$ glasses, where the hole area is normalized to unity at the burning temperature. It is obvious that the hole area decreases as the temperature increases. It is also interesting to note that the hole-erasing behavior is strongly dependent on the glass composition; that is, the holes are observed up to increasing temperatures in the order $Al_2O_3-SiO_2 > SiO_2 > P_2O_5-SiO_2$.

The dotted lines shown in Figure 6 are the fits of the data to eq 2. Among the fitting parameters, the barrier heights, V, of the burnt state over the unburnt state were estimated to be 0.14, 0.30, and 0.40 eV for $P_2O_5-SiO_2$, SiO_2, and $Al_2O_3-SiO_2$ glass, respectively. It is interesting to note that the largest V value is obtained for the glass containing a large amount of the hydroxyl groups up to the highest temperature. The V-value is a measure of the stability of PSHB and dependent on the

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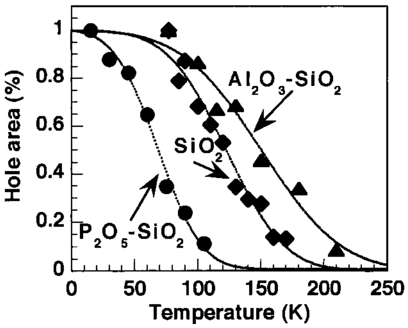

Figure 6. Relation between the hole area and the cycling temperature of Eu^{3+}-doped SiO$_2$, Al$_2$O$_3$−SiO$_2$, and P$_2$O$_5$−SiO$_2$ glasses. The dotted curves indicate a fit to data based on a Gaussian distribution function (see text).

strength of the hydroxyl bonding to the Eu^{3+} ions, although the physical reasons for this barrier are not clear at present. The hydroxyl groups are coordinated to the Eu^{3+} ions, and the hydrogen-bonding strength is strongly dependent on the bond strength between oxygen and the glass-network-forming cations, such as Al, P, and Si ions. Because the POH group exhibits the strongest extent of hydrogen bonding, the hydroxyl bond is easily changed by the small energy, resulting in small *V* values. This discussion, which will be presented in a future paper, should be instructive for developing glasses exhibiting PSHB up to high temperatures.

Conclusion

We could burn persistent holes in the $^7F_0 \rightarrow {}^5D_0$ line of Eu^{3+}-doped SiO$_2$, Al$_2$O$_3$−SiO$_2$, and P$_2$O$_5$−SiO$_2$ glasses prepared by the sol−gel method from metal alkoxides. It was first found that the hole area increased proportionally with the content of hydroxyl groups in the glass. The proposed mechanism for hole burning is the laser-induced rearrangement of the hydroxyl groups surrounding the Eu^{3+} ions. The barrier height of the burnt state over the unburnt state was determined as 0.14, 0.30, and 0.40 eV for P$_2$O$_5$−SiO$_2$, SiO$_2$, and Al$_2$O$_3$−SiO$_2$ glass, respectively. Fluorescence line-narrowing spectra indicate that the Eu^{3+} ions clustered in SiO$_2$ glass. The addition of Al$_2$O$_3$ or P$_2$O$_5$ promotes better dispersion of Eu^{3+} in the glass matrix, though two sites exist for Eu^{3+} ions in Al$_2$O$_3$−SiO$_2$ glass.

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