Room-temperature photochemical hole burning of Eu^{3+} in sodium borate glasses

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Abstract

Persistent spectral hole burning (PSHB) has been observed at 77 K to room temperature for Eu^{3+} in sodium borate glasses with compositions of xNa$_2$O $\cdot$ $(100 - x)$B$_2$O$_3$ ($x = 10, 25, 35$). Glasses melted in air do not show the phenomenon of PSHB, while room-temperature PSHB occurs in the glasses prepared by melting in reducing conditions. ^{151}Eu Mössbauer spectra reveal that europium ions are present as both Eu^{3+} and Eu^{2+} in glasses melted in reducing conditions. The relative hole area increases with an increase in the molar ratio of Eu^{2+} to Eu^{3+} when the content of Eu^{2+} is low, whereas the relative hole is almost independent of the molar fraction of Eu^{2+} when the content of Eu^{2+} is high. Furthermore, a comparison of hole burning among sodium borate glasses with the molar fraction of Eu^{2+} being almost the same as one another shows that the hole area grows larger as the content of Na$_2$O becomes higher. These observations are interpreted in terms of the photoinduced redistribution of electric charges between Eu^{3+} and Eu^{2+}. The effect of the glass composition on hole widths is also discussed based on the structural change in sodium borate glasses.

1. Introduction

The phenomenon of spectral hole burning has attracted considerable attention because of its potential application to the high-density optical storage utilizing frequency domain. Recent efforts of the studies on spectral hole burning have been devoted to the discovery of high-temperature persistent spectral hole burning (PSHB) in amorphous materials such as glasses. This is of great importance for the application of spectral hole burning to information storage, and it produces persistent spectral holes that can be used as high-resolution spectral probes

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in glasses. Sm^{2+}-doped glasses have been reported as room-temperature PSHB materials and showed various interesting material properties [1–3].

For Eu^{3+}-doped glasses, on the other hand, it is known that an optical pumping which leads to a redistribution of electrons among $^7F_0$ sublevels split due to nuclear hyperfine interactions bring about spectral hole burning at very low temperatures. The spectral hole burning caused by the optical pumping mechanism has been observed in Eu^{3+}-doped silicate glass below 10 K [4, 5]. However, Mao *et al* [6] showed that a glass with $74.8SiO_2 \cdot 22.0Al_2O_3 \cdot 3.2Eu_2O_3$ composition prepared in a helium atmosphere exhibits PSHB at a liquid nitrogen temperature. Nogami and Abe [7, 8] also reported high-temperature PSHB of Eu^{3+} in sol–gel-derived SiO_2 and Al_2O_3–SiO_2 glasses. For instance, the spectral hole burning is observed at 200 K for the Eu^{3+}-doped Al_2O_3–SiO_2 glass prepared by the sol–gel method.

Recently, our research group found that the PSHB is observed even at room temperature for Eu^{3+} in sodium aluminosilicate and silicate glasses [9, 10]. As for the sodium silicate glasses, glasses prepared in air do not show PSHB at room temperature, whereas the room-temperature PSHB is observed in glasses melted in a nitrogen atmosphere. Similar room-temperature PSHB has also been reported in other Eu^{3+}-doped silicate glass systems [11, 12]. In all the reported cases, europium ions were present as both Eu^{3+} and Eu^{2+}; Eu^{3+} was partly reduced to Eu^{2+} during melting under reducing conditions. Hence, the degree of reduction which brings about the formation of Eu^{2+} inevitably has an influence on the occurrence of PSHB. We briefly reported the effect of the degree of reduction on PSHB of Eu^{3+} in glasses with $35Na_2O \cdot 65B_2O_3$ composition, and observed that the efficiency of hole burning changes with the concentration of the coexisting Eu^{2+} [13]. Nonetheless, the mechanism of room-temperature PSHB of Eu^{3+} in glasses prepared by melting in reducing conditions is less clear.

It is anticipated that different glass hosts lead to changes in the hole-burning properties of Eu^{3+}, which may give an indication about the hole-burning mechanism of Eu^{3+}. In the present paper, we investigate the dependence of the hole-burning efficiency on the composition of glass as well as on the concentration of coexisting Eu^{2+}. Binary sodium borate glasses were selected as hosts because the electronic structure and basicity of glass vary systematically with sodium contents. The variation of the hole width with the glass composition is also discussed based on the structural change of sodium borate glasses.

2. Experimental procedure

Glasses were prepared from reagent-grade Eu_2O_3, Na_2CO_3 and B_2O_3 as starting materials. First the raw materials were mixed thoroughly to produce a composition of $xNa_2O \cdot (100 - x) B_2O_3 \cdot 2.0Eu_2O_3$ with $x = 10$, 25, and 35 in molar ratio, and the mixture was melted in air at $1100\,°C$ for 30 min in a platinum crucible. The resultant Eu^{3+}-containing glass was remelted under an N_2 or a 50% N_2–47.5% Ar–2.5% H_2 atmosphere at 1100–$1400\,°C$ for 30–60 min using a glassy carbon crucible in an electronic furnace made of a graphite heater, an insulator and a water jacket. The melt was cooled slowly to room temperature. The glass thus obtained was cut into a rectangular parallelepiped with dimensions of 10 mm × 10 mm × 5 mm and the surfaces were polished by CeO_2 slurry.

^{151}Eu Mössbauer effect measurements were performed to estimate the molar fraction of Eu^{2+} and Eu^{3+} ions in the resultant glass samples. The measurements were carried out at room temperature using a conventional transmission geometry (Laboratory Equipment Corporation) with a 1.85 GBq $^{151}Sm_2O_3$ as a 21.5 keV γ-ray source. Calibration of the Doppler velocity was done with the magnetic hyperfine spectrum of α-Fe foil obtained by using a 14.4 keV γ-ray of ^{57}Co doped in metallic rhodium. The Mössbauer spectrum of EuF_3 was used as a standard for the isomer shift.

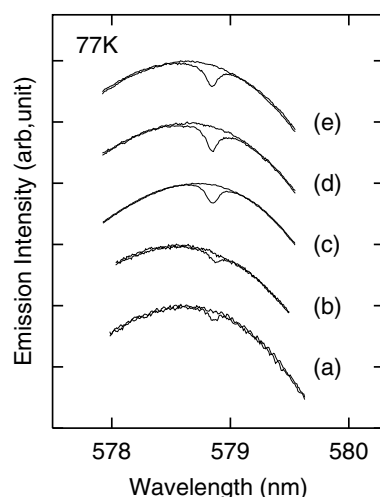**Figure 1.** Hole burning for the $^5D_0$–$^7F_0$ transition of Eu^{3+} in $25Na_2O \cdot 75B_2O_3$ glasses at 77 K. The holes were burned at a wavelength of 578.8 nm for 300 s. The glasses were prepared by melting at various reducing conditions. The symbols (a) to (e) correspond to the melting conditions as follows: (a) 1100 °C for 30 min, N_2, (b) 1200 °C for 30 min, N_2, (c) 1300 °C for 30 min, N_2, (d) 1300 °C for 30 min, N_2+Ar+H_2, and (e) 1400 °C for 30 min, N_2+Ar+H_2.

Spectral holes were burned into $^5D_0$–$^7F_0$ transition of Eu^{3+} using a Rhodamine 6G dye laser (Spectra Physics 375B, linewidth $\sim$1.3 cm^{-1}) pumped by an Ar^+ laser. A typical laser intensity under the burning was 10 W cm^{-2}, and the burning time was 300 s. For hole detection the laser wavelength was scanned, while the fluorescence of $^5D_0$–$^7F_2$ transition of Eu^{3+}, selected with a monochromator combined with a red glass filter, was detected with a photomultiplyer tube (Hamamatsu Photonics R928). The laser power for reading was $\sim$0.25% of that for burning. For the measurements below the room temperature, the sample was fixed in a cryogenic refrigerator (Iwatani Plantech, Model CRT-006-2000) equipped with a compressor (Iwatani Plantech, Model CA101). In this apparatus, low temperatures can be accomplished by the adiabatic expansion of helium gas supplied by the compressor.

3. Results

A persistent spectral hole was readily observed from 77 K to room temperature in all of the Na_2O–B_2O_3 glass systems. Irradiation with a dye laser for about 30 s was usually enough to produce a measurable hole at room temperature. The lifetime of the hole was several days. Figure 1 shows hole spectra at 77 K for $25Na_2O \cdot 75B_2O_3$ glasses prepared by melting in various reducing conditions. It is clear that the hole area changes with the degree of reduction.

In order to clarify the relationship between the relative hole area and the molar fraction of Eu^{2+} in the total number of europium ions, ^{151}Eu Mössbauer effect measurements were carried out so that the molar fraction of Eu^{2+} was estimated. In figure 2 are shown the room-temperature Mössbauer spectra of the $25Na_2O \cdot 75B_2O_3$ glasses prepared under different conditions. Two absorption bands centred at around IS = -13 mm s^{-1} and 0 mm s^{-1}, where IS represents the isomer shift, are ascribed to Eu^{2+} and Eu^{3+} ions, respectively, according to previous reports on several glass systems [14–17]. The fraction of the absorption area of Eu^{2+} with respect to the total absorption area was estimated from the spectra.
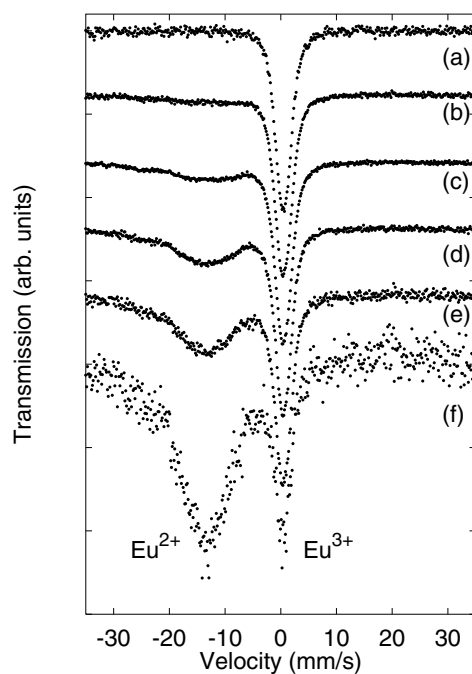
Figure 2. Room-temperature Mössbauer spectra of $25Na_2O \cdot 75B_2O_3$ glasses prepared under various melting conditions: (a) air, (b) $1100\,^{\circ}C$ for 30 min, N_2, (c) $1200\,^{\circ}C$ for 30 min, N_2, (d) $1300\,^{\circ}C$ for 30 min, N_2, (e) $1300\,^{\circ}C$ for 30 min, N_2+Ar+H_2, and (f) $1400\,^{\circ}C$ for 30 min, N_2+Ar+H_2.
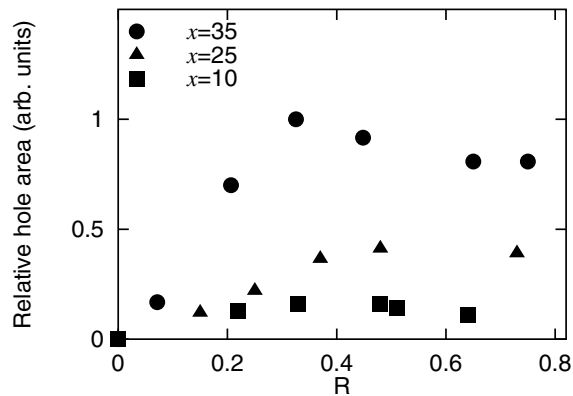

Figure 3. Dependence of relative hole area at 77 K on the relative absorption area of Eu^{2+} in the total area of Mössbauer spectrum, R, for $xNa_2O \cdot (100-x)B_2O_3$ glasses with $x = 10$, 25, and 35. The hole was burned at the wavelength of 578.8 nm for 300 s.

In figure 3, the relative hole area is plotted against the fraction of the absorption area of Eu^{2+} in the Mössbauer spectrum, R. In the figure, the hole area in the ordinate is normalized to the observed maximum value. In all the glasses, the relative hole area increases with an increase of the relative absorption area of Eu^{2+} in the range below $R \sim 0.35$, and then becomes
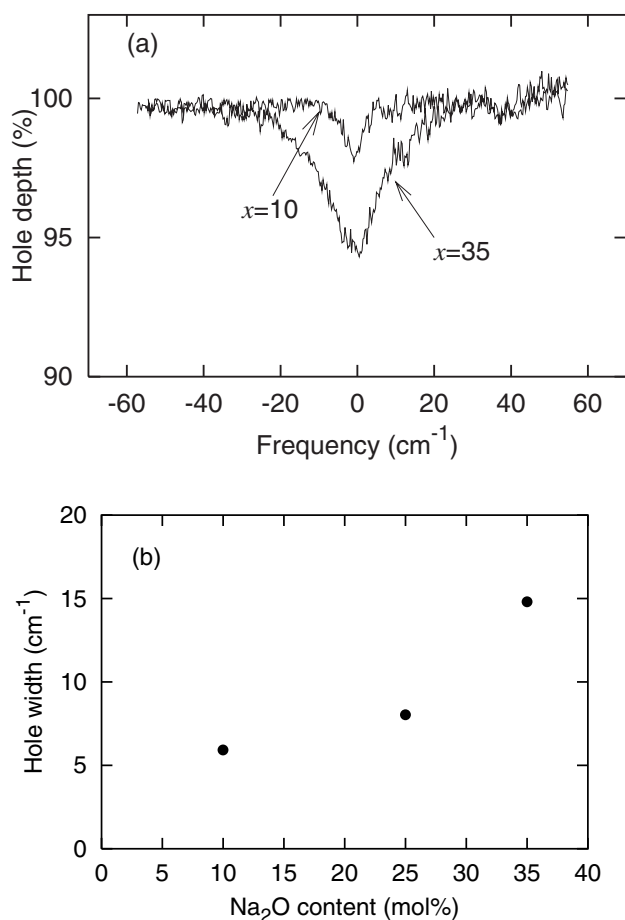
Figure 4. (a) Hole spectra at room temperature for the $^5D_0$–$^7F_0$ transition of Eu^{3+} in xNa$_2$O · $(100-x)$B$_2$O$_3$ glasses with $x = 10$ and 35. The holes were burned at a wavelength of 578.8 nm for 300 s. The glasses with $x = 10$ and $x = 35$ were prepared by melting at 1300 °C for 30 min in an N$_2$ atmosphere and at 1300 °C for 30 min in an N$_2$ + Ar + H$_2$ atmosphere, respectively. Both the glasses contain nearly equal concentration of Eu^{2+}. (b) Hole width at room temperature as a function of Na$_2$O content for xNa$_2$O · $(100-x)$B$_2$O$_3$ glasses with $x = 10$, 25, and 35. The measurements of hole burning were performed under the same condition as in (a).

almost independent of R. It should be stressed that the absorption area ratio is not equal to the molar ratio of Eu^{2+} to Eu^{3+}, since the temperature dependence of recoil-free fraction of Eu^{2+} is different between Eu^{2+} and Eu^{3+}. Coey *et al* [14] reported that the Debye temperatures were 145 and 261 K for Eu^{2+} and Eu^{3+}, respectively, in a fluorozirconate glass. These values were obtained by analysing the temperature dependence of recoil-free fraction. The recoil-free fraction, f, is expressed as

$$f = \exp\left\{-\frac{3E_R}{2k\theta_D}\left[1 + 4\left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x}{e^x - 1}\,\mathrm{d}x\right]\right\} \tag{1}$$

where E_R is the recoil energy, T is the temperature, θ_D is the Debye temperature, and k is the Boltzmann constant. By substituting the above Debye temperatures into equation (1), one can find that the molar fraction of Eu^{2+} in the total number of europium ions is about

0.5 at $R \sim 0.35$. Thus, the efficiency of hole burning becomes almost independent of the concentration of Eu^{2+} when the content of Eu^{2+} exceeds that of Eu^{3+}.

Figure 4(a) shows the room-temperature hole spectra for Eu^{3+} doped in $10Na_2O \cdot 90B_2O_3$ glass and $35Na_2O \cdot 65B_2O_3$ glass where the molar fraction of Eu^{2+} is nearly identical. Both the hole spectra were obtained by subtracting the excitation spectrum of the sample before laser irradiation from that after laser irradiation. The hole area is about five times larger for $35Na_2O \cdot 65B_2O_3$ glass than for $10Na_2O \cdot 90B_2O_3$ glass. The dependence of the hole width on Na_2O content is shown in figure 4(b). The hole width becomes wider as the concentration of Na_2O is increased.

4. Discussion

4.1. Relationship between hole area and Eu^{2+} content

As shown in figure 3, the efficiency of hole burning increases with an increase of the molar fraction of Eu^{2+} when the content of Eu^{2+} is low. This result, along with the absence of the persistent hole in glasses without Eu^{2+}, indicates that reduced species such as Eu^{2+} play an essential role in the process of the high-temperature PSHB of Eu^{3+} in glasses prepared by melting in reducing conditions. Although the detailed hole-burning mechanism still remains open, we tentatively assume the photoinduced redistribution of electric charges between Eu^{3+} and Eu^{2+};

$$Eu^{3+} + Eu^{2+} \xrightarrow{\hbar\omega} (Eu^{3+})^- + (Eu^{2+})^+. \tag{2}$$

Here, $(Eu^{3+})^-$ and $(Eu^{2+})^+$ represent the apparent change in charge states of Eu^{3+} and Eu^{2+}, respectively. Our previous analysis by a fluorescence line narrowing (FLN) technique revealed that the stable environments around divalent and trivalent rare-earth are significantly different from each other in binary sodium borate glasses, owing to the difference in their valences and ionic radii [18]. As a result, the photoproducts are metastable compared with the original states, since the local structural rearrangement is not completely achieved in the rigid state below room temperature. In such a sense, the $(Eu^{3+})^-$ and $(Eu^{2+})^+$ are similar but not identical to Eu^{2+} and Eu^{3+}, respectively. The spatial redistribution of the 2+ and 3+ charge states of europium ions modifies the frequency of the $^5D_0$–$^7F_0$ transition of Eu^{3+}, and consequently, a persistent spectral hole is burned at the corresponding wavelength.

As we already reported [10], the room-temperature PSHB in Eu^{3+}-doped glasses occurred through a one-photon process. However, the equation (2) is presumably not initiated by the change in the valence state of Eu^{3+} when irradiated with the dye laser at a wavelength of ~ 580 nm, because the $^5D_0$ and $^7F_0$ states are strongly localized on Eu^{3+}. In such a situation, it is highly probable that Eu^{2+}, as well as Eu^{3+}, is active while irradiating with the visible radiation. An intense optical absorption band due to the $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} in glasses extends from UV to visible regions, and permanent refractive-index changes attributable to the photoionization of Eu^{2+} are induced using a visible laser light which lies on the far-red edge of the large absorption [19]. We propose that the modification of the electronic state relevant to Eu^{3+} takes place following the change in the valence state of Eu^{2+}, leading to the phenomenon of PSHB.

On the other hand, figure 3 also indicates that when the content of Eu^{2+} is large enough compared with the content of Eu^{3+}, the excess Eu^{2+} centres become inefficient for the hole-burning process. This is because equal concentrations of Eu^{2+} and Eu^{3+} are needed to form Eu^{3+} and Eu^{2+} pairs, as indicated by equation (2). Thus, the efficiency of hole burning tends to saturate in glasses containing a large amount of Eu^{2+} ions.

4.2. Compositional variation of hole area

The efficiency of hole burning is also significantly affected by the composition of sodium borate glasses, as shown in figure 4(a). It is also obvious from figure 3 that the efficiency of hole burning increases with the increase in Na$_2$O content when the molar fraction of Eu^{2+} remains constant. In the Na$_2$O–B$_2$O$_3$ glass system, the electron density on oxide ions, i.e. the basicity of glass, increases with an increase in Na$_2$O content because the electronegativity of Na (χ_{Na} = 1.01) is smaller than that of B (χ_B = 2.05) [20]. The experimental estimation of the local basicity around rare-earth ions in a Na$_2$O–B$_2$O$_3$ glass system led to a similar conclusion [21]. Since valence alternative europium ions favour the higher valence state in the glasses with higher basicity [15], the photoionization of Eu^{2+} to (Eu^{2+})$^+$, which initiates equation (2), is more pronounced in the borate glasses with higher Na$_2$O content. This makes the variation of electronic states concerning Eu^{3+} easy and induces the efficient PSHB. Namely, the dependence of the hole area on glass composition, as well as on Eu^{2+} content as mentioned in section 4.1, can be qualitatively interpreted according to the photochemical reaction of equation (2).

4.3. Compositional variation of hole width

The results of figures 4(a) and (b) also indicate that the hole width increases with an increase in sodium content. Our preliminary experiments revealed that the hole width grows larger as the burning time, t_b, is increased. As for 35Na$_2$O · 65B$_2$O$_3$ glass, for instance, the hole width at t_b = 30 s decreases by a factor of about two with respect to that at t_b = 300 s. In other words, the hole width becomes narrower at the smaller burning time. However, the relation between the hole width and the Na$_2$O content holds when the burning time remains constant; the hole width is larger in the sodium borate glass with higher Na$_2$O content. This tendency is the same as the compositional dependence of homogeneous width obtained from FLN measurements on Eu^{3+} in Na$_2$O–B$_2$O$_3$ glasses at room temperature [22]. Hence, it is reasonably assumed that the hole width observed reflects the homogeneous width, although the homogeneous width should be determined by one-half of the hole width at zero burning. On the other hand, Morgan and El-Sayed [23] found that the temperature dependence of the homogeneous width exhibits a T^2 dependence above 300 K for sodium borate glasses with low and high Na$_2$O contents by means of the FLN technique. Similar T^2 dependence was observed for the same transition of Eu^{3+} in various glasses in very wide temperature ranges above about 10 K [24, 25]. Some theories [26] have revealed that the nearly quadratic temperature dependence of the homogeneous width in glasses can be explained by the phase relaxation due to a two-phonon Raman process, allowing for low-frequency vibrational modes in glasses. Thus, we discuss the compositional dependence of hole width at room temperature based on the Raman process.

The probability of the Raman scattering of phonons is sensitive to the structural change of glass, because the density of states of phonons depends on the strength of the chemical bonds of the glass network. The high-frequency vibrational mode between oxygen and boron does not directly affect the homogeneous width, but the lower-frequency vibrational mode which originates from longer-range arrangements of ions contributes to the broadening of the homogeneous width via the Raman scattering of phonons. According to ^{11}B nuclear magnetic resonance (NMR) measurements on sodium borate glasses [27], the amount of three-coordinated boron decreases and that of four-coordinated boron increases up to 33 mol% Na$_2$O content. The molar fraction of four-coordinated boron increases in accordance with the equation

$$N_4 = \frac{x}{1-x} \qquad (3)$$

where x denotes the molar fraction of Na_2O. The dependence of N_4 upon Na_2O content begins to deviate from equation (3) at 29 mol% Na_2O, reaches a maximum at 35 to 40 mol% Na_2O and then gradually decreases with increasing Na_2O content. This fact indicates that non-bridging oxygen starts to form at 29 mol% and that the number of non-bridging oxygens increases as the Na_2O content increases further. The presence of the large amount of non-bridging oxygens weakens the average bond strength of glass-network structure. This enhances the density of states of low-frequency vibrational modes, and therefore, brings about the increase in the interaction of Eu^{3+} with low-frequency phonons. Consequently, the hole width becomes much larger in the $35Na_2O \cdot 65B_2O_3$ glass than in the $10Na_2O \cdot 90B_2O_3$ glass and $25Na_2O \cdot 75B_2O_3$ glass, indicating that the presence of non-bridging oxygens largely affects the hole width. The slightly large hole width for $25Na_2O \cdot 75B_2O_3$ glass compared with $10Na_2O \cdot 90B_2O_3$ glass may be ascribed to the variation in electron–phonon coupling strengths due to the increase in the four-coordinated boron as mentioned above. The structural units composed of the four-coordinated boron, in contrast to the three-coordinated boron, possess a negative charge, by which the positive charge of Eu^{3+} is satisfied. This makes Eu^{3+} close to its surrounding host glasses, which enhances the coupling strength between 4f electrons and low-frequency phonons even if the density of states of the phonons is not so largely varied. Thus it appears that the structural change from three-coordinated boron to four-coordinated boron also contributes to the increase in hole width.

5. Conclusions

We have demonstrated PSHB at 77 K to room temperature for binary sodium borate glasses prepared under reducing conditions. The efficiency of hole burning depends strongly on the composition of glasses as well as the reduction treatment of the glasses which alters the concentration of Eu^{2+}. Based on these results, it is suggested that the photoinduced recharging between Eu^{3+} and Eu^{2+} is responsible for the room-temperature PSHB phenomenon of Eu^{3+} in glasses. Furthermore, the hole width increases with the increase in sodium content. This trend can be related to structural changes of sodium borate glasses, which result from the variation of oxygen coordination number to boron ions and the change of the number of non-bridging oxygens. The existence of non-bridging oxygens more largely influences the dynamic properties, i.e. the magnitude of the hole width.

Acknowledgments

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