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Influences of Al^{3+} and Eu^{3+} concentration on PSHB properties of melt-quenched Al_2O_3–SiO_2 glasses

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Abstract

Spectral hole-burning has been carried out for glasses with compositions of Eu_2O_3-doped xAl_2O_3–$(100 - x)SiO_2$ ($x = 10, 20, 30, 40$) glasses prepared by melt-quenching. We investigated the effect of Al_2O_3 and Eu^{3+} ions on persistent spectral hole burning (PSHB). The spectral holes were burned on the excitation spectra of the $^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+} ions. Hole-depth increases with the content of Eu_2O_3. The content of Al_2O_3 influenced the hole-width rather than hole-depth. The hole-burning was presumably related to the electron transfer between the Eu^{3+} and the defect.

Keywords: Spectral hole-burning; Eu^{3+}-doped glass; Rare earth ion; Aluminosilicate

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1. Introduction

Persistent spectral hole-burning (PSHB) is an intriguing field in both academic and application [1]. PSHB is known to a powerful tool for high-resolution spectroscopy of the local environments of light absorbing centers in solids. At the same time, PSHB has the strong potential for application to frequency-domain optical memory. For this reason, various materials have been extensively studied for the PSHB material. However, most materials showed PSHB only at extremely low temperature, which is the most vital hindrance for routine use as a PSHB memory. Eu^{3+} embedded glasses are frequently cited as high temperature PSHB materials. For instance, Eu^{3+} in Al_2O_3–SiO_2 [2] or Na_2O–B_2O_3 [3] glass is a novel example that exhibits the hole-burning even at room temperature, although its actual mechanism in these glass systems is not yet clarified. It is well known that the PSHB is hypersensitive to the composition of glass matrix. Thus, systematic studies of PSHB along with compositional variation of the glasses are required to rational design or discovery of PSHB materials. For this purpose, we prepared the glass composition of xAl_2O_3–$(100 - x)SiO_2$ and have investigated Eu_2O_3 and Al_2O_3 ion concentration effect on PSHB.

2. Experimental

Five and 10 wt.% Eu_2O_3 contained glasses in the compositions of xAl_2O_3–$(100 - x)SiO_2$ ($x = 10, 20, 30, 40$) have been prepared by mixing reagents of SiO_2, Al_2O_3 and Eu_2O_3. The glasses were prepared using the technique of radio-frequency melting in air at ~1600 °C.

The spectral hole burning was observed on the excitation spectra of the $^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+} ions utilizing a cw Ar^+-ion laser-pumped Rhodamine 6G dye laser (Coherent, CR599) with a line width of $\sim 1.0\,cm^{-1}$ full-width at half maximum (FWHM) and a power of $\sim 300\,mW/mm^2$ for 30 min at 10 K. The hole spectra were taken by scanning the laser wavelength within the $^7F_0 \rightarrow {}^5D_0$ transition while monitoring the fluorescence of the $^7F_0 \rightarrow {}^5D_2$ transition of the Eu^{3+} ions. The fluorescence was detected by a monochromator (Jobin Yvon, HR 320) equipped with a photomultiplier (Hamamatsu, R955).

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3. Results and discussion

Hole was burned on the excitation spectrum of the $^7F_0 \rightarrow {}^5D_0$ transition with a laser power of 300 mW for 30 min. Fig. 1 shows the typical results of PSHB measurement performed at 10 K and room temperature (RT) for the 10% Eu^{3+}-doped $40Al_2O_3$–$60SiO_2$ glasses. A hole is clearly seen at the center of the spectrum. The hole-width (FWHM), estimated from a Lorentzian function fitting the curve of the hole profile, is 1.8 and 4.4 cm^{-1} at 10 K and RT, respectively. The hole-depth is 15 and 5%, respectively, of the total fluorescence intensity. The hole-depth was increased to the saturated value within a few hundred second of burning time independent of the burning temperature. This RT spectral hole-burning of the Eu^{3+} is quite intriguing because usually Eu^{3+} in aluminosilicate based matrix needs special treatments such as H_2 gas, X-ray treatment to achieve room temperature PSHB [4]. But our glasses are prepared without any treatment in ambient atmosphere. Similar result has been found in $10Al_2O_3$–$90SiO_2$ glass made by melt quenching [5].

The thermal stability of the hole is further studied in detail by the temperature-dependent hole-erasure measurement. The glass was initially burned at 10 K, heated up to a certain temperature above the 10 K, and then kept there for 15 min, followed by cool to 10 K. The hole was once more measured after such a procedure and compared with the initial hole. Fig. 2 shows relation between the hole-depth and the cycling temperature. The hole was partially filled during the cycling process, where the hole-depth decreased and hole-width increased as temperature increased. The hole was clearly observed even at RT independent of the glass composition although hole-depth is small. The shape of the cycling temperature curve was almost independent of the glass composition. The most difference is in the depth of the initial hole in which deeper hole is observed when the concentration of the Eu_2O_3 is high.

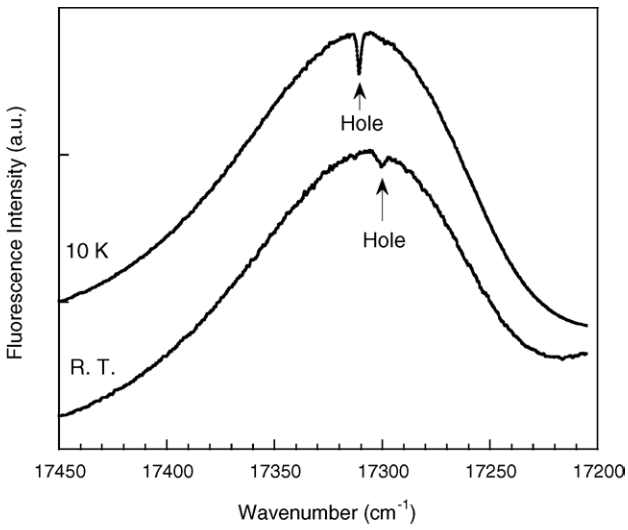

Fig. 1. Hole-burning spectra for the 10% Eu^{3+}-doped $40Al_2O_3$–$60SiO_2$ glasses. Holes were burned and measured at 10 K and room temperature.

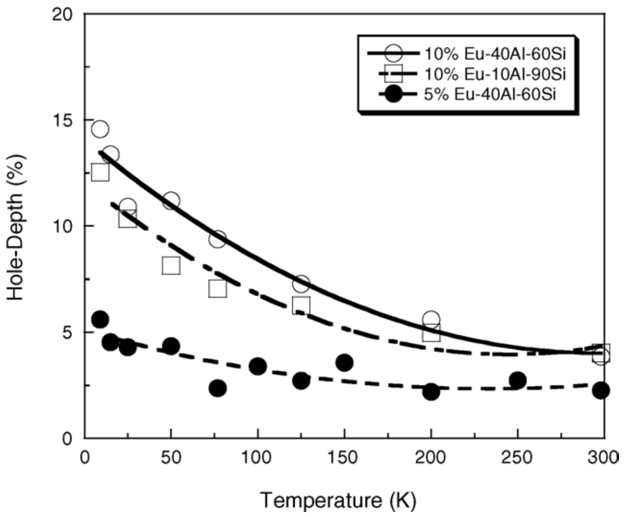

Fig. 2. Relation between the hole-depth and cycling temperature of Eu^{3+}-doped xAl_2O_3–$(100-x)SiO_2$ glasses ($x = 10$ and 40; denoted by 10Al–90Si and 40Al–60Si, respectively). Hole was burned at 10 K.

The effect of Al_2O_3 and Eu_2O_3 on the hole-burning efficiency such as hole-depth and hole-width is further analyzed at low temperature (10 K). Fig. 3 shows the dependence of the hole-depth and hole-width on the Al_2O_3 concentration. The hole-width is gradually decreased with the concentration, while the hole-depth is roughly constant. The structural units of Al^{3+} in aluminosilicate glasses are generally considered to be tetrahedral AlO_4 and octahedral AlO_6. In Al_2O_3–SiO_2 glasses, Nogami and Abe suggested that Eu^{3+} ion acts as network modifier ion in the glass and that its positive charge is compensated by the non-bridging oxygen bonded to both the Si^{4+} and Al^{3+} ions, in which the Al^{3+} ions form AlO_6 [6]. The decrease of the hole-width might be due to the weak interaction between Eu^{3+} and non-bridging oxygen bonded to Al^{3+} ions in AlO_6 that suppress the low frequency mode generation. Fujita et al. also has been conclude

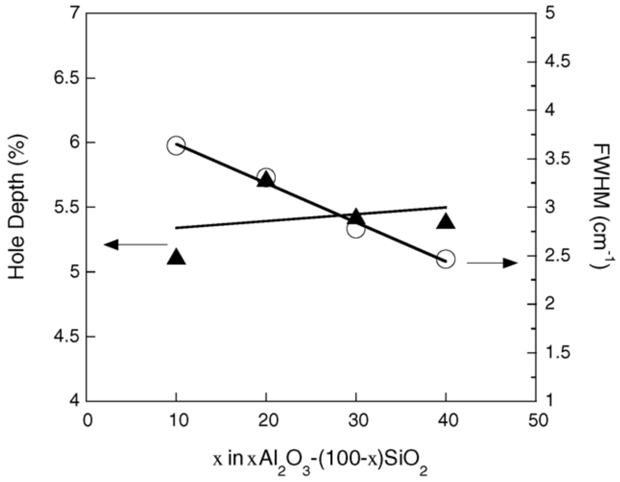

Fig. 3. Dependence of hole-width (◯) and depth (▲) on the Al_2O_3 concentration for the 5% Eu^{3+}-doped xAl_2O_3–$(100-x)SiO_2$ glasses.

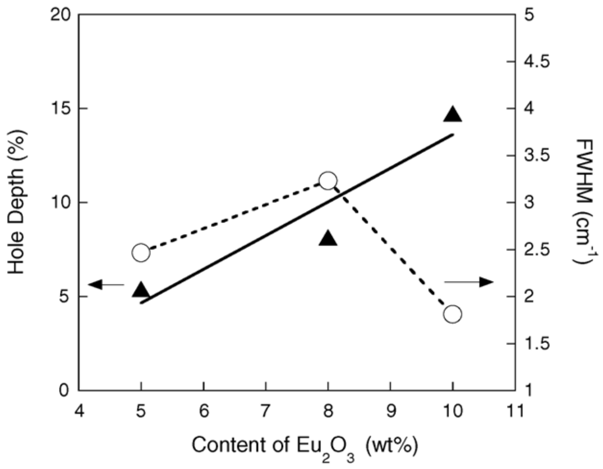

Fig. 4. Dependence of hole-width (○) and depth (▲) on the Eu_2O_3 concentration for $40Al_2O_3$–$60SiO_2$ glasses.

similar interpretation on the decrease of the hole-width in NaO–Al_2O_3–SiO_2 glasses with excess Al_2O_3 [7].

Fig. 4 shows the dependence of the hole-depth and hole-width on the Eu_2O_3 concentration. The hole-depth is drastically increased with the concentration, while the hole-width appears to be almost independent of the concentration. It has been found that a high field strength of modifier ions such as rare earth ions lead to highly disordered structures in aluminosilicate glasses and Utegulov et al. reported that structural disorder associated with Al^{3+} site increases as the concentration of Eu_2O_3 increases [8]. Such structural deformation could be happen in our samples and it must be accompanied with the oxygen related defect formation around Eu^{3+} ions. These defects would serve as hole-trapping centers during the hole-burning process though its exact nature is unclear at this point. This would explain why the hole-depth increased along with the content of Eu_2O_3. Though Eu^{2+} ions also could act as the hole-trapping center [3], we could not found any notable relationship between the concentration of the Eu^{2+} ions and the glass composition by ESR measurement. Nevertheless, the role of Eu^{2+} cannot totally be neglected, because the increased content of Eu_2O_3 also may result in shortened distance between the Eu^{3+} and Eu^{2+} independent of the total Eu^{2+} content. Considering usual absorption density near the burning-laser wavelength (around 576 nm) is small, it is reasonable to think that role of the defect is more important. Thus, we tentatively surmise that most significant factor for the current RT. PSHB is the energy or electron transfer between the Eu^{3+} and the defect in close proximity. On the other word, the burning laser resonates with defect center and resulting ejected electron from the defect is captured by Eu^{3+} to yield Eu^{2+}.

4. Conclusions

We have investigated the influence of Al_2O_3 and Eu_2O_3 on PSHB in Eu^{3+}-doped Al_2O_3–SiO_2 glasses. Hole-depth increased with the content of Eu_2O_3. On the other hand, it appears that the presence of large amount of Al_2O_3 unit more largely influences the hole-width rather than the hole-depth. Though a mechanism of the hole-burning is not clear at this point, we suppose that the process is the electron transfer between the Eu^{3+} and the defect center.

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