

## Persistent Spectral Hole Burning in $\text{Eu}^{3+}$ -doped Calcium Oxide- and Calcium Fluoride-based Aluminoborate Glasses

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$\text{Eu}^{3+}$ -doped oxyfluoride glasses with composition of  $30\text{CaF}_2\text{-}10\text{Al}_2\text{O}_3\text{-}60\text{B}_2\text{O}_3$  (mol %) and oxide glasses of  $30\text{CaO-}10\text{Al}_2\text{O}_3\text{-}60\text{B}_2\text{O}_3$  (mol %) were prepared in a reducing atmosphere. The persistent spectral hole burning (PSHB) was characterized over a temperature range from 10 to 300 K, and the hole-burning efficiency between  $\text{Eu}^{3+}$ -doped glass matrix of  $30\text{CaF}_2\text{-}10\text{Al}_2\text{O}_3\text{-}60\text{B}_2\text{O}_3$  and  $30\text{CaO-}10\text{Al}_2\text{O}_3\text{-}60\text{B}_2\text{O}_3$  was compared.

Recently, there has been considerable interest in the study of persistent spectral hole burning (PSHB) for its attractive applications in frequency domain optical storage (FDOS), spectral filtering, and optical waveform processing.<sup>1</sup> Up to now, different kinds of materials showing PSHB properties at low temperature have been studied.<sup>2,3</sup> However, for practical applications, materials exhibiting desirable PSHB properties at elevated temperature are definitely necessary. Rare earth ion-doped glasses have attracted special attention. Some  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Sm}^{2+}$ -doped glasses showing PSHB properties have been reported.<sup>4,5</sup> Many researches have been carried out on oxide glasses doped with rare earth ions.<sup>6</sup> However, to our knowledge, little attention has been paid to PSHB properties in rare earth ion-doped oxyfluoride glasses. Fluorine is well known as a powerful network disrupter, and the incorporation of fluorine into the glass matrix will give rise to changes in glass structure and properties.<sup>7</sup> In this study, the  $\text{Eu}^{3+}$ -doped oxyfluoride glasses of  $30\text{CaF}_2\text{-}10\text{Al}_2\text{O}_3\text{-}60\text{B}_2\text{O}_3$  were prepared, and the comparison of PSHB properties between  $\text{Eu}^{3+}$ -doped these glasses of  $30\text{CaF}_2\text{-}10\text{Al}_2\text{O}_3\text{-}60\text{B}_2\text{O}_3$  and  $30\text{CaO-}10\text{Al}_2\text{O}_3\text{-}60\text{B}_2\text{O}_3$  was performed.

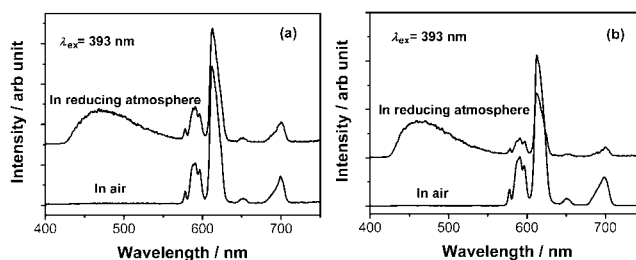
The samples with a composition of  $30\text{CaF}_2\text{-}10\text{Al}_2\text{O}_3\text{-}60\text{B}_2\text{O}_3$  (mol %, referred as F-O glass) doped with 5 wt %  $\text{Eu}_2\text{O}_3$  were prepared from reagent grade  $\text{B}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaF}_2$ , and  $\text{Eu}_2\text{O}_3$ . The raw materials were mixed homogeneously. The mixture was melted at  $1100^\circ\text{C}$  in a platinum crucible for 30 min in air, and then the melt was poured onto a stainless steel mold to quench. The obtained optically transparent glass pieces were pulverized and remelted in a reducing atmosphere (a mixture of 90%  $\text{N}_2$  and 10%  $\text{H}_2$ ) by using a RF furnace at  $1100^\circ\text{C}$  for 1 h. Finally, the glass samples were obtained by cooling down to room temperature with the RF furnace in situ. The resulting materials were optically transparent and yellow in color. The final sample was well polished for the optical measurements. The process for melting glasses of  $30\text{CaO-}10\text{Al}_2\text{O}_3\text{-}60\text{B}_2\text{O}_3$  (mol %, referred as O glass) was the same unless the starting material was  $\text{CaCO}_3$  instead of  $\text{CaF}_2$ . The emission spectra of the samples were measured with a fluorescence spectrophotometer (Hitachi, F-4500) at room temperature. The presence of a considerable amount of fluorine in the F-O glasses was confirmed by EDX (Hitachi, S-3000 HXS) and XPS (Axis

165x, Shimadzu) measurements. The PSHB was performed in the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  of the  $\text{Eu}^{3+}$  ions on the excitation spectrum while monitoring the luminescence of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  at 612 nm of  $\text{Eu}^{3+}$  ion with a rhodamine 6G dye laser (Spectra Physics, 375) pumped by a Nd:YVO<sub>4</sub> green laser (Coherent, Verdi-5). The typical burning power was 150 mW and probing power was 40  $\mu\text{W}$ . The samples were placed in a helium cryostat system, and the temperature was kept constant by a temperature controller. A photomultiplier tube (Hamamatsu Photonics, R649) combined with a monochromator (Nikon, G-250) was used to record the fluorescence spectra.

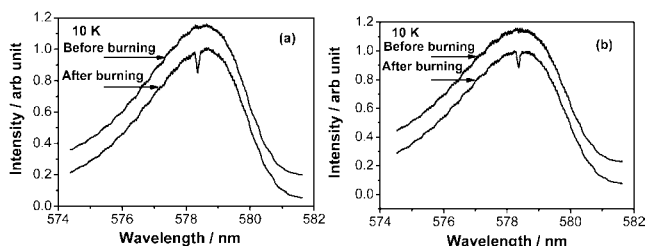
Figure 1 shows the emission spectra of  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ions in the F-O and O glasses prepared in air and reducing atmosphere, respectively. Excitation was carried out at a wavelength of 393 nm. Only strong emission peaks at about 579, 590, 612, 650, and 698 nm exist in the sample prepared in air according to the transitions of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ , and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  of  $\text{Eu}^{3+}$  ion, respectively, whereas the emission spectrum for glasses melted in a reducing atmosphere involves a broad emission due to the transition from  $4f^65d^1$  to  $4f^7$  ( ${}^8\text{S}_{7/2}$ ) of  $\text{Eu}^{2+}$  ion except for the strong line emissions mentioned above. It indicates that the reduction from  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  ion happens during the remelting process in a reducing atmosphere.

Figure 2 shows the typical excitation spectra before and after laser irradiation of  $\text{Eu}^{3+}$  ion at 10 K in F-O and O glasses, respectively. A hole is clearly observed at the burning wavelength after the F-O sample was exposed to a 150-mW laser beam for 20 min. The hole depth and width are about 14% and  $2.6\text{ cm}^{-1}$ , respectively. For the O glass, a hole depth of 11% and width of  $2.5\text{ cm}^{-1}$  are observed under the same burning condition.

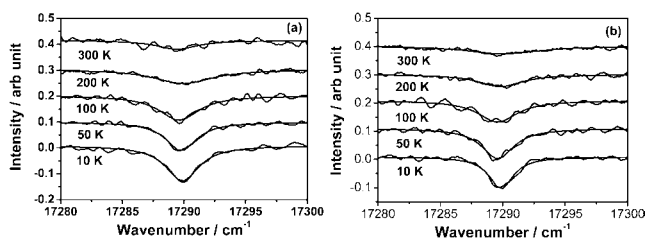
Figure 3 shows the difference spectra of  $\text{Eu}^{3+}$  ion in F-O and O glasses after exposure to 150-mW laser irradiation for 10 min at 10, 50, 100, 200, and 300 K, respectively. With increasing the burning temperature, the hole depth decreases and the hole width increases. At each burning temperature, the



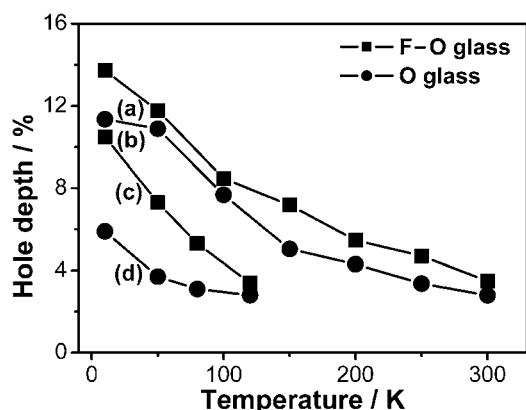
**Figure 1.** Emission spectra of  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ions observed on the (a) F-O glass and (b) O glass prepared in air and reducing atmosphere, respectively.



**Figure 2.** Excitation spectra of  $\text{Eu}^{3+}$  ion before and after laser irradiation at 10 K for 20 min in (a) F–O and (b) O glasses.



**Figure 3.** Difference curves between the excitation spectra of  $\text{Eu}^{3+}$  in (a) F–O and (b) O glasses before and after laser irradiation at various temperatures: 10, 50, 100, 200, and 300 K.



**Figure 4.** Temperature dependence of the hole depth on laser power for the  $\text{Eu}^{3+}$ -doped F–O and O glasses observed under laser irradiation conditions: (a), (b) 150 mW and (c), (d) 38 mW.

burned holes are deeper in F–O glasses than those in O glasses.

The dependence of hole depth on the burning power at different temperature in F–O and O glasses is shown in Figure 4. The hole depth for both samples increases with enhancing the burning power and decreases with increasing the burning temperature. Compared with the results of  $\text{Eu}^{3+}$ -doped F–O glasses, the burned holes are shallower in the  $\text{Eu}^{3+}$ -doped O glasses under the same burning condition.

For the samples in this research, no antihole is observed in the excitation spectra of  $\text{Eu}^{3+}$  ion in both F–O and O glasses. Even the difference spectra do not reveal any obvious antiholes. Therefore, the photophysical mechanism is not significant for our case. For both glasses, a plausible mechanism for the PSHB is the chemical state change from  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  ion.<sup>8</sup> The appearance of the  $\text{Eu}^{2+}$  ion in the glasses proves to be crucial in obtaining the PSHB properties during the burning process since no hole can be burned even at 10 K in the sample prepared in air

in which only  $\text{Eu}^{3+}$  ion exists. However, the hole spectra are clearly recorded even at room temperature in the glasses melted in a reducing atmosphere in which  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ions coexist.

Our experimental results reveal that the hole-burning efficiency is higher in F–O glasses than that in O glasses. Halogen elements such as F, Cl, and Br are well known to coordinate directly to metal cations in crystalline or vitreous metal oxyhalides.<sup>9</sup> Usually, the valence state of europium in europium halides tends to be stabilized in divalent state compared with trivalent one.<sup>10</sup> It means that the  $\text{Eu}^{3+}$  ions in oxyfluoride glasses are expected to be more reducible than those in oxide glasses. In our study, by the direct coordination of  $\text{F}^-$  ions to  $\text{Eu}^{3+}$  ions in the glass matrices, the valence condition of  $\text{Eu}^{3+}$  ions is modified, so that the reduction to  $\text{Eu}^{2+}$  ions becomes much easy, and then the hole formation rate is accelerated. Another reason that causes the higher hole-burning efficiency in F–O glasses is the change of mechanical strength of the glass. It has been tested that fluorine is a powerful network disrupter. When the fluorine substitutes the bridging oxygen by nonbridging fluorine, the network connectivity is reduced and the network motion seems active compared with O glasses. Accordingly, the mechanical strength of F–O glass possibly becomes lower compared with that of O glass. The higher the mechanical strength, the higher the power required burning a hole.<sup>11</sup> Therefore, under the same burning condition, the burned holes become deeper in  $\text{Eu}^{3+}$ -doped F–O glasses than those in  $\text{Eu}^{3+}$ -doped O glasses.

In summary, the PSHB properties were compared between  $\text{Eu}^{3+}$ -doped oxyfluoride glasses of  $30\text{CaF}_2\text{--}10\text{Al}_2\text{O}_3\text{--}60\text{B}_2\text{O}_3$  and oxide glasses of  $30\text{CaO--}10\text{Al}_2\text{O}_3\text{--}60\text{B}_2\text{O}_3$ . The F element in F–O glasses plays an important role in improving the hole-burning efficiency.

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