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Light-induced change of charge transfer band in one europium doped aluminosilicate glass

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Abstract

Ultraviolet light-induced spectral change in one Eu^{3+} doped aluminosilicate glass was studied. It was observed that the excited charge-transfer band decreased after irradiation. The intensity at the irradiated site decreased linearly with the power density of the irradiation light. This means that the light-induced change is a one-photon process. Irradiations at different wavelengths indicate that the spectral change is frequency-selective. The dark decay of the spectral change was also studied. At least two time constants were obtained. One constant is ~2.5 h, and the other is longer.

1. Introduction

Rare earth ions have attracted much attention, because they have large practical and potential applications in many fields, such as laser crystals, fiber amplifiers, phosphors, electro-luminescent devices, and high-density optical storage [1–3]. Among them, trivalent europium ions are attracting current interests. On the one hand, europium ions have potential application in high-density optical storage and phosphors. On the other hand, trivalent europium is an activator to detect local environments [4–8]. As well known, the resonant excitations cross sections of f–f transitions for trivalent rare earth ions are generally small and thus the charge-transfer (CT) states play an important role in the excitation of Eu^{3+}. The variation of CT band with host composition was systematically studied by Su [9]. However, the origin of CT band is not very clear until now. In Y_2O_3:Eu^{3+}, it is considered that the electronic transition from 2p orbital of O^{2-} to the 4f orbital of Eu^{3+} produces excited CT band [9,10]. The origin of CT band in oxide glasses should be similar.

Recently, we observed that the CT band changed after the irradiation of ultraviolet (UV) lights in nanocrystalline Y_2O_3:Eu^{3+}. This change strongly depends on the particle size [11]. In this Letter, we report the UV light-induced change of CT band in oxide glasses.

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2. Experiment

The aluminosilicate glass containing 1 wt% Eu_2O_3 was prepared by melting. The compositions of the glass were $65.1SiO_2$–$22.6Al_2O_3$–$4.2Li_2O$–$0.6MgO$–$0.9Na_2O$–$0.6K_2O$–$2.0TiO_2$–$2.3ZrO_2$–$1.2P_2O_5$–$0.5Sb_2O_3$ in wt%. During the preparation, they were mixed together and stirred to be homogeneous. Then, the mixture was melted in air. After being kept at 1550–1600 °C for 2 h, the glass melt was poured into a stainless-steel plate. The glass was annealed for 2 h at 600 °C and cooled to room temperature slowly. Then colorless transparent glass was formed.

The excitation and emission spectra were measured with a Hitachi F-4500 florescence spectrometer. The continuous lights (200–300 nm) separated from a xenon-lamp were used for irradiation, with a line width of 10 nm and power density of 10–100 $\mu w/cm^2$. A stronger 266-nm pulsed laser with a line width of 0.2 cm^{-1}, pulse duration of 10 ns and repetition frequency of 10 Hz was used for irradiation. It came from a Nd:YAG laser combined with a fourth-harmonic-generator. During this experiment, the power density was adjusted by a neutral density filter. A monochromatic spectrometer, a Boxcar averager and a computer were used for detection.

3. Results and discussion

Fig. 1 shows the excitation spectra of Eu^{3+} in the aluminosilicate glass. The band extended from 200 to 360 nm is associated with the CT transition and the sharp line near 360 nm is associated with $^7F_0$–$^5D_4$ transition of Eu^{3+}. It appears that the intensity of the CT band decreased after irradiation, while the intensity of the sharp line did not change. This implies that the local environment surrounding Eu^{3+} changed after UV light-irradiation, but the population of Eu^{3+} did not change.

Figs. 2a and b show the emissions of $^5D_0$–^7F_J under the excitation of 280 and 394-nm lights, respectively. On excitation of the CT band with 280-nm light, the emission intensity of $^5D_0$–^7F_J decreased after irradiation. Corresponding to the

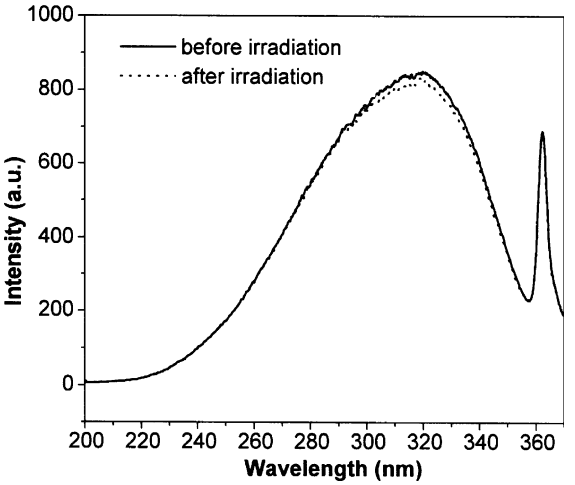

Fig. 1. Excitation spectra of Eu^{3+} ions monitoring 610 nm. The spectra were measured before and after irradiation at 325 nm for 30 min.

394-nm resonant excitation, the emission intensity did not change. This is well in consistent with the result of Fig. 1.

The irradiation was also performed with lights at different wavelengths. Fig. 3 shows the difference between the spectra before and after irradiation. It can be observed that a hole was formed after irradiation. The shorter the wavelength of irradiation light, the shorter the central location of the hole. This indicates that the CT band is frequency-selective. Because the linewidth of the irradiation light is as wide as 10 nm, the hole is quite wide. A narrower hole is expected to be burned by a narrower laser. It should be noted that the central location of the hole is not exactly at the irradiation site.

Fig. 4 shows the time-dependence of the intensity at the irradiated site. It is obvious that the stronger the laser power, the larger the spectral change. The spectral change is proportional to the power density of the irradiation light, indicating that it is a one-photon process. Even after the irradiation by strong 266-nm light, Eu^{3+} ions were not reduced to Eu^{2+}. The decrease of the CT band was thus attributed to the UV light-induced local environment surrounding Eu^{3+} ions change. A number of vacancies may exist in the glass network. We suggest that the electrons are captured

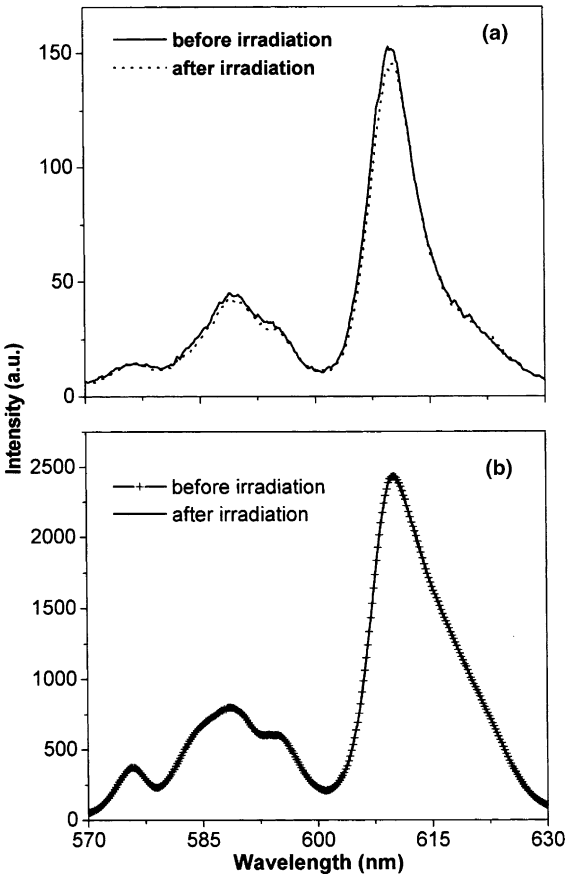

Fig. 2. Emission spectra before and after irradiation at 325 nm for 30 min. The excitation wavelength is (a) 280 nm, and (b) 394 nm.

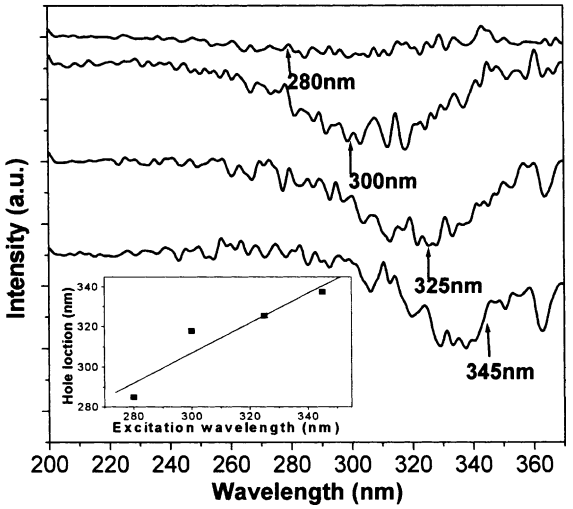

Fig. 3. Difference of the excitation spectra between before and after irradiation at different wavelengths. Inset: dependence of the hole location on wavelength of the irradiation light.

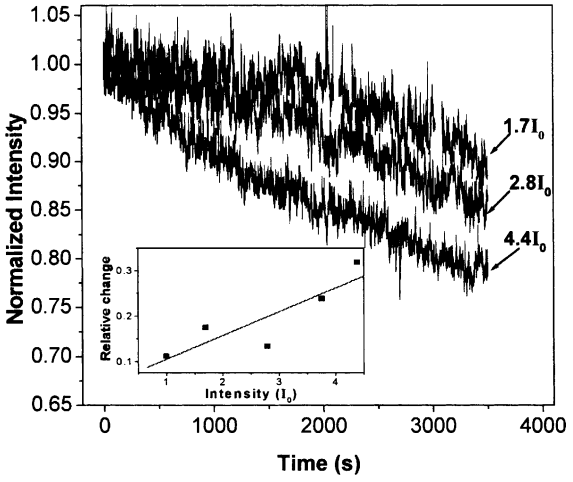

Fig. 4. Normalized emission intensity at the irradiated site as a function of time and power density of 266-nm pulsed laser light ($I_0 \sim 1$ mw/mm^2). Inset: relative spectral change at the irradiated site as a function of power density.

by some vacancies by tunneling when they are excited into the excited states of O^{2-}. This process leads the electrons transferred to Eu^{3+} and the intensity of CT band to decrease.

Fig. 5 shows the excited CT bands at various aging time. The intensity of the CT band decreased after irradiation, then increased again and tended to restore its original state as the irradiation light was shut off. The relative change as a function of recovery time in the dark was drawn in the inset. The solid line in the inset is a bi-exponential fitting function. It appears that there exists at least two recovery time constants. One is ~2.5 h and the other is much longer. The component with the shorter constant is ~50%. This result suggests that two kinds of vacancies may exist and capture the electrons of O^{2-}. It is also possible that the formation mechanisms of light-induced spectral changes are different.

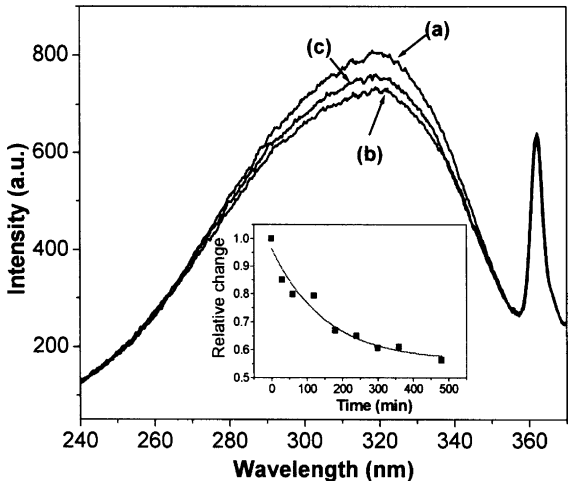

Fig. 5. Excitation spectra measured at different aging time: (a) before irradiation; (b) immediately after the irradiation light of 320 nm was shut off; (c) after the irradiation light was shut off 5 h. Inset: dependence of relative change of CT band as a function of recovery time in the dark.

4. Conclusions

In conclusion, the CT band in the aluminosilicate: Eu^{3+} glass decreased after the irradiation of UV lights. The light-induced change is a one-photon process and frequency-selective. Two recovery time constants were obtained by fitting. One is 2.5 h and the other is longer. The light-induced change of CT band was attributed to local structure change surrounding Eu^{3+} ions. Because the UV light-induced spectral change is frequency-selective, it may have potential use in frequency-domain optical storage. Further irradiation work should be performed by a narrower UV laser.

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