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Femtosecond laser-induced reduction in Eu-doped sodium borate glasses

Ki-Soo Lim[a,*], Sunkyun Lee[a], Minh-Tuan Trinh[a], Suk-Ho Kim[a], Myeongkyu Lee[b], Douglas S. Hamilton[c], George N. Gibson[c]

[a] *Department of Physics and Basic Science Research Institute, Chungbuk National University, Cheongju 361-763, Korea*
[b] *Departent of Materials Science and Engineering, Yonsei University, 134 Shinchon-dong, Seoul 120-749, Korea*
[c] *Department of Physics, University of Connecticut, Storrs, CT 06269, USA*

Abstract

In this work, we report permanent reduction of Eu^{3+} to Eu^{2+} in sodium borate glasses by irradiation of near-infrared femtosecond laser. Glass composition of sodium borate was $85B_2O_3$–$15Na_2O$. The glasses were doped with 0.05, 0.1, and 0.5 mol% Eu_2O_3. Absorption and fluorescence dynamics were studied to investigate valence state change of europium ions and the energy transfer between Eu^{2+} and Eu^{3+} ions. As the femtosecond laser intensity or exposure time increases, the emission band at 400 nm becomes stronger. However, the photoreduction efficiency decreases as the dopant concentration increases. We discuss the photoreduction mechanism under multiphoton absorption.

Keywords: Eu^{2+}; Eu^{3+}; Photoreduction; Laser irradiation; Sodium borate glass; Energy transfer

1. Introduction

Microscopic modifications of optical properties in glasses using femtosecond pulsed laser irradiation is very attractive in both scientific and technological aspects [1]. The photomodified region is well defined due to the nonthermal character of light–matter interaction. Therefore, the femtosecond laser can be effectively used in patterning structures for optical memories and waveguides [2]. Recently, Qiu et al. [3] reported that femtosecond laser irradiation changed the valence state of europium ions in fluorozirconate glass, which was confirmed by observing the change of the absorption. However, fluoride glasses are not so stable as ordinary oxide glasses and need rather a complicated synthesis process. In this report, we present the observation of the change of photoluminescence characteristics due to photoreduction of europium ions in sodium borate glasses after femtosecond laser irradiation.

2. Experimental

The composition of the glass used in this study was $(100-x)(0.85B_2O_3$–$0.15Na_2O)$–xEu_2O_3 (mol%), where $x=0.05$, 0.1 and 0.5. Powders of reagent grade were mixed together and melted in a Pt crucible for 30 min at 1250 °C. Then, the melt was poured onto a stainless plate and pressed to a thickness of about 2 mm by another plate. The glasses were annealed for 1 h at 500 °C and mechanically polished. A regeneratively amplified 800-nm Ti: sapphire laser system with a 1-kHz repetition rate and 100-fs pulse duration was employed as the irradiation source. A pulsed laser beam was focused by a lens inside the sample on an x–y–z stage. The absorption, excitation, and fluorescence spectra of the irradiated area were measured by a spectrophotometer and a fluorescence spectrometer. The fluorescence dynamics was measured by using a digital oscilloscope and a 266-nm pulsed Nd:YAG laser.

3. Results and discussion

The absorption spectra of the Eu^{3+}-doped glass before (a) and after (b) the femtosecond laser irradiation are

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*Corresponding author. Tel.: +82 43 261 2239; fax: +82 43 271 1653.
E-mail address: kslim@chungbuk.ac.kr (K.-S. Lim).

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shown in Fig. 1. In the visible range, the absorption coefficient of the unirradiated sample was nearly constant with wavelengths for both glasses. In the UV range, the induced absorption increased significantly as the wavelength decreased. The differential spectrum shows a broad band peaking at approximately 300 nm.It can be ascribed to the absorption due to the 4f–5d transition of Eu^{2+} [4]. Fig. 2 shows the photoluminescence spectra of the 0.1 mol% Eu^{3+}-doped glass before (a) and after (b) the laser irradiation with 400 mW under excitations at 266 and 325 nm.The emissions between 550 and 750 nm can be attributed to the well-known transitions from $^5D_0$ to ^7F_J $(J = 0, 1, 2, 3, 4)$ levels of Eu^{3+} [5]. It can be seen that the concentration of Eu^{2+} ions is negligible in the unirradiated sample, because no emission from Eu^{2+} ions was found. The new broad bands at 400 nm formed after laser irradiation in both spectra might be assigned to the lowest 5d–4f transition of Eu^{2+} in the host. The emission due to the f–d transitions is broadened because of the large spatial extension of the 5d wave function and the lattice vibration of the surroundings. The emission bands under 266- and 325-nm excitations are basically the same, but the spectrum under the excitation at 325 nm was cut in the shorter wavelength region because of a cut-off filter used to block the excitation light. Intensity of Eu^{2+} ions increased, while the intensity of Eu^{3+} slightly decreased with irradiation intensity and exposure time. The change of photoluminescence implies that the femtosecond laser irradiation produced photoreduction from Eu^{3+} to Eu^{2+}. The excitation spectrum for the emission from Eu^{3+} in Fig. 3 shows a group of 4f intra-configurational transitions from the $^7F_0$ level to $^7D_4$, $^5G_3$ $^5L_6$, $^5D_3$, $^5D_2$, and $^5D_1$ levels in the region of 350–500 nm and the charge transfer band at 270 nm corresponding to the electrons transfer energy from 2p orbits of O_2^- to 4f levels of Eu^{3+} [6].

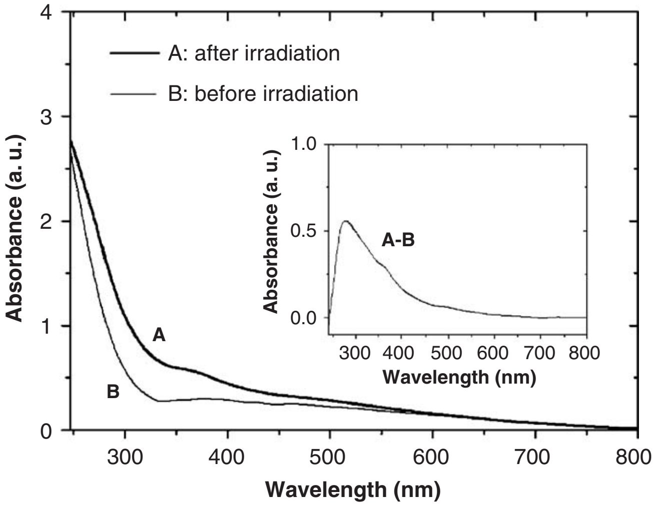

Fig. 1. Laser-induced absorption in Eu-doped sodium borate glasses.

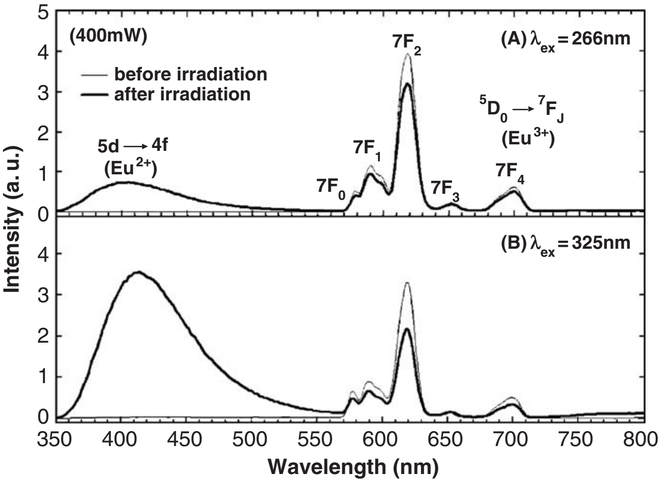

Fig. 2. Spectral change due to photoreduction of Eu ions in sodium borate glasses after femtosecond laser irradiation.

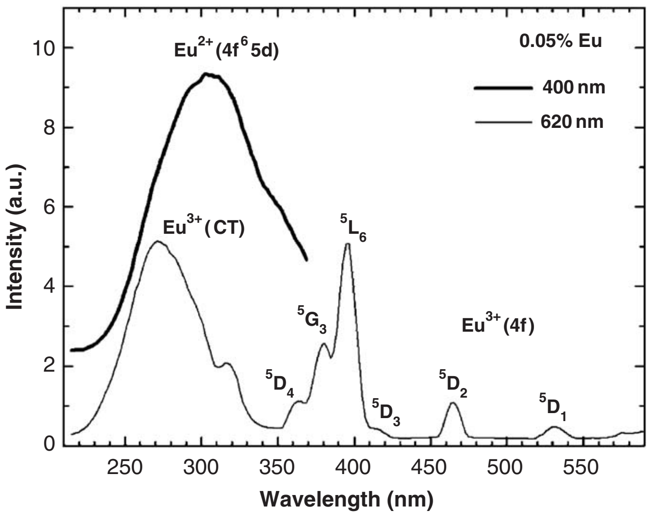

Fig. 3. Excitation spectra for Eu^{2+} (400 nm) and Eu^{3+} (620 nm) emissions for the irradiated 0.05% Eu-doped glass.

We also observed the 5d band of Eu^{2+} in the excitation spectrum for the emission at 400 nm.The 5d orbital is split into two components of E_g and T_{2g} at 310 and 350 nm by the crystal field strength of neighbors surrounding Eu^{2+} ions. The weak band at 310 nm in excitation spectrum of Eu^{3+} is ascribed to 4f–5d transition of Eu^{2+}, which indicates some energy transfer from the 5d level of Eu^{2+} to the 4f levels of Eu^{3+}. The overlap between broad blue emission band of Eu^{2+} and excitation bands of Eu^{3+} in the region around 400 nm causes the energy transfer from Eu^{2+} to Eu^{3+}, resulting in emission from Eu^{3+}. The energy transfer process can be accomplished via re-absorption or resonance transfer [7]. The excited Eu^{2+} in the 5d level nonradiatively relaxes to the ground state $^8S_{7/2}$, and the released energy causes the excitation of Eu^{3+} ions. We also observed another evidence of energy transfer from Eu^{2+} to Eu^{3+} ions by measuring the temporal behavior of Eu^{2+} emission at 400 nm and Eu^{3+} emission at 620 nm. Under the excitation of 266 nm emissions of Eu^{2+} ions at 375, 400, and 450 nm decay non-exponentially with

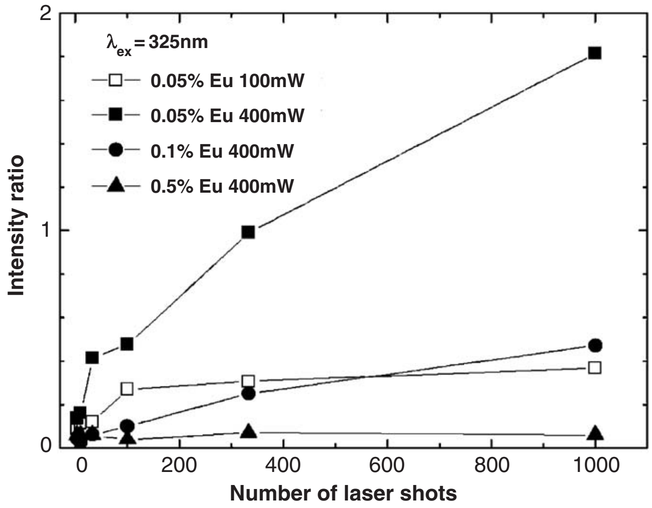

Fig. 4. Ratio of Eu^{2+} (400 nm) and Eu^{3+} (620 nm) emission intensities for 0.05, 0.1 and 0.5% Eu-doped glasses as a function of laser irradiation. For a 0.05% Eu-doped glass, irradiations of 100 and 400 mW were used to see the power dependence of photoreduction.

the same characteristic time of ~0.9 μs. The emission of Eu^{3+} ions at 620 nm with its rise time corresponding to the lifetime of Eu^{2+} ions and the long decay time of 2.6 ms, which indicates the energy transfer from Eu^{2+} to Eu^{3+} ions. As expected from the excitation spectra, the excitation at 325 nm produces the stronger blue emission than the excitation at 266 nm does as shown in Fig. 2.

The mechanism of the photoreduction can be explained as follows. The multiphoton absorption of infrared laser pulses creates active electrons and holes. Then, the electrons are trapped in oxygen vacancies or Eu^{3+} ions, resulting in photoreduction. The electron donation ability of oxygen around Eu^{3+} ions reduces Eu^{3+} to Eu^{2+}. The holes are likely to be trapped in non-bonding oxygen, leading to the formation of V-type hole trapped defect centers. In addition, the trap levels of defect centers can be deep, resulting in stable Eu^{2+} at room temperature. The photoreduction efficiency increased with the number of laser shots, but decreased with concentration of Eu^{3+} ions in 0.05, 0.1 and 0.5 mol% glass samples as shown in Fig. 4. The enhanced photoreduction with more laser exposure is expected because more electrons are trapped in Eu^{3+} ions. The decrease of the photoreduction efficiency in the high concentrated samples can be explained because the laser produces only a finite number of electrons to be trapped in more available Eu^{3+} sites for the higher concentrated samples. Thus, the ratio of Eu^{2+} and Eu^{3+} ion concentrations will decrease in the higher concentrated samples.

In summary, we observed permanent photoreduction of Eu^{3+} to Eu^{2+} by an infrared femtosecond pulsed laser. Photoreduction efficiency was dependent on the initial Eu^{3+} concentration, irradiation intensity and exposure time. We also observed the energy transfer from Eu^{2+} to Eu^{3+} ions in the irradiated samples.

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