Blue emission from Eu$^{2+}$-doped high silica glass by near-infrared femtosecond laser irradiation

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Eu$^{2+}$-doped high silica glass (HSG) is fabricated by sintering porous glass which is impregnated with europium ions. Eu$^{2+}$-doped HSG is revealed to yield intense blue emission excited by ultraviolet (UV) light and near-infrared femtosecond laser. The emission profile obtained by UV excitation can be well traced by near-infrared femtosecond laser. The upconversion emission excited by 800 nm femtosecond laser is considered to be related to a two-photon absorption process from the relationship between the integrated intensity and the pump power. A tentative scheme of upconverted blue emission from Eu$^{2+}$-doped HSG was also proposed. The HSG materials presented herein are expected to find applications in high density optical storage and three-dimensional color displays.

I. INTRODUCTION

Considerable interest has been focused on multiphoton absorption upconversion luminescence materials because of its promising applications such as infrared-pumped visible lasers, optical data storage, three-dimensional display, and so on.$^{1-6}$ To date, various multiphoton absorption upconversion luminescence phenomena have been studied in rare earth$^{7-9}$ or transition metal$^{10}$ ion-doped materials. However, it is noticed that most reports on upconversion luminescence excited by femtosecond laser are focused on organic,$^{2}$ crystals, or glass-ceramics hosts.$^{7-10}$ Few similar phenomena were reported in conventional ion-doped glasses due to their low laser damage threshold. Most of the glasses cannot endure the irradiation of the high intensity femtosecond laser pulses. Long time excitation under femtosecond laser always results in laser-induced optical breakdown of the glasses.

In this paper, we develop an approach to fabricate Eu$^{2+}$-doped high silica glass (HSG) based on sintering porous glass. With an aim of improving their emission properties, numerous efforts have been devoted to porous glass containing rare earth or transition metal ions.$^{11-15}$ However, the porous glasses they prepared were not sintered to dense glasses. Those glasses could not represent intense luminescence because of the impurity quenching effect of residual OH$^-$ groups and the strong scattering of ultraviolet (UV) excitation lights due to the microscopic pores. Our previous study indicated that sintering active-doped porous glass in air or a reducing atmosphere may be an important step in the process of fabricating strong emission HSG.$^{14,15}$ Silica glass is an attractive host matrix for rare earth ions because of its fine optical and mechanical properties, such as good chemical stability, high UV transparency, and large tensile fracture strength. Furthermore, its strong thermal resistance and high surface damage threshold to lasers make it suitable for femtosecond laser induced upconversion luminescence material. The content of SiO$_2$ in HSG is over 96 wt %, close to pure silica glass. Blue emission from Eu$^{3+}$-doped HSG by UV light and near-infrared femtosecond laser irradiation was described in the present work. The blue emission by near-infrared femtosecond irradiation is associated with a multiphoton process. It is the first report on upconversion luminescence of Eu$^{2+}$-doped silica glass or porous silica glass as far as we know. Our study is helpful to expand applications of silica glass or HSGs in high density optical storage and three-dimensional color displays.

II. EXPERIMENTAL

Porous silica glass was obtained by removing the borate phase from phase-separated alkali-borosilicate glass. Detailed fabrication of porous glass was described in a previous paper.$^{16}$ The analytical composition of the porous glass obtained by phase separating and acid treating was 97.0SiO$_2$ −2.1B$_2$O$_3$ −0.8Al$_2$O$_3$ −0.1(Na$_2$O+CaO) (in wt %). The porous glasses were immersed in 0.1 mol/L solutions of Eu$^{3+}$ (obtained from dissolving Eu$_2$O$_3$ in 1mol/L HNO$_3$) for 1 h and dried at room temperature. Then these glasses impregnated with Eu$^{3+}$ ions were sintered at 1150 °C in a reducing atmosphere (CO) to obtain Eu$^{2+}$-doped HSGs. The final Eu$^{2+}$-doped HSGs looked compact and transparent. Blank HSGs (without ions doped) was also fabricated for comparison. All glass samples were cut and polished to a size of 10.0 × 10.0 × 1.5 mm$^3$.

Absorption spectra were recorded with a Jasco V-570 UV/visible/near-infrared spectrophotometer. Excitation and emission spectra of the samples in UV and visible wave-
length ranges were recorded on a Jasco FP-6500 spectrofluorometer equipped with a xenon lamp source. A regeneratively amplified Ti: sapphire laser system was used as an infrared femtosecond laser pump source with an operating wavelength of 800 nm, a repetition rate of 1 kHz, and a pulse duration of 120 fs. The laser beam was focused on the interior of the sample through an optical lens with a focal length of 150 mm. Upconversion emission spectra were obtained by introducing the femtosecond laser into the Jasco FP-6500 spectrofluorometer. All of the measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of Eu2+-doped HSG and blank HSG. There are two strong absorption peaks around 201 and 255 nm. Compared with the blank HSG, Eu2+-doped HSG has a broad and flat UV absorption band located about from 250 to 300 nm. There is no other absorption band in the entire visible and near-infrared region up to 900 nm.

When porous glasses impregnated with Eu3+ ions were heat treated below 800 °C in air, the samples showed a weak red emission band at about 610 nm excited by 250 nm UV light. However, a very intense blue emission appears excited by UV light when the porous glass is sintered at 1150 °C in a reducing atmosphere. Figure 2 presents the excitation and emission spectra of Eu2+-doped HSG. The excitation and emission peaks located at 321 and 435 nm, respectively, correspond to the \( {4f}^{5}5d \rightarrow {4f}^{7}(S_{7/2}) \) transition of the Eu2+ ions.17 There was no red emission from the Eu3+ ions, even after being excited by a monochromatic light at 394 nm which is the energy of the \( ^{7}F_{0} \rightarrow ^{5}I_{6} \) transition of Eu3+. It is evident that the Eu3+ ions are reduced to Eu2+ by CO gas. The inset of Fig. 2 shows the photographs of Eu2+-doped HSG before (a) and after (b) irradiated by a 365 nm UV light.

Figure 3 depicts the emission spectra of Eu2+-doped HSG excited by 800 nm femtosecond laser and 400 nm monochromatic light. The spectral profile pumped by infrared femtosecond laser is almost the same as that excited by UV monochromatic light, indicating that the emission in both cases come from an identical origin. The photographs of the sample irradiated by 405 nm diode laser (a) and 800 nm femtosecond laser (b) are shown in the inset of Fig. 3. The beam from the 405 nm diode laser was focused on the interior of the sample through an optical lens with a focal length of 150 mm. A bright blue emission line could be clearly observed near the focus spots when the sample was pumped by infrared femtosecond and 405 nm diode lasers. The photographs have no visible difference when the sample was excited by both laser sources.

Generally, it is difficult to obtain visible emissions excited by near-infrared wave bands in oxide glasses. Here the blue emission from Eu2+-doped HSG excited by 800 nm femtosecond laser is considered to be related to a multiphoton absorption process. Log-log plots of the upconverted
The slope takes an initial value of \( \sim 2.0 \) and is eventually saturated to a unity. The decrease in the slope may be associated with breakdown of glass network or emergence of color centers induced by an ultrashort laser with high power density. Since there is no resonant absorption at 800 nm, the upconversion luminescence of Eu\(^{2+}\)-doped HSG is attributed to a two-photon excitation process. We propose a tentative scheme of upconverted blue emission from Eu\(^{2+}\)-doped HSG as shown in Fig. 5. For Eu\(^{2+}\), its 4f levels are little influenced by the ligand field of the first coordinating sphere because of the screening effect of the outside electron clouds. However, the 5d levels are affected by this ligand field greatly. Especially in oxide glasses, the strong ligand around Eu\(^{2+}\) due to the large effective charges of oxygen ions results in large splitting of 5d level. The lowest level of 5d is, in most cases, lower than that of \( 6P_{7/2} \) in oxide glasses. When Eu\(^{2+}\)-doped HSG was irradiated by the 800 nm femtosecond laser, Eu\(^{2+}\) ions in the ground state absorb two photons to one of the higher 5d levels with the help of a virtual energy level, then relax to the lower 5d levels via a nonemission multiphonon relaxation process. Subsequently, the transition from the lower 5d levels to \( ^4S_{7/2} \) occurs and a broad blue emission around 435 nm is observed.

### IV. CONCLUSIONS

In conclusion, Eu\(^{2+}\)-doped HSG was fabricated by sintering porous glass impregnated with europium ions. Intense blue emissions were observed when Eu\(^{2+}\)-doped HSG was excited by both UV light and near-infrared femtosecond laser. And the emission profile obtained by UV excitation can be well traced by near-infrared femtosecond laser, indicating that the emission in both cases come from an identical origin. The upconversion emission excited by 800 nm femtosecond laser is considered to be related to a two-photon absorption process from the relationship between the integrated intensity and the pump power. The tentative mechanism of upconverted blue emission from Eu\(^{2+}\)-doped HSG was proposed. The HSG materials presented herein are expected to find applications in high density optical storage and three-dimensional color displays.

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**FIG. 4.** Log-log plots of the upconverted blue emission integrated intensity vs pump power for infrared femtosecond excitation.

**FIG. 5.** (Color online) Mechanism for upconverted blue emission from Eu\(^{2+}\)-doped HSG.