Paper

Space selective reduction of europium ions via SrF$_2$ crystals induced by high repetition rate femtosecond laser

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We report using high repetition rate near-infrared femtosecond laser to reduce Eu^{3+} into Eu^{2+} inside oxyfluoride glass. SrF$_2$ crystal was space-selectively precipitated with the irradiation of femtosecond laser and we successfully realized the reduction of Eu ions, confirmed with the observation of blue emission of Eu^{2+} at laser irradiated spots. The mechanism of the reduction is different from those in previous work which is based on the active electron and holes created by the infrared laser pulse. This work could extend selection of host composition of Eu-doped glass for 3D optical information storage.
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1. Introduction

Direct micro-structuring inside glass materials with near-infrared femtosecond laser has been an attractive research topic recently.[1),2)] Depending on focusing condition, the energy is compressed in ultrashort time scale so that the strength of the electric field can reach as much of $100\,TW/cm^2$ which is sufficient to cause non-linear optical process including multi-photon absorption, tunnelling ionization and avalanche ionization inside transparent materials at non-resonant wavelength. Therefore the femtosecond laser was used in manufacturing integrated optics such as waveguide and optical data storages.[3),4)]

The reduction of europium ions inside glass by femtosecond laser has been previously reported,[5),6)] however, these results are highly depended on the glass composition of glass. To our best knowledge, the photon reduction of Eu^{3+} inside glass are only reported in fluoride and borate glasses with 1 KHz femtosecond laser, which limited the selection of glass host. Recently, reduction of Eu^{3+} inside glass ceramic containing SrF$_2$ was described.[7)] In this work, we present the reduction of Eu ions with SrF$_2$ crystals which is induced by 250 KHz femtosecond laser inside oxyfluoride glass.

2. Experiments

The glass samples were prepared by traditional melting-quench method. The composition of glass sample is listed in **Table 1**. Appropriate raw materials (SiO$_2$, Al$_2$O$_3$, NaF, SrF$_2$, EuF$_3$, LaF$_3$) was mixed and put in a covered Al$_2$O$_3$ crucible in normal atmosphere, then the crucible is heated up to 1430°C for 45 min. the melt was poured on a brass mold and then pressed by another brass plate. All of these glass samples were cut and polished for laser experiment. A regenerative amplified 800 nm Ti: sapphire

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Table 1. Composition of glass sample

Glass	SiO$_2$	Al$_2$O$_3$	NaF	EuF$_3$	SrF$_2$	LaF$_3$
ESG	50	22	6	2	20	—
SG	50	22	6	—	20	—
ELG	50	22	6	2	—	20

laser (RegA 9000, Coherent Inc.) was used which emitted 70 fs, 250 KHz mode-lock pulses with wavelength of 800 nm to irradiate the glass sample. During the experiment laser beam was focused 100 μm below the glass surface via a 20× objective lens (NA = 0.45).

The method to measure the luminescent spectra of modified region was to use a fiber detector under excitation with the abovementioned pulse laser. The X-ray diffraction (XRD) measurement was performed by using Cu Kα radiation (Rigaku RINT-2500HF diffractometer) to identify the crystalline phase. It is difficult to obtain the XRD pattern for single irradiated spot (tens of micrometer), so laser-modified line arrays were created by translate the glass in the vertical direction of propagation direction of laser, then the sample was polished until the line arrays reached the glass surface. The polished sample was used for XRD measurement.

3. Results and discussion

The top view of the structure induced by laser is shown in **Fig. 1**(a) and the concentric-ring-shaped structure is observed, which is much larger than the laser focal spot size due to the thermal expansion. The outer structure is due to strain generated by the residue thermal stress after femtosecond laser irradiation.[1)] We also found the centre of focal spot becomes black when exposure time exceeds 30 s, small bubbles ascribed to the micro explosion should be responsible for this observation.[8)] Figure 1(b) shows the time-depend size variation of the structure induced by femtosecond laser with defferent power. The size of modified structure increases dramatically during the first 2 s of
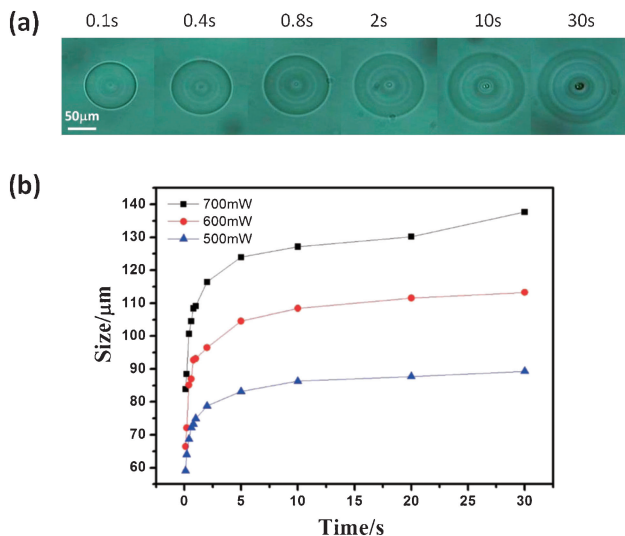
Fig. 1. (a) Optical microscopic image of the microstructures induced with static exposure of femtosecond laser pulse for various times. (b) Dependence of the diameter of the laser induced zone on the irradiation time.
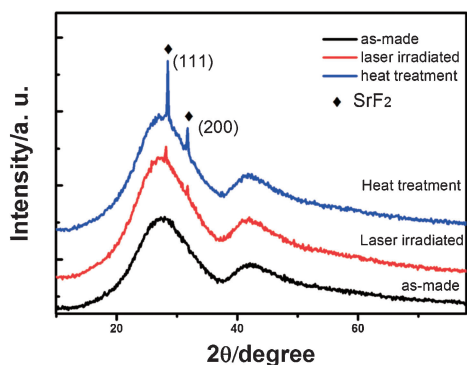

Fig. 2. XRD patterns for the ESG glass modified region, glass and glass ceramics.

Fig. 3. Emission spectra before and after laser irradiation for ESG, ELG and SG.

time, but the speed of growth slows down and approaches saturation because the heat fluctuation reached balance.

Figure 2 presents the X-ray diffraction patterns of ESG glass and laser-modified region. The as-made glass has no diffraction peaks, but two peaks are observed in the pattern for the laser-modified area. For comparison the XRD pattern of ESG glass heat treated at 580°C for 30 min is also presented in Fig. 2. According to JCPDS standard card these two peaks belong to SrF_2 crystal, and no second phase of crystalline was found. When irradiated by high repetition rate femtosecond laser, heat accumulation occurred at the focal spot. The thermal effect could cause the nucleation and crystal growth near the laser focal spot,[9] SrF_2 could be space-selectively precipitated inside glass with femtosecond laser irradiation.

In **Fig. 3** the luminescence spectra is presented. Although femtosecond pulse laser is used as the excitation source, the laser beam was attenuated to $0.08\,\mu J$ so the multi-phonton absorption process was only enough to excite luminescence of rare earth ions and the structure of modified region is not compromised during the measurement.[2] The emission peaks from 560 to 710 nm could be attributed to the $^5D_0$ energy level to ^7F_J ($J = 0$, 1, 2, 3, 4) levels of Eu^{3+} and the broad band emission peaked at around 470 nm is regarded to the $4f^65d$ to $4f^7$ transition of Eu^{2+}.
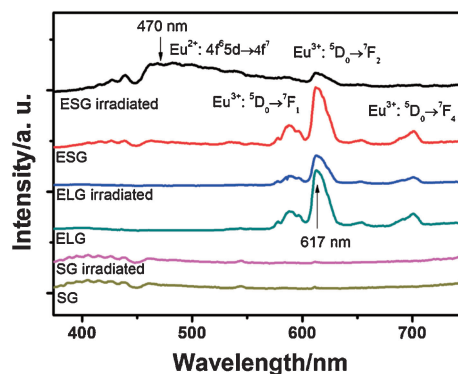
The luminescence of non-irradiated area shows only the Eu^{3+} emission, indicating that the concentration of Eu^{2+} in as-made glass is negligible. A strong emission of Eu^{2+} is observed at the center of focal spot, suggesting the reduction from Eu^{3+} to Eu^{2+} was realized inside ESG glass under femtosecond laser irradiation. We also investigated the luminescent property in the SG and ELG glass before and after laser irradiation. In SG glass no emission from Eu ions is observed, except a weak emission at 400 nm which is ascribed to the nonlinear effect of femtosecond laser. In ELG glass only the Eu^{3+} emission is observed, suggesting Eu ions are usually unable to be reduced in oxy-fluoride glass. We also confirmed that LaF_3 crystal was precipitated after femtosecond laser irradiation inside ELG, however, the reduction of Eu ions is not observed. Therefore, the precipitation of SrF_2 crystal is responsible for the reduction process which we observed in the ESG sample.

The mechanism of this photo reduction is not based on the active electron from glass host trapped by Eu^{3+} ions which is proposed in the earlier work.[5),6] During high repetition rate laser irradiation, heat was accumulated at the focal spot due to multi-photon absorption and plasma with high temperature is induced. The extremely high temperature at the focal spot formed temperature gradient[10] which induced the nucleation and growth of SrF_2 crystal. In such condition, Eu^{3+} from the glass host would be inevitably doped into SrF_2 crystalline. During this doping process, two Eu^{3+} would substituted for three Sr^{2+} ions, and a cation vacancy defect with two negative charges would be created. The vacancy acted as a donor of electron and transferred electrons to Eu^{3+} in the crystal host under thermal stimulation, reducing Eu^{3+} to Eu^{2+}.[7] Besides, compare with the size of Eu^{3+} (121 pm), the size of Eu^{2+} (139 pm) is much closer to the size of Sr^{2+} (140 pm),[11] so the reduction of Eu ions is favored because it could reduce the lattice distortion of doped SrF_2 crystal.

Figure 4 shows the intensities of the emissions associated with Eu^{2+} (470 nm) and Eu^{3+} (617 nm) as the function of the distance from the center of laser modified region. Eu^{2+} emission is weak at around the center but the intensity increases dramatically as the distance increases from 6 to 10 μm. The intense luminescence from Eu^{2+} indicates that the SrF_2 is mainly precipitated at this region since reduction could not occur without SrF_2.

Figure 4 also shows that the emission from Eu^{3+} increases at the region where SrF_2 precipitated. This variation is related to the elemental redistribution induced by the laser irradiation. The glass network modifier tends to migrate to the outer region and network former has the tendency to be enriched at the center during high repetition femtosecond laser irradiation.[12] Although
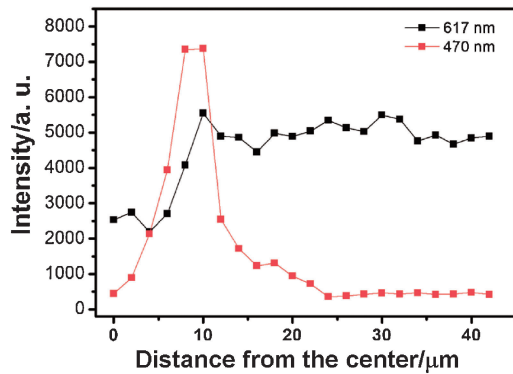
Fig. 4. Variation of peak intensity as the function of the distance to the center of laser modified spot, which induced by irradiation of femto-second laser with 700 mW for 30 s, before any bubble is produced by femtosecond laser. During the luminescence measurement, the excited area was about 2 μm in diameter.
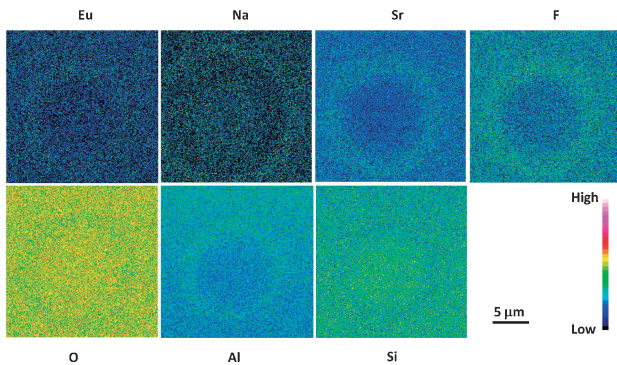

Fig. 5. The EPMA mapping showing only the relative concentration changes of the different ions in the glass around the focal point after the femtosecond laser irradiation.

the SrF$_2$ reduced a fraction of Eu^{3+} to Eu^{2+}, the luminescence at 617 nm is still increased due to the total concentration of Eu ions is increased at this region.

The composition variation of ESG due to femtosecond laser irradiation is also measured with EPMA, as is shown in **Fig. 5**. The enrichment of Sr and F at the ring-shaped region is accordant with our above deduction where the SrF$_2$ is mainly precipitated. In addition, the mapping of Eu shows the concentration increase in the same region.

In Fig. 4, when the distance is larger than 10 μm, the emission at 470 nm is keeping decreasing until no luminescence from Eu^{2+} could be observed. There are two reasons for this phenomenon.

The first one is the element redistribution region is only in a short distance from the center, the concentration of Eu would be decreased to reach the initial glass composition as distance is further increased. The other reason is the temperature decreases rapidly along radical direction from the focal spot when femtosecond laser is irradiating,[10] so the nucleation and growth of SrF$_2$ crystal decreased and could not occur at the region where the temperature is too low. Assuming doping concentration is proportional to the volume fraction of SrF$_2$, the reduction of Eu^{3+} to Eu^{2+} decreased as less SrF$_2$ was precipitated. The Eu^{2+} emission could be observed until the distance increased to 22 μm. When the distance is further than 22 μm the reduction of Eu ions could not be observed because of the absence of SrF$_2$ crystallization.

4. Conclusions

In summary, we have successfully realized the reduction of Eu^{3+} to Eu^{2+} in a oxyfluoride glass with high repetition rate femtosecond laser. The precipitation of SrF$_2$ is observed in the laser modified region and works as a new type of photo-reduction mechanism of ultra short pulse laser. These results may extend application of Eu-doped glass in the 3D optical data storages.

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