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The photosensitive effect of Ce on the precipitation of Ag nanoparticles induced by femtosecond laser in silicate glass*

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This paper studies the photosensitive effect of cerium oxide on the precipitation of Ag nanoparticles after femtosecond laser irradiating into silicate glass and successive annealing. Spectroscopy analysis and diffraction efficiency measurements show that the introduction of cerium oxide may increase the concentration of Ag atoms in the femtosecond laser-irradiated regions resulting from the photoreduction reaction $Ce^{3+} + Ag^{+} \rightarrow Ce^{4+} + Ag^{0}$ via multiphoton excitation. These results promote the aggregation of Ag nanoparticles during the annealing process. It is also found that different concentrations of cerium oxide may influence the Ag nanoparticle precipitation in the corresponding glass.

Keywords: femtosecond laser, glass, photosensitive effect
PACC: 4270G, 4280W

1. Introduction

The femtosecond laser has become a powerful tool to study the interaction between light and matter in recent decades due to its characteristics of ultrahigh light intensity and ultrashort pulse, and a lot of novel phenomena have been observed during and after femtosecond laser irradiation into glass, crystal, metal and other dielectric materials.[1−8] Significantly, space-selective precipitation of noble metal nanoparticles inside the glass matrix induced by the femtosecond laser and successive annealing has been intensively studied owing to the ultrafast all optical response and large third-order non-linear susceptibility of the nanoparticle-doped glasses,[9−11] which opens a new route for the fabrication of integrated optical elements.[12,13]

It is known that in Ag^{+} and Ce^{3+} co-doped silicate glasses, Ag^{+} may be reduced to atom Ag^{0} because Ce^{3+} can release free electrons after exposure of ultraviolet (UV) light, on the basis of redox reaction $Ce^{3+} + Ag^{+} \rightarrow Ce^{4+} + Ag^{0}$.[14] However, up to now, the photoreaction mechanism of Ag^{+} and Ce^{3+} co-doped silicate glasses induced by a femtosecond laser has not been clearly understood. Recently, Hongo *et al* reported that Ce^{3+} had no effect on the precipitation of Ag nanoparticles in the photosensitive glass Foturan after femtosecond laser irradiation.[15] In addition, Qiu *et al* have achieved space-selective precipitation of Ag nanoparticles in the silicate glass without Ce^{3+}.[11] In our previous investigation, it was suggested that cerium oxide in the glass may promote the formation of the Ag atoms after femtosecond laser irradiation, but the amount dependence of the doped cerium was not clear.[16] Here we studied the photosensitive mechanism of Ce with different concentrations after focused femtosecond laser irradiation and successive annealing. The results show that the addition of cerium oxide into glass may increase the concentration of Ag atoms and promote the precipitation of Ag nanoparticles induced by the femtosecond laser. Meanwhile, we also found the extravagant Ce^{3+} may consume the greater part of the energy of the incident pulse, which influenced the precipitation of Ag nanoparticles.

2. Experimental

We prepared glass samples with compositions of $20Na_2O{\cdot}10CaO{\cdot}70SiO_2{\cdot}0.05Ag_2O{\cdot}xCeO_2$ in mol% (x = 0, 0.05, 0.1, 0.2). Reagent grade Na_2CO_3, $CaCO_3$, SiO_2, CeO_2 and $AgNO_3$ were used as raw

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materials. Mixtures of raw materials of about 40 g were melted in a Pt crucible at 1550 °C for 1 hour under ambient atmosphere. Then the melts were quenched into transparent and colorless glasses by pouring them onto a stainless steel plate at room temperature. Finally the glasses were cut and polished into glass samples with thickness of 1.5 mm. Our experiments used a commercial regeneratively amplified 800-nm Ti: Sapphire laser (Spitfire, Spectrum-Physics) that emits 120 fs, 1 kHz, mode-locked pulses. The laser beam with an average power of 20 mW was focused by a 10× objective lens with a numerical aperture of 0.3, and the position of the focus was 200 μm beneath the sample surface with the help of a computer controlled 3-dimensional (3-D) *XYZ* stage. Grating structures with a period of 10 μm were inscribed into the glass samples by laser directly writing with a rate of 1000 μm/s. The size of the grating was 3 mm×3 mm. After exposure to the femtosecond laser, all four samples were annealed at various temperatures for 30 min. Optical absorption spectra and photoluminescence spectra of the glass samples were measured using a Jasco V-570 spectrophotometer and a Jasco FP-6500 fluorescence spectrophotometer, respectively. A frequency doubled Nd:YAG laser beam (532 nm) was employed to examine the diffraction efficiency of the scanning gratings. All the samples were measured at room temperature.

3. Results

From Fig.1, we may observe the absorption spectra of the glass samples before and after femtosecond laser irradiation, and successive annealing at 200 °C, 350 °C, 450 °C, 500 °C and 600 °C, respectively. Before femtosecond laser irradiation, all the samples were colorless and transparent, and there was no apparent absorption in the wavelength region longer than 300 nm in sample Ce0, but the absorption edges showed a little red shift in the other samples doped with cerium because of the intrinsic absorption of the

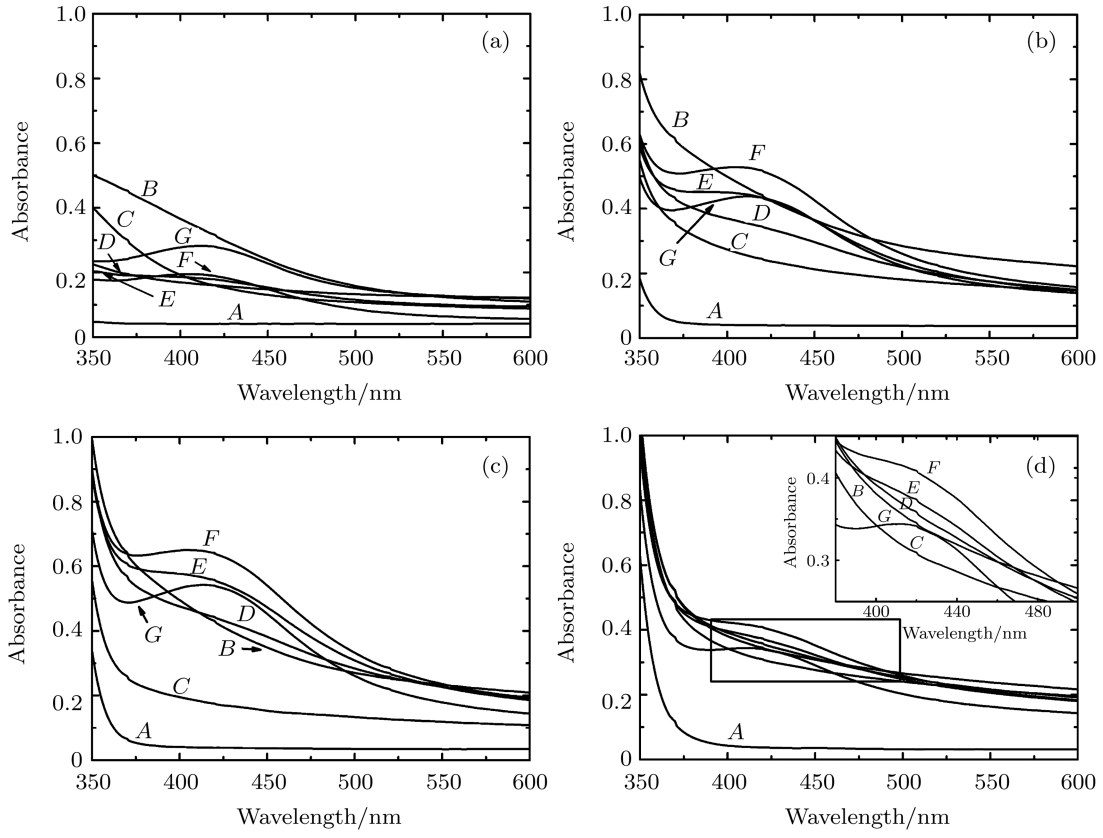


Fig.1. Absorption spectra of (a) sample Ce0, (b) sample Ce0.05, (c) sample Ce0.1, (d) sample Ce0.2 before (curve *A*) and after (curve *B*) femtosecond laser irradiation, and subsequent annealing at various temperatures of 200 °C (curve *C*), 350 °C (curve *D*), 450 °C (curve *E*), 550 °C (curve *F*) and 600 °C (curve *G*) for 30 min. The inset is the amplification of the curves inside the box in Fig.1(d).

cerium ions.[17] Since the formation of hole trap centers was generated from nonbridging oxygen near Ag^+ after the femtosecond laser irradiation,[18] the exposure regions became darkish gray. With annealing at 200 °C for 30 min, the color centers with absorption peaks at 340 nm disappeared and the samples became colorless again. Furthermore, an absorption band with peak at about 415 nm due to surface plasmon resonance of Ag nanoparticles appeared in the samples Ce0.05, Ce0.1 and Ce0.2 after annealing at 350 °C. Nevertheless, no obvious absorption peak due to Ag nanoparticles was found for the sample Ce0 till the temperature reached 450 °C.

In order to study the formation process of Ag nanoparticles in different samples during the annealing process, we plotted temperature dependence of the intensity of the absorption peak due to Ag nanoparticles in Fig.2(a). Here we simply calculated the intensity of the absorption peak by the absorbability difference between the original glass and the femtosecond laser irradiated region at temperatures from 350 to 650 °C. From the curves, the intensity of the absorption peak of Ag nanoparticles in the samples Ce0.05, Ce0.1 and Ce0.2 increased with increasing annealing temperature from 350 °C to 500 °C, and then decreased with the temperatures beyond 500 °C. It was due to the Ag nanoparticles dissolving into the glass matrix. Finally, Ag nanoparticles began to precipitate in the whole bulk glass as a result of thermal chemical effect at high temperature.[19] But in sample Ce0, the intensity of the peak due to Ag nanoparticles increased with increasing annealing temperature. Obvious dissolution was not observed through the whole annealing process.

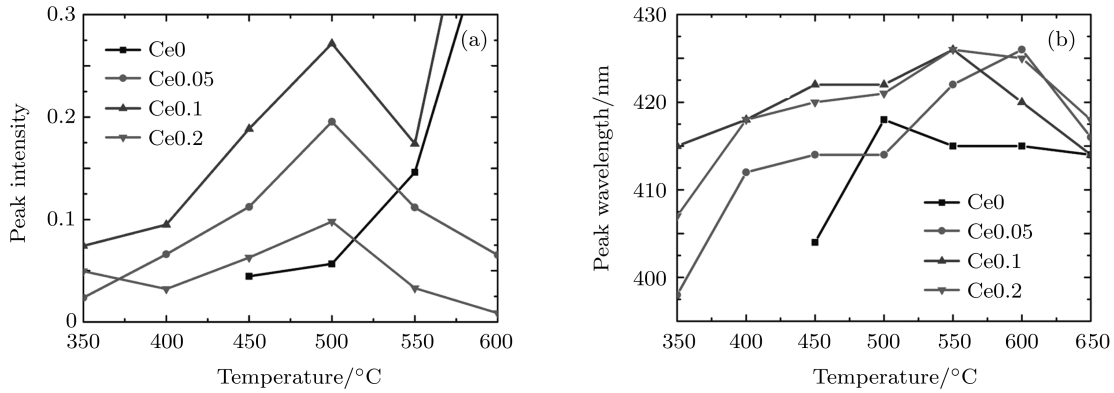


Fig.2. (a) Temperature dependence of intensity of the absorption peak due to Ag nanoparticles; (b) temperature dependence of the position of the absorption peak due to Ag nanoparticles.

According to the quantum size effect and dielectric confinement effect,[19,20] the absorption peak of samples shifted toward a longer wavelength with the increasing size of Ag nanoparticles. In this experiment, the absorption peak of Ag nanoparticles showed some red shift with increasing annealing temperature, and then the absorption peak shifted to a shorter wavelength because of the Ag nanoparticles dissolving into the glass with further treatment at high temperature ($T > 550$ °C), as shown in Fig.2(b).

We also measured the first order diffraction efficiency of the grating in the samples after the direct scanning of the femtosecond laser and successive annealing. The diffraction efficiency (η) was calculated by measuring the light intensity of each diffraction spot. Here the diffraction efficiency is ordinarily defined by the ratio of the diffraction beam intensity of each order to the incident beam intensity. The beam energy of each diffraction spot of a certain order (0^{th}, $\pm1^{\text{st}}$, $\pm2^{\text{nd}}$, so on) was measured by a power meter. As shown in Fig.3(a), the first order diffraction efficiency η was only 3.9% in the sample Ce0 immediately after femtosecond laser irradiation, while the ones of the other samples with cerium can exceed 13%, which is much higher than the diffraction efficiency of the samples without cerium. Based on the Kogelnik's coupled wave theory,[21] the diffraction efficiency can be expressed as $\eta = (\pi\Delta nd/\lambda\cos\theta)^2$, where d is the thickness of the grating, λ is the vacuum wavelength of readout light, and θ is the angle between the surface

normal and readout beam inside the grating. Therefore, we calculated the change of refractive index Δn of the sample in Fig.3(b). We assume that the concentration of colour centre associating with Ag atoms is an important reason for changes of refractive index after femtosecond laser irradiation.[10,22] The colour centre disappeared gradually with increasing annealing temperature due to the thermal stimulation and the phonon vibrations, thus the diffraction efficiency decreased to the bottom at 350 °C. With annealing at higher temperatures, the precipitation of Ag nanoparticles became the key factor influencing the changes of refractive index, so the diffraction efficiency increased along with the increase of refractive index, which is coincident with the formation and growth of Ag nanoparticles.

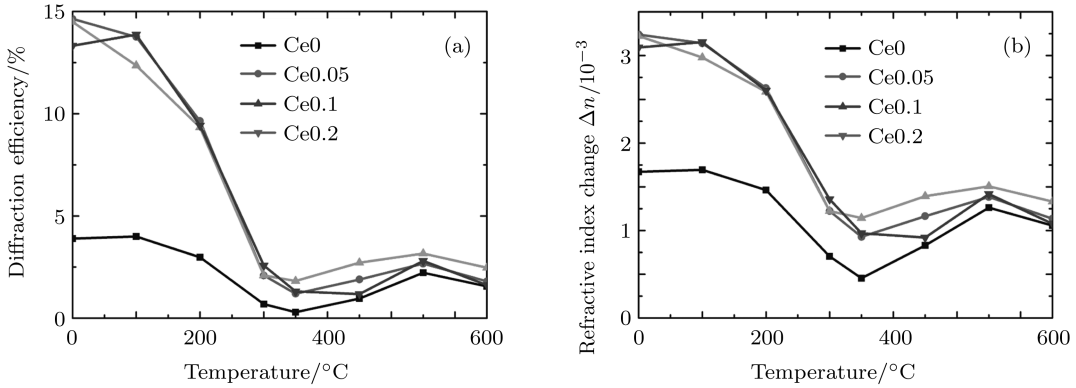


Fig.3. Temperature dependence of (a) the first order diffraction efficiency of the grating and (b) the calculated refractive index changes of the laser irradiation regions.

4. Discussion

Since the samples have no intrinsic absorption at 800 nm, we think that the interaction of laser and matter in this experiment should be a nonlinear optical process of multiphoton absorption and excitation induced by the femtosecond laser. Based on our experimental results, we conclude that the Ce^{3+} may give up a free electron via multiphoton excitation during the femtosecond laser irradiation, and these electrons would be trapped by the Ag^{+} to form Ag^{0} because the threshold of photoionization energy of the conversion of Ce^{3+} to Ce^{4+} is about 3.94 eV,[18,23,24] which is much lower than the band gap (∼8 eV) of the glass matrix.[17,25] Therefore the free electrons were excited much easier from the Ce^{3+} than the ones from the glass matrix. Meanwhile, another part of the laser energy may also excite few free electrons from the $2p$ orbital of the nonbridging oxygen in the SiO_4 polyhedron and induce avalanche ionization via the nonlinear process, but the number of these free electrons from this channel was fewer consequentially because this process needs more rigorous conditions, i.e., larger power density. Finally, the avalanche ionization may produce plasma expansion and microexplosion, and result in permanent structural changes in the focusing regions. In short, the samples with cerium may produce more Ag atoms than the one without cerium after femtosecond laser irradiation, because the power density for generating free electrons from Ce^{3+} was smaller than the one from the glass matrix. It indicated the increase of the concentration of Ag atoms and reasonably promoted the Ag nanoparticle formation at successive annealing. Hence we can explain the formation process of Ag nanoparticles as follows:

$$\text{I.}\quad Ce^{3+} + Ag^{+} \xrightarrow{nh\nu} Ce^{4+} + Ag^{0}(n \geq 3), \tag{1}$$

$$\text{II.}\quad \text{glass} \xrightarrow{nh\nu} h^{+} + e(n \geq 5), \quad Ag^{+} + e \rightarrow Ag^{0}, \tag{2}$$

$$\text{III.}\quad mAg^{0} \xrightarrow{\text{annealing}} Ag_{m}, \tag{3}$$

where n is the number of photons involved in the multiphoton process, and m is the number of Ag atoms aggregating into Ag nanoparticles.

In addition, we found that different concentrations of cerium oxide may influence the precipitation of Ag nanoparticles. According to the above results, we can observe that both the intensity and position of

the absorption peak of Ag nanoparticles of the sample with cerium exceed those of the sample without cerium after femtoseocond laser irradiation and successive annealing, which is consistent with the concentration dependence of cerium and Ag atoms. However, the amount of Ag atoms generated in the sample Ce0.2 may be too small to promote diffusion and aggregation of the Ag atoms. A plausible explanation is that most of the energy is consumed as the 4f–5d transition energy of the Ce^{3+} and then released via a radiative transition process. Notably, Wang *et al* have investigated this phenomenon in Ce^{3+} doped BK7 glass.[26] A broad emission band at about 450 nm associated with the 5d–4f transition of the cerium ion was observed, and the intensity of photoluminescence of Ce0.2 was higher than other samples with 800 nm femtosecond laser excitation or under 365 nm UV light excitation, as shown in Fig.4. The above results agree with our hypothesis on the energy transform competition between free electron combining with Ag^{+} and electron radaitive transition of cerium ions in glass samples. So the extravagant cerium ions may activate their luminescence performances according to the present results.

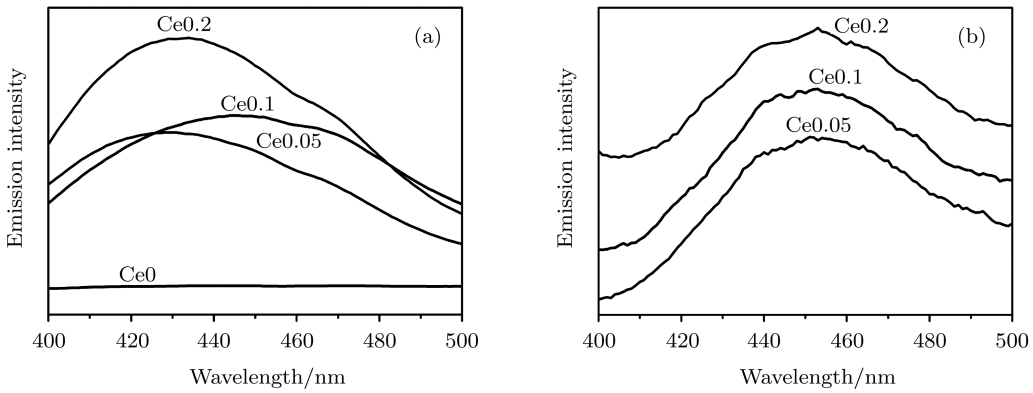


Fig.4. Photoluminescence spectra (a) under 365 nm ultraviolet Xe lamp excitation, and (b) under 800 nm femtosecond laser excitation.

In the previous experiments, the cerium ions doped in conventional and commercially available photosensitive glass like Foturan have been investigated, and cerium ions have no effect of Ag nanoparticles aggregation after femtosecond laser irradiation and successive annealing because most free electrons are considered from the inter-band excitation of the glass matrix.[15] But we would like to point out that the Ce^{3+} concentration in the glass may play an important role in the generation process of free electrons.

5. Conclusion

In conclusion, we studied optical absorption and photoluminescence spectra, as well as the first order diffraction efficiency of scanning grating in a series of silicate glass with doped cerium oxide after femtosecond laser irradiation and successive annealing, in order to clarify the effect of cerium oxide for the precipitation of Ag nanoparticles. The results show that the addition of cerium oxide can increase the concentration of Ag atoms after femtoseocnd laser irradiation and promote the aggregation of Ag atoms to form Ag nanopartiocles at the annealing process, but excessive cerium oxide may consume the laser energy via the radiation transition process, which inhibits the Ag atom formation. According to these results, we think that the photoreduction mechanism induced by the femtosecond laser is the key reason for promoting the concentration of Ag atoms in our experiment. The above results may be used in integrated optical devices and 3-D micromaching in photosensitive glass.

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