Effect of Pulsed Nd:YAG Laser Energy on Crystallization in $Li_2O \cdot Al_2O_3 \cdot SiO_2$ Glass

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Abstract

A 355 nm (3.5 eV) neodymium:yttrium aluminum garnet laser, produced by a harmonic generator, was used to create silver metallic particles as seeds for nucleation in photosensitive glass containing Ag+ and Ce3+ ions. The pulse width and frequency of the laser were 8 ns and 10 Hz, respectively. Heat treatment was conducted at 570 C for 1 h, following laser irradiation, to produce crystalline growth, after which a LiAlSi3O8 crystal phase appeared in the laser-irradiated Li2O Al2O3 SiO2 glass. For the present study, we compared the effect of laser-induced crystallization on glass crystallization with that of spontaneous crystallization by heat treatment.

1. Introduction

Photosensitive glasses are well known as materials that react to light or electromagnetic radiation. Silver and gold cations typically are added to the glasses as metallic ions, to induce photosensitivity under ultraviolet (UV) beam irradiation, with Ce3+ ions used as a sensitizer. The photosensitive mechanism in glasses was investigated by Stookey,1 3 among other researchers, in the 1940s and 1950s. According to Stookey's theory, Ce3+ ions4 can be ionized by photons with an energy of 10 100 mJ/cm2 in the region of 310 nm wavelength light. The electrons produced by photoionization reduce the ions to metallic particles that play the role of nuclei in the glasses. Subsequent heat treatment then develops microcrystalline components in the glasses. This mechanism5 applies mostly to nucleation6 and crystallization produced in photosensitive glasses2 irradiated by a UV beam.

Most glasses are photosensitive to radiation by high-energy photons, such as X rays or gamma rays. However, in the present study, we investigated experimental results for neodymium:yttrium aluminum garnet (Nd:YAG) laser-induced nucleation and crystallization at lower energy than that of X rays or gamma rays and crystallization7 produced by subsequent heat treatment. We studied the effect8 of adopting laser beams9,10 as a photon source.

2. Experimental Procedure

A glass of base composition (in wt%) 8.03 Li2O, 27.39 Al2O3, and 64.58 SiO2 was used for the present study, to which were added (in wt%) 3 K2O, 0.2 Sb2O3, 0.1 Ag2O, and 0.05 CeO2. The batch was calcined at 800 C for 6 h, melted at 1550 C for 2 h, and then held at 1500 C for 2 h for refining. The melts were cooled rapidly, by pouring them onto a carbon plate, to prevent the reduction and precipitation of silver.

The resultant glass was sliced into rectangular bars measuring 2 mm 10 mm 10 mm and finely polished for irradiation by an Nd:YAG laser. The glass specimens were irradiated with a 355 nm wavelength of a third-harmonic-generated Nd:YAG laser emitting an intrinsic beam of a 1064 nm wavelength. The procedure used to create the 355 nm beam is illustrated in Fig. 1. The parameters of the laser were 90 and 130mJ mJ of energy per pulse, an 8 ns pulse width, and a 10 Hz frequency. The generated laser beam was irradiated without a focusing lens for 9 min and 20 min.

After irradiation, heat treatment was conducted at 570 C for 1 h, to precipitate crystal phases in the glasses. Differential Scanning Calorimeter (DSC) was applied to trace the crystallization temperature. Growth of the crystal phases in the glass was observed by optical transmission polarized microscopy (OPTM). X-ray diffractometry (Model No. Q301-33000118 DX-D1, Shimadzu Corp., Tokyo, Japan) was adopted to define the crystals precipitated in the laser-irradiated area of the glasses.

3. Results and Discussion

Figure 1 shows the DSC traces of laser-irradiated glass with 130mJ(A) and 90mJ(B) and the base glass(C). Although the exothermic peaks in Fig. 1 are located in the area of 620 C, we adopted 570 C for the crystallization starting temperature of the exothermic peaks, in order to allow a more sophisticated comparison of the crystallization caused by laser-induced nucleation and by spontaneous nucleation. As shown in Fig. 1, the intensities and temperatures of the exothermal peaks of crystallization are different in the same composition. In the Fig. 1, the glass A shows lower peak temperature and more peak intensity than the others. It is considered that nucleation sites induced in laser-treated glass can be increased by more laser energy of 130mJ. The peak of glass B are located near the same temperature as that of glass C, but the glass B peak also has more exothermic energy than does the glass C peak. This energy difference occurs because the laser-treated glass has more nuclei for nucleation, as a result of photochemical ionization caused by photons from the laser, which creates silver metallic particles to act as seeds in the glass (see Eq. (1)).

$$Ce3+ + Ag+ \quad Ce4+ + Ag0 \qquad (1)$$

Thus, laser-induced nucleation caused by photons and spontaneous nucleation caused by heat treatment occur at the same time in the laser-irradiated glass, but spontaneous nucleation alone occurs in the non laser-irradiated glass. Consequently, the laser-irradiated glass has more exothermic energy of crystallization and lower peak temperature, as indicated in Fig. 1.

Figure 2 shows the XRD patterns of photosensitive glass containing Ag+ and Ce3+ ions. In glass A and B after heat treatment of 570 C for 1hour, crystals of LiAlSi3O8 occur in the Li2O Al2O3 SiO2 within an angular range, whereas hardly any crystallization occurs in the non laser-irradiated glass C after the heat treatment. This result agrees with that from the DSC patterns.

Figure 3 and 4 are SEM photographs of $LiAlSi_3O_8$ phases in the photosensitive glasses A and B after laser irradiation with 90mJ and 130mJ after the heat treatment. The acid leaching with dilute HF was carried out.

Figure 5 is OTPM photograph of the photosensitive glass heat-treated after laser irradiation with 90mJ and 130mJ. In the Fig. 7, the precipitated crystal phases are dispersed within the glass, which is shown at 400 times magnification. The white and black spots indicate $LiAlSi_3O_8$ crystal phases created by laser-induced nucleation; the smaller spots are $LiAlSi_3O_8$ crystal phases resulting from spontaneous nucleation by heat treatment. After laser and heat treatment, the only visible change observed in the present specimens was a color change to amber, caused by crystallization.

The typical method for producing nucleation and crystallization[11] in most glass-ceramics[12] generally is two-step heat treatment, but we propose using laser-induced nucleation, followed by a one-step heat treatment. Thus, we propose that the photoionization of Ce^{3+} by laser photons with an energy of 90 and 130 mJ/cm^2 at a 355 nm wavelength, corresponding to the ionization energy of Ce^{3+} by a UV beam for the creation of novel metallic particles in a photosensitive glass, induces a nucleation process in the glass, whereas spontaneous nucleation by heat treatment in non laser-irradiated glass scarcely affects crystallization, because the heating rate at 570 C is not enough heating rate.

Because no special features or damage to the glass surface were observed before laser irradiation, the crystallization is most likely resulted from silver metallic particles, nuclei, produced by the laser irradiation. In addition, a nanosecond pulse-width laser beam with a 355 nm wavelength proved able to create photoionization, causing nucleation. Thus, we have demonstrated that $LiAlSi_3O_8$ crystals can be precipitated by laser-induced nucleation and crystallization in the photosensitive glass.

4. Conclusion

We have demonstrated the precipitation of different $LiAlSi_3O_8$ crystal phases in an Li_2O Al_2O_3 SiO_2 glass by a laser-induced nucleation process with energy of 90mJ and 130mJ, followed by heat treatment. This laser-induced process apparently creates silver metallic seeds by the photoreduction of electrons from Ce^{3+}, as a result of the photon energy of the laser. The laser method, we expect, offers a unique and sophisticated way of producing desired crystal-phase growth and properties optically or electronically different from those created by typical two-step heat treatment.

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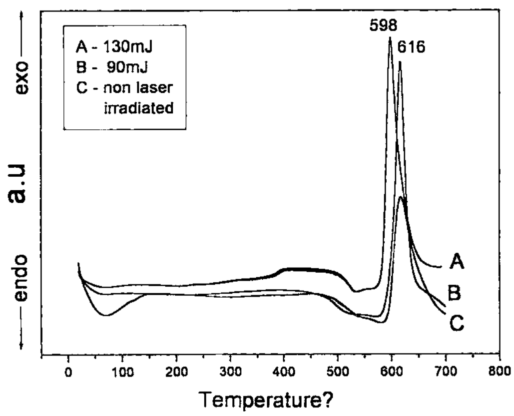

Fig. 1. DSC traces of laser-irradiated glass A, B and non-laser irradiated glass C. The exothermic peaks are indicating crystallization in each glass

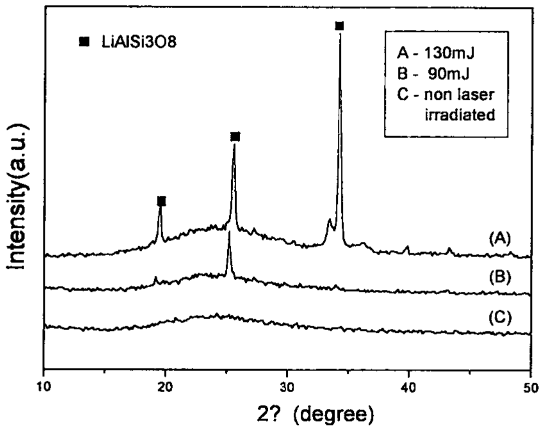

Fig. 2 X-ray diffraction patterns of photosensitive glasses containing Ag+ and Ce3+. Glass A and B were laser irradiated with nanosecond pulses at a wavelength of 355nm with an energy of 90 and 130mJ/cm2/pulse, and shows crystallization after heat-treatment at 570 C for 1hour. LiAlSi3O8 is indicated in the figure.

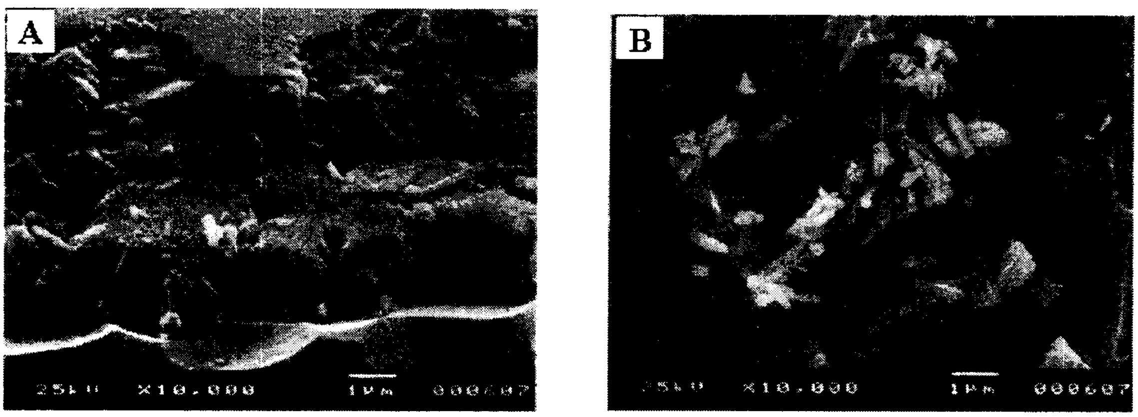

Fig. 3 SEM photograph of LiAlSi3O8 phases in the photosensitive glass after laser irradiation of 130mJ energy and heat treatment at 570 for 1h. The acid leaching with dilute HF was carried out.

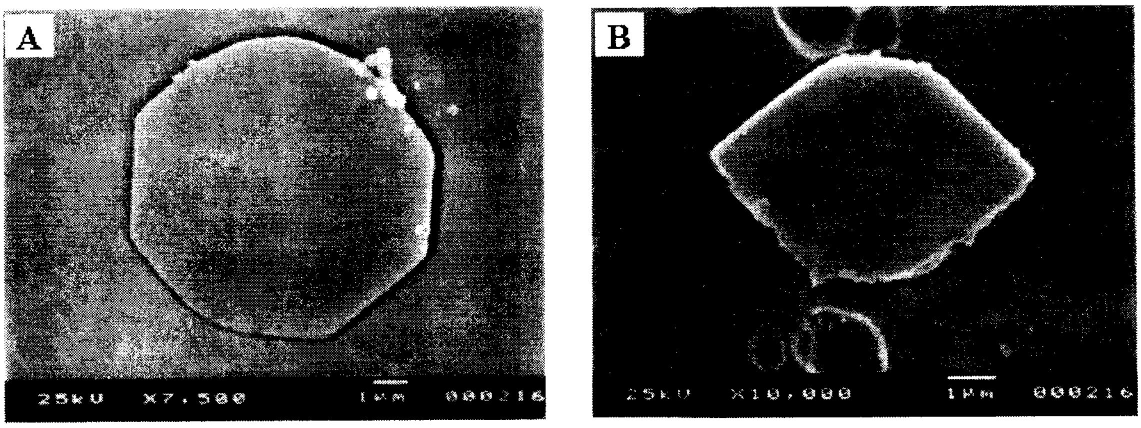

Fig. 4 SEM photograph of LiAlSi3O8 phases in the photosensitive glass after laser irradiation of 90mJ energy and heat treatment at 570 for 1h. The acid leaching with dilute HF was carried out.

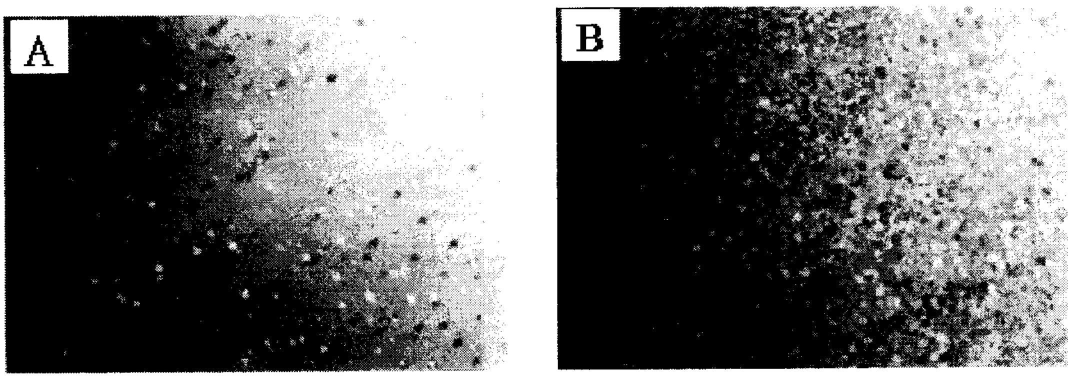

Fig. 5 Photographs of Optical Transmission Polarized Microscope for the photosensitive glass containing Ag+ and Ce3+ heat-treated after the irradiation of 8 nano-second pulses at a wavelength of 355nm with 90(A) and 130(B)mJ/cm2 at 10Hz repetition for 20min and 9min, respectively.