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Crystallization in Li_2O-Al_2O_3-SiO_2 Glass induced by 355 nm Nd:YAG Laser Irradiation

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Abstract : Nd:YAG laser of 355 nm wavelength, which amounts to 3.5 eV, produced by a harmonic generator was used to create Ag metallic particles as seeds for nucleation in photosensitive glass containing Ag^+ and Ce^{3+}. The pulse widths and frequency of the laser were 8ns and 10 Hz, respectively. For crystalline growth, heat-treatment following laser irradiation was carried out at 570°C for 1h. Then, the $LiAlSi_3O_8$ crystal phase appeared in the laser irradiated lithium aluminum silicate glass. We present the effect of laser-induced nucleation compared with spontaneous nucleation by heat treatment for crystallization in the glass.

Keywords : Crystallization, Photosensitive glass, 355 nm, Irradiation, Nucleation

1. Introduction

Photosensitive glasses were well known for the reacting materials to light or electromagnetic radiations. Ag and Au cations in the glass are the typical metallic ions to have the photosensitivity by UV beam irradiation with the help of Ce^{3+} ion as a sensitizer. The photosensitive mechanism in glasses is due to Stookey[1-3] in the 1940s and 1950s.

According to their theory, Ce^{3+} ion[4] can be ionized by photons with the energy of 10 mJ-100 mJ/cm^2 in the region of 310 nm wavelength light. The electrons produced by the photo-ionization can reduce the ions to metallic particles that play a role of nuclei in the glasses. Then, the subsequent heat-treatment can develop the microcrystalline consisting of the components in the glasses. This mechanism[5] is mostly applied from the nucleation[6] and crystallization in the photosensitive glasses[2] irradiated by UV beam.

Most glasses are photosensitive to a radiation with high-energy photons such as X-rays or γ-rays. In this article, however, it is reported that the experimental results of Nd:YAG laser-induced nucleation with lower energy comparing with X-rays or γ-rays and crystallization[7] by subsequent heat-treatment. We studied the effect[8] of the laser beams,[9,10] which that is adopted as a photons source.

2. Experiment

The glass of base composition of 8.03Li_2O, 27.39Al_2O_3 and 64.58SiO_2(in wt%) as used, to which 3 wt% K_2O, 0.2Sb_2O_3, 0.1Ag_2O, 0.05CeO_2 were added. The batch was calcined at 800°C for 6 hrs and melted at 1550°C for 2 hrs, and held at 1500°C for 2 hrs for refining. The melts were cooled rapidly by being pouring onto a carbon plate to prevent reduction and precipitation of silver. The glass was sliced in 2 mm×10 mm×10 mm in size and polished finely to be irradiated by Nd:YAG laser. The glass specimen were irradiated with 355 nm wavelength of 3rd harmonic generated Nd:YAG laser emitting intrinsic beam of 1064 nm wavelength. The process of 355 nm laser beam was illustrated in Fig. 1. The parameters of the laser were 8ns pulse width, 10 Hz frequency and 90 mJ/pulse, and generated laser beam was irradiated without focusing lens for 20 min. After the irradiation, heat treatment at 570°C for 1 hr was carried out to precipitate crystal phases in the glasses. Differential Scanning Calorimeter to trace crystallization

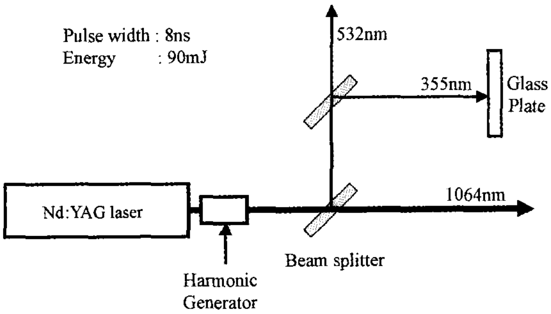

Fig. 1. Schematic of Nd:YAG laser emitting Third Harmonic Generated 355 nm wavelength with repetition of 10 Hz and 8ns pulse duration.

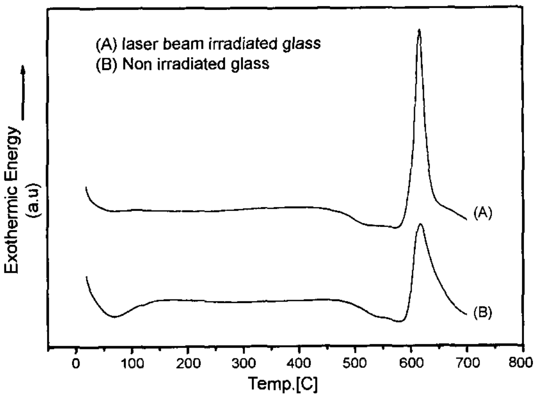

Fig. 2. Differential Thermal Calorimetry traces of laser irradiated glass(A) and non irradiated glass(B). The exothermic peaks are indicating crystallization in each glass.

temperature was applied. We have observed growth of crystal phases in the glass with Optical Transmission Polarized Microscope (OTPM). X-ray diffraction analysis (SIMATZU, DX-D1) was adopted to define crystals precipitated in the laser irradiated area in the glasses.

3. Results and Discussion

Fig. 4 is SEM photograph of $LiAlSi_3O_8$ phases in the photosensitive glass after laser irradiation of 355 nm wavelength and heat treatment at 570°C for 1 h. The acid leaching was carried out by diluted HF. After laser and heat treatment, the only visible change observed in the present specimens was a color change to amber, caused by the agglomeration of silver. Fig. 2 shows DSC(differential scanning calorimeter) traces of the

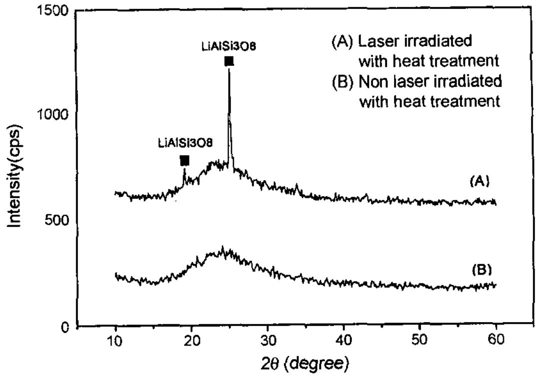

Fig. 3. X-ray diffraction patterns of photosensitive glasses containing Ag^+ and Ce^{3+}. Only sample(B) was laser-irradiated with nanosecond pulses at a wavelength of 355nm with an energy of 90mJ/pulse, and each sample was heat-treated.

non laser-irradiated glass(B) and laser irradiated glass(A). Though the exothermic peaks are located in the area of 620, we adopted 570°C for the crystallization as starting temperature of the exothermic peaks for more sophisticated comparison of the crystallizations caused by laser induced and spontaneous nucleation. In Fig. 2, the glasses show the different intensities of the exothermal peaks of the crystallization in the glasses. The peak of the laser irradiated glass(A) locates around same temperature with non laser-irradiated glass(B), but has more exothermic energy comparing with the other. This phenomenon is due to the fact that the nucleation of the laser treated glass has more nuclei with help of photochemical ionization, $Ce^{3+}+Ag^+ \rightarrow Ce^{4+}+Ag^0$, by photons of laser, which creates Ag metallic particles acting as seeds in the glass. Thus, it is considered that laser-induced nucleation by photons and spontaneous nucleation by heat treatment occur in the laser-irradiated glass at the same time, but only the spontaneous nucleation is happened in non laser-irradiated glass. As the result of it, laser irradiated glass have more exothermic energy of crystallization as we present in Fig. 2. Fig. 3. shows X-ray diffraction patterns of photosensitive glass containing Ag^+ and Ce^{3+}. In the laser irradiated glass (A) after heat treatment, the $LiAlSi_3O_8$ crystals of lithium aluminum silicate was indicated in the angular range while the crystallization scarcely occurs in the non irradiated

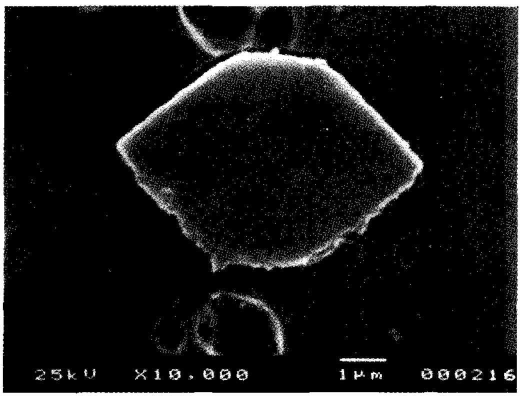

Fig. 4. SEM photograph of $LiAlSi_3O_8$ phase in the photosensitive glass after laser irradiation of 355 nm wavelength and heat treatment at 570°C for 1h. Fine polishing and acid leaching with diluted HF was carried out.

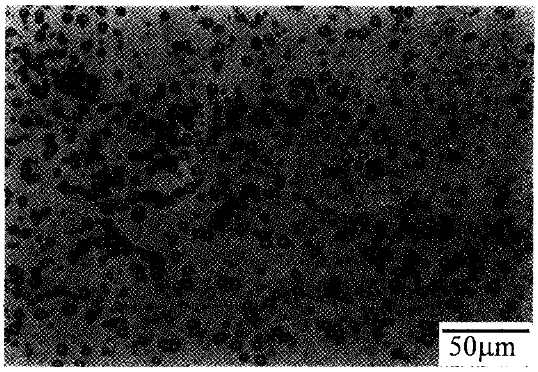

Fig. 5. $LiAl_3SiO_8$ crystal phases are showed in the Photograph of Optical Transmission Polarized Microscope for the photosensitive glass containing Ag^+ and Ce^{3+}. The glass was heat-treated after the irradiation of 8ns pulses at a wavelength of 355 nm with 90 mJ/pulse at 10 Hz repetition for 20 min. The picture was taken after acid treatment of the glass with diluted HF.

glass after heat treatment. This result also agrees with that of the DSC patterns. Fig. 4~Fig. 5 is the photograph of Optical Transmission Polarized Microscope. In the Fig. 5, the precipitated crystal phases, $LiAlSi_3O_8$, are dispersed in the glass, which is observed by 400X magnitude.

After laser and heat treatment, any visible changes, such as crack, has not been observed except the color change to amber due to the agglomeration of Ag colloid particles.

Generally, the two-step heat treatment for nucleation and crystallization[11] is the typical process in most glass ceramics,[12] but the proposed method for crystallization in this article is to utilize laser induced nucleation followed by one-step heat treatment. Thus, we propose that the photo-ionization of Ce^{3+} by laser photons energy with 10-100 mJ/cm^2 at 300-350 nm wavelength, which is corresponding to ionization energy of Ce^{3+} by UV beam for creation of novel metallic particles in a photosensitive glass, offers nucleation process in the glass while the spontaneous nucleation by heat treatment in non laser irradiated glass hardly effect on the crystallization due to not enough heating rate at 570°C. Since any features or damages on the glass surface were not observed before heat treatment, we consider that the crystalline was created from silver metallic particles caused by the laser irradiation. We also proved that nanosecond pulse width laser beam with 355 nm wavelength can create photo-ionization causing nucleation process. For the first time, to our knowledge, we demonstrated that $LiAlSi_3O_8$ crystals can be precipitated by laser induced nucleation like as UV beam causing lithium methasilicate[13] or sodium fluoride crystals in typical photosensitive glass.

4. Conclusion

We demonstrated the precipitation of $LiAlSi_3O_8$ crystals phases in the lithium aluminum silicate glass with laser induced nucleation process followed by heat treatment. This process for the crystallization is proposed to create Ag metallic seeds by photo reduction with electrons from Ce^{3+}, which is caused by laser photon energy. This method can be a unique and sophisticated way to control a desired crystal phase growth, and would give optically or electronically different properties distinguished from the typical two-step heat treatment.

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