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Micro-crystallization of the infrared transmitting chalcogenide glass in $GeSe_2$–As_2Se_3–PbSe system

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Abstract

Micro-crystallization of the chalcogenide glass $40GeSe_2$–$50As_2Se_3$–10PbSe has been studied in order to obtain infrared transmitting glass ceramics. Differential scanning calorimetry, IR transmission spectroscopy, X-ray diffraction, scanning electronic microscopy and thermal dilatancy have been used for characterizing the crystallization process. Performing thermal treatment on the glass sample at 250 °C (40 °C higher than T_g) for 10 h, we obtained a glass ceramic containing well-dispersed micro-crystals (<50 nm) and the obviously decreased thermal expansion coefficient.

Keywords: D. Glass ceramics; Micro-crystallization; Chalcogenide glass

1. Introduction

Chalcogenide glasses have long been studied due to their practical and potential usages in fields such as infrared optics, opto-electronics and photonics [1–5]. In particular, chalcogenide glasses are the good candidate for replacing costly germanium single crystal for thermal imaging application. To reach this target, they are facing with the challenge of improvement on thermal and mechanical properties because of their relatively low phonon energy and weak chemical bonds that are desired by the longer IR cut-off edge for mid and far infrared transmitting glasses [3–5].

Micro-crystallization procedure has widely been known as an effective way to improve properties of the original glass. For example, glass ceramic composites containing micro-crystals can have very low thermal expansion coefficient and other outstanding thermal mechanical properties [4–5]. In general, the optical transparence declines after the glass being crystallized due to refraction of crystals separated from the glass matrix. Thus it becomes essential to control the size of crystals in the course of crystallization process in order to decrease the scattering loss as much as possible to confine the affected wavelength region out of the application window in the middle and far IR region [4,5].

For realization of the controlled crystallization process, the original glass is desired to be stable enough to avoid extra growth of crystals during the thermal treatment [4,6]. In this communication, we report our latest micro-crystallization experiments on the selected glass from the novel $GeSe_2$–As_2Se_3–PbSe system [7]. The proper thermal treatment conditions were explored under which glass samples were heated and characterized by IR transmission spectroscopy, scanning electronic microscopy (SEM), X-ray diffraction (XRD) and thermal expansion coefficient (TEC) measurements.

2. Experimental

The glass composition for the present micro-crystallization experiment is selected from a newly developed $GeSe_2$–As_2Se_3–PbSe system ($40GeSe_2$–$50As_2Se_3$–10PbSe, mol%). Glass samples were prepared by using the traditional melt-quenching

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method with high purity elements (5N) Ge, As, Pb and Se as starting materials. They were weighed in the appropriate quantities and introduced into a silica ampoule which was then sealed under vacuum. The mixture in the sealed ampoule was heated in a rocking furnace at about 850 °C for 12 h to ensure homogenization of the melt. The ampoule with the melts was then cooled in air and annealed at 200 °C for 2 h. The XRD pattern which shows no crystal diffraction peak confirmed that the as-prepared samples were homogeneous glasses.

Samples were cut into slices of 3 mm in thickness and double-face polished for optical measurements. Thermal treatments were performed on these samples at different temperatures (higher than T_g) for different durations. Differential scanning calorimetry (DSC) (TA DSC 2010) analysis was used to determine the glass transition temperature T_g. The IR transmission spectra (BRUKER VECTOR22) and TEC (TA TMA 2940) were measured on samples before and after thermal treatment to evaluate the effect of crystallization process. The morphology of micro-crystals on section was observed directly by SEM (JSM6301F JEOL) while the crystal type was identified using XRD (PHILIPS PW3230).

3. Results and discussion

The DSC curve of the base glass measured at a heating speed of 10 °C/min is shown in Fig. 1. It is seen that an endothermal peak for determining T_g is at 210 °C while no exothermic crystallization peaks detectable. The latter is an indication of the fairly high thermal stability of the glass that facilitates fabrication of chalcogenide glass ceramics via controlled crystallization treatment.

Controlled crystallization of the glass samples were performed under the different conditions as shown in Table 1. As an important parameter for crystallization process, the annealing temperatures T_a was chosen in the range between 20 °C and 60 °C above T_g. These temperatures are below the softening temperatures of glass samples thus the figuration of samples remained unchanged. It is known that the optical transmittance of glass ceramics will decrease as the size of crystals is close to the wavelength [8]. Thus, the aim of annealing is to keep crystals precipitated from the glass matrix small enough to ensure the optical transmission in the required wavelength region. So far as the crystallization process is concerned, it contains two steps: nucleation and crystal growth. The suitable annealing temperatures are those at which nuclei forms quickly while crystal grows slowly. As mentioned above, transmittance of glasses is sensitive to the size of precipitated crystals, so that Vis–NIR–IR transmission curve can be served as an evaluation criterion for crystallization treatment.

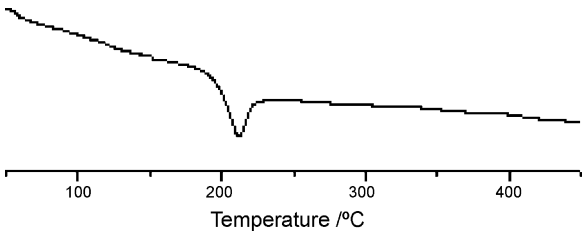

Fig. 1. DSC curve of the base glass at the heating rate of 10 K/min.

Table 1
Samples and thermal treatment conditions

	Code				
	GC1	GC2	GC3	GC4	GC5
T_a (°C)	230	230	230	250	270
t (h)	10	20	40	10	10

Fig. 2 shows the variation of the Vis–NIR–IR spectra as samples were annealed under different conditions. When the sample was heated at 230 °C for 10 h, its IR transmission spectrum did not exhibit remarkable variation compared with the base glass. When the duration extended to 40 h, the cut-off edge at the short wavelength end showed a small red shift. As annealing at 250 °C for 10 h, the heated sample showed a decline of transparence from 890 nm to 1500 nm, but kept the original transmission level in the longer wavelength region. Further increasing T_a to 270 °C for 10 h, the heated sample became opaque with the cut-off edge shifted to the 1700 nm.

SEM photographs on sections of some thermally treated samples are shown in Fig. 3 for visual representation of crystal morphology under different annealing conditions. After heat treatment at 230 °C for 20 h, only sparse and small crystals were precipitated from glass matrix (a). The increasing amount of crystals with the average diameter smaller than 50 nm was observed for the heated sample at 250 °C for 10 h (b). As the annealing temperature increased up to 270 °C for 10 h, the amount of crystal decreased with the growing size about 100 nm (c). SEM observations correspond well to the above IR transmission spectra. The decline of IR transmission is mainly due to the scattering loss caused by micro-crystals, so the volume and amount of crystals distributed in glass matrix determine the variation of IR transmission spectra. When the degree of crystallization is low as shown in Fig. 3(a), the IR transmission spectra of sample GC3 shows almost imperceptible change. As T_a rose to 250 °C (sample GC4), the growth of crystals speeds up, and causes the scattering loss in the short wavelength region. As the size of micro-crystals become larger (sample GC5), the range of influence on IR transmission spectra by scattering loss expands to the longer wavelength region.

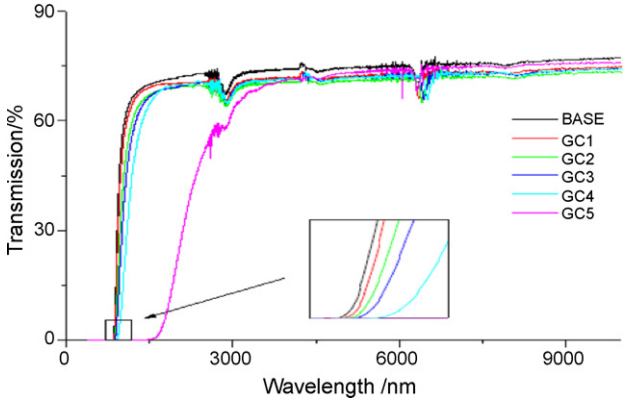

Fig. 2. Vis–NIR–IR transmission spectra of some glasses ceramic.

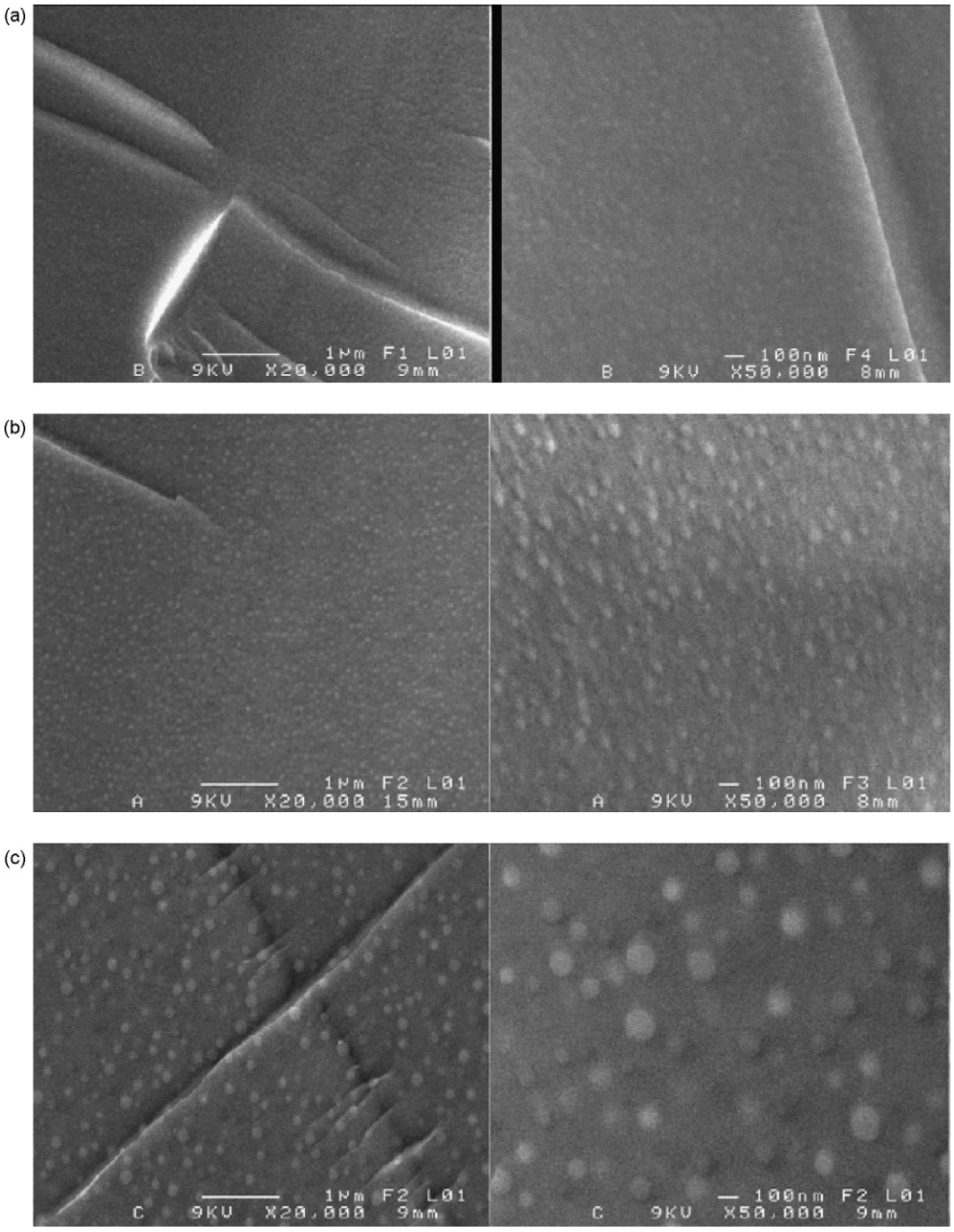

Fig. 3. SEM photographs of glass samples after annealing at 230 °C for 20 h (a); 250 °C for 10 h (b); 270 °C for 10 h (c).

From these results it is clear that availability of glass ceramics preserving good IR transmission requires a control of the increasing amount of nuclei with negligible crystal growth. So far as the present work is concerned, it can be concluded that the nucleation step was dominant in the annealing temperatures from 230 °C to 250 °C, while crystal growth speeded up with the increasing temperature and time. As T_a was up to 270 °C, crystal growth progressed more intensively, making the crystallization process hard to control.

The types of precipitated crystals have been identified by the XRD measurement on the treated sample in this system [7]. It can be seen from Fig. 4 that crystals consist of As_2Se_3, AsSe and PbSe. From viewpoint of glass formation, the complication of glass formers is another factor to ensure the thermal stability of the system, as the ''competition'' of different crystal species is beneficial to the control of the nucleation-crystallization process.

TEC (α) is an important parameter to appraise the thermal shock resistance of glass ceramics. Thermal expansion of glass ceramics is known to be determined by TEC of both glass and micro-crystal phases [9]. For the same composition, glass normally has the larger TEC than crystal due to the looser

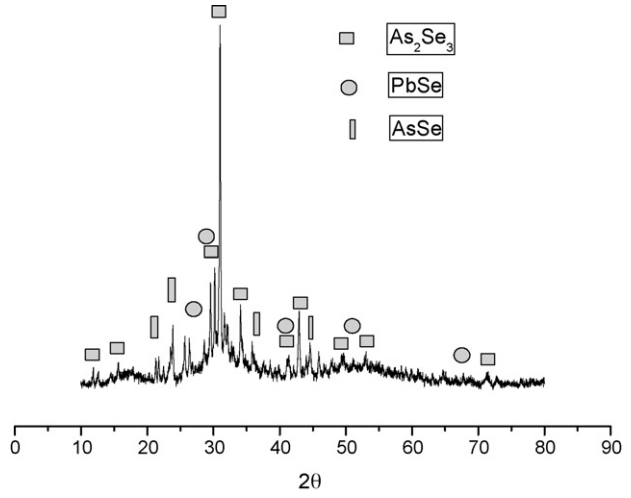

Fig. 4. X-ray diffraction patterns of glass ceramic.

Table 2
Thermal expansion coefficient

Code	α (μm/m °C)
Base	12.93
GC1	12.13
GC2	11.94
GC3	11.7
GC4	9.41
GC5	8.79

structure [10]. Table 2 shows measured TEC of the present glass samples. As expected, the samples showed a decrease α with the increased annealing temperature and/or duration due to a significantly increased crystal/glass ratio, which is consistent with the variations of IR transmittance spectra (Fig. 2) and SEM observations (Fig. 3).

4. Conclusions

The selected base glass $40GeSe_2$–$50As_2Se_3$–10PbSe has the good thermal stability for crystallization treatment. For the sample treated at the annealing temperatures from 230 °C to 250 °C, the nucleation step is dominant while crystal growth speeds up with the increasing temperature and time. The size of crystals precipitated from the glass matrix can be controlled smaller than 50 nm with the obviously decreased TEC.

Acknowledgement

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