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Time-temperature-transformation diagrams for crystallization of the oxyfluoride glass system

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ABSTRACT

Isothermal crystallization studies were performed on the glass $37.26SiO_2$-$28.11Al_2O_3$-7.73CaO-$26.89CaF_2$-$4.5K_2O$ (wt%) in the crystallization region between the glass transition (T_g) and end of crystallization temperature (T_f), resulting in a time-temperature-transformation (T.T.T.) diagram for crystallization. The crystallized fraction calculated by "Ohlberg-Strickler" method. By fitting Avrami curves on experimental data kinetic properties of isothermal crystallization of CaF_2 has been determined. It is concluded that the crystallization of the mentioned glass is a process controlled by Avrami nucleation and three-dimensional diffusion controlled growth. The (T.T.T.) "C" shape diagrams with a nose at 690 °C resulted in from fitted Avrami "S" shapes Diagrams.

Introduction

Wang and Ohwaki [1–6] proposed oxyfluoride-based glass-ceramics consisting of fluoride nanocrystals with RE^{3+} incorporated ions into fluoride nanocrystals. Usually, glass-ceramics are prepared using controlled heat treatment. Nucleation and growth of fluoride crystals such as pbF_2, LaF_3, CaF_2 and etc occur in the base glass during heat treatment and RE^{3+} prefers to segregate into the fluoride nanocrystals [1].

Time-temperature-transformation (T.T.T.) diagrams indicate the transformation rate of equal phase transformation [7]. T.T.T. diagrams are used mostly for steels and alloys [8], metallic-glasses [9,10], glass and glass ceramics [11–15]. In the processing of glass-based materials, T.T.T. diagrams help to predict the characteristics of crystallization, state of nucleation and conversion to a certain degree of crystallinity. In general, T.T.T. diagrams are "C-shape" curves for metals and glass-based materials [10,13]. In order to propose a T.T.T. diagram, degree of crystallinity should be measured.

Most conventional method for determination of crystallization percentage in glass-ceramics is the investigation of X-ray diffraction (XRD) patterns. The Ohlberg and Strickler [16] XRD based method is used especially to study the crystallization procedure on glasses with different heat treatment conditions. It is based on the XRD patterns comparison of heat treated glass–ceramic samples with totally amorphous and mechanical mixture specimens. Intensities of X-ray patternsin2θ which the nanocrystalline scattering intensity is high for fully amorphous glass and in the same time is not overlapped with the crystalline peaks of both heat-treated glass and mechanical mixture sample.

This paper proposes primary T.T.T. diagrams for the crystallization of an oxyfluoride-based glass. These T.T.T. diagrams can now be used to predict the crystallization degree of an oxyfluoride-based glass for isothermal annealing and can give suitable guidance for isothermal heating steps. In this study, we report on crystallization study of $37.26SiO_2$-$28.11Al_2O_3$-7.73CaO-$26.89CaF_2$-$4.5K_2O$ (%wt). Heat treating this glass in different temperature and times then measuring the crystallinity enabled us to measure the complete T.T.T. diagrams for crystallization of parent glass.

Experimental procedures

$37.26SiO_2$-$28.11Al_2O_3$-7.73CaO-$26.89CaF_2$-$4.5K_2O$ (wt%) glasses with some dopants were prepared using precursor powders. The composition of initial glass which is the most typical one, have been used by other scientists [17–25] has been shown in Table 1.The main starting materials are high purity leached SiO_2(99% purity), Al_2O_3 (Merck 101077) and CaF_2 (Dae Jung 2508145), $CaCO_3$ (Merck 102069) and K_2CO_3 (Sigma-Aldrich P5833) were used to introduce CaO and K_2O. To avoid the bubbles in the samples, Sb_2O_3 and As_2O_3 were used as refining agents. Pr_2O_3, Y_2O_3, and V_2O_5 were added as dopants to improve crystallization and optical properties. K_2O was added to the batch to have a melt with favorable viscosity [17]. 50 g of the mixed batch in alumina crucibles was melted at 1450 °C for 1 h in an electric furnace. The prepared molten glass was poured into molds which preheated at 500 °C. Finally obtained glassy discs with 0.5 cm thickness were

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Table 1
The composition of the initial glass (in wt.%).

SiO_2	Al_2O_3	CaF_2	CaO	K_2O	Pr_2O_3	V_2O_5	Y_2O_3
37.26	28.11	26.89	7.73	4.5	1.5	1.5	1.5

annealed at 500 °C for 30 min to release the internal stresses due to thermal shock. In order to construct the T.T.T. diagram for glass-oxy-fluoride nanocrystals, the parent glass was heat treated at temperatures of 620, 640, 660, 690 and 720 °C (between *Tg* and *Tf*) in the time range of 1 until 18 h with the step of 2 h.

Differential thermal analysis of 50 mg powdered glass samples was done with the rate of 10(°C/min) by DTG-60AH Shimadzu to determine crystallization temperatures.

Crystal phase analysis of glass-ceramics was carried out by X-ray diffraction (XRD, Siemens D-500). In this study X-ray diffraction used to identify the phase analysis and measure the crystallinity of mechanical mixture of glass, initial amorphous glass, and partially crystallized glass to plot T.T.T. diagrams.

Results and discussion

Fig. 1 shows the conventional DTA curves of $37.26SiO_2$-$28.11Al_2O_3$-$7.73CaO$-$26.89CaF_2$-$4.5K_2O$ (wt%) at a heating rate of 10(°C/min). The glass transition temperature T_g, the end of the first crystallization T_f and especially the crystallization temperature of desired CaF_2 phase, T_{p1} is shown.

The temperatures for crystallization of CaF_2 nanocrystals was selected in the region of T_g to T_f (where the crystallization completes).

To investigate the crystallization mechanism and plotting T.T.T. diagrams, several glass samples were heat treated at various temperatures of 620, 640, 660, 690 and 720 °C which selected based on DTA results, for various times. All the samples heat treated in selected temperatures crystallized partially. But with increasing temperature, the time needed for definite crystallized fraction decreases. In Fig. 2 XRD patterns of the two glass-ceramic samples which heat-treated at 690 °C for 6 h and 9 h, the parent glass and the mechanical mixture of the crystalline compound with chemical composition equivalent to parent glass are shown. Based on Ohlberg & Strickler model [16] the XRD pattern of the mechanical mixture is used for correction of background. The values of 2θ are selected in the regions that the scattering intensity for amorphous glass is high and is not overlapped with the crystalline peaks in both partially crystallized sample and mechanical mixture. The Ohlberg & Strickler equation which shows the crystallinity of partially crystallized is as following:

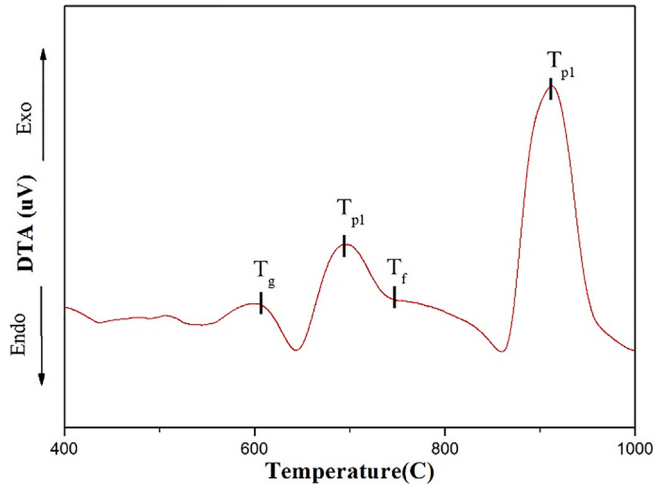

Fig. 1. DTA curves of the oxy-fluoride glass measured at different heating rates.

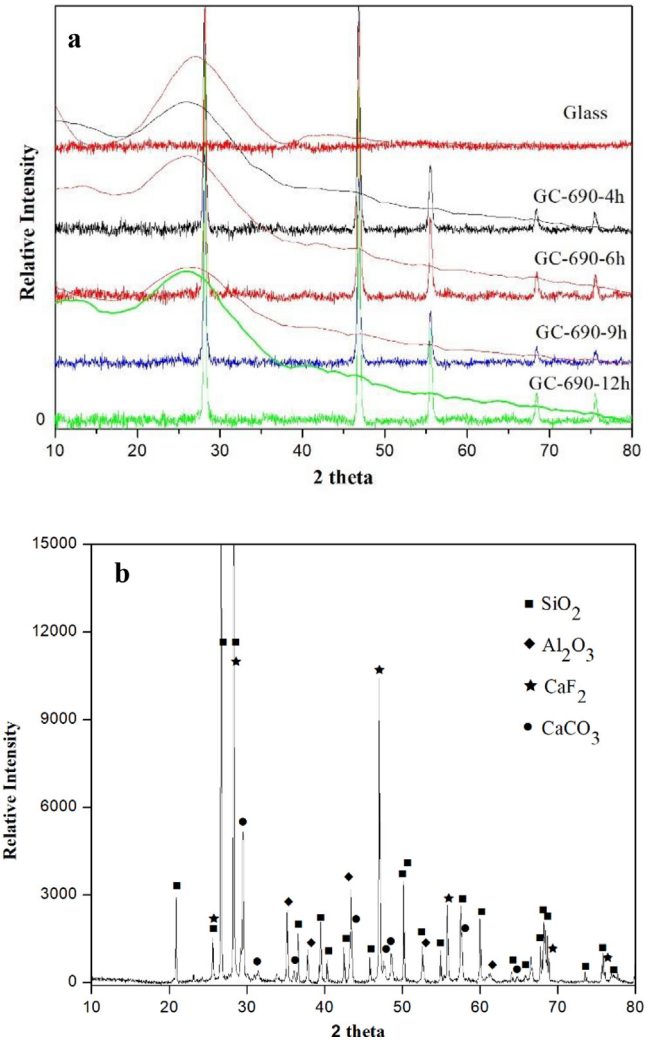

Fig. 2. XRD patterns of: (a) the parent glass (fully-amorphous sample) and partially heat-treated glasses at 690 °C for different times with their backgrounds (b) mechanical mixture of crystalline compounds.

$$\%C = \left(\frac{I_g - I_x}{I_g - I_b}\right) \times 100$$

In this equation, I_g, I_x, and I_b are the XRD intensity scattered by the parent glass, the partially crystallized glass and a mechanical mixture of crystalline powders. It is clear from Fig. 2 that crystalline phase was formed in the expense of amorphous phase and the scattering intensity of amorphous phase proportionally was reduced because of crystallization.

The calibration curve for this study was obtained using the mixture of CaF_2 and the parent glass at different ratios. Parent glass, parent glass-CaF_2 mixtures and pure crystalline CaF_2 were used to ensure I_g, I_x and I_b intensities. The results are plotted in Fig. 3 and summarized in Table 2. It can be seen that the amounts of determined and calculated crystallinity are in good agreement with each other.

The isothermal reaction kinetics of nucleation and growth in solid-solid phase transformations can be quantified using the Johnson-Mehl-Avrami equation [26–28], and we will also employ this description in this study. In this approach, the transformed fraction, A_t, for samples after a time t is given by:

$$A_t = 1 - \exp(-(kt)^n) \quad (1)$$

where A_t is the transformed fraction mentioned in the, n is the Avrami exponent and k is the reaction rate constant that includes nucleation