

NON-ISOTHERMAL CRYSTALLIZATION IN ZrF_4 - BaF_2 - GdF_3 - AlF_3 FLUORIDE GLASSES *

KAZUMASA MATUSITA, HIDEKI YAMAMOTO and TAKAYUKI KOMATSU

Department of Materials Science and Technology, Technological University of Nagaoka, 1603-1 Kamitomiokacho, Nagaoka, Niigata-ken 940-21 (Japan)

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ABSTRACT

The crystallization kinetics of 50 mol.% ZrF_4 -40 mol.% BaF_2 -4 mol.% GdF_3 -6 mol.% AlF_3 were studied by DSC and optical microscopy. The crystallization kinetics were analysed on the basis of the non-isothermal kinetic theory. The viscosity of glass was measured by the penetration method. In the course of heating at a constant rate, metastable β - $BaZrF_6$ crystals were found to precipitate first and transform into stable α - $BaZrF_6$ crystals at higher temperatures. It was found that a constant number of crystal particles, irrespective of heating rate, grow three-dimensionally in bulk specimens. The activation energy determined for crystal growth was 469 kJ mol^{-1} , much less than that for viscous flow. The apparent activation energy determined for viscous flow was 920 kJ mol^{-1} in the narrow temperature range of measurement but the activation energy was observed to decrease extraordinarily with temperature. The mechanism of crystal growth is discussed in relation to the discrepancy between the activation energies for crystal growth and viscous flow.

INTRODUCTION

Thermal analysis has been used as a rapid and convenient method for studying crystallization kinetics. The non-isothermal crystallization kinetics of materials heated at a constant rate have been analysed theoretically [1–7], and a method for obtaining kinetic parameters, such as an activation energy for crystal growth, has been proposed. Matusita and coworkers [6,7] derived the following expression based on the nucleation and growth processes:

$$\ln[-\ln(1-x)] = -n \ln \alpha - 1.052m(E_a/RT) + \text{constant} \quad (1)$$

where x is the volume fraction of crystals precipitating in a glass heated to a temperature T at a heating rate α , E_a is the activation energy for crystal growth, n is a numerical factor depending on the nucleation and growth

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mechanisms and m is a numerical factor depending on the growth mechanism. MacFarlane et al. [8] derived almost the same expression for crystallization in which crystal growth is controlled by diffusion. The values of n and m are already shown in tables in several previous papers [6,7,9,10].

Recently, fluoride glasses based on $\text{ZrF}_4\text{-BaF}_2$ have attracted much attention because of their potential uses in numerous optical applications, especially as IR transmission materials [11]. Usually, useful properties arising from an amorphous state are lost on crystallization. Therefore, it is very important to elucidate crystallization behaviour in order to evaluate the thermal stability of amorphous materials. Several studies have been reported on the crystallization behaviour of fluoride glasses using thermal analysis, microscopic observation and X-ray diffraction [8–10,12–18]. However, many more studies and comparisons with other amorphous materials, such as oxide glasses and metallic glasses, are desirable to obtain a systematic understanding of the crystallization mechanisms of fluoride glasses.

In the present study, the crystallization kinetics of $\text{ZrF}_4\text{-BaF}_2\text{-GdF}_3\text{-AlF}_3$ glasses which are promising for IR optical fibres [19] were investigated by DSC, optical microscopy and X-ray diffraction, and the activation energy for crystal growth was determined from non-isothermal analysis. The growth mechanisms are discussed by comparing the activation energy for crystal growth with that for viscous flow.

EXPERIMENTAL

The composition of the glass used in the present study is 50 mol.% ZrF_4 –40 mol.% BaF_2 –4 mol.% GdF_3 –6 mol.% AlF_3 . The raw materials used were high purity fluoride powders. Batches producing 25 g glass on addition of 10 g $\text{NH}_4\text{F}\cdot\text{HF}$ were placed in platinum crucibles and put into an electric furnace preheated at 900°C. After melting at 900°C for 20 min, the melts were cast onto a steel plate and pressed quickly with another piece of steel. All operations were carried out under a nitrogen atmosphere.

The DSC measurements were made under an argon gas flow with a Rigaku Denki thermal analysis apparatus which has a platinum sample holder of inner diameter 4 mm and a depth of 2 mm. Bulk samples of about 0.1 g and of thickness 1–2 mm were used, and the heating rates were 0.25, 0.5, 1 and 2 K min^{-1} . Higher heating rates were not used in order to avoid a sharp temperature rise in the sample owing to the rapid evolution of the crystallization heat. The viscosity was measured by a penetration method [20] in the range $10^7\text{--}10^{11}$ poise using a Rigaku Denki thermomechanical analysis apparatus.

The crystals precipitated in the glasses were identified by X-ray diffraction analysis and the morphology of the crystals was observed with a polarized optical microscope.

RESULTS

Figure 1 shows the DSC curve of the glass heated at 2 K min^{-1} as an example. In each DSC curve, an exothermic peak is observed around $360\text{--}400^\circ\text{C}$, which was confirmed by X-ray diffraction to be due to the

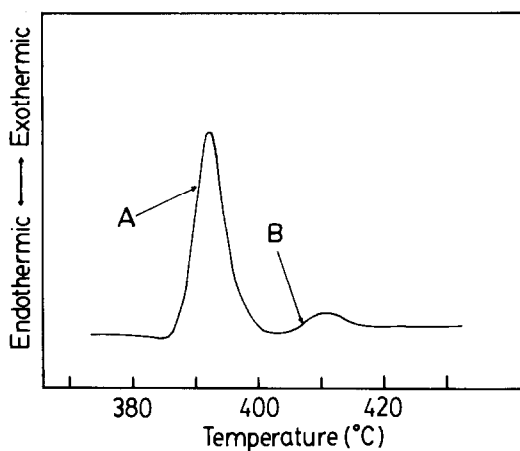


Fig. 1. DSC curve for glass heated with a heating rate of 2°C min^{-1} .

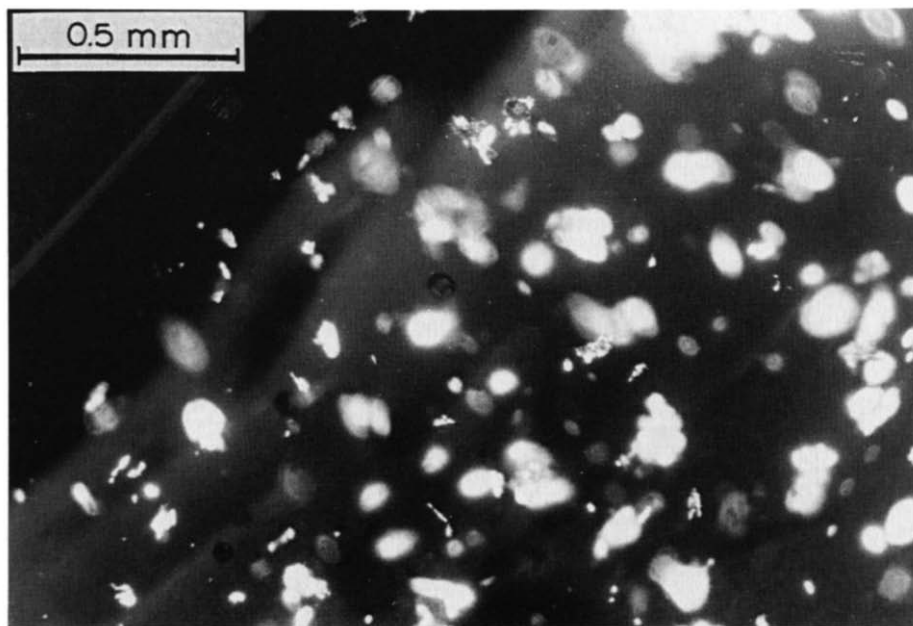


Fig. 2. Optical micrograph of crystals precipitated in glass heated at a rate of 2°C min^{-1} to 382°C .

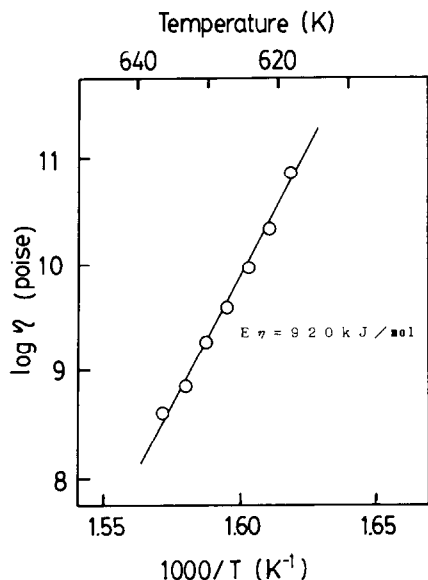


Fig. 3. Viscosity of glass measured by the penetration method as a function of the reciprocal temperature.

precipitation of metastable β -BaZrF₆ crystals [21,22]. These crystals transform into the stable α -BaZrF₆ crystals around 410°C where a small exothermic peak is observed.

Figure 2 is an optical micrograph of crystals precipitated in the glass heated at 2 K min⁻¹ to 382°C. It is seen that no surface nucleation is observed and the crystal particles grow three-dimensionally in the bulk specimens. It was also seen that the number of crystal particles was almost the same irrespective of the heating rate.

Figure 3 shows the logarithmic viscosity of the glass as a function of the reciprocal temperature. It may be said that the viscosity obeys the Arrhenius equation in this narrow temperature range:

$$\eta = A \exp(E_{\eta}/RT) \quad (2)$$

where E_{η} is the activation energy for viscous flow. The activation energy for viscous flow is found to be 920 kJ mol⁻¹, being slightly higher than those of ZrF₄-BaF₂-AlF₃-NaF glasses reported previously [9,10].

DISCUSSION

When a glass specimen is heated at a constant rate α , the volume fraction of crystal increased with temperature, obeying eqn. (1). The volume fraction of crystal can be obtained from DSC curves as described previously [6,23].

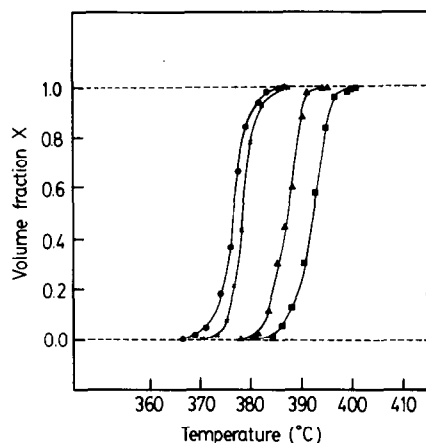


Fig. 4. Variation with temperature in volume fraction of crystals precipitated in glass heated at various heating rates: ●, $0.25^{\circ}\text{C min}^{-1}$; ×, $0.5^{\circ}\text{C min}^{-1}$; ▲, $1^{\circ}\text{C min}^{-1}$; ■, $2^{\circ}\text{C min}^{-1}$.

Figure 4 shows the variation in the crystal volume fraction with temperature for various heating rates. As the heating rate increases, crystallization starts at higher temperatures. Figure 5 shows the relation between $\ln[-\ln(1-x)]$ and $\ln \alpha$, where x is the volume fraction of crystal when the temperature reaches 380°C . According to eqn. (1), the value of the parameter n is given by the slope of the straight line of this equation, which was determined to be three within the experimental error. As shown in Fig. 2, the crystal particles

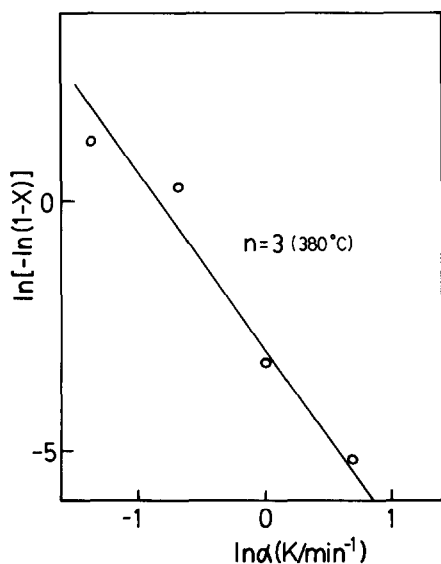


Fig. 5. Variation in $\ln[-\ln(1-x)]$ at 380°C with the natural logarithm of the heating rate.

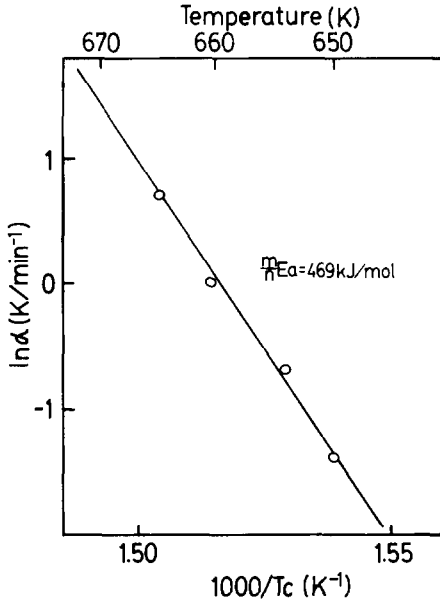


Fig. 6. Relation between the natural logarithm of the heating rate and the reciprocal of the peak temperature in DSC curves.

seem to grow three-dimensionally in bulk specimens and the value of the parameter m is estimated to be three [6,7,23]. This corresponds to the crystallization mechanism in which a constant number of crystal particles, irrespective of heating rate, grow three-dimensionally. Figure 6 shows the plot of $\ln \alpha$ against the reciprocal of the peak temperature of a DSC curve. It has already been reported that the crystal volume fraction at the peak temperature is almost the same irrespective of the heating rate [6]. In the present study, the crystal volume fraction at the peak temperature is nearly 50% as shown in Table 1. Therefore, the slope of the straight line in Fig. 6 gives the activation energy E_a for crystal growth directly. The E_a value thus obtained is 469 kJ mol⁻¹, being similar to those of ZrF₄-BaF₂-NaF-AlF₃ reported previously [9,10]. This value of E_a is much lower than the activation energy for viscous flow, E_η .

TABLE 1

Volume fraction of crystal at exothermic peak temperature

Heating rate (°C min ⁻¹)	Peak temperature (°C)	Volume fraction x
0.25	376	0.50
0.5	379	0.53
1	388	0.54
2	392	0.49

It is assumed that the viscosity of glass is controlled by the chemical bonds of a network structure, and that the crystal growth rate is controlled by the migration of components in the liquid and reaction at the crystal-liquid interface. It is reported that when the composition of a crystal is the same as that of the mother glass, E_a is equal to E_η [7]. However, it is observed that the activation energy for viscous flow in fluoride glasses changes extraordinarily with temperature [24]. Around the glass transition temperature, E_η is reported to be 700–850 kJ mol⁻¹, and near the liquidus temperatures (800–900 °C), E_η is 40–60 kJ mol⁻¹ [9,10,24–28]. Actually, it seems that the viscosity data in Fig. 3 show a slight curvature and the activation energy decreases with temperature. The temperature range where the exothermic peak in DSC is observed is about 25 °C higher than that where the viscosity is measured. It is difficult to estimate the value of the activation energy for viscous flow in the temperature range where the exothermic peak is observed in the DSC curve. Viscosity measurements at higher temperatures are desired to elucidate crystal growth.

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