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CRYSTALLIZATION KINETICS OF LITHIUM DIBORATE GLASS BY DTA

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Abstract

The crystallization process of $Li_2B_4O_7$ in the glass of stoichiometric composition, characterized by the crystal growth of pre-existing nuclei, was analyzed kinetically by means of DTA. Because the number of pre-existing nuclei for the subsequent growth varies depending on the cooling rate of the glass-forming melt and heating rate of the as-prepared glass, a modified Kissinger plot was applied for evaluating the apparent activation energy to the crystal growth in the glass samples with three different thermal histories, i.e., the pre-annealed, slowly quenched and quickly quenched glasses. The process was characterized by the three dimensional growth of pre-existing nuclei with the apparent activation energy of ca 340 kJ mol^{-1}.

Keywords: crystallization, DTA, kinetics, Kissinger plot, lithium diborate glass

Introduction

Kinetics of crystal nucleation and growth of $Li_2B_4O_7$ in the glass of stoichiometric composition have been investigated by microscopic measurements of number of nuclei formed by a certain thermal treatment [1] and linear growth rate at a temperature [2–4], respectively. To understand the overall crystallization behavior, it is important to characterize the relation of the nucleation and growth kinetics on a time scale of the kinetic measurements. Recently, several interesting behaviors of the glass formation and devitrification of $Li_2B_4O_7$ were revealed by thermoanalytical measurements [5]. (1) The glass sample of $Li_2B_4O_7$ can be prepared by cooling the glass-forming melt in DTA apparatus even at very slow cooling rate, i.e., ~2 K min^{-1}. (2) Temperature range of the nucleation corresponds closely to that of the glass transition, showing the maximum nucleation rate at 770 K. (3) Rate behaviors of the nucleation during cooling the glass-forming melt and during heating the as-prepared glass are comparable. (4) On the time scale of thermal analysis, temperature ranges of the crystal nucleation and growth in the glass are separated satisfactorily from each other.

On the basis of the experimental evidences, the exothermic peak of the crystallization recorded by DTA can be treated as the growth of pre-existing nuclei, where

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the number of nuclei varies depending on the thermal history of the sample. Kinetic analysis of the crystal growth has to be carried out by taking account of the number of pre-existing nuclei. Such kinetic approach has been proposed by modifying the Kissinger and Ozawa methods [6, 7], where the crystallization processes of as-quenched glasses were analyzed by considering the effect of heating rate Φ_h on the number of pre-existing nuclei. Later, the corresponding kinetic equation was derived rigorously [8] and the significance was discussed elsewhere [9, 10]. For the present crystallization process, it is expected from the characteristics of glass formation and nucleation behaviors that the number of pre-existing nuclei for subsequent growth is influenced by the cooling rate Φ_c of the glass-forming melt and heating rate Φ_h of the as-prepared glass. In this paper, series of DTA curves for the crystallization of pre-annealed, slowly quenched and quickly quenched glasses are analyzed kinetically on the basis of the Kissinger method with a correction of the number of pre-existing nuclei.

Experimental

Crystalline $Li_2B_4O_7$ of about 8.0 mg was weighed onto a platinum crucible (5 mm in diameter and 2.5 mm in height). Using an instrument of TG-DTA (ULVAC TGD9600), the sample was heated up to 1225 K at 30 K min^{-1}, where a sharp endothermic peak of melting was observed at 1183.9±0.3 K. Subsequently, the glass-forming melt was cooled down below the glass transition temperature at Φ_c=30 K min^{-1}. During cooling the glass-forming melt, an annealing treatment at 770 K for 10 min was performed in some selected runs. The as-prepared glasses with and without the pre-annealing treatment are designated pre-annealed glass and slowly quenched glass, respectively. Separately, the sample in the platinum crucible was melted at 1225 K for 10 min in an electric furnace. The melt was quenched quickly by placing the platinum crucible on a cold metal plate. The glass sample is designated quickly quenched glass.

The three kinds of glass samples prepared were subjected to DTA measurements at various Φ_h in the instrument mentioned above.

Results and discussion

Pre-annealed sample

Figure 1 shows typical DTA curves at various Φ_h for the pre-annealed glass. For the crystal growth of pre-existing nuclei, the following kinetic equation is assumed with the kinetic model function $f(\alpha)$ of the Johnson-Mehl-Avrami-Erofeyev-Kolgomorov (JMAEK) type [11].

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha)$$

with

$$A=(gN)^{1/m}\,\nu_0 \text{ and } f(\alpha)=m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m} \tag{1}$$

where α, g, N and ν_0 are the fractional crystallization, a geometric factor depending on the growth dimension m, number of pre-existing nuclei and pre-exponential factor in the rate equation of linear growth, respectively. Other symbols are in standardized meanings. The first derivation of Eq. (1) with respect to time gives [12]

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}=A\exp\left(-\frac{E}{RT}\right)f(\alpha)\left[\frac{\mathrm{d}f(\alpha)}{\mathrm{d}\alpha}A\exp\left(-\frac{E}{RT}\right)+\frac{\Phi_\mathrm{h}E}{RT^2}\right] \tag{2}$$

At the peak maximum

$$\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}\right)_\mathrm{p}=0 \tag{3}$$

where subscript p denotes the value at the peak maximum. The general kinetic equation of the Kissinger method is obtained by combining Eqs (2) and (3).

$$f'(\alpha_\mathrm{p})A\exp\left(-\frac{E}{RT}\right)+\frac{\Phi_\mathrm{h}E}{RT_\mathrm{p}^2}=0 \quad \text{with}\, f'(\alpha)=\frac{\mathrm{d}f(\alpha)}{\mathrm{d}\alpha} \tag{4}$$

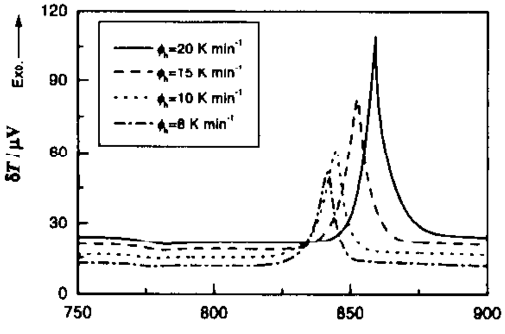

Fig. 1 Typical DTA traces at various Φ_h for the pre-annealed glass

Because a nearly saturated number of nuclei forms by the annealing at 770 K for 10 min during cooling the glass-forming melt [5], the pre-exponential factor A of the crystal growth in the pre-annealed glass is constant irrespective of Φ_h. For such a process, the conventional Kissinger plot [13] is applicable without any corrections.

$$\ln\frac{\Phi_\mathrm{h}}{T_\mathrm{p}^2}=-\frac{E}{RT}+\ln\left[\left|f'\left(\alpha_\mathrm{p}\right)\right|\frac{AR}{E}\right] \tag{5}$$

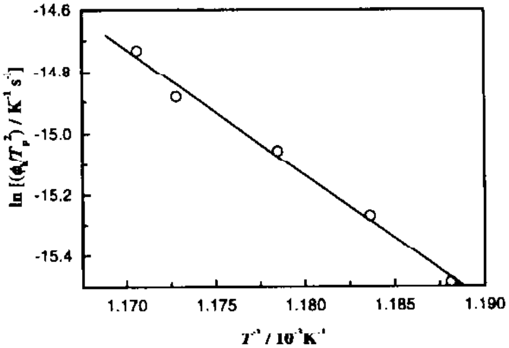

Fig. 2 The Kissinger plot for the crystal growth in the pre-annealed glass

Figure 2 shows the plot of $\ln(\Phi_h/T_p^2)$ *vs.* T_p^{-1} for the crystal growth in the pre-annealed glass. From the slope of the plot, the apparent value of E=340.3±17.6 kJ mol^{-1} was calculated. Although the value of $f'(\alpha_p)$ in Eq. (5) changes slightly with E/RT_p for the process with the growth dimension m other than unity, the error in the slope of the Kissinger plot is less than 5% provided that E/RT_p>10 [14].

Slowly quenched glass

Figure 3 shows typical DTA curves at various Φ_h for the slowly quenched glass. Comparing with the pre-annealed glass (Fig. 1), the DTA curves for the slowly quenched glass shift to higher temperature range with a decrease in the height of the peak maximum. This results from that the number of pre-existing nuclei is smaller in the slowly quenched glass than in the pre-annealed glass.

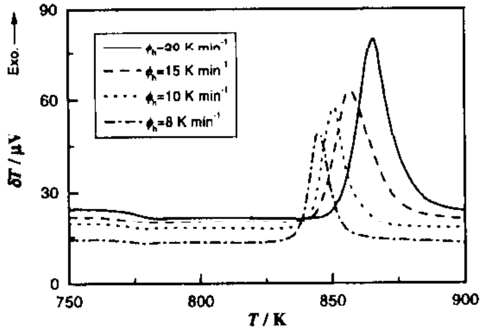

Fig. 3 Typical DTA traces at various Φ_h for the slowly quenched glass

When a glass-forming melt is cooled at Φ_c and the as-prepared glass is heated at Φ_h, the number of nuclei N including in the pre-exponential factor A can be expressed by [7–10]

$$N=\int_0^t I(T)\mathrm{d}t=F(\Phi)N_0 \text{ with } N_0=\int_{T_1}^{T_2} I(T)\mathrm{d}T=\text{const. and } F(\Phi)=\frac{1}{\Phi_c}+\frac{1}{\Phi_h} \qquad (6)$$

where $I(T)$ is the rate of nucleation per unit volume. By taking account of Eq. (6), Eq. (5) is modified as

$$\ln\left\{\frac{\Phi_h}{T_p^2}\left[\frac{1}{F(\Phi)}\right]^{1/m}\right\}=-\frac{E}{RT_p}+\ln\left[\left|f'\left(\alpha_p\right)\right|\frac{A'R}{E}\right] \text{with } A'=(gN_0)^{1/m}\nu_0 \qquad (7)$$

Figure 4 shows the plots of $\ln[(\Phi_h/T_p^2)/F(\Phi)^{1/m}]$ *vs.* T_p^{-1} by assuming various m. Although fairly linear plots were obtained irrespective of m assumed, the slope changes with m. Table 1 lists the apparent values of E calculated from the slope of the plots. When m=3 is assumed, the value of E is in good agreement with that determined for the pre-annealed glass.

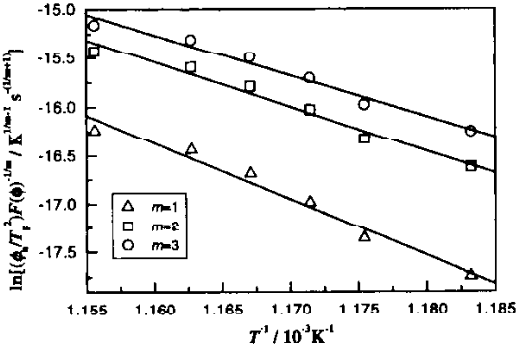

Fig. 4 The extended Kissinger plots with various m for the crystal growth in the slowly quenched glass

Quickly quenched glass

Broader exothermic peak of crystallization, compared with those of the pre-annealed and slowly quenched glasses at the corresponding Φ_h, was observed for the quickly quenched glass, indicating that the number of growing nuclei is smaller. For the quickly quenched glass, the term of $1/\Phi_c$ in $F(\Phi)$ is negligible because the glass-forming melt was quenched at a very high Φ_c. The plots of $\ln[(\Phi_h/T_p^2)/F(\Phi)^{1/m}]$ *vs.* T_p^{-1} by assuming various m are shown in Fig. 5. Slope of the plot decreases with increasing m, as is the case of the slowly quenched sample. Apparent values of E calculated for the quickly quenched glass are also listed in Table 1. The value of E obtained by assuming m=3 is comparable with those obtained for the pre-annealed glass and for the slowly quenched glass by assuming m=3.

Table 1 Apparent values of E determined from the extended Kissinger plots by assuming various m

m	Slowly quenched glass		Quickly quenched glass	
	E/kJ mol^{-1}	$-\gamma^*$	E/kJ mol^{-1}	$-\gamma^*$
1	483.3±46.5	0.9864	487.0±26.5	0.9956
2	381.0±36.1	0.9867	361.7±19.9	0.9956
3	346.9±32.7	0.9869	320.0±17.7	0.9955

*Correlation coefficient of the linear regression analysis.

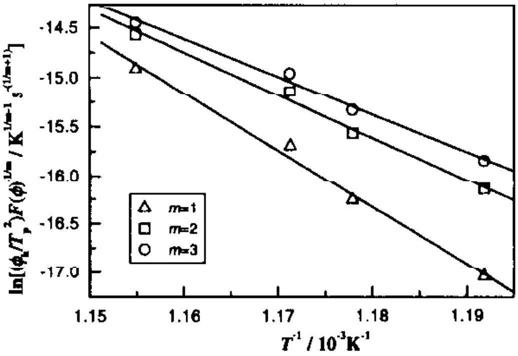

Fig. 5 The extended Kissinger plots with various m for the crystal growth in the quickly quenched glass

Conclusions

Crystallization of $Li_2B_4O_7$ in the stoichiometric glass was analyzed kinetically on the basis of the previous experimental results that the process is described by the crystal growth of pre-existing nuclei, where the number of pre-existing nuclei varies with thermal history of the glass sample. For the pre-annealed glass, the conventional Kissinger method is applicable for obtaining the apparent value of E, because the number of pre-existing nuclei remains constant irrespective of Φ_h in the DTA measurements. The apparent value of E=340.3±17.7 kJ mol^{-1} was determined by the Kissinger plot. When the glass-forming melt was quenched slowly at Φ_c and the as-prepared glass was heated at Φ_h, the number of pre-existing nuclei for the crystal growth changes depending on Φ_c and Φ_h. A modified form of the Kissinger equation was proposed by taking account of the change in the number of pre-existing nuclei. From the extended Kissinger plots with m=3, the apparent values of E, comparable to that determined for the pre-annealed glass, were obtained for the slowly and quickly quenched glasses. Accordingly, the crystallization process is characterized by the three dimensional growth of pre-existing nuclei.

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