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Note

STUDY ON CRYSTALLIZATION KINETICS IN GLASS BY DIFFERENTIAL THERMAL ANALYSIS

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Thermal analysis is a very useful tool for studying crystallization of glass. It has been used not only for qualitative analysis [1,2] but also for quantitative analysis [3—12]. In a previous report [9], the authors proposed a method for determining the activation energy for crystal growth by differential thermal analysis based on the nucleation and growth equations. It was indicated that the mechanism of crystallization, that is, whether crystallization proceeds from bulk nucleation or surface nucleation, is important for the determination of the activation energy. In this study, a method for determining the mechanism of crystallization was derived by referring to nucleation and growth kinetics [13].

Usually, the rate of crystal nucleation in glass reaches the maximum at a temperature somewhat higher than the glass transition temperature and then decreases rapidly with increasing temperature [14—17], while the rate of crystal growth reaches the maximum at a temperature much higher than the temperature at which the nucleation rate is highest [15—20]. When glass is heated at a constant rate, crystal nuclei formed at lower temperatures grow in size at higher temperatures without any increase in number [18,19]. The number, N, of nuclei per unit volume formed during heating from room temperature, T_r, to a temperature, T, is expressed as

$$N = \int_0^t I(T)\,\mathrm{d}t = \frac{1}{\alpha}\int_{T_r}^{T} I(T)\,\mathrm{d}T = \frac{N_0}{\alpha} \tag{1}$$

where

$$N_0 = \int_{T_r}^{T} I(T)\,\mathrm{d}T$$

Here $I(T)$ is the rate of nucleation and α is the heating rate. N_0 does not depend on temperature if T is much higher than the temperature at which the nucleation rate is highest. The rate of crystal growth, $U = \mathrm{d}r/\mathrm{d}t$, is expressed by [9]

$$U = U_0 \exp(-E/RT) \tag{2}$$

where E is the activation energy for crystal growth. The radius, r, of crystal particle is expressed by [9]

$$r = \int_0^t U(T)\,\mathrm{d}t = \frac{U_0}{\alpha}\int_{T_r}^{T} \exp(-E/RT)\,\mathrm{d}T$$

$$\simeq \frac{r_0}{\alpha}\exp(-E/RT) \tag{3}$$

It should be noted here that there are two types of crystallization: one based on bulk nucleation in which each crystal particle grows three-dimensionally in glass, and the other based on surface nucleation in which each crystal grows one-dimensionally from surface to inside of glass. In bulk nucleation, variation of the volume fraction of crystal, x, is expressed by [9]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = 4\pi N r^2 (1-x)\frac{\mathrm{d}r}{\mathrm{d}t} \tag{4}$$

From eqns. (1—4)

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{4N_0 r_0^2 U_0}{\alpha^3}(1-x)\exp\left(-\frac{3E}{RT}\right) \tag{5}$$

In surface nucleation, the nuclei are formed at the surface but not in the inner part of the sample. If we assume the glass sphere of radius R_0 in which the surface layer of the thickness r is crystallized, variation of the volume fraction of crystal is expressed as [9]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{3U_0}{R_0}(1-x)^{2/3}\exp\left(-\frac{E}{RT}\right) \tag{6}$$

In the previous report [9], it was shown that the following relation holds in DTA process

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1}{KA}\left[C_\mathrm{p}\frac{\mathrm{d}(\Delta T)}{\mathrm{d}t} + K\Delta T\right] \tag{7}$$

where ΔT is the temperature difference between the sample and the reference material, C_p is the heat capacity of the sample and the sample holder, K is the heat transfer coefficient between the sample and its environment and A is the area under the peak due to crystallization in the DTA curve. Combining eqns. (5—7), the following general expression can be derived

$$\log\left[C_\mathrm{p}\frac{\mathrm{d}(\Delta T)}{\mathrm{d}t} + K\Delta T\right] = -n\log\alpha - \frac{mE}{2.3RT} + \text{const.} \tag{8}$$

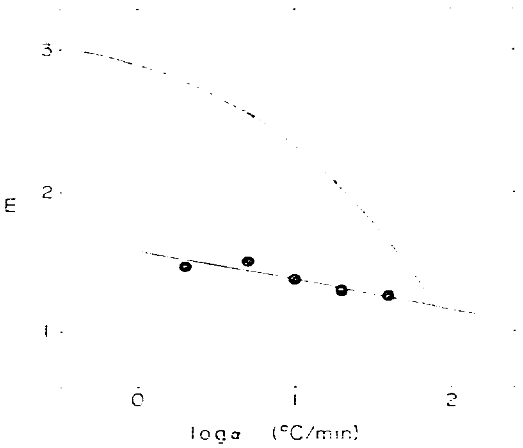
where $n = m = 3$ in the case of bulk nucleation, and $n = 0$ and $m = 1$ in the case of surface nucleation. It should be noticed that the crystal volume fraction should be small in order for the terms $\log(1-x)$ and $\log(1-x)^{2/3}$ to be regarded as constant and accordingly, for eqn. (8) to be valid. The values of n and m are summarized in Table 1 for various crystallization mechanisms.

TABLE 1

Values of n and m for various crystallization mechanisms

Crystallization mechanism	n	m
Bulk nucleation		
Three-dimensional growth	3	3
Two-dimensional growth	2	2
One-dimensional growth	1	1
Surface nucleation	0	1

In the previous work [9], the authors obtained the m values for $Li_2O \cdot 2\ SiO_2$ and $33.3\ Li_2O \cdot 66.7\ SiO_2 \cdot 3\ TiO_2$ (mole ratio) glasses by plotting log $[C_p d(\Delta T)/dt + K\Delta T]$ against $1/T$ and comparing with the kinetic data. These are reproduced in Fig. 1 as a function of heating rate. Using the same DTA curves as in the previous report [9], log $[C_p d(\Delta T)/dt + K\Delta T]$ is plotted against log α for various temperatures in Figs. 2 and 3 for $Li_2O \cdot 2\ SiO_2$ and $33.3\ Li_2O \cdot 66.7\ SiO_2 \cdot 3\ TiO_2$ glasses, respectively. Generally, these lines are not linear and the gradient decreases with increase in heating rate. According to eqn. (8), the gradients of these lines represent n-values. It is seen that for $Li_2O \cdot 2\ SiO_2$ glass, n is close to 3 at low heating rates and decreases gradually as the heating rate increases. For the glass containing TiO_2, n is less than unity even at low heating rates and decreases further as the heating rate increases. It is already known that bulk nucleation is dominant in $Li_2O \cdot 2$



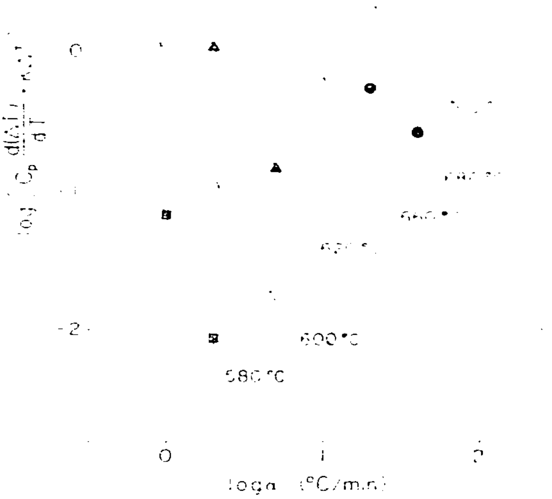


Fig. 1. m-values as a function of heating rate. : $Li_2O \cdot 2\ SiO_2$; ●: $33.3\ Li_2O \cdot 66.7\ SiO_2 \cdot 3\ TiO_2$.

Fig. 2. Log $[C_p(d\Delta T/dt) + K\Delta T]$ as a function of heating rate for $Li_2O \cdot 2\ SiO_2$.

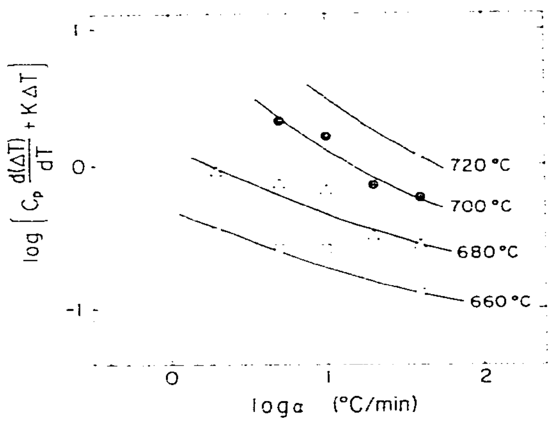


Fig. 3. Log [$C_p(d\Delta T/dt) + K\Delta T$] as a function of heating rate for 33.3 Li_2O · 66.7 SiO_2 · 3 TiO_2.

SiO_2 glass, especially at low heating rates, and each particle grows three-dimensionally [9,14—18], which agrees with the fact that n and m are close to 3. The contribution of surface crystallization increases as the heating rate increases [9], which agrees with the gradual decrease in the values of n and m (Figs. 1 and 2). In the glass containing TiO_2, surface crystallization is dominant and the crystal grows one-dimensionally, especially at high heating rates [9], which agrees with the fact that n is much less than unity and m is close to unity.

The general agreement of the analysis of DTA curves with the crystallization mechanism found by inspection under microscope indicates that eqn. (8) is valid and useful for studying the crystallization mechanism and obtaining the activation energy for crystal growth.

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