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Nucleation in glass and differential thermal analysis

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The crystal nucleation of Li_2O–$2SiO_2$ glass is studied by differential thermal analysis. A simple method, based on the shift of the differential thermal analysis (DTA) crystallization-peak temperature, for evaluating the influence of temperature and time of heat-treatments on bulk nucleation, is described. The experimental results are in good agreement with results obtained by other workers.

1. Introduction

As differential thermal analysis (DTA) allows quick investigation of simple properties over a wide range of temperatures, using only a small amount of sample, it has been extensively applied to the study of glass de-vitrification.

Although the bulk crystal nucleation in glass is of great importance in the formation of glass-ceramic materials the several methods so far proposed for obtaining kinetic data from DTA curves have been only concerned with crystal growth [1–6].

In this paper a method for evaluating the effectiveness of the nucleation heat treatment from the temperature of DTA crystallization-peak is described. The proposed procedure allows the estimation of temperature of maximum nucleation-rate to be made more quickly than is usually the case.

The de-vitrification of Li_2O–$2SiO_2$ glass has been investigated because the results can be compared with those that have been obtained using the other techniques and which are reported in the literature.

2. Experimental procedure

Samples of Li_2O–$2SiO_2$ glass were prepared by melting pure reagents at 1450° C in a Pt-crucible placed in an electric oven. The melt was cast in Fe-moulds at high cooling-rate. From the as-quenched glass small bulk samples were cut of a size suitable for the DTA sample-holder.

The nucleation heat-treatments were performed in the DTA furnace so that the temperature and time-of-treatment data were easily and exactly detected on isothermal DTA curves. Nucleation times were measured starting from the time at which the sample, heated at a rate of $50^\circ\,C\,min^{-1}$, reached the selected temperature.

To detect the crystallization-peak temperature, DTA curves, recorded in air at a healing rate of $20^\circ\,C\,min^{-1}$, from the as-quenched sample and from the previously heat-treated samples were recorded.

A Netzsch 404M thermoanalyzer was used and the reference material was Al_2O_3. To improve the heat transfer in the holder, Al_2O_3 powder was added to the sample.

3. Theoretical considerations and results

The non-isothermal de-vitrification of glass is the result of two individual processes: nucleation and crystal growth.

The total number of nuclei per unit volume, N, is given by the sum of (a) the surface nuclei, N_S, (b) the bulk nuclei formed during the DTA run, N_B, and (c) the bulk nuclei formed during the previous heat treatment of nucleation, N_H:

$$N = N_S + N_B + N_H. \qquad (1)$$

N_S and N_B are, respectively, proportional to the specific surface of the sample and to the reciprocal of the heating rate, β [7]. N_H is related to the time of the nucleation heat treatment, t_n, by

$$N_H = I(t_n)^b, \qquad (2)$$

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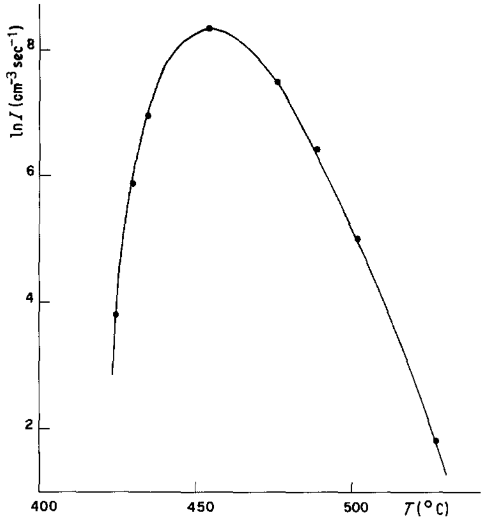

Figure 1 Nucleation rate, I, against temperature, T, curve for Li_2O–$2SiO_2$ glass, from [10].

where b is a constant related to the nucleation mechanism [8]. The rate constant, I, for nucleation in a super-cooled liquid may be expressed as a function of the absolute temperature, T, by

$$I = A \exp\left(-\frac{w+E_n}{RT}\right), \tag{3}$$

where, w and E_n are, respectively, the thermodynamic and the kinetic barriers to nucleation, and A is a constant [9].

Equation 3 predicts that the rate of nucleation should be very sensitive to variations in temperature, since it depends exponentially on a quantity w which, itself, varies rapidly with temperature. The nucleation rate increases as the temperature falls until the kinetic barrier begins to exert a controlling influence; when this happens the nucleation rate decreases with decreasing temperature so that the I–T relationship has the form shown in Fig. 1 [10].

As the crystallization takes place, the heat-of-crystallization is evolved and an exothermic peak appears on the DTA curves, as shown in Fig. 2.

The extent of crystallization, α, at time t is well described [8] by a Johnson–Mehl–Avrami (JMA) equation [11, 12]

$$\alpha = 1 - \exp(-kt)^n, \tag{4}$$

where n is a parameter related to both the crystallization mechanism and to the crystal shape [8] and the rate constant, k, is related to the absolute temperature, T, by an Arrhenius-type equation

$$k \propto N \exp\left(-\frac{E_c}{RT}\right). \tag{5}$$

For glass crystallized at temperatures well above the temperatures of high nucleation-rates, the number of nuclei already present cannot appreciably change during the crystallization process (DTA peak) [5, 7]. As a result the crystals grow from a nearly-fixed number of nuclei and E_c represents the kinetic barrier for crystallization.

Assuming that, in a DTA curve, Fig. 2, the ΔT deflection from the baseline is at each temperature, T, proportional to the reaction rate $d\alpha/dt$ [13], the condition that, at peak temperature, T_p, the ΔT deflection has a null temperature derivative leads at $T = T_p$ to

$$\frac{d\Delta T}{dT} = \frac{d}{dT}\left(\frac{d\alpha}{dt}\right) = 0. \tag{6}$$

Since the degree of crystallization, α, is related to both time and temperature by a JMA equation, Equation 6 is satisfied if [5]

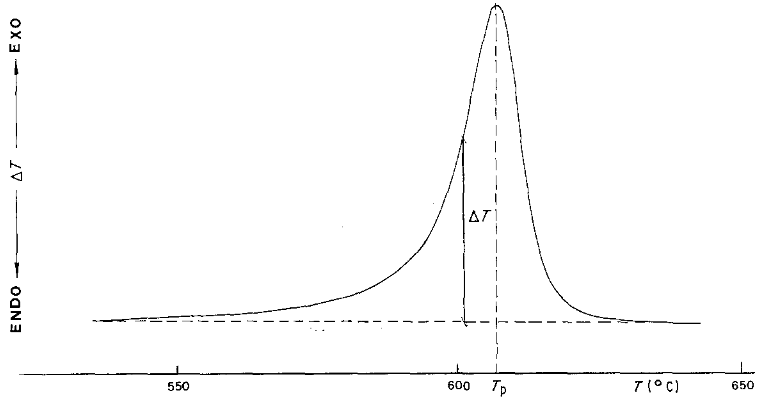

Figure 2 Crystallization peak of Li_2O–$2SiO_2$ glass detected by DTA.

$$kt = 1 \quad \text{when} \quad T = T_p. \tag{7}$$

Therefore, the peak of the DTA curve occurs when the argument of the exponential of the JMA equation is close to unity [6].

Taking into account Equation 5 and assuming that the time, t, of heating at each temperature, T, is proportional to the reciprocal of the heating rate, β [1], the logarithms of Equation 7 lead to

$$\ln \beta - \ln N = -\frac{E_c}{R}\frac{1}{T_p} + \text{constant}. \tag{8}$$

If the DTA runs are carried out at the same heating rate (β = constant, N_B = constant) on samples of the same specific surface (N_S = constant), the total number of nuclei per unit volume is the sum of a constant nuclei number, N_0, and of a nuclei number N_H depending on the time and temperature of the heat treatments (for the as-quenched sample $N_H = 0$),

$$N = N_0 + N_H. \tag{9}$$

Substituting for N in Equation 8 from Equation 9, and, taking into account the fact that the value of E_c is not dependent on the crystallization mechanism [14, 15], the following equation can be obtained

$$\ln (N_0 + N_H) = c_1 \frac{1}{T_p} + c_2, \tag{10}$$

where c_1 and c_2 are constants.

Assuming that $N_0 \ll N_H$, owing to the low specific surface of the bulk sample and to the high heating-rate (20° C min^{-1}), the difference between the crystallization-peak temperature, T'_p, of the as-quenched sample and the value of T_p for a previously-nucleated sample can be expressed as a function of the nuclei number, N_H, formed during the heat treatments

$$T'_p - T_p = c_3 \ln N_H + c_4, \tag{11}$$

where c_3 and c_4 are constants.

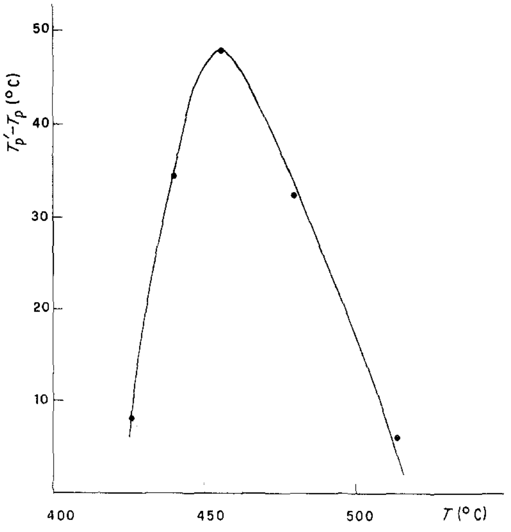

Figure 3 $T'_p - T_p$ plotted against temperature of heat-treatment for $Li_2O{-}2SiO_2$ glass.

If the samples are previously held for the same times (t_n = 2 h, N_H = constant) at different nucleation temperatures, a plot, shown in Fig. 3, of $T'_p - T_p$ against the temperatures of the heat treatments gives a nucleation rate–temperature curve which shows the same shape and a maximum at the same temperature of the curve reported in Fig. 1.

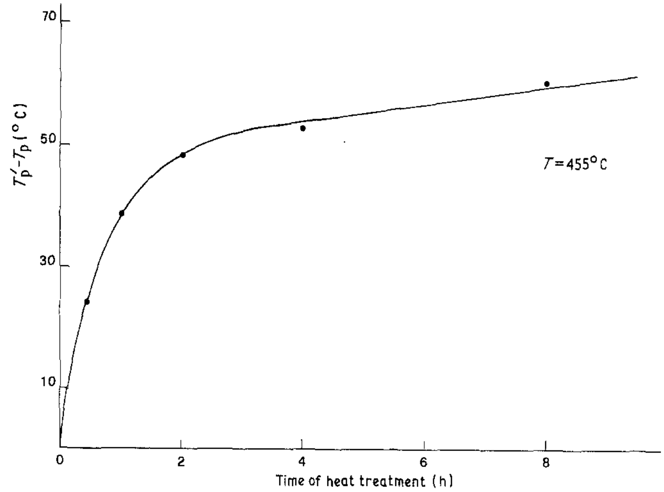

Figure 4 $T'_p - T_p$ against time of heat-treatment for $Li_2O{-}2SiO_2$ glass.

If the samples are previously held for different times at this so-determined temperature of maximum nucleation rate ($T = 455°$ C, N_H = constant $\times t_N^b$) a plot, in Fig. 4, of $T_p' - T_p$ against the times of the heat treatments gives an isothermal nucleation curve which shows how the nuclei number-order of magnitude is increased by the duration of the heat treatments.

4. Conclusions

The DTA method proposed has the following advantages over other techniques currently in use:

(a) the measurements are rather quick (a DTA curve for each temperature or time investigated is required) and easily achieved (only the peak temperature has to be detected on the DTA curve);

(b) only a small amount of glass sample is required;

(c) as the heat treatments are performed inside the DTA furnace only the DTA apparatus is used.

The described procedure can be applied to all glass systems which undergo internal crystal nucleation and its validity is confirmed by the good agreement between the experimental results and the data reported by other workers who have used the alternative methods.

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