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THE INFLUENCE OF P_2O_5 ON THE NON-ISOTHERMAL DEVITRIFICATION OF 30 $Li_2O \cdot 70$ SiO_2 GLASS

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ABSTRACT

The nucleation and crystal growth in 30 $Li_2O \cdot 70$ SiO_2 and 30 $Li_2O \cdot 69$ $SiO_2 \cdot 1$ P_2O_5 were studied by differential thermal analysis. The temperature of maximum nucleation rate, the activation energy for crystal growth and the crystallization mechanism were evaluated from DTA and DDTA curves. The influence of P_2O_5 on the devitrification process was also examined.

INTRODUCTION

In previous papers [1–4] the non-isothermal devitrification of $Li_2O \cdot 2$ SiO_2 glass was studied by differential thermal analysis (DTA) in order to point out the advantages and the limits of this rapid technique in the study of crystallization kinetics. From the experimental results some conclusions were drawn.

(a) The activation energy of devitrification, calculated from the shift of the crystallization peak as the heating rate is changed, represents only the kinetic barrier for the crystal growth [2].

(b) To avoid misinterpretation of the kinetic parameters, surface and bulk crystallization must be studied separately, using as-quenched, finely powdered samples and well-nucleated bulk samples, respectively [2].

(c) The temperature of maximum nucleation rate can be detected on a nucleation rate-temperature like curve obtained from the shift of the DTA peak temperature with increase of the number of nuclei [3].

(d) The crystallization mechanism can be evaluated from the inflection point temperatures of the DTA crystallization peak detected on the derivative differential thermal analysis (DDTA) curve [4].

In this paper the investigation has been extended to the devitrification of non-stoichiometric (30 $Li_2O \cdot 70$ SiO_2) glass. The effect of a small amount of P_2O_5 on nucleation and crystal growth kinetics has been also examined.

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EXPERIMENTAL

Samples of 30 $Li_2O \cdot 70\ SiO_2$ (glass A) and 30 $Li_2O \cdot 69\ SiO_2 \cdot 1\ P_2O_5$ (glass B) were prepared by melting pure reagents at 1450°C in a Pt crucible placed in an electric oven. The melts were cast in an Fe mould at a high cooling-rate. From the as-quenched glasses, small bulk samples were cut, of a size suitable for the DTA sample holder.

The nucleation heat treatment was 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°C min^{-1}, reached the selected temperature.

Differential thermal analysis (DTA) curves and their first derivative (DDTA) curves were recorded in air at different heating rates (5–50°C min^{-1}) on ~ 90 mg bulk samples. A Netzsch 404 M 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.

RESULTS AND DISCUSSION

When a glass devitrifies during a DTA run, the heat of crystallization is evolved and an exothermic peak and a double peak appear on the DTA and DDTA curves, respectively. The maximum and the minimum of the DDTA

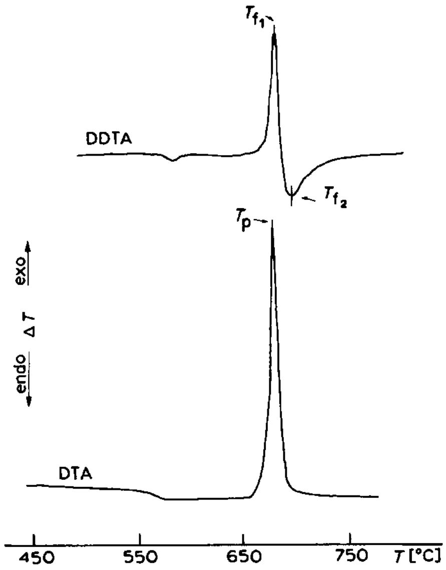

Fig. 1. DTA and DDTA curves of glass A nucleated for 14 h at 470°C, recorded at 20°C min^{-1}.

double peak correspond to the two inflection points (i.e. the maximum and the minimum slopes) of the DTA peak (Fig. 1). The crystalline phase was identified by X-ray diffraction as lithium disilicate in both cases.

Kinetic equations

The non-isothermal devitrification of glasses is well described by the equation proposed by Matusita and Sakka [5]

$$-ln(1-\alpha)=C\frac{N}{\beta^n}\exp\left(-\frac{nE}{RT}\right) \tag{1}$$

where α is the volume fraction crystallized at temperature T, β is the DTA heating rate, E is the activation energy for crystal growth, n is a parameter related to crystal shape [5] and C is a constant. The number of nuclei, N, per unit volume is the sum of the surface nuclei, N_s, which is proportional to the specific surface area of the sample, the bulk nuclei, N_b, formed during the DTA run and proportional to the reciprocal of the DTA heating rate, and the bulk nuclei, N_h, formed during a previous heat treatment of nucleation and proportional to its duration [2].

$$N=N_s+N_b+N_h \tag{2}$$

Assuming that the ΔT deflection from the baseline is proportional, at each temperature T, to the instantaneous reaction rate [6], the condition that at the peak temperature, T_p

$$\frac{d\Delta T}{dT}=0 \tag{3}$$

and at the inflection points temperature, T_f

$$\frac{d^2\Delta T}{dT^2}=0 \tag{4}$$

are satisfied, respectively, by [1,4]

$$x=1 \tag{5}$$

$$x^2-3x+1=0 \tag{6}$$

where

$$x=C\frac{N}{\beta^n}\exp\left(-\frac{nE}{RT}\right) \tag{7}$$

Temperature of maximum nucleation rate

Taking into account eqn. (7), the logarithms of eqn. (5) lead to

$$\ln N-n\ln\beta=\frac{nE}{R}\frac{1}{T_p}+\text{const.} \tag{8}$$

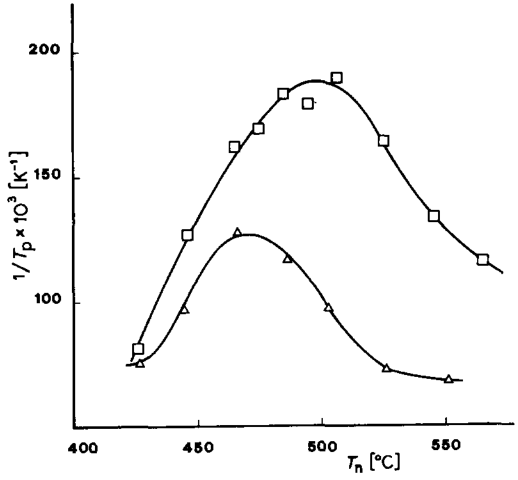

Fig. 2. Nucleation rate-temperature like curves. Δ, Glass A; □, glass B.

If the DTA runs are carried out at the same heating rate (N_b = const.) on samples of the same specific surface area, and assuming that $N_h \gg N_s + N_b$ owing to the low specific surface of the bulk sample and to the high heating rate (20°C min^{-1}), the following equation can be derived

$$\ln N_h = a \frac{1}{T_p} + b \tag{9}$$

where a and b are constants.

If the samples are previously held for the same time (t_n = 2 h) at different nucleation temperatures, T_n, a plot of $1/T_p$ vs, T_n gives a nucleation rate-temperature like curve as shown in Fig. 2.

The bell-shaped curves for the two glasses investigated show a maximum at 470°C for glass A and at 500°C for glass B.

Kinetic parameters for crystal growth

To study bulk crystallization the DTA runs were carried out on samples which had previously been nucleated for a long time (t_n = 14 h) at a high nucleation rate temperature (T_n = 470°C). In this way, the high number of bulk nuclei formed during the heat treatments of nucleation makes the number of surface nuclei and the number of bulk nuclei formed during the DTA run negligible. Hence the crystals grow in the bulk from the same fixed number of nuclei at each heating rate and eqn. (8) can be rearranged as

$$\ln \beta = -\frac{E}{R} \frac{1}{T_p} + \text{const.} \tag{10}$$

Moreover, from the two solutions of the quadratic eqn. (6), the following

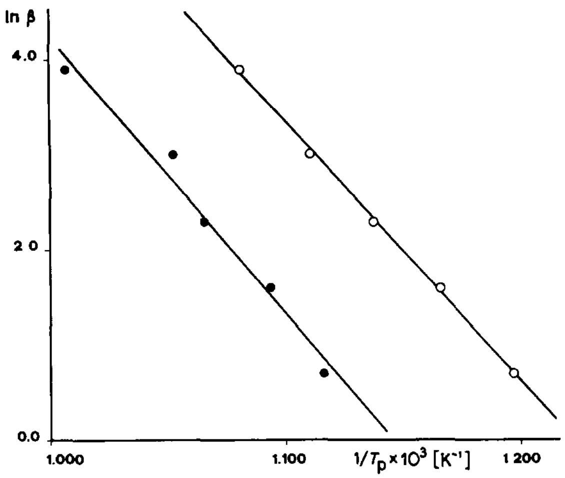

Fig. 3. Plot of ln β vs. $1/T_p$. ●, Glass A; ○, glass B.

relationship between nE and the two inflection point temperatures T_{f_1} and T_{f_2} can be derived [4]

$$nE = \frac{1.92}{1/T_{f_1} - 1/T_{f_2}} \tag{11}$$

By plotting ln β vs. $1/T_p$ straight lines were obtained for each glass, as shown in Fig. 3. The values of the activation energy, E, as calculated from their slopes, and the values of the product nE, as calculated by eqn. (11) from the two inflection point temperatures, are reported in Table 1.

The values of the n parameter obtained by comparing the nE and E values suggest three-dimensional growth in both cases.

The effectiveness of the heat treatments on nucleation were evaluated from eqn. (8) by comparing the crystallization peak temperature, T_p°, found from DTA curves carried out at the same high heating rate (50°C min^{-1}), on an as-quenched ($N_h = 0$) bulk sample and a sample which had been nucleated for a long time (14 h) at a temperature (470°C) of high nucleation rate

TABLE 1

Kinetic parameters

Sample	E (kcal mole^{-1})	nE	n
Glass A	58	195	3.36
Glass B	54	171	3.30

$(N_h \gg N_s + N_b)$.

$$\ln \frac{N_h}{N_s + N_b} = \frac{nE}{R}\left(\frac{1}{T_p} - \frac{1}{T_p^\circ}\right) \tag{12}$$

From eqn. (12) values of

$$\left(\frac{N_h}{N_s + N_b}\right)_A \cong 10000$$

$$\left(\frac{N_h}{N_s + N_b}\right)_B \cong 50000$$

were calculated for glass A and B, respectively.

CONCLUSIONS

From the DTA study described the conclusions drawn are: (a) the temperature of maximum nucleation rate for glass A and B are 470°C and 500°C, respectively; (b) the number of homogeneous nuclei formed during a heat treatment of nucleation at a temperature very close to T_g is remarkably increased by the presence of P_2O_5; (c) in both glasses the crystals grow in three-dimensions in the bulk, with nearly the same activation energy value.

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REFERENCES

1 A. Marotta and A. Buri, Thermochim. Acta, 25 (1978) 155.
2 A. Marotta, A. Buri and F. Branda, Thermochim. Acta, 40 (1980) 397.
3 A. Marotta, A. Buri and F. Branda, J. Mater. Sci., 16 (1981) 341.
4 A. Marotta, S. Saiello, F. Branda and A. Buri, J. Mater. Sci., 17 (1982) 105.
5 K. Matusita and S. Sakka, Bull. Inst. Chem. Res. Kyoto Univ., 59 (1981) 159.
6 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.