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Activation energy for the crystallization of glass from DDTA curves

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A simple method, based on the measurements of two peak temperatures on a single derivative differential thermal analysis (DDTA) curve for determining the activation energy for bulk or surface crystallization in glasses is described. The devitrification of $Li_2O{-}2SiO_2$ glass has been investigated; the experimental results agree well with those obtained by alternative techniques and with the activation energy of viscous flow in the crystallization-range temperatures.

1. Introduction

The usual method of obtaining kinetic data on glasses involves a series of experiments carried out under isothermal conditions at different temperatures. This process is laborious and considerable interest exists in the study of reaction kinetics by a dynamic method such as differential thermal analysis (DTA).

Two methods of analysis for determining the activation energy for the crystallization of glass from DTA curves have been proposed [1–8]. One method [1–5] utilizes the linear relation between peak crystallization temperature, T_p, see Fig. 1, and DTA heating rate. The measurements are easily achieved (only the peak temperatures have to be detected on the DTA curves) but multiple DTA curves have to be recorded; in this way the main advantage of the non-isothermal technique is lost. The other method [6–8] is based on the evaluation of the heights, ΔT, and/or the areas, a, under a single crystallization peak, see Fig. 1. These parameters are difficult to measure if the peak is sharp and strongly affected by a correct interpolation of the baseline under the peak.

In the present paper, a method of analysis for obtaining the activation energy for the crystallization of a glass from a single derivative differential thermal analysis (DDTA) curve has been derived and applied to the devitrification of $Li_2O{-}2SiO_2$ glass.

The results were compared with those obtained by the alternative DTA methods and with those obtained under isothermal conditions in order to discuss the validity of the present method.

2. Experimental procedure

Samples of $Li_2O{-}2SiO_2$ glasses were prepared by melting the pure reagents in a Pt-crucible in an electric oven and casting them in Fe-moulds at a high cooling rate.

The as-quenched glass was crushed in an agate mortar and then sieved in order to obtain very fine (− 170, + 230 mesh) particles. Small bulk samples were also cut, of a size suitable for the DTA sample-holder. In this case Al_2O_3 powder was added to improve the heat transfer between the sample and the sample-holder.

The heat-treatment of nucleation was performed in the DTA furnace. The sample was

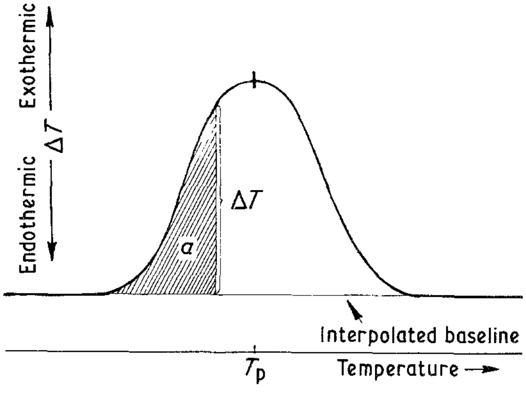

Figure 1 A typical DTA curve.

heated at a rate of 50° C min^{-1} up to the temperature of maximum nucleation rate, 455° C [9], and the time of nucleation (2 h) was measured on the isothermal curve recorded at this temperature.

Differential thermal analysis (DTA) and derivative differential thermal analysis (DDTA), of 90 mg of powdered or bulk glass, were undertaken, in air.

A Netzch differential thermal analyzer, model 404 M, was used and Al_2O_3 powder was used as reference material.

3. Theoretical considerations and results

There are two types of crystallizations which take place in a glass, based on surface and bulk nucleations.

In the case of surface nucleation, nuclei are formed only on the surface and the crystals grow from the surface to the inside of the glass one-dimensionally.

The volume-fraction of the crystals, α, is expressed as [10]

$$1-(1-\alpha)^{1/3} = kt, \qquad (1)$$

where k is a constant and t is time.

In the case of bulk nucleation, in which each crystal particle grows three-dimensionally, the volume-fraction of the crystals, α, is expressed as

$$-\ln(1-\alpha) = (kt)^3. \qquad (2)$$

The constant k is related, in both cases, to the absolute temperature, T, by an Arrhenius-type equation

$$k \propto N_0 \exp\left(-\frac{E}{RT}\right), \qquad (3)$$

where E is the activation energy for crystal growth, N_0 the number of nuclei and R is the gas constant.

As a glass crystallizes at a temperature well above that of the maximum nucleation rate, the number of nuclei already formed increases appreciably during the crystal growth (DTA peak). Therefore the crystals grow, in all cases, from a fixed number of nuclei [11, 12].

Assuming that the ΔT deflection from the baseline is, at each temperature, T, proportional to the crystallization rate [6, 8],

$$\Delta T \propto \frac{d\alpha}{dt}, \qquad (4)$$

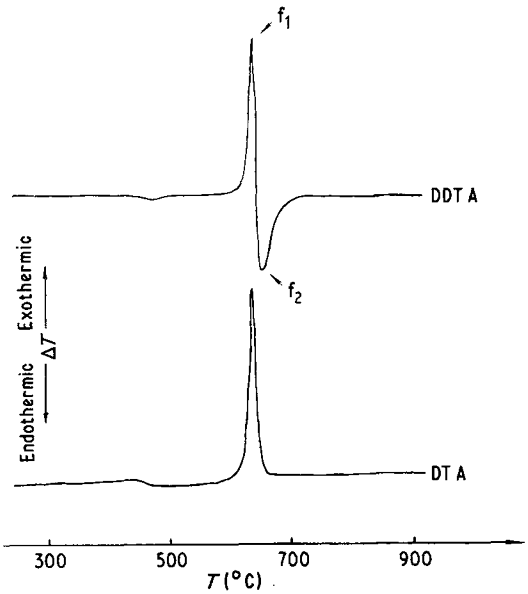

Figure 2 DTA and DDTA curves of a bulk sample of Li_2O–$2SiO_2$ glass.

then the inflection-point temperature, T_f, of the DTA crystallization peak can be obtained, provided the DTA run is carried out at constant heating rate $dT/dt = \beta$, by setting

$$\frac{d^2\Delta T}{dT^2} = \frac{d^2}{dT^2}\left(\frac{d\alpha}{dt}\right) = \frac{d^3\alpha}{dT^3} = 0 \qquad (5)$$

and solving for T_f.

This leads, taking into account Equations 1 and 2, respectively, to

$$\frac{d^3}{dT^3}[1-(1-kt)^3] = 0 \qquad (6)$$

and

$$\frac{d^3}{dT^3}\{1-\exp[-(kt)^3]\} = 0. \qquad (7)$$

Assuming that the time of heating, t, proportional to the reciprocal of the DTA heating rate, β, at each temperature, T, [2], and neglecting small quantities [5] the nth temperature derivative of (kt) is

$$\frac{d^n}{dT^n}(kt) = \left(\frac{E}{RT}\right)^n (kt) \qquad (8)$$

and Equations 6 and 7 are, respectively, satisfied if

$$9(kt)^2 - 8(kt) + 1 = 0 \qquad (9)$$

and

$$(kt)^6 - 3(kt)^3 + 1 = 0. \qquad (10)$$

As, for each of the Equations 9 and 10, there exist two solutions which correspond to the two inflection points, the following relationships between the activation energy E of crystal growth and the temperatures of the two inflection-points, T_{f_1} and T_{f_2}, can be derived, that is

TABLE I Activation energy for crystal growth in $Li_2O-2SiO_2$ glass

Sample	E (kcal mol^{-1})			
	Calculated from Equations 11 and 12	From isothermal data [13]	Calculated from Equation 13	Calculated from Equation 14
Powder	73	65	67	104
Bulk	76	65	59	82

$$\frac{E}{R}\left(\frac{1}{T_{f_1}}-\frac{1}{T_{f_2}}\right) = 1.59 \qquad (11)$$

for surface crystallization and

$$\frac{E}{R}\left(\frac{1}{T_{f_1}}-\frac{1}{T_{f_2}}\right) = 0.64 \qquad (12)$$

for bulk crystallization.

If the DTA curve and its derivative are simultaneously recorded, the two inflection points, i.e., the maximum and the minimum slopes, of the DTA peak correspond to the maximum and the minimum of the DDTA double-peak, as shown in Fig. 2.

Therefore, the temperatures T_{f_1} and T_{f_2} can be easily and exactly detected on the DDTA curve.

For studying the surface and bulk crystallization separately, as-quenched powdered samples and well-nucleated bulk samples have to be used, as pointed out in a previous paper [12].

In very fine powder of as-quenched glass, the high specific surface area of the sample makes surface crystallization dominant; on the contrary, surface crystallization can be neglected in well-nucleated bulk samples owing both to the high number of bulk nuclei formed during the previous nucleation heat-treatment and to the low specific surface area of the samples.

The values of activation energy for the crystal growth, calculated from Equations 11 and 12 from DDTA curves recorded at 20° C min^{-1} and 10° C min^{-1} for powdered and bulk samples, respectively, are reported in Table I. These values agree well with those obtained under isothermal conditions [13] and are consistent with the value $E_\eta = 70$ kcal mol^{-1} of the activation energy for viscous flow in the temperature range of the exothermic peaks [14].

For the sake of comparison the values of activation energy for crystal growth were also evaluated from DTA curves by the following alternative equations

$$\ln \beta = -\frac{E}{R}\frac{1}{T_p} + \text{constant} \qquad (13)$$

and

$$\ln \Delta T = -\frac{nE}{R}\frac{1}{T} + \text{constant}, \qquad (14)$$

where $n = 1$ for surface crystallization and $n = 3$ for bulk crystallization.

Equation 13 [3, 8] is based on the shift of the crystallization-peak temperature, T_p, as the heating rate, β, is changed. Equation 14 [8] is based on the assumption that in the initial part of the crystallization peak the change in temperature has a much larger effect on the change in ΔT compared with the change in extent of crystallization, α [15].

The values of activation energy calculated from the slopes of the straight lines obtained by plotting $\ln \beta$ against T_p^{-1} and $\ln \Delta T$ against T^{-1} are reported in the last two columns of Table I.

4. Conclusions

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

(a) the measurements are rather quick (a single DDTA curve is required);

(b) the measurements are easily achieved (only two peak temperatures have to be detected on the DDTA curve).

The described procedure can be applied to all glass systems which devitrify from the surface or in the bulk and its validity is confirmed by the good agreement between the experimental results and the data obtained by the alternative methods.

The applicability of this procedure to a devitrification process in which the crystallized-phase composition is different from that of the matrix glass requires further investigation.

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