

HETEROGENEOUS BULK NUCLEATION AND DIFFERENTIAL THERMAL ANALYSIS

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The effect of the addition of Ag_2O on the mechanism of non-isothermal devitrification of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass has been studied by differential thermal analysis. In both bulk and powdered samples, the presence of heterogeneous nuclei lowers the crystallization temperatures but not the value of the crystal growth activation energy.

The influence of the catalyst on the crystallization mechanism is not affected by a previous heat treatment at the temperature of the maximum nucleation rate.

In previous papers [1–3] the non-isothermal devitrification of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ 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 the following conclusions were drawn:

a) The activation energy of devitrification, calculated from the shift of the crystallization peak temperature as the heating rate is changed, represents only the kinetic barrier for the crystal growth [1] and in accordance with the results obtained under isothermal conditions [4], its value is the same for both surface and bulk crystallization [2].

b) The shapes and the temperatures of the DTA crystallization peaks suggest a good evaluation of the crystallization mechanism and of the effectiveness of the nucleation heat treatment [2].

c) 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].

d) A nucleation rate *vs.* temperature curve can be obtained from the shift of the DTA peak temperature with increase of the number of nuclei [3]. In this paper the investigations have been extended to the effects of silver particles as heterogeneous nucleation catalyst on the non-isothermal kinetics of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass devitrification.

Experimental procedure

Samples of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (NC) and $\text{Li}_2\text{O} \cdot 2\text{SiO}_2 + 1\% \text{Ag}_2\text{O}$ (C) glasses were prepared by melting the pure reagents at 1450° in a Pt crucible in an electric oven. The melts were cast in Fe moulds at a high cooling rate. The as-quenched glasses were crushed or cut in order to obtain powdered samples ($-240 + 350$ mesh) and small bulk samples (suitable for the size of the sample holder of the DTA).

apparatus), respectively. The nucleation heat treatments were performed on ~90 mg specimens in the DTA furnace to eliminate temperature gradients. The nucleation time (8 h) was measured on isothermal DTA curves from the time at which the samples, heated at $50^\circ \text{ min}^{-1}$, reached the selected temperatures (455°).

Differential thermal analysis (DTA) curves were recorded on ~90 mg specimens different heating rates ($5-20^\circ \text{ min}^{-1}$) in air. Powdered Al_2O_3 was added to improve heat transfer between bulk samples and the sample holder. A Netzsch 404 M thermoanalyzer was used and Al_2O_3 was employed as reference material.

Theoretical considerations and results

Glass is metastable with respect to the crystalline phase at temperatures below its equilibrium liquid temperature and it would achieve a lower free energy by crystallizing. The devitrification process occurs in a range of temperatures at which the values of viscosity allow the structural rearrangement necessary for the crystal growth from the nuclei present in the glass.

Two types of nuclei have to be considered:

- a) Heterogeneous nuclei such as surface defects or bulk nucleating particles.
- b) Homogeneous nuclei formed in the bulk during the DTA run or during a previous heat treatment at temperatures of high nucleation rate.

The numbers N_S and N_C of the former type are proportional to the specific surface area of the sample and to the amount of nucleation catalyst, respectively. The numbers N_B and N_H of the latter type are proportional to the reciprocal of the heating rate and to the duration of the heat treatment, respectively. In the most general theoretical case the total number of nuclei N for unit volume is:

$$N = N_S + N_C + N_B + N_H \quad (1)$$

In the cases examined in this paper the numbers of some kinds of nuclei are, as later proved, very much higher than those of the others, so that the latter can be neglected.

However, in all cases when a glass crystallizes in a range of temperatures well above the temperatures of high nucleation rates, the number of nuclei already present in the glass cannot appreciably increase during crystallization (DTA peak) and the crystals grow from a nearly fixed number of nuclei [5]. The kinetics of crystal growth are well described by the Johnson-Mehl-Avrami (J. M. A.) equation [6, 7]:

$$-\ln(1 - \alpha) = (kt)^n \quad (2)$$

where α is the volume fraction crystallized at time t and the constant k is an Arrhenius type function of the absolute temperature T

$$k = AN \exp\left(-\frac{E_C}{RT}\right) \quad (3)$$

where E_c is the activation energy for the crystal growth, N is the number of nuclei and A is a constant. The parameter n is related to the crystallization mechanism, ranging between $n = 1$ (surface crystallization) and $n = 3$ (bulk crystallization) for $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2$ devitrification [4, 5].

Assuming that the deflection ΔT from the baseline (Fig. 1) at each temperature is proportional to the reaction rate $\frac{d\alpha}{dt}$ [8], the condition that the deflection ΔT has a zero temperature derivative at the peak temperature T_p (Fig. 2) leads to:

$$\frac{d\Delta T}{dT} = \frac{d}{dT} \left(\frac{d\alpha}{dt} \right) = 0 \quad (4)$$

As the crystallization degree α is related to the time and the temperature by the J. M. A. equation, Eq. 4 is satisfied at $T = T_p$ if [1, 9]

$$kt = 1 \quad (5)$$

Taking Eq. 3 into account and assuming that the duration of heating at each temperature is proportional to the reciprocal of the heating rate β [10], the logarithms of Eq. 4 lead to:

$$\ln \beta - \ln N = -\frac{E_c}{R} \frac{1}{T_p} + \text{const.} \quad (6)$$

If the DTA runs are carried out at the same heating rate β , taking into account as previously shown [2, 4, 5] that the value of the activation energy does not depend on the crystallization mechanism, the following relationship can be derived

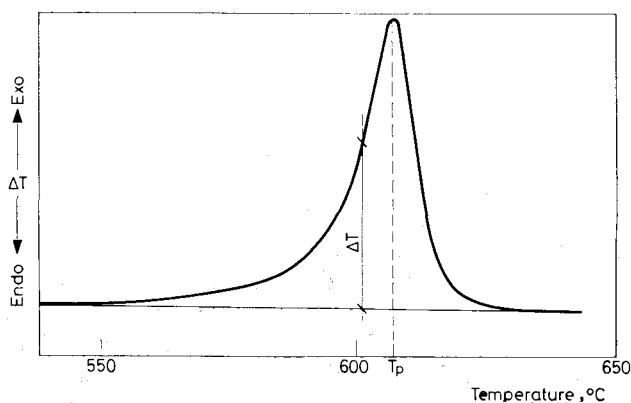


Fig. 1. A typical DTA curve. ΔT = Temperature difference between sample and reference;
 T_p = peak temperature

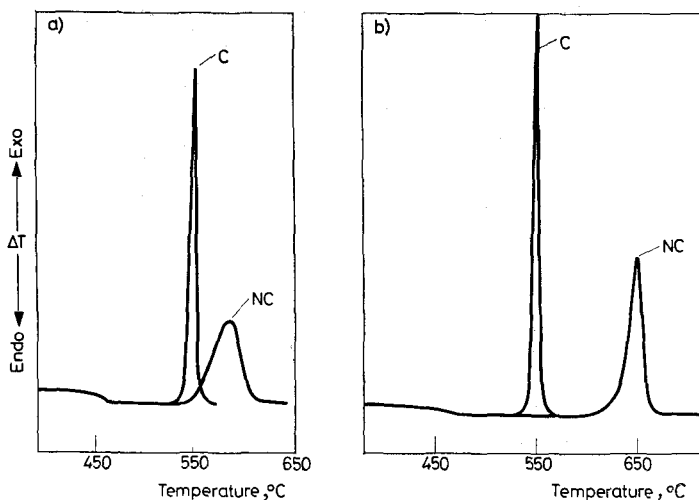


Fig. 2. DTA curves recorded at $5^{\circ} \text{ min}^{-1}$ on as-quenched glasses a) powdered samples; b) bulk samples

between the total number of nuclei for unit volume N and the peak temperature T_p from Eq. 6:

$$\ln N = c_1 \frac{1}{T_p} + c_2 \quad (7)$$

where c_1 and c_2 are constants.

Moreover, the shape of the peak is strongly affected by the value of the parameter n ; the higher the latter, the narrower the former [9]. Therefore, surface ($n = 1$) and bulk ($n = 3$) crystallization correspond to large and sharp peaks, respectively.

The DTA curves recorded at $5^{\circ} \text{ min}^{-1}$ on the as-quenched glasses are shown in Fig. 2.

The roles of the sample specific surface and of the nucleating catalyst are evident.

In the NC glass the small number of homogeneous bulk nuclei formed during the DTA run makes bulk crystallization negligible (large peak) in the very finely powdered sample, due to its high specific surface, and comparable with surface crystallization only in the bulk sample. In the C glass the large number of heterogeneous bulk nuclei makes bulk crystallization dominant in both powdered and bulk samples. The DTA peaks are therefore narrower and shifted towards lower temperatures than those of the NC glass, in accordance with Eq. 6.

The DTA curves recorded at $5^{\circ} \text{ min}^{-1}$ on the glasses previously heated for 8 h at 455° (temperature of maximum nucleation rate) are shown in Fig. 3. By comparing the shapes and the temperatures of the peaks in Fig. 2 with those of the peaks in Fig. 3, it is evident that only the crystallization mechanism of the NC

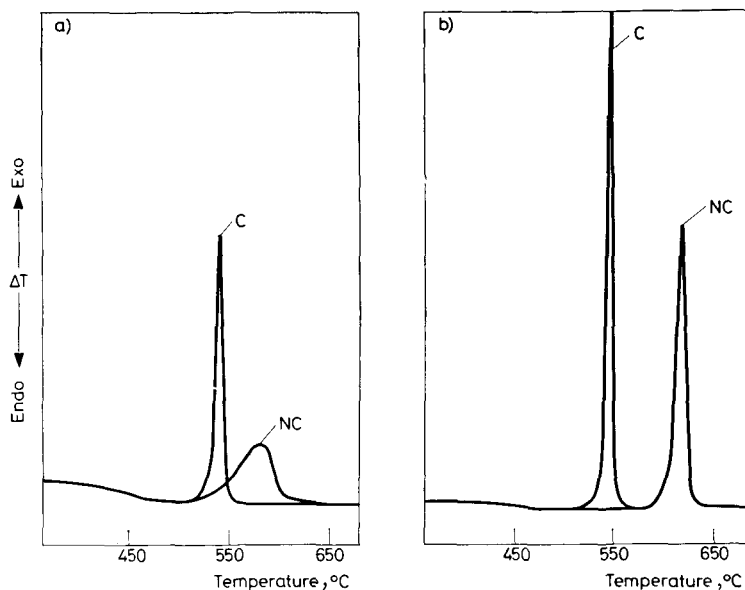


Fig. 3. DTA curves recorded at $5^{\circ} \text{ min}^{-1}$ on previously heated for 8 h at 455° glasses
 a) powdered samples; b) bulk samples

glass bulk sample is strongly affected by the heat treatment of nucleation. Only in this case is the peak shape changed and the peak temperature markedly (36°) lowered.

From the above remarks, the type of nuclei whose number is predominant in each case can be pointed out as reported in Table 1.

Table 1

Predominant type of nuclei and activation energy of crystal growth

Sample	NC				C			
	Q		H		Q		H	
	N	E_c	N	E_c	N	E_c	N	E_c
Bulk	$N_S N_B$	167	N_H	247	N_C	255	N_C	289
Powdered	N_S	293	N_S	264	N_C	301	N_C	368

NC = no catalyst; C = with catalyst

Q = as-quenched; H = heated at 455° for 8 h

N = predominant type of nuclei

E_c = activation energy for crystal growth (kJoule mole^{-1})

If the total number of nuclei for unit volume is not affected by the heating rate β , the activation energy E_c for the crystal growth can be calculated via the following relationship between the peak temperature T_p and the heating rate β derived from Eq. 5:

$$\ln \beta = - \frac{E_c}{R} \frac{1}{T_p} + \text{const.} \quad (8)$$

The values (error $\pm 10\%$) of E_c calculated by plotting $\ln \beta$ against $\frac{1}{T}$ (see Table 1) are in good agreement with the value of 260 ± 40 kjoule mole⁻¹ obtained under isothermal conditions for both surface and bulk crystallization [4, 5]. In the as-quenched NC glass bulk sample the number of bulk nuclei N_B formed during the DTA run cannot, as in the other cases, be neglected. This number decreases with the increase of the heating rate and the crystals grow from a different number of nuclei at each heating rate, so that the peak temperature is shifted not only by the change in the heating rate, according to Eq. 8, but also by the change in the number of nuclei. In the case, therefore, the decrease in the activation energy is not real. In the preheated C glass powder sample the very great number of nuclei present in the glass owing to the nucleating particles, the high specific surface and the heat treatment allow the crystallization in a range of temperatures lower than in the other cases. The high value of the activation energy is consistent with that of the viscous flow activation energy in the same range of temperatures [10].

Conclusions

The addition of 1% Ag₂O to a Li₂O · 2 SiO₂ glass gives rise to such a great number of heterogeneous bulk nuclei that a) bulk crystallization becomes dominant in the very finely powdered sample, in spite of its high specific surface, and b) the number of homogeneous bulk nuclei is negligible after an extended heat treatment at the temperature of the maximum nucleation rate.

The presence of the nucleation catalyst lowers the crystallization temperatures but not the activation energy for the crystal growth.

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RÉSUMÉ — On a étudié, par analyse thermique différentielle, l'effet de l'addition d'Ag₂O sur le mécanisme de dévitrification non-isotherme du verre Li₂O · 2 SiO₂. La présence de noyaux hétérogènes abaisse les températures de cristallisation, mais pas la valeur de l'énergie d'activation de la croissance des cristaux, que les échantillons soient massifs ou pulvérisés.

L'influence du catalyseur sur le mécanisme de la cristallisation n'est pas altérée par un traitement thermique préalable à la température de la vitesse maximale de nucléation.

ZUSAMMENFASSUNG — Die Wirkung des Einflusses von Ag₂O auf den nicht-isothermen Entglasungsmechanismus von Li₂O · 2 SiO₂-Glas wurde durch Differentialthermoanalyse untersucht.

Die Gegenwart heterogener Kerne setzt die Kristallisierungstemperaturen herab, jedoch nicht die Werte der Aktivierungsenergien des Kristallwachstums in grob- als auch in feinpulverisierten Proben.

Die Wirkung des Katalysators auf den Kristallisationsmechanismus wird durch eine vorhergehende Wärmebehandlung bei der Temperatur der maximalen Keimbildungsgeschwindigkeit nicht beeinflusst.

Резюме — С помощью дифференциального термического анализа изучено влияние добавки окиси серебра на неизотермический механизм реакции расстекловывания стекла Li₂O · 2SiO₂. Наличие гетерогенных центров кристаллизации понижает температуры кристаллизации, но не энергию активации роста кристаллов как в массивных, так и порошкообразных образцах. Влияние катализатора на механизм кристаллизации не затрагивается ранее проведенной тепловой обработкой при температуре максимальной скорости образования зародышей кристаллов.