

NUCLEATION KINETIC DATA FROM DTA CURVES

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ABSTRACT

Non-isothermal kinetic data relative to five silicate glasses are compared. A new parameter is proposed, whose usefulness in roughly estimating the ability of different glass compositions to form nuclei and, so, give fine grained glass ceramics, is discussed.

INTRODUCTION

Differential thermal analysis (DTA) allows to evaluate glass devitrification kinetic parameters very rapidly and by using very small amount of glass if compared to the traditional isothermal methods. In this work the data relative to five silicate glasses are compared.

THEORETICAL CONSIDERATION

In fig. 1, a typical DTA curve of a glass is reported. After the slope change in the glass transformation range, an exothermic peak appears due to crystallization. The non-isothermal devitrification of a glass is well described by the following equation (1,2):

$$-\ln(1-\alpha) = \frac{AN}{\beta^m} \exp\left(-\frac{m E_c}{RT}\right) \quad (1)$$

where α is the volume fraction crystallized at temperature T , β is the DTA heating rate, A is, for each glass, a constant whose value depends on the preexponential factor, U^0 , of the crystal growth rate, U , equation:

$$U = U^0 \exp\left(-\frac{E_c}{RT}\right) \quad (2)$$

N is the nuclei number, E_c is the crystal growth activation energy, m is the Avrami parameter, whose value depends on the devitrification mechanism and crystal growth morphology. For crystal-glass interface reaction controlled mechanism, m ranges from $m=1$ for one-dimensional growth (or growth from surface nuclei) to $m=3$ for three-dimensional growth. For diffusion controlled growth, the corres-

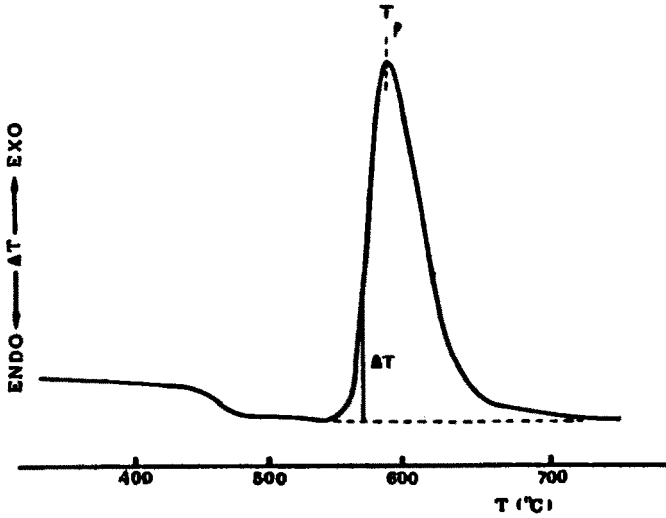


Fig.1 Typical DTA curve.

ponding m range is 0.5-1.5. Taking into account that (3) at the peak temperature, T_p , the crystallization degree reaches the same value not dependent on the heating rate, a shift of the peak must be expected, with the heating rate, so that

$$\ln \beta = - \frac{E_c}{RT_p} + \text{const} \quad (3)$$

Moreover the deflection from the baseline ΔT is proportional to the instantaneous reaction rate (4) and, in the initial part of the DTA crystallization peak, the change in temperature has a much greater effect than α on the ΔT deflection (5); so the following equation can be derived:

$$\ln \Delta T = \frac{m E_c}{RT} + \text{const} \quad (4)$$

The peak becomes sharper, the lesser is the sample specific surface. This is because the "bulk" nuclei formed during the DTA run become progressively dominant with respect to the ones heterogeneously formed at the surface of powder grains. By this way, the Avrami parameter can increase by a factor of three. Therefore, when changing the sample powder size, that is the specific surface, a change in the slope of the DTA peak is expected and observed (6), as shown in fig.2. If a sample is preventively heat treated at a temperature of efficient nucleation rate, equation (1) predicts a DTA shift so that:

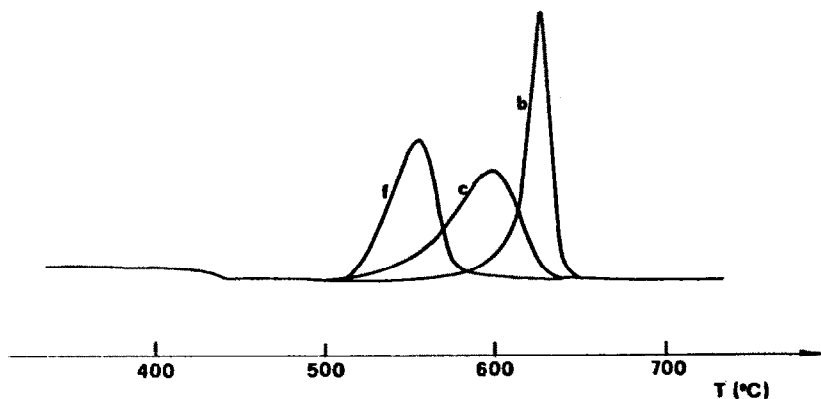


Fig.2 DTA curves recorded at 5°C/min heating rate of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ samples: (f) fine (- 240 + 350 mesh) powder sample; (c) coarse (-30 + 52 mesh) powder sample; (b) bulk sample.

$$\ln \frac{N}{N^0} = \frac{m E_c}{R} \left(\frac{1}{T_p} - \frac{1}{T^0} \right) \quad (5)$$

where T_p^0 and N^0 are, respectively, the peak temperature and nuclei number relative to the as quenched sample. If bulk samples are heat treated for the same time at different temperatures in the range of efficient nucleation rate, a nucleation rate like curve can be obtained by plotting $\left(\frac{1}{T_p} - \frac{1}{T^0} \right)$ vs the heat treatment temperature, as described in (7). In fig.3, as an example, is reported the plot relative to a $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass (7). The temperature of maximum nucleation rate can be so determined. By means of equations (3-5) it is possible, by changing the specific surface or the length and temperature of heat treatments, to get information about the devitrification mechanism. It is worth noting that equation (3) is derived by supposing that the nuclei number present at the onset of the devitrification peak is not depending on the heating rate. Therefore the real value of E_c can be obtained either by using samples of very high specific surface, in which surface nuclei, which form in amount proportional to the specific surface, are dominant, or, better, by using samples heat treated for a long enough time at temperatures of efficient nucleation rate.

RESULTS AND DISCUSSION

The above kind of analysis was performed on the five glasses compositions reported

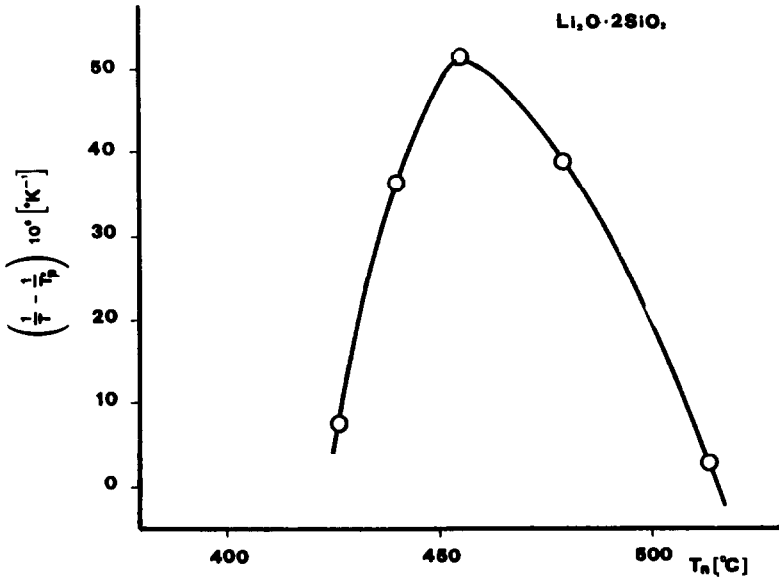


Fig.3 Nucleation rate like curve relative to $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass.

in table (1) (6,8-11). All reported data are taken from the original papers. All glasses show a crystal-glass interface reaction controlled mechanism. When using samples of low specific surface, the Avrami parameter assumes the value $m=3$, indicative of crystal morphology similarity. The reported E_c values are those obtained by means of equation (3) by using samples of low specific surface heat treated, as indicated in the table footnotes, at temperatures of efficient nucleation rate for times long enough to make dominant the bulk nuclei so formed. The reported peak temperatures are those detected on the DTA curves recorded at a heating rate of $10^\circ\text{C}/\text{min}$ for the same kind of sample. In the last column is reported the nuclei number which, following references (12,13), should be present in each glass after the specified heat treatment. In order to discuss the reported data, it is useful rearrange equation (1) as follows:

$$\frac{E_c}{RT_p} = \frac{1}{m} \ln \frac{AN}{\beta^m} + \text{const} \quad (6)$$

Therefore, submitting to DTA runs at the same heating rate different glasses samples whose devitrification can be characterized by the same value of the Avrami parameter, the value of the dimensionless ratio E_c/RT depends on the nuclei number and the factor A. As long as A can be considered constant, a plot

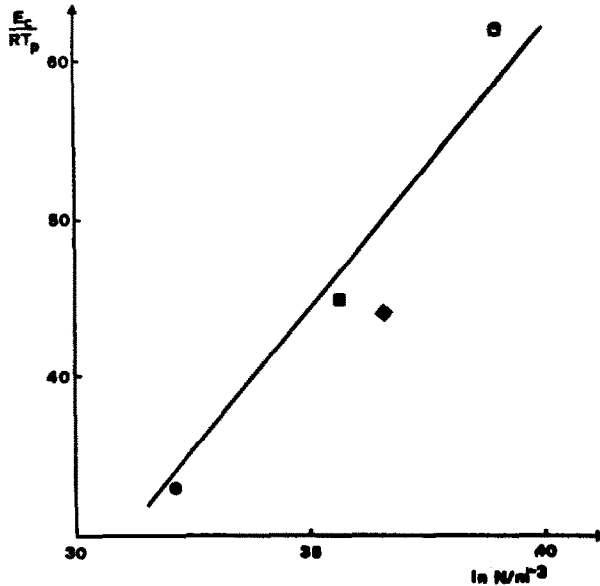


Fig.4: Plot of the parameter E_c/RT_p (defined in the text) vs the natural logarithm of the nuclei present, after the heat treatments reported in Table 1, in the following glasses: (●) $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, (◻) $0.9\text{Li}_2\text{O} \cdot 0.1\text{BaO} \cdot 2\text{SiO}_2$; (◆) $\text{BaO} \cdot 2\text{SiO}_2$, (●) $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$, (●) $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$.

of (E_c/RT) vs. the logarithm of the nuclei number should give straight line. It is effectively obtained, as shown in fig 4, with the data reported in table 1.

It is worth noting that the crystal growth activation energy is usually equal to the viscous flow activation energy, E_η . It's known that in wide temperature range, the viscosity, η , variations are well described by the Vogel equation (14):

$$\log \eta = A + \frac{B}{T - T^\circ}$$

where A, B and T° are constants whose value depends on the glass composition. By comparing the Arrhenius type dependence with the Vogel one, the following relation can be obtained:

$$E_\eta = BR \left(\frac{T}{T - T^\circ} \right)^2$$

that is the viscous flow activation energy progressively decreases as the temperature is increased. Therefore, taking into account eq.6, when a glass is heated in a DTA apparatus, the devitrification temperature range depends on the nuclei number formed, the viscosity-temperature curve shape and the factor A, that is

TABLE 1

Non-isothermal kinetic data for the glasses studied

Glass composition	E_c Kcal mol ⁻¹	T_p (°K)	$\left(\frac{E_c}{RT_p}\right)$	$N^{10^{-13}}$ (m ⁻³)
Li ₂ O.2SiO ₂ a	59	899	33	9
0.9Li ₂ O.0.1BaO.2SiO ₂ b	70	933	38	20
BaO.2SiO ₂ c	99	1119	44	800
Na ₂ O.2CaO.3SiO ₂ d	89	982	45	300
2Na ₂ O.CaO.3SiO ₂ e	107	864	62	8000

a 14 h at 475°C b 750h at 480°C c 2h at 700°C d 2h at 580°C e 2h at 480°C

on the preexponential factor of crystal growth rate equation. As long as A can be considered constant, the dimensionless ratio E_c/RT_p , evaluated as described before, is a measure of the nuclei number present. The described parameter, therefore, allows to make a rough estimate of the ability of different glass compositions to form nuclei and, therefore, to give fine grained glass ceramics.

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