

THE COMPOSITION OF GLASS CERAMICS DETERMINED BY DTA

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ABSTRACT

The thermoanalytical data of various silicate glasses are compared. It is pointed out that the higher activation energy values obtained with non-isothermal devitrification techniques are not necessarily indicative of a lower tendency to devitrification. A criterion is proposed for evaluating the relative ease of different vitreous compositions to form glass-ceramic materials.

INTRODUCTION

Glass ceramics are prepared by a two-step heat treatment. A first step at a temperature of efficient nucleation rate is followed by a second one in which the crystal growth upon the nuclei is allowed. An important criterion in selecting the glass composition for glass-ceramic production is that it must be capable of being crystallized without the use of prohibitively long heat treatments [1].

In this paper a discussion on the meaning of the activation energy value obtained by means of thermoanalytical techniques leads to the definition of a method to evaluate the relative ease with which different compositions form glass ceramics.

RESULTS AND DISCUSSION

Figure 1 shows the differential thermal analysis (DTA) curves of some different kinds of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass [2]. After a slope change in the glass transformation range, an exo-peak due to the heat evolution during crystallization appears in all cases. Figure 2 shows the DTA curves, stopped just before the melting temperature [3], of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$. As can be seen, no exo-peak appears on the bulk-sample curve. The coarse-powder curve exhibits two slope changes before crystallization occurs. The second slope change is linked to the softening and consequent wetting of the sample-holder

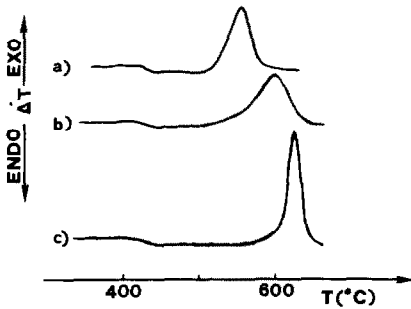


Fig. 1. DTA curves of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass: (a) $-240 + 350$ mesh; (b) $-30 + 52$ mesh; (c) bulk sample.

walls which changes the heat-transfer coefficient. Comparison of the two sets of curves suggests that devitrification occurs with greater difficulty in the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glass, in which, during a DTA cycle, it occurs at temperatures of lower viscosity and only from surface nuclei.

The devitrification kinetic parameters were evaluated [2–6] by means of the thermoanalytical techniques based on the well-known equation [7,8]

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

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

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

where E_c is the crystal growth activation energy and m is the Avrami parameter which depends on the mechanism and morphology of the crystal growth.

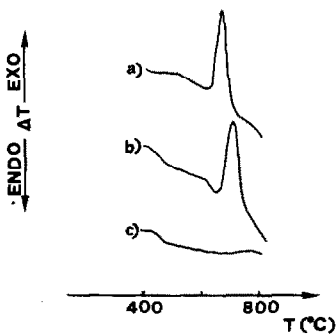


Fig. 2. DTA curves of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glass: (a) -350 mesh; (b) $-170 + 230$ mesh; (c) bulk sample.

TABLE 1

Peak temperatures (T_p , K), undercooling (ΔT , K), activation energies (E_c , E_η , E'_η , kcal mol⁻¹) and the E_c/RT_p parameter as defined in the text

	E_c	E'_η	E_η	ΔT	T_p	E_c/RT_p
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ -170 + 230 mesh	36	53	54	200	949	19
-350 mesh	51	62	58	250	893	29
$\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ -30 + 52 mesh	61		65	400	909	34
-240 + 350 mesh	70		70	434	872	40

The results obtained are reported in Table 1 in which T_p is the peak temperature from a DTA curve recorded at 10°C min⁻¹, ΔT is the undercooling, and E_η is the viscous flow activation energy evaluated from literature data [9,10] in the devitrification temperature range. The difference between the E_c and E_η values relative to $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glass is to be linked [3] to the crystal growth thermodynamic barrier which must to be taken into account when the undercooling is small. As long as the thermodynamic barrier can be taken as proportional to ΔT [11] and a Vogel-Fulcher equation holds for the viscosity [12], the following relation can be derived [3]

$$E_c = RB \left(\frac{T}{T - T^0} \right)^2 - \left(\frac{1.75RT^2}{\Delta T} \right) = E - \left(\frac{1.75RT^2}{\Delta T} \right) \quad (3)$$

where B and T^0 are constants of the Vogel-Fulcher equation. By using eqn. (3) the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ E_c values give the viscous flow activation energy values, E'_η , reported in Table 1, which are very close to the E_η values [3].

As can be seen, despite the early observation that $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass devitrifies more easily than $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glass, the latter appears to convert into crystalline form with a lower activation energy. In order to discuss the results, taking into account that the peak temperature corresponds to equal fractions crystallized [13], it is useful to rearrange eqn. (1) as follows

$$\frac{E_c}{RT_p} = \frac{1}{m} \ln \left(\frac{AN}{\beta^m} \right) + \text{constant} \quad (4)$$

Therefore, taking into account that, following eqn. (2), the E_c values decrease progressively as the temperature is increased, the apparent contradiction can be overcome: owing to greater nucleation rates and/or greater A constant values, devitrification can be performed, in the case of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass, in temperature ranges of greater crystal growth activation energies. However a better parameter for comparing the tendencies to devitrification during heating seems to be the ratio (E_c/RT_p) evaluated in conditions where the Avrami parameter is the same. The (E_c/RT_p) values calculated from the data in Table 1, relative to conditions in which $m = 1$ (devitrification from surface nuclei), are reported in the same table. The

TABLE 2

Glass transformation, peak and liquid temperatures (T_g , T_p , T_l , K), activation energies (E_c , kcal mol⁻¹), (E_c/RT_p) as defined in the text, and K_{gl} parameter values

	T_g	T_p	T_l	E_c	E_c/RT_p	K_{gl}
$Li_2O \cdot 2SiO_2$	743	899	1306	59	33	0.383
$BaO \cdot 2SiO_2$	983	1119	1693	99	44	0.237
$Na_2O \cdot 2CaO \cdot 3SiO_2$	843	982	1557	89	45	0.242
$2Na_2O \cdot CaO \cdot 3SiO_2$	763	865	1414	107	62	0.186

higher values of the (E_c/RT_p) parameter, increasing as the specific surface increases owing to the greater number of nuclei, show that the $Li_2O \cdot 2SiO_2$ glass has a greater tendency to devitrify on heating.

Table 2 gives the E_c values relative to bulk samples of four different silicate glasses previously nucleated for 2 h at the maximum nucleation-rate temperature [2,4–6], so that the Avrami parameter $m = 3$ is obtained. Also used in Table 2 are the glass transition temperatures from the DTA curves recorded at 10°C min⁻¹, the liquid temperatures (T_l), and the peak temperature from DTA curves recorded at 10°C min⁻¹ (T_p) for the same sample described above. Again higher (E_c/RT_p) values should be indicative of a greater aptitude to form nuclei and/or higher pre-exponential factors of the crystal growth-rate equation. Moreover, as long as the induction times at the maximum nucleation-rate temperature can be neglected, as in the cases of the $Li_2O \cdot 2SiO_2$, $Na_2O \cdot 2CaO \cdot 3SiO_2$ and $2Na_2O \cdot CaO \cdot 3SiO_2$ glasses [14,15], eqn (4) leads, for two generic glasses i and j nucleated for the same time at the maximum nucleation rate temperature, to the following relation

$$\frac{E_{ci,j}}{RT_{pi,j}} - \frac{E_{cj,j}}{RT_{pj,j}} = \frac{1}{m} \ln \left(\frac{I_i A_i}{I_j A_j} \right) \quad (5)$$

The (E_c/RT_p) parameter, evaluated as reported above, could therefore be used as a measure of the ability to form glass ceramics.

Recently, a method has been proposed [16,17] for comparing the glass thermal stability by using characteristic temperatures evaluated from the DTA curves: the method makes use of the parameter

$$K_{gl} = \frac{T_p - T_g}{T_l - T_p}$$

where T_p , T_g and T_l are the peak, glass transformation and liquid temperatures, respectively. It was proposed that the lower this parameter is, the higher the tendency to devitrify should be.

In the last two columns of Table 2, the (E_c/RT_p) and K_{gl} values are reported. These values are also plotted in Fig. 3. In terms of the above

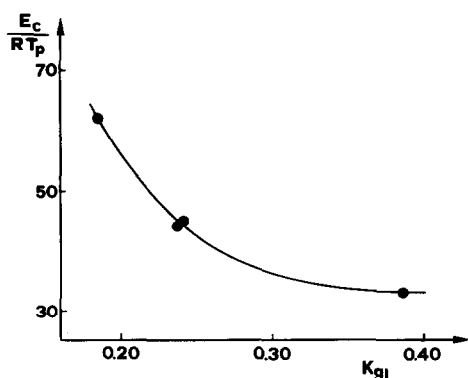


Fig. 3. Plot of (E_c/RT_p) versus K_{g1} .

discussion, less values of the K_{g1} parameter must be expected, the higher the (E_c/RT_p) value is. This is indeed found, as shown in Fig. 3.

It is worth noting that as long as the variation in the A values in eqn. (1) can be neglected, the proposed parameter can be used to select glass compositions suitable for producing fine-grained glass ceramics [18].

CONCLUSIONS

Higher activation-energy values obtained by thermoanalytical methods are not necessarily linked to greater glass thermal stability on heating. If T_p is the peak temperature taken from the DTA curves recorded at the same heating rate, a better parameter seems to be the ratio (E_c/RT_p) . Comparisons should be made when the Avrami parameter is the same. When using samples preheated for the same length of time at the maximum nucleation-rate temperature, the defined parameter should allow the relative ease with which different vitreous compositions form glass ceramics to be defined.

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