

CRYSTALLIZATION OF GLASSES IN THE $2 \text{Na}_2\text{O} \cdot \text{CaO} \cdot 3 \text{SiO}_2 - \text{Na}_2\text{O} \cdot 2 \text{CaO} \cdot 3 \text{SiO}_2$ COMPOSITION RANGE

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ABSTRACT

The devitrification behaviour of specimens with compositions $(2-x)\text{Na}_2\text{O}(1+x)\text{CaO} \cdot 3 \text{SiO}_2$, $0 \leq x \leq 1$, was studied. The crystalline phases were identified by X-ray diffraction and the glass transition temperatures were determined by differential thermal analysis. The activation energies for the crystal growth were calculated from the inflection point temperatures detected on the derivation differential thermal analysis curves.

INTRODUCTION

This work is part of a more general study on the devitrification behaviour of soda-lime-silica glasses for producing glass ceramics from cheap raw materials. In previous papers [1,2] the non-isothermal devitrification of $2 \text{Na}_2\text{O} \cdot \text{CaO} \cdot 3 \text{SiO}_2$ (N_2CS_3) and $\text{Na}_2\text{O} \cdot 2 \text{CaO} \cdot 3 \text{SiO}_2$ (NC_2S_3) glasses has been studied by differential thermal analysis. The temperature of maximum nucleation rate, the activation energy for crystal growth, and the crystallization mechanism were evaluated and the results were compared with those obtained under isothermal conditions by other workers [3,4].

In the present paper a series of glasses in the ternary system $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{SiO}_2$ whose compositions lie on the line joining N_2CS_3 with NC_2S_3 glasses has been studied in order to evaluate the effect of replacing Na_2O by CaO , in molecular equivalent amounts, on the glass transition temperature and devitrification kinetics.

EXPERIMENTAL

Five specimens were prepared of general formula $(2-x) \text{Na}_2\text{O} \cdot (1+x) \text{CaO} \cdot 3 \text{SiO}_2$, where $x = 0.0, 0.25, 0.50, 0.75, 1.0$ (Table 1).

The extreme values $x = 0.0$ and $x = 1.0$ correspond to the stoichiometric compounds N_2CS_3 and NC_2S_3 , respectively. Specimens were prepared by melting analytical grade reagents in a Pt crucible in an electric oven and keeping them at 1400°C for 6 h. The melts were cast at a high cooling rate by plunging the bottom of the crucible in cold water. The as quenched glasses thus obtained were studied by:

(a) differential thermal analysis (DTA) of 60 mg powdered samples at a heating

Table 1

Composition of glasses

x	Na ₂ O (wt.%)	CaO (wt.%)	SiO ₂ (wt.%)
0.00	34.4	15.6	50.0
0.25	30.2	19.6	50.2
0.50	26.0	23.5	50.5
0.75	21.8	27.6	50.6
1.00	17.5	31.7	50.9

rate of 20°C min⁻¹ in air; the particles were -170 + 270 mesh and the reference material was Al₂O₃. A Netzsch 404 M thermoanalyzer was used; and

(b) X-ray diffraction (XRD) to identify phases crystallizing after thermal treatment; a Guinier de Wolff camera and CuK α radiation were used. The glass was milled and passed through a 270 mesh sieve and then placed in the specimen holder provided.

RESULTS AND DISCUSSION

Glass transition temperature

Figure 1 shows the DTA curves for the five specimens. All the glasses exhibit a slope change between 468 and 610°C which may be attributed to the glass transition. As a glass is heated its heat capacity, as other properties, changes abruptly in a narrow temperature range, called the glass transition or transformation temperature, at which the glass network acquires mobility, changing from a rigid to a plastic structure [5]. When a glass, heated in a DTA furnace, passes through the glass transition temperature range the slope of the DTA curve is changed and a peak appears on the DDTA curve as shown in Fig. 2.

In this work the DDTA peak temperature was taken as the glass transition temperature T_g and the values for the five investigated glasses are plotted as a function of x in Fig. 3. The linear increase of T_g values with respect to the progressive substitution of Ca²⁺ ions for Na⁺ ions (Ca²⁺ \rightarrow 2 Na⁺) agrees well with the increase of the coordination number from 6 for Na⁺ ions to 8 for Ca²⁺ ions [6] and with the increase of the field strength (expressed in terms of Z/r^2 where Z and r are the charge and the radius of the cations, respectively) from 1.11 for Na⁺ ions to 2.04 for Ca²⁺ ions [7].

Glass devitrification kinetics

When a glass is heated at a constant rate crystal nuclei are formed at a temperature somewhat higher than the glass transition temperature and grow in size at higher temperatures without any increase in number [8]. As the crystallization

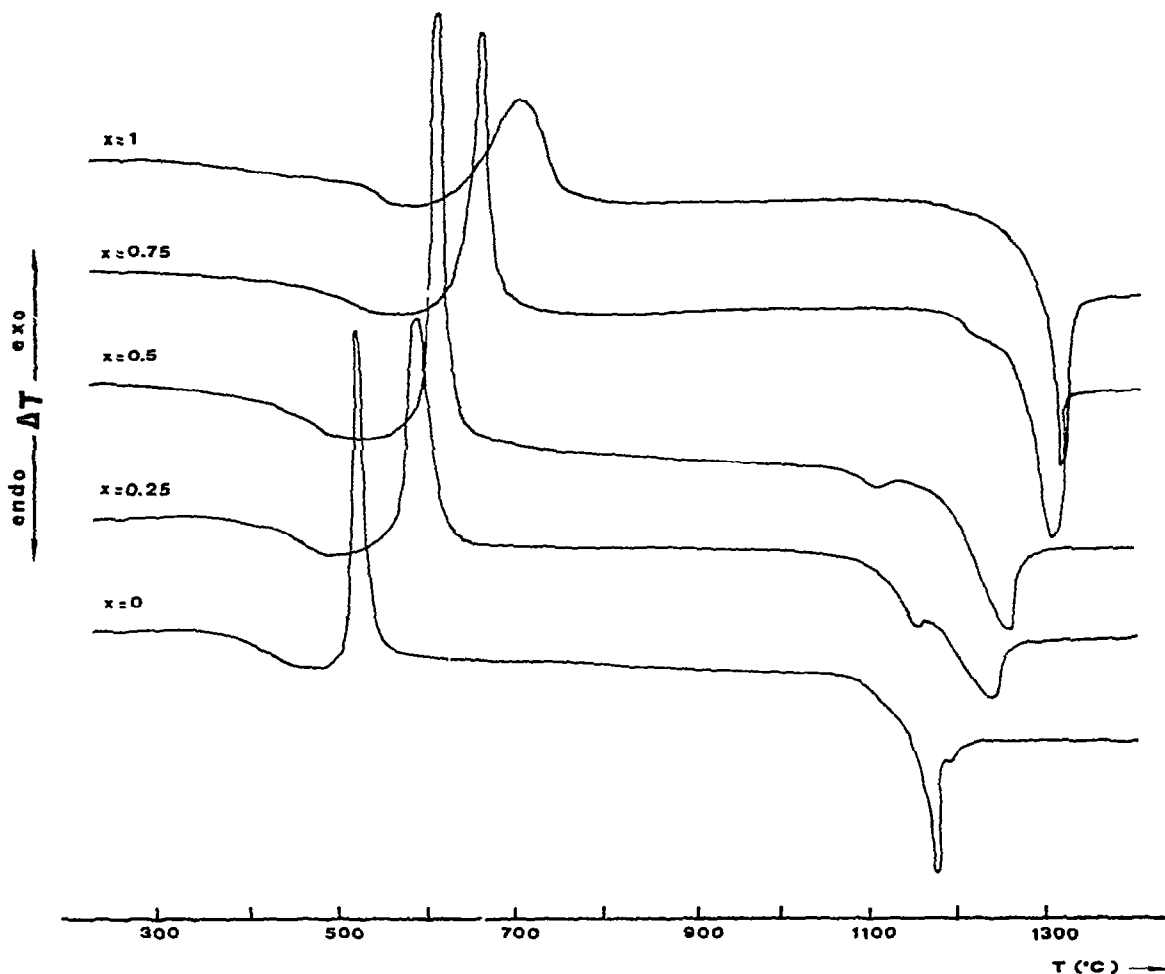


Fig 1 DTA curves of glasses with λ values indicated

proceeds, the heat of crystallization is evolved and an exothermic peak appears on the DTA curve (Fig. 1)

As very fine-powdered samples were used, surface crystallization is dominant [9] and the non-isothermal devitrification process can be described by [9]

$$-\ln(1 - \alpha) = A \frac{N}{\beta} \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where α is the degree of crystallization, N is the number of nuclei, β is the DTA heating rate, E is the activation energy for crystal growth, T is the absolute temperature, and A is a constant.

If the DTA runs are carried out at the same heating rate ($\beta = \text{constant}$) on samples of the same specific surface, eqn. (1) can be rewritten as

$$-\ln(1 - \alpha) = K \quad (2)$$

where

$$K = A' \exp\left(-\frac{E}{RT}\right) \quad (3)$$

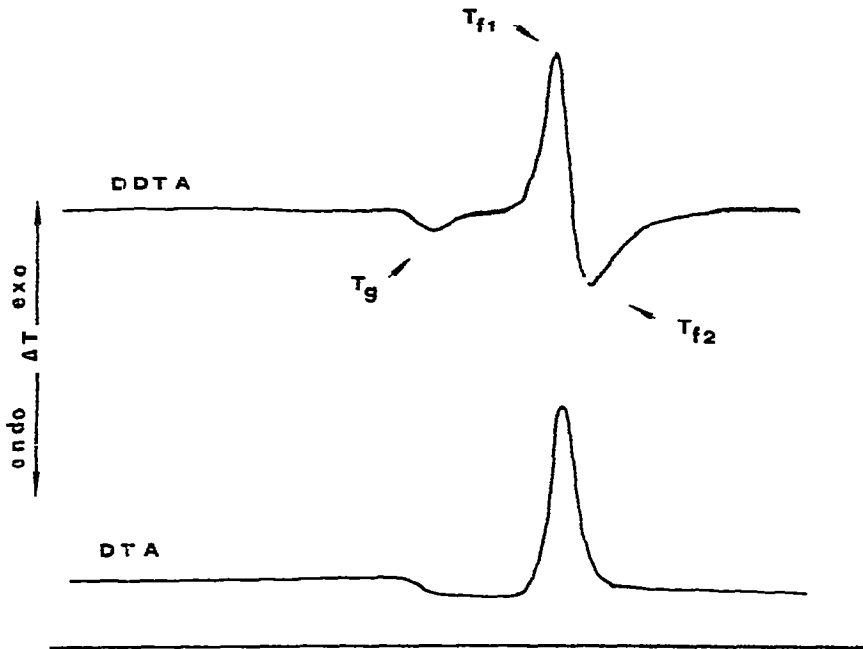


Fig 2 DTA and DDTA curves of $\nu=0$ glass

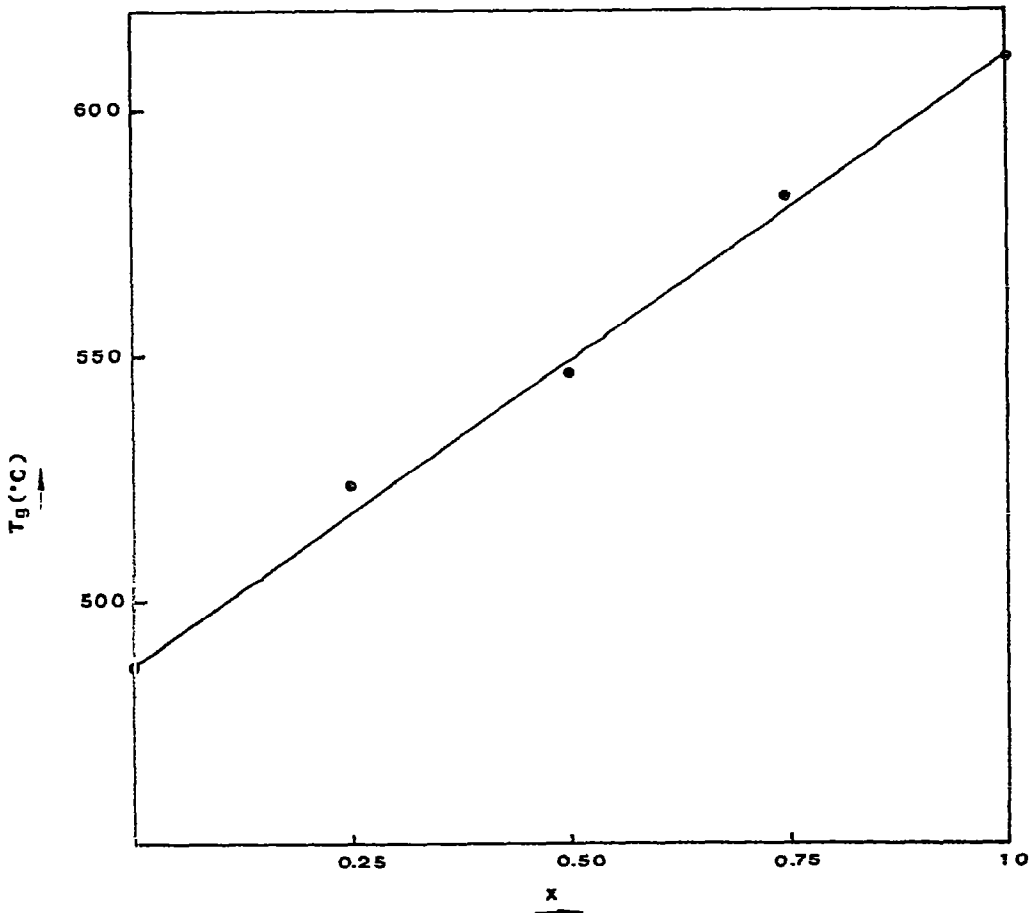


Fig 3 T_g as a function of the composition (x) of glasses

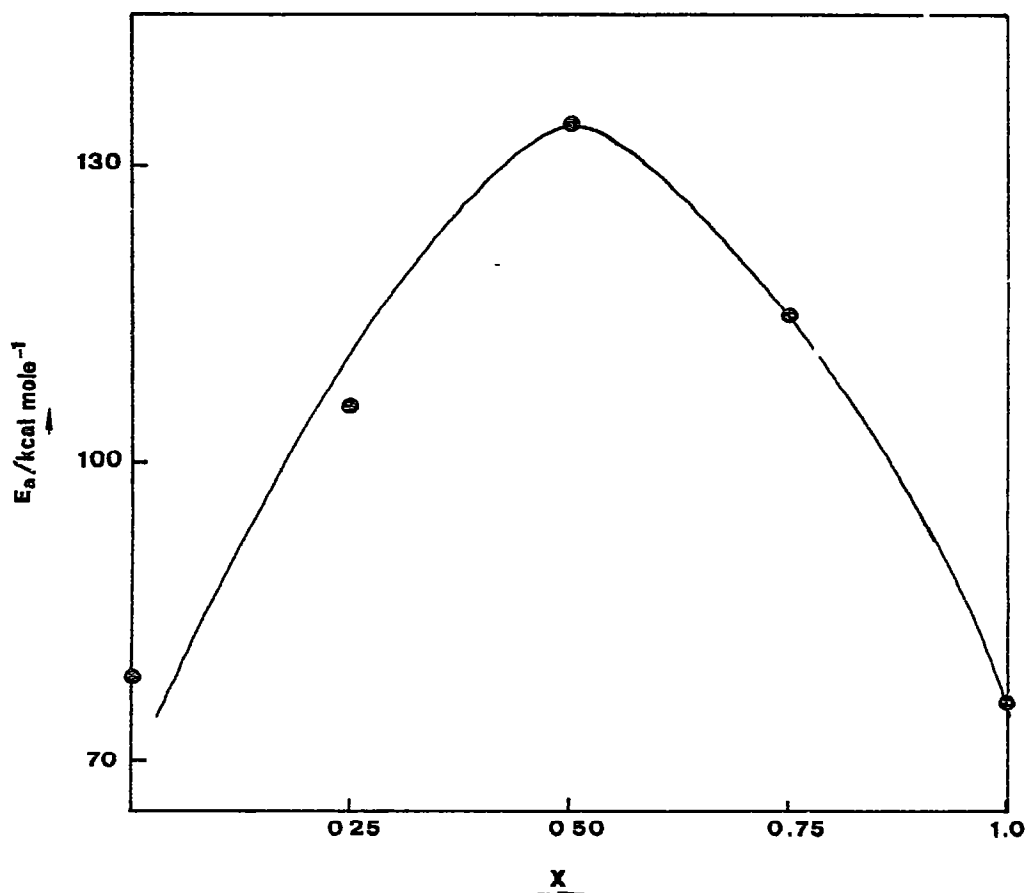


Fig 4 Activation energy E for crystal growth as a function of the composition (x) of glasses

Assuming that ΔT deflection from the baseline is, at each temperature, proportional to the instantaneous crystallization rate [10], the inflection point temperature T_f of the DTA crystallization peak can be obtained by setting

$$\frac{d^2 \Delta T}{dT^2} = \frac{d^3 \alpha}{dT^3} = \frac{d^3}{dT^3} [1 - \exp(-K)] = 0 \quad (4)$$

In a previous paper [11] it was shown that eqn. (4) is satisfied if

$$K^2 - 3K + 1 = 0 \quad (5)$$

As for this equation there exist two solutions which correspond to the two inflection points (i.e. the maximum and the minimum slopes of the DTA peak), the following relationship between the activation energy E for the crystal growth and the inflection point temperatures T_{f_1} and T_{f_2} can be derived

$$\frac{E}{R} \left(\frac{1}{T_{f_1}} - \frac{1}{T_{f_2}} \right) = 1.92 \quad (6)$$

If the DTA curve and its derivative are simultaneously recorded, the two inflection points of the DTA peak correspond to the maximum and the minimum of

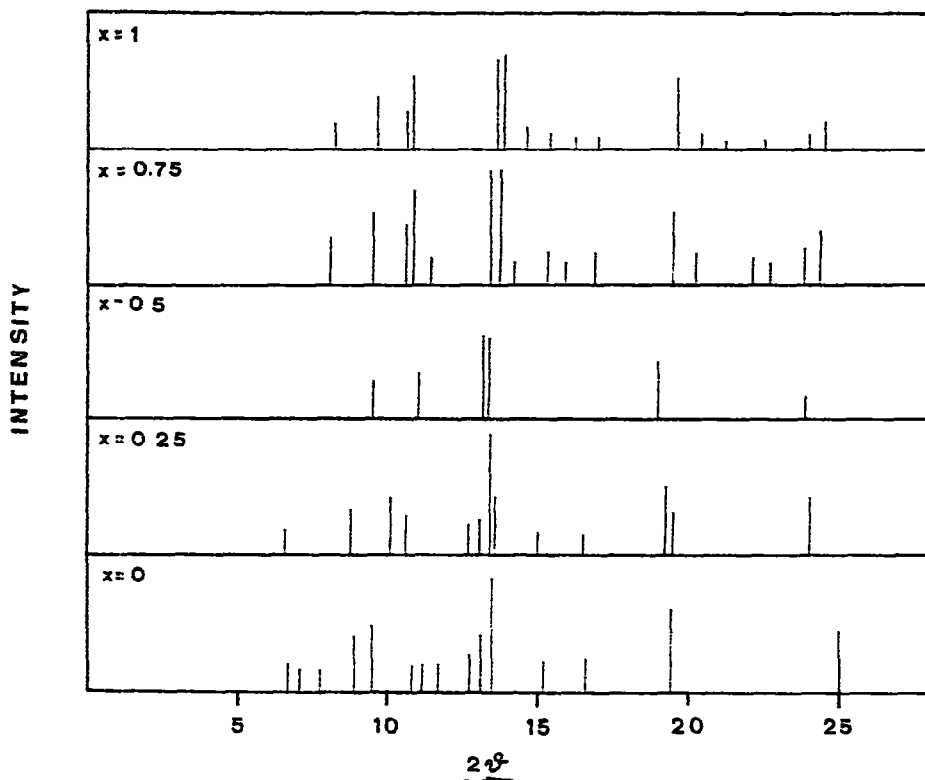


Fig 5 X-ray diffraction patterns of crystallized samples

the DDTA double peak as shown in Fig. 2. The activation energy values calculated by eqn. (6) are reported as a function of x in Fig. 4. The bell shape of the plot with a maximum for the specimen with $x=0.5$ can be attributed to the long-range diffusion required for the crystallization of phases with chemical composition different from that of the mother glass.

Crystallized phases

The phases crystallized during the DTA runs were identified by X-ray diffraction (Fig. 5). In the end members a single crystallized phase was formed, N_2CS_3 in the specimen with $x=0$ and NC_2S_3 in that with $x=1$. The presence of a single crystallized phase is confirmed by DTA curves (Fig. 1). In the DTA curves of $x=0$ and $x=1$ samples, sharp endothermic peaks appear at the melting point temperatures $T=1141^\circ\text{C}$ and $T=1284^\circ\text{C}$ for N_2CS_3 and NC_2S_3 crystals, respectively. In the intermediate terms both N_2CS_3 and NC_2S_3 crystals were formed, as confirmed by the presence, in these cases, of two broad endothermic peaks on the DTA curves.

CONCLUSIONS

Within the glass series studied the transition from the N_2CS_3 composition ($x = 0$) to the NC_2S_3 composition involves a linear increase of glass transition temperature owing to the higher field strength and coordination number of Ca^{2+} ions with respect to those of Na^+ . The more the crystallized phase composition differs from the mother glass, the higher is the value of activation energy for crystal growth owing to the increase of diffusion processes. In spite of a single crystallization peak on the DTA curve for all glasses examined, two crystalline phases were identified by XRD in the intermediate terms ($0 < x < 1$) of the series.

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