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DEVITRIFICATION BEHAVIOUR OF GLASSES NEAR THE $Na_2O \cdot 2\,SiO_2$ COMPOSITION

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ABSTRACT

The influence of small substitutions of different cations for Na^+ ions on the devitrification behaviour of $Na_2O \cdot 2\,SiO_2$ glass has been investigated by differential thermal analysis.

The stability of the glasses has been related to the glass transition temperature/liquidus temperature ratio and to the field strength of the cations.

INTRODUCTION

In previous papers [1,2] the effect of a progressive substitution of several different M^{n+} cations for Na^+ ions ($M^{n+} \rightarrow nNa^+$) in sodium disilicate glass on the glass transition temperature, T_g, has been investigated. From the experimental results, conclusions were drawn about the role of such cations in the glass structure. Moreover, T_g values have been indirectly related to the degree of cross-linking and of tightness of packing.

The effect of small substitutions of Li^+, K^+, Ca^{2+}, Ba^{2+}, La^{3+}, Y^{3+} and In^{3+} cations for Na^+ ions on the devitrification behaviour of sodium disilicate glass has been studied in this work. A non-isothermal technique, i.e., differential thermal analysis (DTA), that allows the kinetic parameters of crystal growth to be evaluated more quickly than the isothermal techniques, was used.

EXPERIMENTAL

The glasses examined, whose compositions can be expressed by the general formula

$$0.9\,Na_2O \cdot \frac{0.1}{m} M_nO_m \cdot 2\,SiO_2$$

with $M_nO_m = Li_2O$, K_2O, CaO, BaO, La_2O_3, Y_2O_3 and In_2O_3, have the same polymerization degree, i.e., the same O/Si = 2.5 molar ratio.

Samples of such glasses were prepared by melting pure reagents in a Pt crucible in an electric oven at 1100 °C for 5 h.

The melts were quenched by plunging the bottom of the crucible into cold water. No crystalline phases were detected by X-ray diffraction in the quenched glasses using a Guinier de Wolff camera and Cu K_α radiation.

The as-quenched glasses were crushed or cut in order to obtain fine powdered samples (− 170 + 230 mesh) and small bulk samples (suitable for the size of the sample holder of the DTA apparatus), respectively.

Differential thermal analysis (DTA) curves of ~ 50-mg specimens at different heating rates (2–20 °C min^{-1}) in air were recorded. Powdered Al_2O_3 was added to improve heat transfer between bulk samples and the sample holder. Derivative differential thermal analysis (DDTA) curves were also simultaneously recorded.

A Netzsch thermoanalyzer (Model 404M) was used, and powdered Al_2O_3 was used as reference material.

RESULTS AND DISCUSSION

When a glass is heated in a DTA furnace the recorded curve shows (Fig. 1) a slope change in the glass transition temperature range, an exothermic

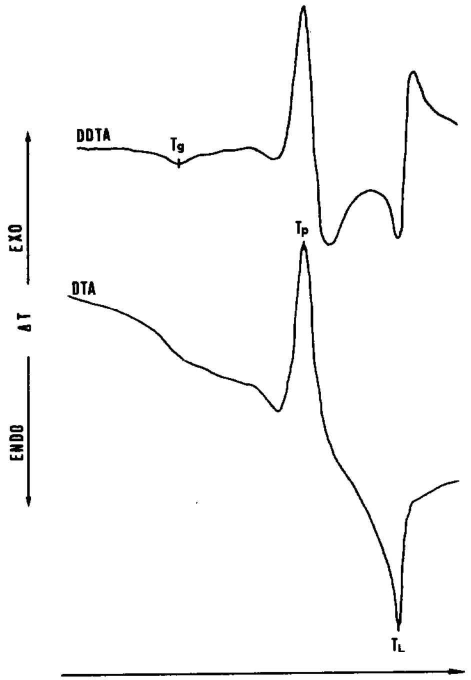

Fig. 1. Characteristic temperatures on DTA and DDTA curves.

TABLE 1

Characteristic temperatures (K), field strengths of the cations ($Å^{-2}$), and activation energies for crystal growth ($kcal\ mol^{-1}$)

M^{n+}	T_g	T_l	T_g/T_l	z/r^2	E
Li^+	718	1101	0.652	2.16	54
K^+	716	1086	0.659	0.56	58
Ba^{2+}	741	1114	0.665	1.11	60
Ca^{2+}	766	1122	0.683	2.04	68
La^{3+}	770	1122	0.686	2.91	80
Y^{3+}	781	1120	0.697	3.76	99
In^{3+}	784	1122	0.699	4.57	88

peak when crystallization takes place, and an endothermic peak when melting occurs. Values of the glass transition temperature, T_g, and of the liquidus temperature, T_l, for the investigated glasses were detected on DTA and DDTA curves as shown in Fig. 1, and are reported in Table 1.

Crystallization in glass can occur either in the volume or on the surface of the sample; when only surface crystallization occurs, no exothermic peak appears on the DTA curves of bulk samples owing to their low specific surface area.

In Fig. 2 are reported the DTA curves of a powdered and bulk sample of $0.9\ Na_2O \cdot 0.1\ BaO \cdot 2\ SiO_2$ glass. The lack of any crystallization peak on the DTA curve of the bulk sample suggests that in this glass the crystals grow only from the surface of the sample.

All glasses examined show the same behaviour. In the case of surface crystallization, nuclei are formed only on the surface of the sample and the crystals grow from the surface to the inside of the glass particles one-dimensionally.

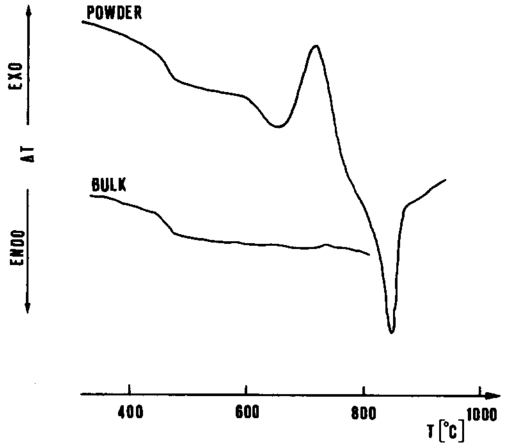

Fig. 2. DTA curves of powdered and bulk samples of $0.9\ Na_2O \cdot 0.1\ BaO \cdot 2\ SiO_2$ glass.

The volume fraction of the crystals, α, can be expressed as [3]

$$1-(1-\alpha)^{1/3}=A\frac{N}{\beta}K \tag{1}$$

where β is the DTA heating rate, and A is a constant. The number of nuclei, N, is proportional to the specific surface area of the samples.

The rate constant, K, can be expressed by the following empirical equation for $Na_2O \cdot 2\,SiO_2$ glass [4], proposed by Hillig and Turnbull [5]

$$K=\frac{B}{\eta}\Delta T^{1.75} \tag{2}$$

where η is the viscosity of the glass, ΔT is the undercooling degree, i.e., the difference between the liquidus temperature and the temperature at which crystallization occurs, and B is a constant.

As eqn. (2) holds for other soda–silica glass compositions [6], and taking into account that the phases crystallized during the DTA runs were identified by X-ray diffraction as $Na_2Si_2O_5$ in all glasses examined, it has to be expected that eqn. (2) well describes the devitrification kinetics of the glasses investigated whose compositions are close to that of the $Na_2Si_2O_5$ glass.

In a narrow range of temperature the viscosity can be related to the absolute temperature, T, by an Arrhenius type equation

$$\eta=c\exp(E/RT) \tag{3}$$

where E is the activation energy for the viscous flow, and c is a constant.

Taking into account eqns. (2) and (3), using the logarithms of eqn. (1), gives

$$\ln|1-(1-\alpha)^{1/3}|=\ln N-\ln\beta+1.75\ln\Delta T-\frac{E}{R}\frac{1}{T}+\text{const.} \tag{4}$$

Taking into account that (a) the DTA runs are carried out on samples of the same specific surface area ($N=\text{const.}$), and (b) at the crystallization peak temperature, T_p, the volume fraction of the crystals, α [7,8], has the same value at each heating rate, β, the following equation can be derived

$$\ln\frac{\Delta T^{1.75}}{\beta}=\frac{E}{R}\frac{1}{T_p}+\text{const.} \tag{5}$$

Plots of $\ln(\Delta T^{1.75}/\beta)$ against $1/T_p$ gave straight lines (Fig. 3) for all glasses examined. The values of the activation energy, E, calculated from their slopes, are reported in Table 1.

The increase in the values of E for crystal growth with an increase in the T_g/T_l ratio (Fig. 4) is consistent with that observed in other glass-forming systems in which the higher the T_g/T_l ratio, the higher the glass stability [9].

In Table 1 the field strengths of the cations are also reported, i.e., the ratio of the cation charge to the square of the ionic radius (ionic radii were taken from IUPAC tables). As can be seen the values of the activation energy

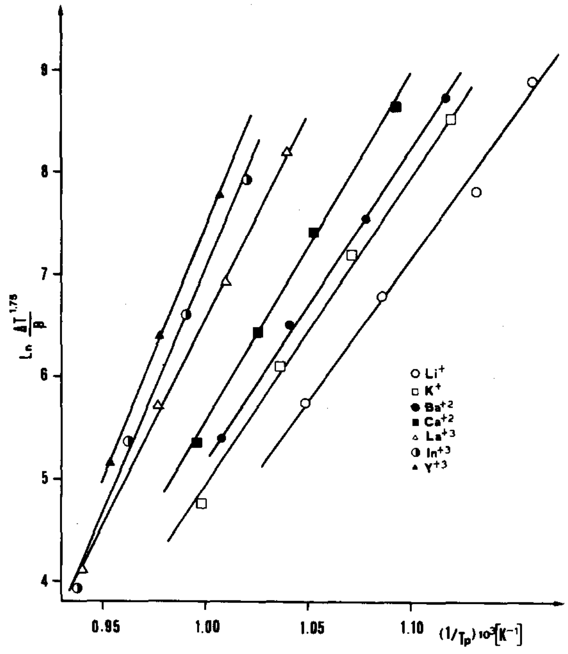

Fig. 3. Plots of ln $\Delta T^{1.75}/\beta$ against $1/T_p$.

increase as z/r^2 is increased. The low value of activation energy for the Li^+ cation can be attributed to its low coordination number.

CONCLUSIONS

From the experimental results the following conclusions can be drawn:

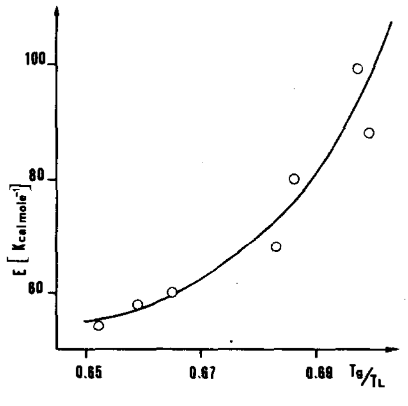

Fig. 4. Plot of E against T_g/T_l.

(a) in all glasses investigated, like $Na_2O \cdot 2\ SiO_2$ glass, only surface crystallization occurs;
(b) the glass stability increases with increasing T_g/T_l ratio and with the field strength value of the M^{n+} cation.

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