NUCLEATION AND CRYSTAL GROWTH IN A $0.9Li_2O \cdot 0.1BaO \cdot 2SiO_2$ GLASS: A DTA STUDY

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ABSTRACT

The devitrification behaviour of a $0.9Li_2O \cdot 0.1BaO \cdot 2SiO_2$ glass has been studied by differential thermal analysis in order to evaluate the effect of substitution of a small amount of BaO for Li_2O on the nucleation and the growth kinetics of lithium disilicate crystals. The value of the activation energy for crystal growth is very close to that for crystal growth in a lithium disilicate glass. A method for evaluating the effect of heat treatments in the nucleation temperature range on bulk crystallization kinetics is also proposed. The results suggest that the bulk nucleation rate of lithium disilicate crystals is lowered remarkably by the presence of BaO.

INTRODUCTION

The devitrification behaviour of a $0.9Li_2O \cdot 0.1BaO \cdot 2SiO_2$ glass has been studied by differential thermal analysis (DTA) in order to evaluate the effect of substitution of a small amount of BaO for Li_2O on the nucleation and the growth kinetics of lithium disilicate crystals.

EXPERIMENTAL

Samples of glass with $0.9Li_2O \cdot 0.1BaO \cdot 2SiO_2$ composition were prepared by melting pure reagents (Li_2CO_3, $BaCO_3$ and SiO_2) at 1400°C in a platinum crucible in an electric oven for 4 h. The melts were cast by plunging the bottom of the crucible into cold water.

Differential thermal analysis (DTA), of about 100 mg of glass samples was carried out in air at various heating rates (2–20°C min^{-1}). The analysis was performed on fine ($-170 + 230$ mesh) and coarse ($-30 + 52$ mesh) powder samples. Small bulk samples suitable for the size of the sample holder of the DTA apparatus were also prepared. In this case, powdered Al_2O_3 was added to improve the heat transfer between the sample and the sample holder. A Netzsch differential thermal analyser model 404M and

Al$_2$O$_3$ as reference material were used. The X-ray diffraction pattern was obtained by means of a Guinier–de Wolff camera (Enraf Nonius, Delft, Netherlands) and CuKα radiation.

RESULTS AND DISCUSSION

The DTA curve recorded at 20°C min^{-1} on a fine powdered sample of the studied glass is shown in Fig. 1. The X-ray diffraction pattern of a sample of 0.9Li$_2$O · 0.1BaO · 2SiO$_2$ taken from the DTA furnace just after the devitrification heat evolution had stopped, is reported in Table 1. It differs from that of a similarly devitrified Li$_2$O · 2SiO$_2$ sample in the presence of a few weak reflections. The weakness of the relative reflections suggests that BaO · 2SiO$_2$ crystals form even if in a small amount as may be expected taking into account the composition of the glass.

The non-isothermal devitrification of glasses is well described by the following equation [1,2]

$$-\ln(1-\alpha) = \frac{A}{\beta^n}\exp\left(-\frac{mE_c}{RT}\right) \tag{1}$$

where α is the volume fraction crystallized at temperature T, β is the DTA heating rate, E_c is the activation energy for crystal growth and A is a constant. The parameter m depends on the mechanism and morphology of crystal growth. For growth controlled by the reaction at the glass–crystal interface it ranges from $m = 1$, for one-dimensional growth (or growth from surface nuclei) to $m = 3$ for three-dimensional growth. For the diffusion-controlled growth the corresponding m range is 0.5–1.5. The parameter n takes into account the possibility that the number of nuclei depends on the heating rate; if this is not the case $n = m$.
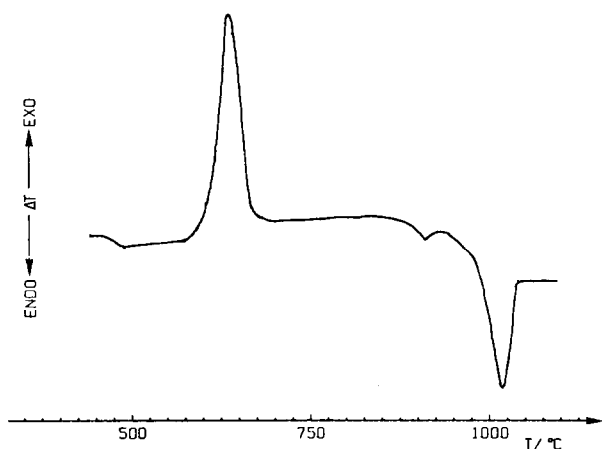

Fig. 1. DTA curve of the studied glass on fine powdered sample recorded at 20°C min^{-1}.

TABLE 1

X-ray diffraction patterns, d spacings and relative intensities

$Li_2O \cdot 2SiO_2$ ASTM Card 17/447	$Li_2O \cdot 2SiO_2$ ASTM Card 30/767	$BaO \cdot 2SiO_2$ ASTM Card 10/45	$Li_2O \cdot 2SiO_2$ Devitrified glass	$0.9Li_2O \cdot 0.1BaO \cdot 2SiO_2$ Devitrified glass
7.34/12	7.30/20			
			7.22 w	7.22 w
5.43/14				
			5.37 m	5.37 m
			4.67 w	4.67 w
		4.05/100		
				3.97 w
3.75/90				
			3.72 s	3.72 s
3.67/100	3.68/50			
			3.63 s	3.63 s
3.59/60	3.60/80			
			3.56 vs	3.56 vs
		3.55/50		
		3.35/40		
			3.29 w	3.29 w
				3.23 w
		3.17/80		
				3.10 w
				3.08 w
	2.95/20			
			2.93 w	2.93 w
2.92/12				
	2.91/20		2.91 m	2.91 m
		2.70/50		
			2.69 w	2.69 w
2.40/14	2.40/100			
			2.38 s	2.38 s
2.36/10				
			2.34 w	2.34 w
			2.32 w	2.32 w
2.30/8				
			2.28 w	2.28 w
		2.26/60		
				2.23 w
		2.22/80		
				2.20 w
2.06/8				
			2.05 w	2.05 w
	2.00/20		2.00 w	2.00 w
			1.99 w	1.99 w
1.97/20				
			1.96 m	1.96 m
	1.85/20			

w, weak; m, medium; s, strong; vs, very strong.
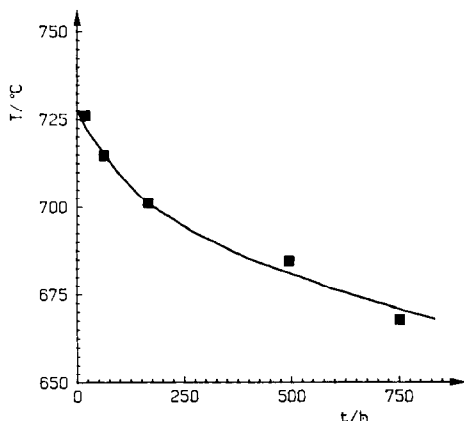
Fig. 2. Peak temperature vs. duration of heat treatment at $480\,^{\circ}$C of $0.9Li_2O \cdot 0.1BaO \cdot 2SiO_2$ bulk samples.

As in ref. 3 at peak temperature T_p, the crystallization degree reaches the same specific value not dependent on the heating rate; the following relation between heating rate and peak temperature is easily obtained:

$$\ln \beta = -\frac{m}{n} \frac{E_c}{RT_p} + \text{const.} \tag{2}$$

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 larger effect on the ΔT deflection [5]; the following equation is thus obtained:

$$\ln \Delta T = -\frac{mE_c}{RT} + \text{const.} \tag{3}$$

If a series of bulk samples of the glass studied are heat treated at $480\,^{\circ}$C, i.e. in the glass transformation range, the devitrification peak shifts towards lower temperatures, as shown in Fig. 2. The behaviour is due to nucleation that occurs during the heat treatment that, improving glass devitrification, causes the temperature to lower. In order to evaluate the devitrification kinetic parameters, a series of DTA runs were performed on fine powder and coarse powder of a series of "as quenched" samples and on bulk samples long nucleated (750 h a $480\,^{\circ}$C). As can be seen in Fig. 3, according to equation (2), straight lines were obtained by plotting (ln β vs. $1/T_p$. The slopes of the lines gave the value $mE_c/n = 70 \pm 4$ kcal mol^{-1}. When a glass is long nucleated a value of $m/n = 1$ must be expected. The same m/n value has to be expected when the glass is crushed to fine powder; in this case, indeed, devitrification starts from surface nuclei which form in an amount proportional to the specific surface. The data, therefore, suggest for the crystal growth activation energy a value $E_c = 70 \pm 4$ kcal mol^{-1} and
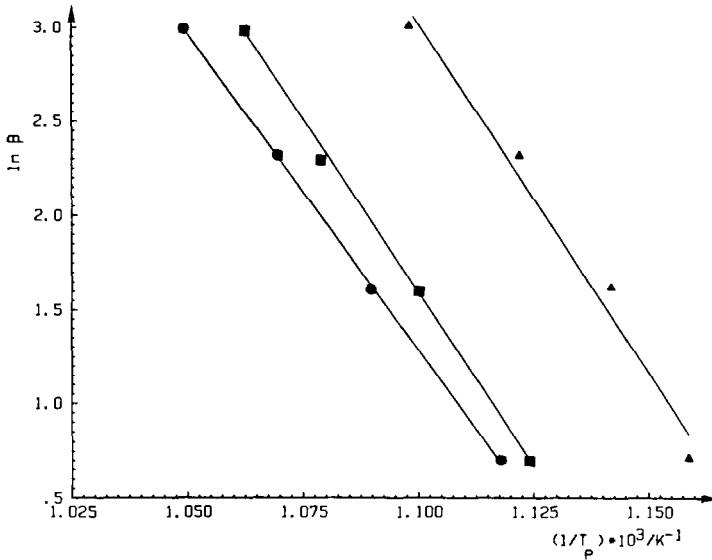
Fig. 3. Plot of ln β vs. $1/T_p$. ▲, fine powders; ●, coarse powders; ■, bulk samples after 750 h at 480 °C.

$m/n = 1$ for coarse powder too. The E_c value found is very close to that found under non-isothermal [6] and isothermal [7] conditions for the $Li_2O \cdot 2SiO_2$ glass devitrification. According to eqn. (3) straight lines were obtained
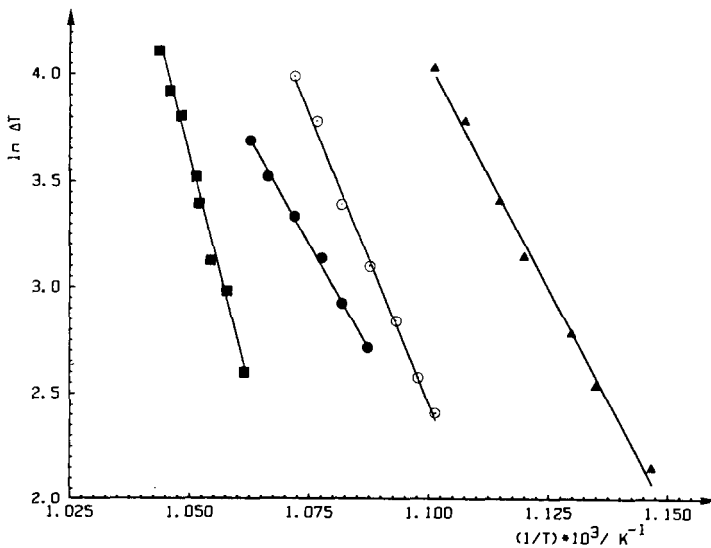

Fig. 4. Plot of ln ΔT vs. $1/T$ (the values of ΔT and T are derived from DTA curves recorded at 5 °C min^{-1}): ▲, fine powders; ●, coarse powders; ○, coarse powders after 70 h at 477 °C; ■, bulk samples after 500 h at 481 °C.

TABLE 2

Sample	mE_c (kcal mol^{-1})
Fine powders	84
Coarse powders	83
Coarse powders 70 h at 477 °C	108
Bulk sample 500 h at 481 °C	172

by plotting $\ln \Delta T$ vs. $1/T$ as shown in Fig. 4. The mE_c values obtained from the slopes of these straight lines by means of eqn. (3) are reported in Table 2. The m values, obtained by comparing these values with the E_c one just determined, change from $m \approx 1$, for "as quenched" fine and coarse powdered samples, to $m = 2.5$ for a long nucleated bulk sample. These changes are consistent with a growth mechanism controlled by the glass–crystal interface reaction $(1 \leqslant m \leqslant 3)$. These results had to be expected, taking into account the closeness of the glass composition to the stoichiometric one of the $Li_2O \cdot 2SiO_2$ crystals. The last data confirm that in fine and coarse "as quenched" samples devitrification starts mainly from surface nuclei. To have crystal growth mainly from bulk nuclei it is necessary to long nucleate bulk samples. The value $m = 1.6$ found for coarse powders nucleated 70 h at 477 °C suggests that in this case surface nuclei and bulk nuclei are competing to convert the glass into crystalline material. In order to get information about the homogeneous nucleation of the glass studied, DTA runs were carried out on a series of bulk samples heat treated at several temperatures in the range 420–500 °C and subsequently crushed to coarse powders. The values of mE for two series of samples heat treated
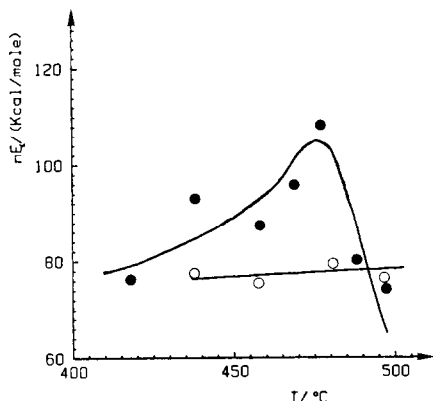

Fig. 5. Plot of nE_c vs. heat treatment temperature. ○, 14 h heat treatment; ●, 70 h heat treatment.

for 16 h or 70 h, evaluated by eqn. (3), are reported in Fig. 5 as a function of the heat treatment temperature. The mE_c values are not affected by the 16 h heat treatments and they remain close to that previously evaluated for the "as quenched" sample. This behaviour suggests that in glasses heat treated for 16 h surface crystallization is still dominant. However, the increase in mE_c values after the 70 h heat treatments can be attributed to an appreciable increase of bulk nuclei so that bulk and surface crystallization become comparable. The maximum at 480°C suggests that this should be the maximum nucleation rate temperature. It is very close to that [8] reported in the literature for this composition. Taking into account that [6] in the case of $Li_2O \cdot 2SiO_2$ glass, 14 h at 480°C are sufficient to have, in coarse powders, devitrification from bulk nuclei $m = 3$, it can be inferred that the substitution of a little amount of Li_2O with BaO hardly lowers the aptitude to devitrify from bulk nuclei. One must expect, therefore, a bulk nucleation rate lower than for the $Li_2O \cdot 2SiO_2$ glass, as was indeed found by traditional methods [8].

CONCLUSIONS

The experimental results suggest that in the $0.9Li_2O \cdot 0.1BaO \cdot 2SiO_2$ glass crystal growth occurs by a mechanism controlled by the glass–crystal interface reaction and with an activation energy close to that of the $Li_2O \cdot 2SiO_2$ glass. The substitution of BaO for Li_2O has a marked effect on the homogeneous nucleation rate. The maximum nucleation rate temperature was found to be $T = 480°C$. The results agree well with literature data on this system.

REFERENCES

1 K. Matusita and S. Sakka, Bull. Int. Chem. Res., Kyoto Univ., 59 (1981) 159.
2 D.R. Macfarlane, M. Matecki and M. Poulain, J. Non-Cryst. Solids, 64 (1984) 351.
3 T. Ozawa, Polymer, 12 (1971) 150.
4 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
5 F.O. Piloyan, I.V. Ryabchicov and O.S. Novikova, Nature (London), 212 (1966) 1229.
6 A. Marotta, A. Buri and F. Branda, Thermochim. Acta, 40 (1980) 397.
7 P. Hautojarvi, A. Vehanon, V. Komppa and E. Pajanni, J. Non-Cryst. Solids, 29 (1978) 365.
8 P.F. James, Nucleation and Crystallization in Glasses, The American Ceramic Society, Columbus, OH, 1982, p. 1.