The Compositional Dependence of Crystal Nucleation in Li_2O-SiO_2 Glasses

Edgar D. ZANOTTO[*][†] and Peter F. JAMES

Department of Ceramics, Glasses and Polymers, University of Sheffield, UK

[†] Present address: Universidade Federal de São Carlos - 13560 S.P., Brasil

Amorphous phase separation can have a significant influence on the kinetics of crystal nucleation in glasses [1,2]. An increase in crystal nucleation rates with time of isothermal heat treatment has been observed in BaO-SiO_2 glasses undergoing phase separation [3,4]. This effect was due to a shift in *composition* of the amorphous baria-rich matrix towards the composition of the precipitating barium disilicate crystal phase. In contrast, it was suggested [5,6] that enhanced crystal nucleation in phase separated Li_2O-SiO_2 glasses was associated with the droplet interfaces. In this paper, new results on the Li_2O-SiO_2 system are presented with the object of clarifying the overall situation.

1. Experimental

Li_2O-SiO_2 glasses with 17.7, 31.0 and 33.2 mole% Li_2O were prepared from Optipur SiO_2 (Merck) and 99.999% Li_2CO_3 (Aldrich). Batches calculated to give 100 g of glass were well mixed and melted in a new Pt-10% Rh crucible at 1550°C (17.7 mole% Li_2O); 1450°C (31.0 mole% Li_2O) and 1350°C (33.2 mole% Li_2O) in electric furnaces. The glasses were homogenized by crushing and remelting five times. Clear samples of the 17.7 mole% Li_2O glass, about 1 mm thick, were obtained by splat cooling. Melts of the other compositions were cast and pressed between steel plates. Clear specimens 1-2 mm thick were obtained. Volatilization of lithium during melting was low (Table 1). Also impurity levels in the glasses were low. Using atomic absorption, the Na_2O contents were below 0.02 wt%, and the Fe_2O_3 and Al_2O_3 contents were below the detection limits (0.0004 and 0.05 wt% respectively).

Table 1 Chemical Analysis of Li_2O-SiO_2 Glasses (FES = Flame Emission Spectroscopy; FP = Flame Photometry; EPMA = Electron Probe Microanalysis)

	mole% Li_2O	wt% Li_2O			
Glass (Code)	Nominal	Nominal	FES	FP	EPMA
17.7	18.0	9.84	9.67	9.69	9.67
31.0	31.0	18.28	18.30	18.49	18.00
33.2B	33.3	19.91	-	-	19.82

The 'water' content determined by infra-red spectroscopy, was about 0.02 wt% in the three glasses. The crystal nucleation kinetics were studied by heat treating

glass specimens of about 3 x 3 x 1 mm^3 at 481°C for times up to 10 hours, quenching them to ambient temperature and developing the nuclei at 570°C or 600°C for 30 to 70 minutes. Some specimens were previously phase-separated at 497°C for 5 hours before the standard double stage heat treatment. The number of particles per unit volume, N_V, was determined from reflection optical micrographs of polished and etched sections through the samples as described elsewhere [7]. The shape of the crystal 'spherulites' in the glasses became increasingly ellipsoidal as the $Li_2O.2SiO_2$ composition was approached. They were nearly spherical in glass 17.7. The statistical error in N_V was ±10-20% (95% confidence limits). There was also a systematic underestimation of N_V values of approximately 5% due to the limited resolution of the optical microscope [4].

2. Results

The silica-rich side of the phase diagram and the miscibility gap of the $Li_2O.$ SiO_2 system are shown in Fig.1. The shaded area represents the range of solid solution formation [8]. The compositions and heat treatment temperatures used here are indicated. It can be seen that glass 17.7 is in the spinodal region; glass 31.0 is in the 'nucleation and growth' region and glass 33.2B is outside the gap, being very close in composition to the stoichiometric $Li_2O.2SiO_2$ crystal phase. Transmission electron microscopy (TEM) of ion beam thinned specimens showed that the shapes of the crystals were different in the three glasses, being nearly spherical in glass 17.7. Also there was a fine scale interconnected phase separation in glass 17.7, while isolated SiO_2-rich droplets were observed in glass 31.0. Glass 33.2B was free of phase separation and the crystalline particles had the well-known rosette morphology [12].

The transformation range of these glasses is around 450°C and a steady-state nucleation rate is rapidly established for temperatures higher than about 475°C [1,7]. Also, the time required for the amorphous separation to reach the final stage (equilibrium composition of the matrix) is about 15 hours at 475°C for a glass with nominally 31.0 mole% Li_2O [6]. This time is expected to be much shorter for glass 17.7, which is in the spinodal region. Therefore, 481°C was chosen for the present study of crystal nucleation. At this temperature phase separation should reach its final stage in a reasonable period and the induction period for crystal nucleation should be negligible.

2.1 Crystal Nucleation Kinetics

In Fig.2 the most striking observation is that the crystal nucleation rates in glasses 17.7 and 31.0 (undergoing phase separation) *increase* with time, and after about 4 hours are *equal* and 3.6 times *higher* than the constant rate in glass 33.2B. Most points in Fig.2 were obtained using a development temperature of 570°C. To test the possible influence of the development treatment some speci-
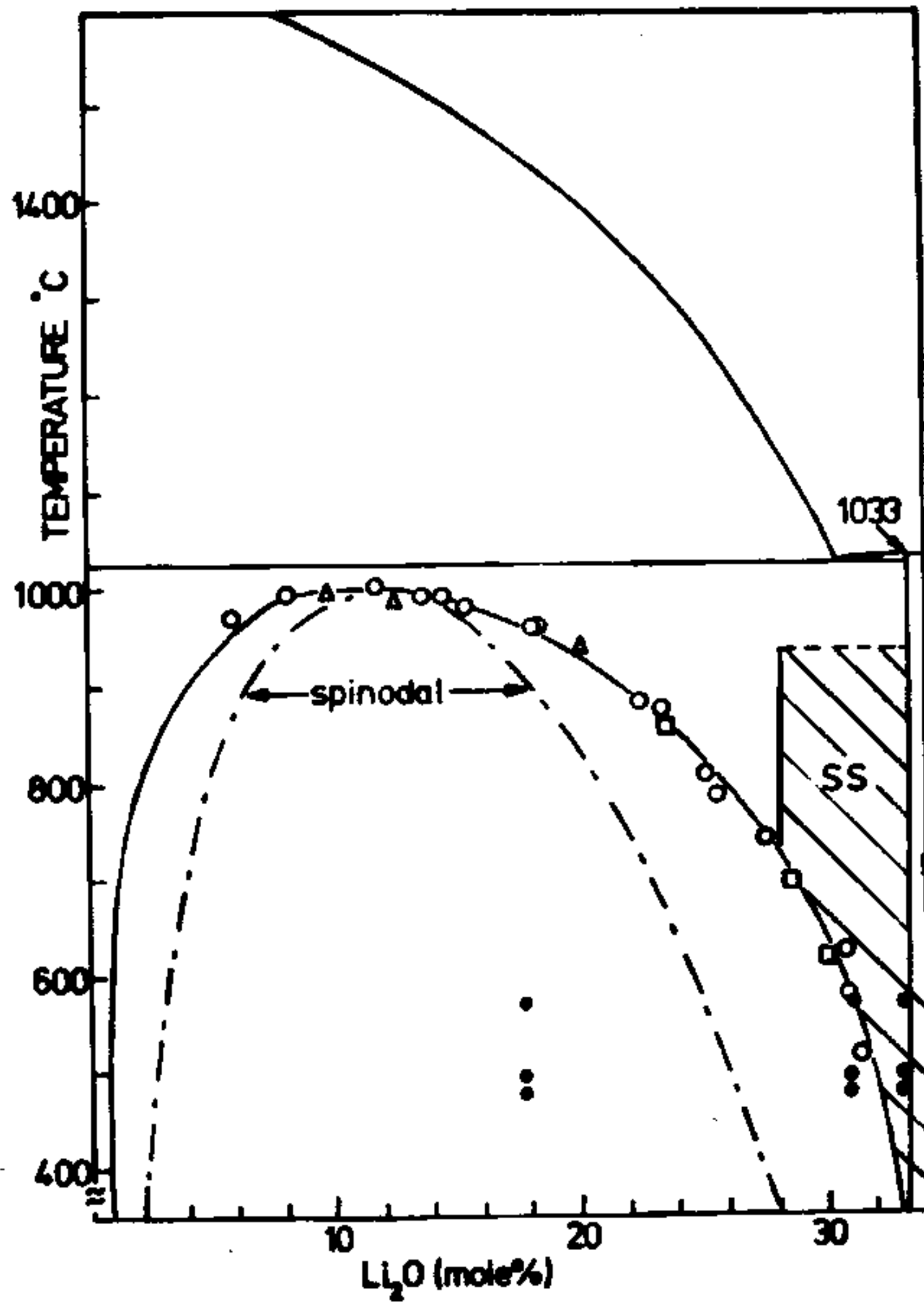
Fig.1: Li$_2$O-SiO$_2$ system: calculated [9] binodal (solid çurve) and spinodal (dashed curve); experimental data O [9], □ [10] and Δ [11]; heat treatments used here ●

Fig.2: Number of crystals per unit volume (N$_V$ x 10^{-4} mm^{-3}) versus time for glasses nucleated at 481°C; 31.0 (O ●), 17.7 (□ ■), 33.2B (Δ). Development temperatures: 570°C (O □), 600°C (● ■).
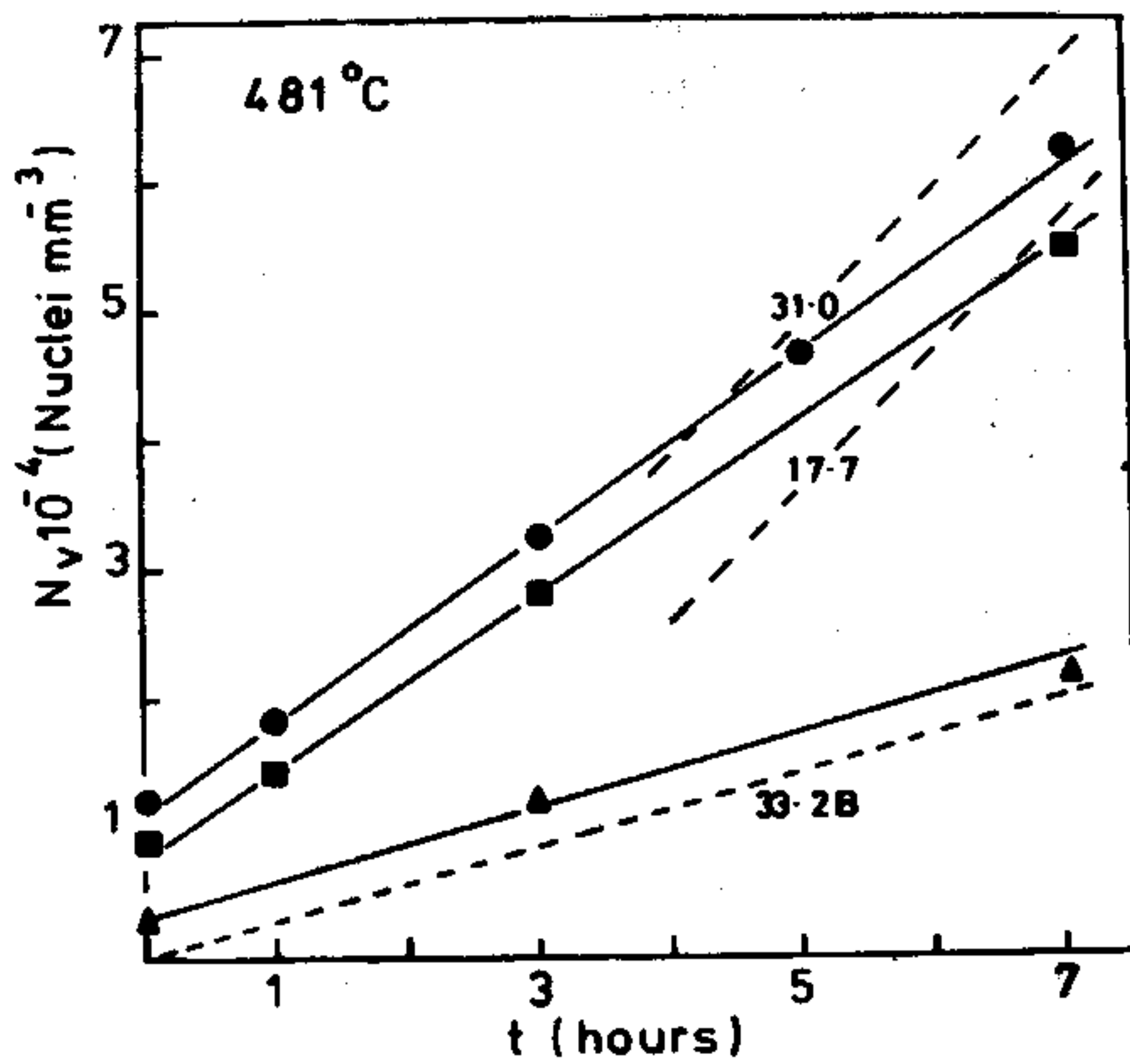

Fig.3: N$_V$ versus time for glasses nucleated at 481°C; 31.0 (●), 17.7 (■), 33.2B (▲); -----as quenched glasses, ——— phase separated for 5 h at 497°C.
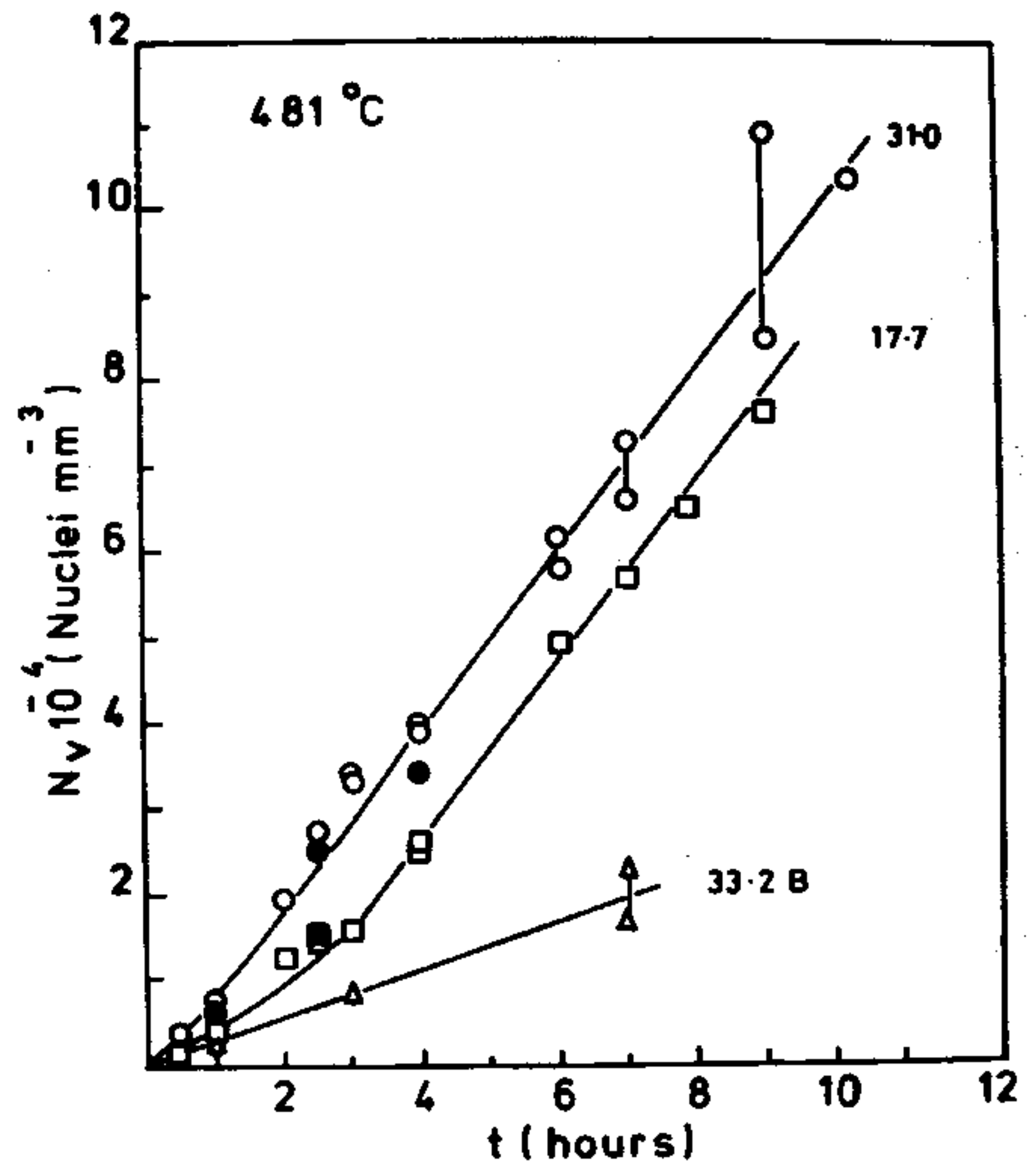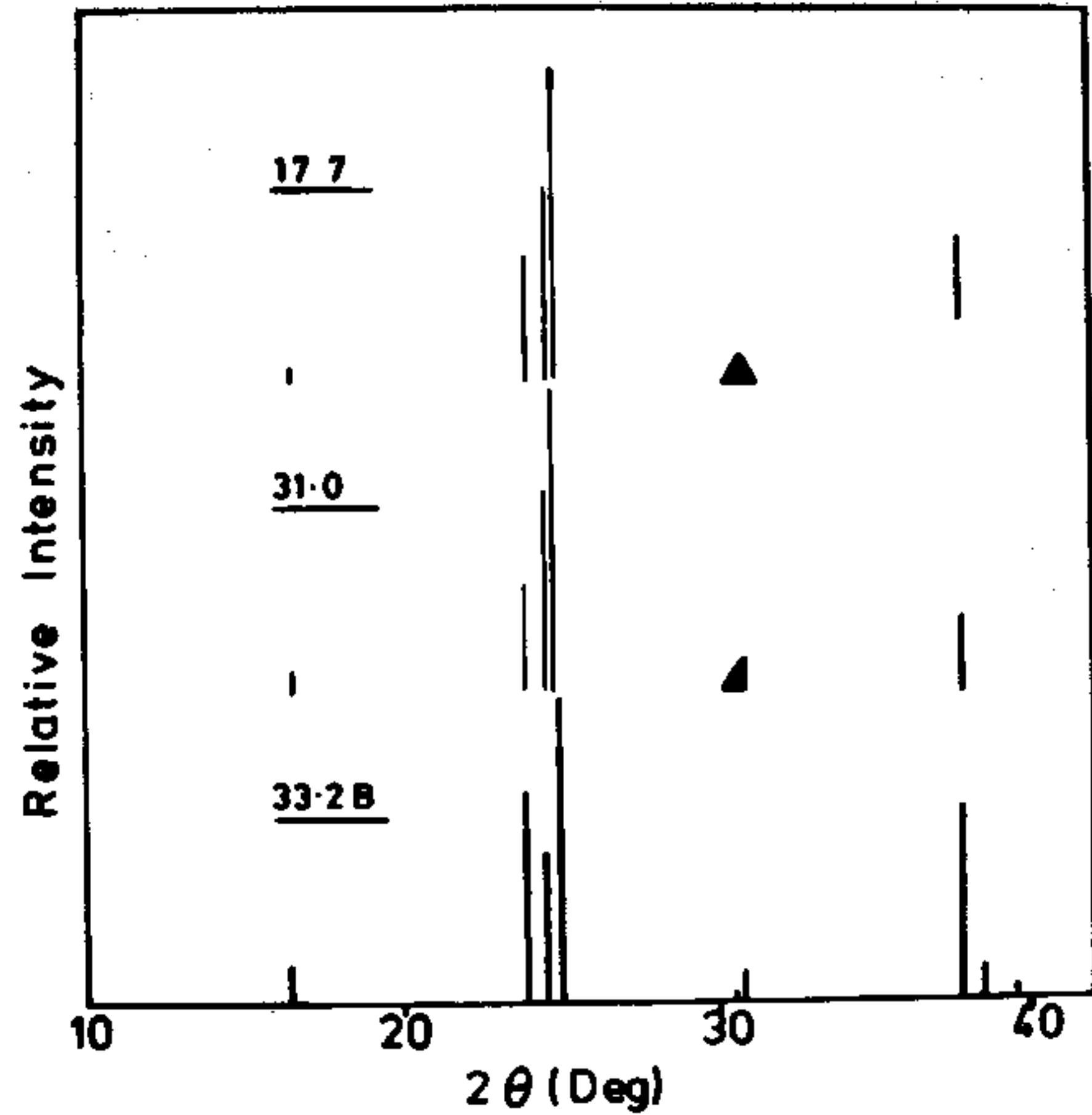

Fig.4: Schematic X-ray diffraction patterns (see text).

mens were heat treated at 600°C. The small differences in N_V observed for the two development temperatures were within the statistical error.

To study the effect of the advanced coarsening stage of amorphous phase-separation on crystal nucleation, another experiment was devised. Specimens of glasses 17.7 and 31.0 were first heated at 497°C for 5 hours to produce phase separation. Samples of glass 33.2B were also given the same treatment for control purposes. Then all samples were nucleated at 481°C and 'developed' at 570°C. Fig. 3 shows that the crystal nucleation rates in glasses 17.7 and 31.0 (previously phase separated at 497°C) are *equal* and constant at all times. They are about 2.4 times higher than the nucleation rates in glass 33.2B. It is clear that the treatment at 497°C eliminates the curvature observed for the as-quenched glasses undergoing phase separation (Fig.2) and *decreases* the nucleation rates (compare with dashed lines in Fig.3). For the non phase-separating glass 33.2B, there is no change in the nucleation rate. The intercepts on the N_V axis are due to nucleation during the initial treatment at 497°C.

2.2 X-ray Diffraction Study

Pieces of glass about $20 \times 10 \times 2 \text{ mm}^3$ in size were nucleated at 464°C for 18 hours and developed at 570°C for 1.5 hours. In this way a large number of randomly oriented crystals were formed in the bulk of the specimens. The crystallized surface layers were removed to minimise preferential orientation of crystals, which usually occurs with powdered specimens. The interplanar spacings (d) and relative intensities of the reflections (I) are given in Table 2.

Table 2   X-ray Diffraction Results for $Li_2O\text{-}SiO_2$ Glasses (Copper $K\alpha$ radiation)

2θ (deg)	d (nm)	I	2θ (deg)	d (nm)	I	2θ deg	d (nm)	I
Glass 17.7			Glass 31.0			Glass 33.2B		
16.55	0.5351	4	16.45	0.5384	7	16.50	0.5368	12
24.00	0.3704	39	23.90	0.3720	34	23.93	0.3715	67
24.60	0.3615	61	24.48	0.3633	60	24.48	0.3633	48
24.95	0.3566	100	24.89	0.3574	100	24.98	0.3561	100
30.80	0.2900	6	30.45	0.2933	4	30.50	0.2928	3
37.60	0.2390	26	30.75	0.2905	7	30.83	0.2898	9
			37.60	0.2390	24	37.73	0.2382	62
						38.35	0.2345	11
						39.45	0.2282	5

The phases crystallizing in glasses 17.7 and 31.0 give very similar X-ray patterns (Fig.4) and can be identified as a lithium disilicate solid solution [8]. The pattern for glass 33.2B is identified with the low temperature form of the $Li_2O.2SiO_2$ crystal phase. The metastable lithium disilicate solid solution, an important first crystallization product of $Li_2O\text{-}SiO_2$ glasses, ranges in composition from 28 to 38 mol% Li_2O. Below 700°C it persists indefinitely [8].

3.   Discussion

The effects of amorphous phase separation on crystal nucleation can be divided

into two main categories associated either with (a) *compositional* variations of the separating liquid phases or with (b) the *interfaces* between the glassy phases [1-6]. It will be shown that the present results can be explained mainly in terms of the first category. However, a small additional effect on the crystal nucleation rates could be associated with the interfaces.

The nucleation curves of Fig.2 show that for the phase separating glasses there are small inflexions (points higher than the 'smooth' curves) between 1 and 3 hours for glass 17.7, and between 2 and 4 hours for glass 31.0. Although these points are within the 95% confidence limits for N_V, they were confirmed by repeated measurements. Similar inflexions were observed elsewhere [5,6] and attributed to enhanced nucleation of crystals in the diffusion zones around the droplets since they occurred in the *early* stages of phase separation. This explanation might account for the very small inflexions observed here.

For longer times the crystal nucleation rates in glasses 17.7 and 31.0 are *equal* but *higher* than the constant nucleation rate of the nearly stoichiometric glass 33.2B. A similar argument used to explain the nucleation in the $BaO-SiO_2$ glasses undergoing phase separation can be applied [1-4], i.e., the only parameter which is the *same* for glasses 17.7 and 31.0, after nucleation at 481°C, is the composition of the amorphous (lithia-rich) matrix phase. The morphologies (and probably kinetics) of the phase separation in the two glasses were quite different. Thus isolated silica-rich droplets were observed in glass 31.0, which were probably produced by nucleation and growth, whereas in glass 17.7 an interconnected microstructure, possibly the result of spinodal decomposition, was observed. Therefore, the nearly identical crystal nucleation rates in these glasses for longer times is due to the same *composition* of the lithia-rich matrix in both glasses after the completion of phase separation. Furthermore, the increase of the nucleation rates with time during the first few hours for glasses 17.7 and 31.0 (Fig.2) may be explained by the gradual shift in *composition* of the amorphous matrix phase towards its equilibrium at 481°C.

Fig.3 shows that the crystal nucleation rates in the fully phase-separated glasses 17.7 and 31.0 (17.7PS and 31.0PS) are equal and constant from the beginning, being lower than the nucleation rates in the as-quenched glasses (dashed lines). Similar behaviour was found in $BaO-SiO_2$ glasses [4]. It is probably due to the slightly lower Li_2O content in the matrix for the glasses first phase separated at 497°C compared with the Li_2O matrix content for glasses only heated at 481°C. In principle, further phase separation (nucleation of new droplets and/or growth of the existing ones) could occur at 481°C for glasses 17.7PS and 31.0PS. However, since the matrix compositions after heat treatment at 497°C would be only *just inside* the miscibility boundary corresponding to 481°C, the

798

kinetics of secondary phase-separation would probably be very slow. Therefore, it is likely that the composition of the matrix phase did not reach the equilibrium value at 481°C even after 7 hours (Fig.3), whereas equilibrium was attained much more quickly in the as-quenched glasses at 481°C (Fig.2).

The fact that the almost stoichiometric glass 33.2B has a *lower* crystal nucleation rate than the phase-separated glasses, differs strikingly from the observations in the BaO-SiO$_2$ glasses [1-4] and cannot be explained by the same (compositional) arguments if the crystal phase is the stoichiometric Li$_2$O.2SiO$_2$ in all glasses. However, it was shown previously that the crystalline phases in glasses 17.7 and 31.0 were *solid solutions* which gave nearly identical diffraction patterns. In glass 33.2B, the low Li$_2$O.2SiO$_2$ stoichiometric crystal phase was clearly identified. Therefore, the crystalline phase in the stoichiometric glass *differs* in composition from that in the phase-separated glasses. Thus the thermodynamic driving force (and interfacial energy) could be more favourable for crystal nucleation in the phase-separated glasses than in the nearly stoichiometric glass, giving higher nucleation rates for the former glasses. The effects of phase separation are, however, clearly shown because the nucleation rates in glasses 17.7 and 31.0, which have widely different overall compositions are *identical* for two heat treatment conditions. In both cases the amorphous matrix has the same Li$_2$O content.

4. References

1   James, P.F., in 'Nucleation and Crystallization in Glasses', Advances in Ceramics, 4 (1982) 1-48, Amer. Ceram. Soc., Inc., Columbus, Ohio.

2   Craievich, A.F., Zanotto, E.D. and James, P.F., Bull. Soc. Franc. Miner. et Crist., (1983) to be published.

3   Ramsden, A.H., 'Crystal Nucleation and Growth in BaO-SiO$_2$ Glasses', Ph.D. Thesis (1977), University of Sheffield, UK.

4   Zanotto, E.D., 'The Effect of Amorphous Phase-Separation on Crystal Nucleation in BaO-SiO$_2$ and Li$_2$O-SiO$_2$ Glasses', Ph.D. Thesis (1982), University of Sheffield, UK.

5   Tomozawa, M., Physics Chem. Glasses, 13 (1972) 161-166.

6   Zanotto, E.D. and Craievich, A.F., J. Mater. Science, 16 (1981) 973-982.

7   James, P.F., Physics Chem. Glasses, 15 (1974) 95-105.

8   West, A.R. and Glasser, F.P. in 'Advances in Nucleation and Crystallization in Glasses', (1971) 151-165, Amer. Ceram. Soc., Inc., Columbus, Ohio.

9   Haller, W., Blackburn, D.H. and Simmons, J.H., J. Amer. Ceram. Soc., 57 (1974) 120-126.

10   Andreev N.S., Goganov, D.A., Porai-Koshits, E.A. and Sokolov, Y.G., in 'The Structure of Glass', Vol. 3 (1964) 47-52, Consultants Bureau, New York.

11   Moriya, Y., Warrington, D.H. and Douglas, R.W., Physics Chem. Glasses, 8 (1967) 19-25.

12   James, P.F. and Keown, S.R., Philos. Mag., 30 (1974) 789-802.