Influence of water content on the rates of crystal nucleation and growth in lithia-silica and soda-lime-silica glasses

C. J. R. GONZALEZ-OLIVER, P. S. JOHNSON[†], P. F. JAMES
Department of Ceramics, Glasses and Polymers, University of Sheffield, UK

Two sets of glasses were studied with compositions close to $Li_2O \cdot 2SiO_2$ and $Na_2O \cdot 2CaO \cdot 3SiO_2$, and with water contents ranging from 0.019 to 0.136 wt % and 0.007 to 0.040 wt %, respectively. The crystal nucleation and growth rates increased markedly with increase in water content, whereas the viscosities of the glasses decreased. For the lithia glasses, increases in nucleation rates at various temperatures closely corresponded to reductions in viscosity, indicating that the main effect of water was to lower the kinetic barrier to nucleation (ΔG_D), rather than to alter the thermodynamic barrier to nucleation (W^*). For the soda-lime glasses, ΔG_D was also lowered by water content but additional effects due to differences in base compositions were observed. The kinetic barriers to growth were lowered by water content for both sets of glasses, increases in growth rates corresponding closely to reductions in the viscosities. It is suggested that the large effects of water on nucleation and growth may be due to an increase in the oxygen ion diffusion coefficient. In the soda-lime glasses addition of sodium fluoride produced similar effects to the addition of water. Liquidus temperature measurements, and the results of DTA, optical microscopy and electron microscopy are also reported.

1. Introduction

Most glasses contain small quantities of dissolved water. Commercial silicate glasses, for example, usually have a water content of 0.01 to 0.03 wt %. Such small quantities of water can have a significant effect on properties. An increase in water content generally increases density, refractive index, thermal expansion and electrical conductivity and lowers viscosity [1]. Water also affects the kinetics of phase transformations in glass-forming systems. Thus it enhances the kinetics of liquid—liquid phase separation in sodium silicate glasses [2] and increases crystal growth rates in vitreous silica [3] and lead borate glasses [4]. Recently, glasses in the La_2O_3—SiO_2 system were melted both from normal oxide batches and from batches prepared by gellation. After heat-treatment, the crystal nucleation in the "gel" glasses was higher than in the "normal" glasses. This was attributed to a greater OH content in the "gel" glasses [5]. Apart from these studies of kinetics, however, there has

been little systematic work on the effects of water content on crystal growth rates and, more particularly, crystal nucleation rates in glasses. Such work would be of interest for a number of reasons. First, the mechanisms of nucleation and growth, which have recently received detailed study [6—11], may be influenced by water content. Secondly, water may influence the formation of glass ceramics, materials made by the controlled crystallization of glasses [12]. Thirdly, glasses prepared by certain non-conventional techniques which are attracting considerable interest, for example the "gel" process referred to above [5, 13, 14], may have different (often higher) water contents than glasses prepared conventionally by fusion of oxides. This may affect the properties and crystallization behaviour of these glasses.

In the present paper, crystal nucleation and growth rates have been measured for two base compositions in which the water contents were deliberately modified, namely $Li_2O \cdot 2SiO_2$ (LS_2)

[†]Present address: British Glass Industry Research Association, Northumberland Road, Sheffield, UK.

TABLE I (a) Lithia—silica glasses (all nominally $Li_2O \cdot 2SiO_2$)

Glass	Melting conditions	Li$_2$O content	H$_2$O content	
		(mol%)	(wt%)	(mol%)
L1	normal (stirred)	33.1	0.020	0.056
L2	normal (stirred)	–	0.024	0.066
L3	bubbled with dried air	–	0.019	0.053
L4	bubbled with wet air	–	0.034	0.096
L5	bubbled with steam	33.0	0.136	0.377

TABLE I (b) Soda-lime—silica glasses (N1 and N2 nominally $Na_2O \cdot 2CaO \cdot 3SiO_2$)

Glass	Melting conditions	Composition (mol%)			H$_2$O content	
		Na$_2$O	CaO	SiO$_2$	(wt%)	(mol%)
N1	normal (stirred)	16.3	33.1	50.7	0.0070	0.023
N2	bubbled with steam	14.7	31.7	53.6	0.0404	0.133
N3	normal (stirred)	14.3	31.6	54.1	0.0070	0.023

and $Na_2O \cdot 2CaO \cdot 3SiO_2$ (NC_2S_3). These compositions were chosen because they both exhibit internal crystal nucleation and the rates of nucleation and growth are not too high to be conveniently measured. Moreover, the precipitating crystal phase in each case has the same composition as the parent glass, thus aiding interpretation of the results. Although these compositions are 'simple' the results should be helpful in interpreting the effects of water on more complex glasses including commercially important compositions. Some commercial glass ceramics, in fact, contain lithium disilicate as a major crystal phase [12]. The $Li_2O \cdot 2SiO_2$ composition without deliberate additions of water has already been extensively studied [6—10]. Recently, Rowlands [8] has carried out a comprehensive study of the nucleation kinetics of both lithium and barium disilicates in the $Li_2O—BaO—SiO_2$ system. Also James et al. [15] showed that neither minute quantities of platinum introduced during melting nor minor impurities in the glass batch significantly affected nucleation in lithium disilicate glass, providing support for the view that the nucleation was predominantly homogeneous rather than heterogeneous. The crystallization kinetics of the $Na_2O \cdot 2CaO \cdot 3SiO_2$ crystal phase have been previously studied in glasses containing 55 and 60 mol% SiO_2 [16].

2. Experimental methods and results
2.1. Preparation of glasses
The glasses were melted (Table I) using analytical reagent grade carbonates of lithium, sodium and calcium and Belgian sand (containing approximately 0.009 wt% total iron and 0.05 wt% alumina

impurities). To further reduce impurity levels, the sand was washed in nitric acid for 4 h at 80° C with stirring, followed by washing in distilled water and thorough drying at 110° C. After this treatment, the alumina content was less than 0.01 wt% and the total iron approximately 0.001 wt%. This washed sand was used for all the glasses except L1 which had been melted for a previous study [7]. Hence there may be very small differences in the impurity levels of L1 and the other glasses. However, there was no evidence from the results to be described and from previous work [15] that these small differences in impurities significantly affected the nucleation and growth behaviour. All the glasses were melted in platinum/ platinum 8% rhodium crucibles using an electric furnace. For the lithia glasses the melting time was 6 h at 1350° C (1400° C for L1) and for the soda-lime glasses 5 h at 1400° C. Melts L1, L2, N1 and N3 were prepared in the normal way without deliberate addition of water, and were stirred for a total time of 2 h using a platinum blade. The largest quantities of water were introduced into melts L5 and N2 by bubbling with steam for 2 to 3 h. The steam was generated by heating distilled water in a safety flask placed in an electric heater. The flask was joined by a plastic tube to a sillimanite tube with a platinum tube cemented to its end. The platinum tube was inserted into the melt. A flow rate of about 1 litre H_2O per hour was used. For comparison purposes one glass (L3) was bubbled with dried air (compressed air passed through a drying column) and another (L4) with wet air (compressed air passed through a conical flask containing water at 80° C). Each glass was cast as 10 mm diameter rod on a grooved steel

block. Glass samples were also prepared as thin discs by pressing between steel plates. 300 to 500 g of each glass was obtained. All the glasses were homogeneous and bubble free.

2.2. Chemical analysis

The results of chemical analysis are given in Table I. Flame photometry was used for lithium analysis (L1, L5). For sodium either flame photometry or the triple uranyl acetate method was used. Calcium was determined by EDTA titration. It was feared that some volatilization of the oxides of lithium, sodium or calcium might occur when bubbling with steam. Hence for glasses L3, L4 and L5 a small extra amount of Li_2CO_3 was added to the batch to correct for this effect. After preparation, L5 was found to be very close in composition to L1, allowing direct comparisons to be made. No correction was attempted for the soda-lime glasses. There was a difference in composition between N1 and N2 (both the same batch composition) probably due to volatilization effects (for N2 the largest loss was in Na_2O content although a significant loss in CaO also occurred). As a result, another glass was melted under ordinary conditions (no steam bubbling) with nominally the same composition as N2. Although the actual compositions of N2 and N3 were not exactly the same (Table I), they were sufficiently close for a useful comparison to be made.

2.3. Water content determination

Thin samples of each glass were ground parallel, polished with cerirouge (paraffin lubricant), washed in acetone and examined in a Grubb Parsons double-beam infra-red spectrometer. Absorption bands due to water were detected in the ranges 2.75 to 2.95 μm, 3.35 to 3.85 μm and around 4.25 μm. The water content associated with each band was determined from the measured peak heights using the Beer—Lambert law,

$$\log_{10}\left(\frac{I_0}{I}\right) = \epsilon c d$$

where I_0 and I are the incident and transmitted light intensities, c the water concentration ($mol\,m^{-3}$), d the sample thickness (m) and ϵ the extinction coefficient for the appropriate wavelength range. The total water content was found by adding the contributions from the three wavelength bands. The spectral curve for each glass was corrected for the approximately constant background absorption including that due to scattering in the sample and reflection from the sample surfaces. The resulting corrected curve was analysed in a digital curve resolver to obtain the three main peaks whose sum matched the experimental curve. A representative absorption curve is shown in Fig. 1. The heights of the resolved peaks were used in the calculation. The water contents are given in Table I. The extinction coefficients employed in the calculations were values given by Scholze [17] for glass compositions similar to those in the present work, since values for the exact compositions used were not available. Although this introduces some uncertainty in the absolute values of water contents in Table I, the results are sufficiently accurate for comparison purposes. The water contents of the lithia glasses were significantly (about 3 times) greater than the similarly prepared soda-lime glasses, but it is interesting to note that the ratio of water contents for the melts bubbled with steam to those prepared under "dry" conditions is approximately the same (about 6) for both sets of glasses. The melt bubbled with dried
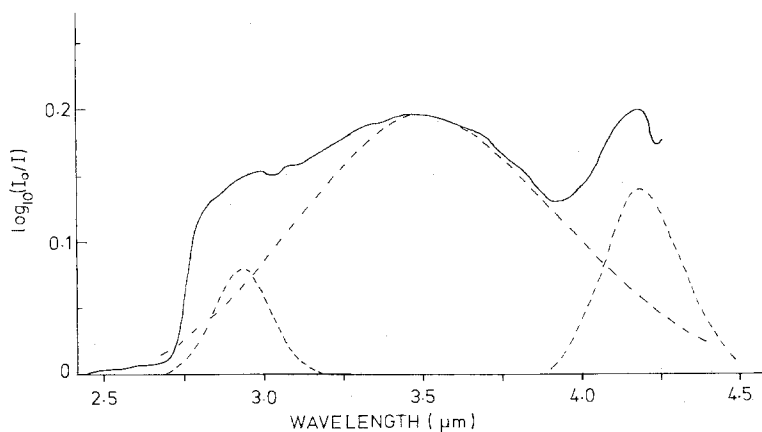

Figure 1 Corrected absorption curve for glass N2. Plot of $\log_{10}$ (I_0/I) versus wavelength, where I_0 and I are the incident and transmitted intensities. The three main absorption peaks due to water content are shown by the dotted curves.

air (L3) had only slightly less water than the "ordinary" melts L1 and L2.

2.4. Nucleation rates

Samples of the glasses 3 mm thick were given a crystal nucleation treatment in a horizontal tube furnace controlled accurately to within $\frac{1}{4}$° C of the heat-treatment temperature. The samples were subsequently heat-treated at a higher "growth" temperature for a few minutes to grow the nucleated crystals to observable dimensions for the optical microscope. At this temperature more rapid growth occurred but negligible nucleation. The method is fully discussed by James [7]. For the lithia glasses, nucleation temperatures from 440 to 516° C were used for a constant time of 4 h. The growth temperature was 560° C for L1 and 600° C for glasses L2 to L5. For the soda-lime glasses nucleation temperatures from 540 to 695° C were used for a constant time of either 40 or 80 min. The growth temperature was 725 to 740° C. The constant nucleation times were chosen to enable a direct comparison to be made between the different glasses in each group. After heat-treatment, polished and etched sections of the samples were prepared for reflected light microscopy and the number of crystal spherulites per unit volume N_v were determined by standard stereological methods, which are described in detail elsewhere [7]. Typical optical micrographs are shown in Figs. 2 and 3. In the lithia glasses the lithium disilicate spherulites had a well-defined prolate ellipsoid shape [18, 19] and this shape was not noticeably affected by higher water content. In the soda-lime glasses the NC_2S_3 crystal particles were spherical in shape, thus simplifying the stereological analysis. Plots of the nucleation densities divided by the time of heat-treatment (N_v/t) as a function of nucleation temperature are given in Figs. 4 and 5. It is evident that a small increase in water content caused a significant increase in nucleation for both sets of glasses.

It should be mentioned that the N_v/t values are a good measure of the nucleation rates, I, particularly at higher temperatures above the maximum where "steady state" conditions apply and I is constant with time at a given temperature. At lower temperatures below the maximum, however, non-steady state conditions increasingly apply as the temperature falls [7–9] and N_v/t values underestimate the steady state nucleation rates. In the present work comparisons between glasses were thus made mainly above the maximum where
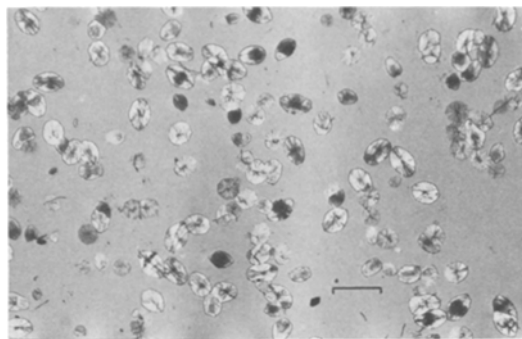

Figure 2 Reflection optical micrograph of polished and etched surface of glass L3 heated at 503° C for 4 h followed by a growth treatment at 600° C for 35 min ($N_v = 4.2 \times 10^6$ cm^{-3}). The bar denotes 100 μm.

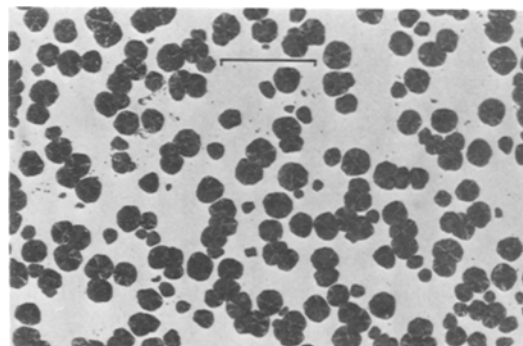*Figure 3* Reflection optical micrograph of polished and etched surface of glass N2 heated at 653° C for 40 min followed by a short growth treatment at 725° C ($N_v = 3.8 \times 10^7$ cm^{-3}). The bar denotes 100 μm.

non-steady state effects could be neglected. In order to compare the different glasses (Figs. 4, 5) it was also necessary for the number of nuclei present in the as-prepared glasses (before heat-treatment) to be negligible compared with the number after heat-treatment. Optical examination of the as-prepared glasses given a single growth treatment showed that this condition held in the present work.

2.5. Crystal growth rates

For the lithia glasses L1 and L5, crystal growth rates were obtained at a series of temperatures by measuring the thickness of the thin surface crystallization layer as a function of time using polished sections prepared normal to the surface and examined by optical microscopy. For the soda-lime glasses N1 and N2, it was more convenient to use the internal crystals, since the thin surface layer was less uniform in thickness than for the lithia glasses. Measurements were made on the maximum sized crystals on the polished optical
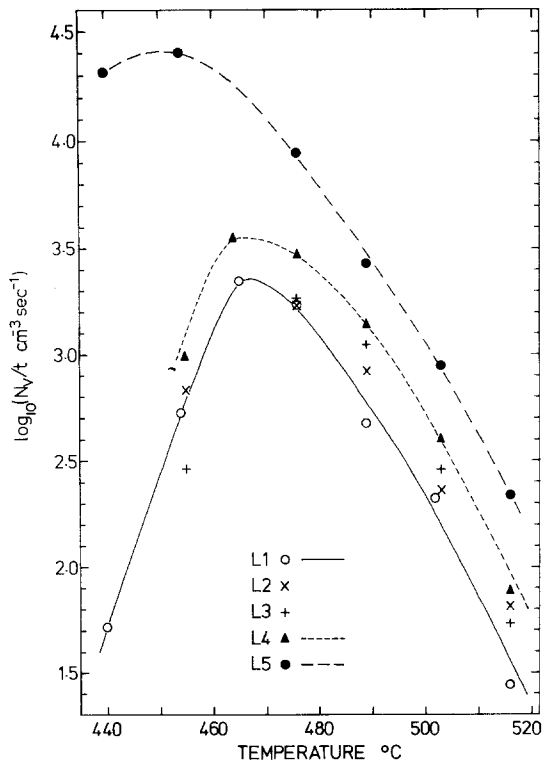
1162

Figure 4 $\text{Log}_{10}\,(N_V/t)$ versus nucleation temperature for lithia—silica glasses, where N_V is the number of crystals per unit volume and t is the time at the nucleation temperature (4 h).
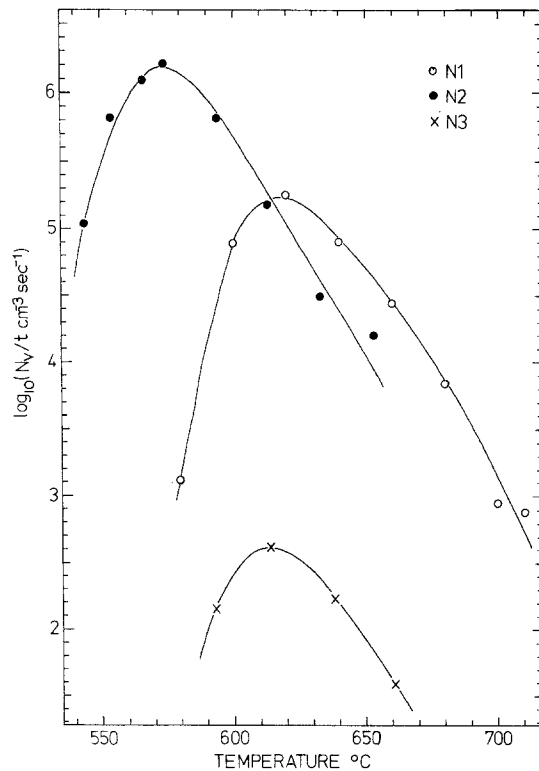

Figure 5 $\text{Log}_{10}\,(N_V/t)$ versus nucleation temperature for soda-lime—silica glasses, where N_V is the number of crystals per unit volume and t is the time at the nucleation temperature (40 min for N1 and N2, 80 min for N3).

section for different heat-treatment times. For all the glasses, crystal growth rates (U) were constant with time at each temperature. For convenience the results are plotted in Fig. 6 in the form $\log_{10} U$ versus $1/T$ (T is the temperature in K). Clearly the growth rates increased markedly with increase in water content.

2.6. Viscosity measurements

Viscosities for compositions L1, L5, N1, N2 and N3 were determined in the range 10^9 to 10^{13} P with a penetration viscometer. The penetration of a steel ball into a sample of each glass was measured as a function of time at constant temperature using a capacitance transducer. The method and
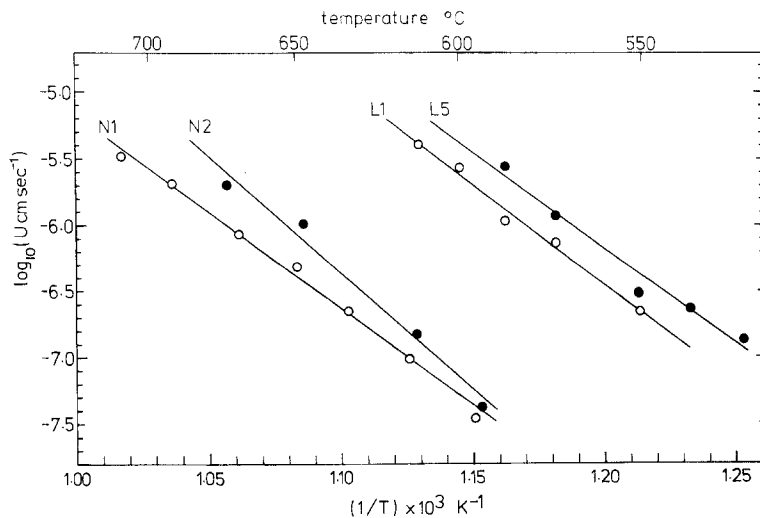

Figure 6 $\text{Log}_{10}\,U$ versus $1/T(\text{K}^{-1})$, where U is the crystal growth rate, for lithia—silica glasses (L1, L5) and soda-lime—silica glasses (N1, N2). The straight lines were obtained by least squares analysis.
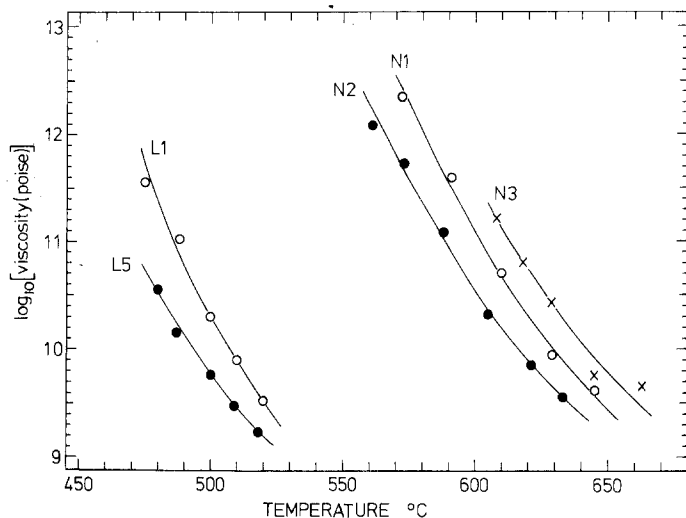
Figure 7 Log$_{10}$ (viscosity) versus temperature (°C) for lithia–silica glasses (L1, L5) and soda-lime–silica glasses (N1, N2, N3).

apparatus is described in detail elsewhere [20, 21]. The apparatus was calibrated with a standard glass (NBS 710), which has a known viscosity–temperature relationship. The upper temperature limit for viscosity measurements for each glass was determined by the occurrence of crystallization. For the range of temperatures used, although some crystal *nucleation* occurred while the viscosity measurements were in progress, the amounts of *overall* crystallization were either negligible or very small. This was shown by optical examination of the glass samples after they had been used for viscosity measurements. Consequently, it is reasonable to assume that the viscosity values obtained are accurate. The results are plotted in Fig. 7. Clearly, increase in water content gave a substantial decrease in viscosity for both sets of glasses.

2.7. X-ray diffraction and electron microscopy

Samples of the crystallized glasses were examined in a Philips X-ray powder diffractometer. This confirmed that the primary crystalline phase was lithium disilicate for the lithia glasses. Also the primary phase for the soda-lime glasses was in each case the low temperature form of NC_2S_3 [22, 23].

Figure 8 Thin film transmission electron micrographs of NC_2S_3 crystals in glasses N1 and N2. Specimens prepared by ion-beam thinning. Micrographs taken at 100 kV. The bars denote 0.5 μm. (a) Glass N1, 580° C for 20 h, (b) glass N2, 572° C for 14 h 20 min, (c) glass N2, 579° C for 10 h.
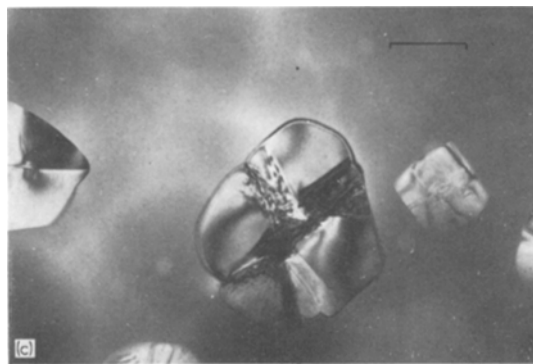
The early stages of crystal growth in the soda-lime glasses were studied by transmission electron microscopy. Glass samples were given a single heat-treatment in the nucleation range. Thin sections were then prepared by ion-beam thinning using an Edwards IBMA2 instrument and examined in a Hitachi HU11A electron microscope operating at 100 kV. Electron microscopy revealed a high density of internally nucleated crystals. Typical micrographs for glass N1 are shown in Fig. 8. The internal crystals were approximately spherical in overall shape and identified as single crystals of the NC_2S_3 phase by electron diffraction. The defects or growth faults clearly visible in the crystals were not identified. These "defects" may not be connected with the growth process itself but may arise during cooling from the heat-treatment temperature, due to a polymorphic change of phase which occurs at 485° C from the high-temperature crystalline form of NC_2S_3 to the low-temperature form [23]. The optical micrograph in Fig. 3 shows the crystal morphology at a much later stage of development in a sample given a *two* stage heat-treatment.

Studies of the early stages of crystal growth in the lithium disilicate glass using electron microscopy are described in other publications [7, 18, 19].

2.8. Other measurements
The liquidus temperatures T_L for a number of the glasses were measured by a quenching method. A small platinum crucible containing the glass specimen was placed inside a moveable platinum-wound tube furnace, with a thermocouple touching the crucible. After 1 h at a given temperature the furnace was quickly lowered and the glass quenched into either water or silicone oil. The glass was examined by optical microscopy for the presence or absence of crystals. By this means T_L could be determined to within 1° C (Table II).

Finely powdered samples of L1, L2, N1 and N2 were examined by differential thermal analysis

TABLE II

Glass	Liquidus temperature, T_L (° C)	Heat of fusion (DTA) (kcal mol^{-1})	T_g (DTA) (° C)
L1	1036	–	451
L5	1034	–	441
N1	1276	20.6	579
N2	1273	21.3	571
N3	1268	–	–

(DTA) in a Standata 6-25 instrument with powdered alumina as a reference and a heating rate of 10° C min^{-1}. The glass transformation temperatures, T_g, were determined from the endothermic dips on the DTA traces (Table II). In addition, estimates were made of the heat of fusion, ΔH_f, of the NC_2S_3 phase from the area under the endothermic melting peak. The DTA apparatus was calibrated using separate runs on NaF and NaCl, which have known heats of fusion. The results (Table II) are in close agreement with an independent value determined by calorimetry [24] of 21.8 kcal mol^{-1}. Further details of the technique, which is similar to that described by Rowlands and James [25], will be given elsewhere.

It is interesting to note that the DTA T_g showed a drop for increase in water content (Table II), as expected from the viscosity results. This was particularly noticeable for L5. The drop in T_g for N2, however, was somewhat less than expected from the viscosity results.

3. Discussion
3.1. Effect of water content on nucleation rates
Before discussing the results in detail, it will be helpful to briefly consider the theory. According to classical theory (see, for example, [26]), the nucleation rate I (number of nuclei formed per unit volume per unit time) may be expressed as a function of temperature, T, by

$$I = A \exp \ [-(W^* + \Delta G_D)/kT] \qquad (1)$$

where A is a constant, approximately independent of temperature, W^* and ΔG_D are the thermodynamic and kinetic free-energy barriers to nucleation, respectively, and k is Boltzmann's constant. For a spherical nucleus, W^* is given by $16\pi\sigma^3/3\Delta G^2$ where σ is the liquid–crystal interfacial free-energy per unit area and ΔG is the bulk free-energy change per mole in the phase transformation.

The kinetic barrier, ΔG_D, or the free energy of activation for transport across the liquid–crystal interface, may be expressed in terms of an effective diffusion coefficient, D, in the liquid given by

$$D = D_0 \exp (-\Delta G_D/kT), \qquad (2)$$

where D_0 is a constant. Moreover, ΔG_D may be regarded as the activation free-energy for diffusion of the slowest diffusing atomic species in the

liquid. In one component systems it is reasonable to assume [6, 7] that D is proportional to $1/\eta$ where η is the viscosity of the liquid. From Equations 1 and 2 we thus obtain

$$I = \frac{A'}{\eta} \exp\left(-W^*/kT\right) \qquad (3)$$

where A' is a constant.

A change in nucleation rate, for example due to the presence of water, may be caused by a change in one or more of the parameters $\Delta G_D, \Delta G$ or σ. Viscosity measurements provide a means of assessing changes in ΔG_D (or D). It is more difficult to know if ΔG has been altered since direct measurements of ΔG are rarely available. In a one component system ΔG is given approximately at temperature T by $-\Delta H_f(T_m - T)/T_m$ where ΔH_f is the heat of fusion (per mol) and T_m the melting point. If a small amount of an additional component (such as water) is added, the expression is modified, assuming ideal mixing, to $-\Delta H_f(T_L - T)/T_L$ where T_L is the liquidus temperature in the now binary system [8]. Thus, changes in liquidus temperature are useful to assess changes in ΔG. Unfortunately, there is no independent way of assessing possible changes in the interfacial energy, σ.

From the nucleation results for the lithia glasses (Fig. 4) it is clear that the number of crystals, N_v, for the standard heat-treatment time at a particular temperature increased progressively with water content, and hence also the nucleation rate, I, increased with water content. The largest effect was observed with the steam-bubbled glass L5 containing most water. The glass bubbled with wet air (L4) also had consistently higher nucleation than the "dry" glasses L1, L2 and L3. The two glasses melted under ordinary conditions (L1 and L2) and the glass bubbled with dried air (L3) were not significantly different in nucleation behaviour. This is not surprising in view of their closely similar water contents (Table I). From the nucleation curves in Fig. 4 the nucleation rates for glass L5 are greater than those for glass L1 by factors of approximately 5.3, 5.4 and 5.8 at temperatures of 510, 490 and 480° C, respectively. Comparing the viscosities of L1 and L5 at these temperatures from the curves in Fig. 7, the viscosity of L5 is less than L1 by corresponding factors of 2.7, 5.6 and 6.3, respectively. Allowing for errors, these changes in nucleation and viscosity are in

close correspondence. This strongly suggests, from Equation 3, that the predominant effect of a small increase in water content in the lithia glasses is to decrease the kinetic barrier, ΔG_D, thereby increasing nucleation and decreasing the viscosity. The effect on the W^* term (including ΔG and σ) appears to be much smaller than on the kinetic term for the water contents involved in the present study. Further support for this conclusion is given by the negligible difference in liquidus temperatures between L1 and L5 (Table II) suggesting a negligible change in ΔG.

A large effect of water content on nucleation was also found for the soda-lime glasses. However, the interpretation is not as straightforward as in the case of the lithia glasses due to larger changes in base composition giving rise to additional changes in $\Delta G_D, \Delta G$ and possibly σ.

Neglecting the effect of water content for the moment, consider an addition of SiO_2 to the NC_2S_3 composition. An addition of SiO_2 is expected to depress nucleation for two reasons. First, the thermodynamic driving force for crystallization, ΔG, at a given temperature will be decreased, and secondly the viscosity (and hence ΔG_D) will be increased. This is supported by the experimental results of Strnad and Douglas [16] and is also shown by the results for glasses N1 and N3 in the present study (Figs. 5 and 7). A detailed experimental study of the effects of variations in composition near NC_2S_3 will be described in a later publication [27].

Glass N2 has 3 mol % more SiO_2 than glass N1, which is closest to the exact NC_2S_3 composition. Thus, ignoring the water contents, N2 is expected to have a lower nucleation rate than N1 at all temperatures. In fact, from Fig. 5, N2 has a higher maximum nucleation rate than N1 by about a factor of 10 (the maximum for N2 is also 40° C lower in temperature than for N1). It is clear that water is responsible for this large increase in nucleation for N2 at lower temperatures. At temperatures above 610° C, however, the curves "cross over" and N2 has somewhat lower nucleation than N1 (Fig. 5). This is due to the combined effect of the greater water content of N2 (tending to decrease ΔG_D and η) and the difference in base compositions (tending to increase ΔG_D and decrease ΔG for N2). Hence at higher temperatures, the higher silica content of N2 overrides the effect of water and gives a net decrease in nucleation. It is interesting to note that the

"cross over" was not observed for the lithia glasses L1 and L5 because the base compositions were the same.

The conclusion that the water has decreased ΔG_D for the soda-lime glasses is supported by the viscosity results (Fig. 7). N2 has a lower viscosity than N1 by a factor varying from 5.6 to 2.3 over the temperature range 560 to 630° C. Clearly, the water content of N2 overrides the increase in SiO_2 content in affecting the viscosity.

Comparison of N2 and N3, which are closer in base compositions, confirms the above conclusions. The nucleation rates in N2 are about two orders of magnitude greater than in N3, and the viscosity of N2 is about an order of magnitude less than N3. The quantitative correspondence between nucleation and viscosity is thus not as close as for the lithia glasses. This may be partly due to the small difference in base compositions between N2 and N3, giving a difference in ΔG for the two glasses. However, there remains the possibility for glass N2 that the water content has caused a reduction not only in ΔG_D but also in W^* (for example, by lowering σ). Further work is needed to clarify this point.

3.2. Effect of water content on crystal growth rates

The crystal growth rate for a one component system may be expressed, according to the normal growth mechanism, in the form [28]

$$U = f\lambda\left(\frac{kT}{h}\right)[1 - \exp(-\Delta G/kT)]$$
$$\exp(-\Delta G'_D/kT), \qquad (4)$$

where λ is the crystal interplanar spacing in the direction of growth ("jump distance" across the interface), f is the fraction of sites on the crystal available for growth and $\Delta G_D{}'$ is the kinetic barrier for crystal growth. At high undercoolings below the melting point, the term involving ΔG can be taken as unity and

$$U = f\lambda\left(\frac{kT}{h}\right)\exp(-\Delta G'_D/kT). \qquad (5)$$

Using the same method as above for nucleation and relating the kinetic term to a diffusion coefficient and then to the viscosity, η, we obtain from Equation 5

$$U = \frac{B}{\eta}, \qquad (6)$$

where B is effectively constant.

This procedure implies that the kinetic barriers for nucleation (ΔG_D) and growth ($\Delta G'_D$) are equal, which is reasonable for a one component system. An expression of the form of Equation 6 is expected, regardless of the exact growth mechanism, provided high undercoolings are involved.

Let us now examine the results. For the lithia glasses the growth rates for L5 are greater than for L1 by a factor of nearly 2 over the range 525 to 587° C (Fig. 6). This increase corresponds very closely with the observed reduction in viscosity of L5 relative to L1 at 520° C (a factor of about 2.1), this being the highest temperature at which viscosities could be measured. Similar behaviour was observed for the soda-lime glasses. The crystal growth rates for N2 are greater than for N1 by a factor of about 2 (with some experimental scatter) in the range 594 to 673° C (Fig. 6). Over a similar range of temperatures (594 to 630° C) the viscosity of N2 is less than N1 by a factor varying between 3.9 and 2.2. This is in agreement with the increase in growth rates, within experimental error.

Hence for both sets of glasses the changes in growth rates due to water content follow changes in the viscosities in accordance with Equation 6. This is to be expected since, for all the present growth measurements, high undercoolings were involved so that the term involving ΔG in Equation 4 could be neglected. In fact, although the ΔG values for N1 and N2 were different, a direct comparison of their growth rates was possible as above. Comparison of the nucleation rates for N1 and N2 was more complex since they were also dependent on ΔG.

It is interesting to note that the growth rates for N2 were greater than N1 in spite of the higher SiO_2 content of the former, again illustrating the very marked effect of the water content.

A final point concerning the plots in Fig. 6 should be made. The free-energy kinetic barrier $\Delta G'_D$ (or ΔG_D) can be expressed as $\Delta H'_D - T\Delta S'_D$ where $\Delta H'_D$ and $\Delta S'_D$ are the enthalpy and entropy of activation, respectively. Thus the slope of the log U versus $1/T$ plot gives $\Delta H'_D/k$ according to Equation 5 and *not* $\Delta G'_D/k$. Changes in $\Delta G'_D$ can only be assessed by examining changes in the growth rate (U) itself (Equation 5). From Fig. 6 we see that the water content has increased U, and hence lowered $\Delta G'_D$, for both sets of glasses. However, from the slopes there is no evidence that water content has appreciably affected $\Delta H'_D$ for the glasses (Table III). Since $\Delta H'_D$, $\Delta S'_D$ and $\Delta G'_D$

1167

TABLE III Activation enthalpies, $\Delta H'_D$, from crystal growth rates (with 95% confidence limits)

| Glass	$\Delta H'_D$ (kcal mol^{-1})	Temperature range ($^\circ$C)
N1	68 ± 6	596 − 710
N2	81 ± 30	594 − 673
L1	69 ± 14	551 − 612
L5	66 ± 20	525 − 587

are dependent on temperature, comparisons of their values for different glasses are only meaningful, of course, if made over similar temperature ranges [8].

3.3. Mechanism of the effect of water content on nucleation and growth rates

The present work has shown that addition of small amounts of water has a pronounced influence on rates of crystal nucleation and growth. The main effect is to alter the kinetic barriers, ΔG_D and $\Delta G'_D$, or the effective diffusion coefficient, D, in the liquid (see Equation 2), rather than to alter the quantities ΔG or σ.

The mechanism of the diffusion processes involved in nucleation and growth is not clearly understood. Recent work, however, suggests that nucleation and growth in silicate glasses may be rate-controlled by the diffusion of oxygen ions. Thus Oishi et al. [29] found that the activation energies (ΔH_D) for diffusion of oxygen ions in several silicate glasses, including a soda-lime−silica composition, were close to those for viscous flow, indicating that viscous flow was rate-controlled by diffusion of oxygen ions in these glasses. Also, diffusion coefficients determined from studies of the kinetics of liquid−liquid phase separation in soda-silica [30] and soda-lime−silica [31] were close to that of oxygen, indicating that oxygen diffusion is the rate-cotrolling process in phase separation.

Incorporation of water into vitreous silica or low alkali silicate glasses probably follows a mechanism of the type [32]

$$\equiv Si-O-Si\equiv + H_2O \rightarrow \equiv Si-OH + HO-Si\equiv$$
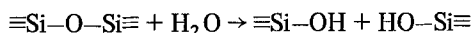
the rupturing of silicon−oxygen bridges resulting in a lowering of viscosity. For high alkali silicate glasses the process is probably more complicated and hydrogen bridge bonds of the type OH ... O also occur.

If diffusion of oxygen ions is the rate-determining process in nucleation and growth, a possible explanation for the large effect of water content is that the presence of water causes an increase in the oxygen diffusion coefficient. The details of this effect remain unclear. However, it would be of great interest to test this hypothesis by carrying out diffusion measurements of oxygen in water-containing glasses.

It should be noted that Eagan and Bergeron [4] in their crystal growth studies of lead borate glasses, found that an increase in water content produced a larger increase in growth rate than predicted from changes in viscosity. This was attributed to a higher concentration of water near the crystal−melt interface than in the bulk melt, leading to a local lowering in viscosity. However, such an effect is unlikely in the glasses studied here due to the close correspondence between changes in nucleation and growth rates and changes in bulk viscosity.

Recent work [27] has shown that addition of a few mol% NaF to the NC_2S_3 composition produces a very similar effect to the addition of water, i.e. a lowering of viscosity and an increase in nucleation and growth rates. This is probably because NaF, like H_2O, causes a rupturing of network bonds, the F^- ion substituting for O^- non-bridging oxygens in the structure. Thus one of the main effects of fluoride is probably to modify the kinetic barriers for nucleation and growth, particularly when used in relatively small quantities, which may, at least in part, explain the well-known action of fluoride as a nucleating agent in many systems [12, 33].

4. Conclusions

Small quantities of dissolved water were found to increase markedly crystal nucleation and growth rates in lithia−silica and soda-lime−silica glasses. Comparison of these increases with the observed decreases in viscosity indicated that the main effect of water was to lower the kinetic barriers to nucleation and growth. The thermodynamic barrier to nucleation, W^*, was probably not significantly affected by water content for the lithia silica glasses, although it may have been modified for the soda-lime glass N2.

It is clear that water content must be carefully considered when carrying out fundamental studies of nucleation and growth kinetics in "simple" systems. Thus different melting conditions, for example the use of electric or gas furnaces, could produce small differences in water content and, as

a result, significant changes in nucleation and growth rates. Such factors deserve further investigation since they could produce differences in the results for nominally the same glass compositions prepared in different laboratories. The effect of water is also of interest in the preparation of glass ceramics. For certain compositions, a deliberate increase in water content could shorten the crystal nucleation and growth times or usefully lower the heat-treatment temperatures required while maintaining the same fine grain microstructure provided, of course, no deleterious effects on the properties of the resultant materials occurred and convenient methods of introducing the higher water contents during melting could be devised. This has already been attempted in the $Li_2O-Al_2O_3-SiO_2$ system [34] by using $LiOH \cdot H_2O$ to introduce OH groups into the glass. Finally, the present results are relevant to crystallization studies of glasses prepared by the "gel" process as mentioned in Section 1. Further work on the effects of water content on more complex compositions of greater technological interest, particularly for glass ceramics would be of considerable interest.

Acknowledgements

References

1. E. N. BOULOS and N. J. KREIDL, *J. Canad. Ceram. Soc.* 41 (1972) 83.
2. M. S. MAKLAD and N. J. KREIDL, Proceedings of the 9th International Congress on Glass, Versailles, France, Vol. 1 (1971) p. 75.
3. F. E. WAGSTAFF, S. D. BROWN and I. B. CUTLER, *Phys. Chem. Glasses* 5 (1964) 76.
4. R. J. EAGAN and C. G. BERGERON, "Advances in Nucleation and Crystallisation in Glasses" (American Ceramic Society, Columbus, 1971) p. 202.
5. S. P. MUKHERJEE, J. ZARZYCKI and J. P. TRAVERSE, *J. Mater. Sci.* 11 (1976) 341.
6. K. MATUSITA and M. TASHIRO, *J. Non-Cryst. Solids* 11 (1973) 471.
7. P. F. JAMES, *Phys. Chem. Glasses* 15 (1974) 95.
8. E. G. ROWLANDS, Ph.D. thesis, University of Sheffield (1976).
9. A. M. KALININA, V. N. FILIPOVITCH and V. M. FOKIN, Proceedings of the 11th International Congress on Glass, Prague, Vol. 2 (1977) p. 11.
10. J. J. TUZZEO, Ph.D. thesis, Ohio State University (1976).
11. W. HINZ, *J. Non-Cryst. Solids* 25 (1977) 217.
12. P. W. McMILLAN, "Glass Ceramics" (Academic Press, London, 1964).
13. B. E. YOLDAS, *J. Mater. Sci.* 12 (1977) 1203.
14. M. YAMANE, S. ASO and T. SAKAINO, *ibid* 13 (1978) 865.
15. P. F. JAMES, B. SCOTT and P. ARMSTRONG, *Phys. Chem. Glasses* 19 (1978) 24.
16. Z. STRNAD and R. W. DOUGLAS, *ibid* 14 (1973) 33.
17. H. SCHOLZE, *Glastech. Ber.* 32 (1959) 81, 142, 278, 314, 381, 421.
18. P. F. JAMES and S. R. KEOWN, *Phil. Mag.* 30 (1974) 789.
19. S. R. KEOWN and P. F. JAMES, Proceedings of the Eighth International Congress on Electron Microscopy, Canberra, Vol. 1 (1974). p. 546.
20. R. W. DOUGLAS, W. L. ARMSTRONG, J. P. EDWARD and D. HALL, *Glass Tech.* 6 (1965) 52.
21. C. E. MAGHRABI, Ph.D. thesis, University of Sheffield (1970).
22. L. S. DENT GLASSER and J. S. MILESON, *J. Amer. Ceram. Soc.* 51 (1968). 55
23. I. MAKI and T. SUGIMURA, *J. Ceram. Assoc. Jap.* 76 (1968) 144.
24. C. KRÖGER and G. KREITLOW, *Glastech. Ber.* 29 (1956) 393.
25. E. G. ROWLANDS and P. F. JAMES, Proceedings of the Symposium on the Structure of Non-Crystalline solids, Cambridge, edited by P. H. Gaskell (1976) p. 215.
26. A. C. ZETTLEMOYER, Ed., "Nucleation" (Marcel Dekker, New York, 1969).
27. C. J. R. GONZALEZ-OLIVER and P. F. JAMES, to be published.
28. D. TURNBULL, in "Solid State Physics" Vol. 3, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956).
29. U. OISHI, H. UEDA and R. TERAI, Proceedings of the 10th International Congress on Glass, Kyoto, Japan, Part I (1974) 8–30.
30. G. F. NEILSON, *Phys. Chem. Glasses* 10 (1969) 54.
31. D. G. BURNETT and R. W. DOUGLAS, *Phys. Chem. Glasses* 11 (1970) 125.
32. C. R. KURKJIAN and L. E. RUSSEL, *J. Soc. Glass Tech.* 42 (1958) 130.
33. S. P. MUKHERJEE and P. S. ROGERS, *Phys. Chem. Glasses* 8 (1967) 81.
34. H. DOI, T. KANDORI and O. KAMIGAITO, *Jap. J. Appl. Phys.* 12 (1973) 742.