

EXPERIMENTAL TESTS OF THE CLASSICAL NUCLEATION THEORY FOR GLASSES

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New data for crystal nucleation rates and viscosities were obtained for $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ and $\text{BaO}\cdot 2\text{SiO}_2$ glasses. Special efforts were made to minimise impurities in the glasses. Good general agreement with previously published nucleation results was found. The new and previous results were used to test the applicability of classical nucleation theory. For both lithium and barium disilicates the temperature dependence of nucleation rates was satisfactorily described by theory, $\ln(I\eta/T)$ vs. $1/\Delta G^2 T$ plots yielding straight lines over a wide range of temperatures (ΔG is the bulk free energy difference per mole between crystal and liquid at temperature T). However, for lithium disilicate, where experimental ΔG data were available, the experimentally determined preexponential factor A in the nucleation equation was much higher than the theoretical value, in agreement with previous studies. This was the case even allowing for reasonable variations in ΔG . A similar result was obtained for barium disilicate using calculated ΔG values. Possible reasons for the discrepancy in A between theory and experiment are discussed including transient nucleation, experimental errors in the nucleation rates and heterogeneous nucleation. None of these effects can account for the observed discrepancy. Other possible explanations are considered.

1. Introduction

The classical nucleation theory for condensed systems derived by Turnbull and Fisher in 1949 [1], is extremely important from both the fundamental and technological points of view. Recently, it has been used by Uhlmann and coworkers [2–6] to establish a kinetic treatment of glass formation. The production of useful glass ceramic articles is also related to the knowledge of the nucleation kinetics of crystalline phases in glasses. Other branches of materials science, such as metallurgy and polymer science, also make extensive use of the nucleation theory. An extensive review of crystal nucleation in glass forming systems has been given by James [7].

In this paper tests of the classical theory are carried out by means of measured values of nucleation rates and viscosities and available thermodynamic data from the literature.

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2. Literature review

Because of the experimental difficulties associated with direct measurements of nucleation rates [1] in liquids, in most studies the critical undercooling for homogeneous crystal nucleation has been simply determined and the resulting information used to estimate the magnitude of the nucleation barrier.

As a result of the strong temperature dependence of the viscosity of glass forming liquids and their solvent nature, the homogeneous nucleation of crystals in a wide temperature range can be arrested by quenching and studied. Evidence for homogeneous internal crystal nucleation in glasses has been presented by Burnett and Douglas [8] and James et al. [9] who melted glasses under different conditions and found no appreciable variations in nucleation rates.

The kinetics of internal (or volume) nucleation have been studied intensively for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass (see for example [7,9–11]), which is one of the few silicate compositions where detailed experimental data for ΔG , the bulk free energy change per mole in crystallization, are available [12,13].

Rowlands and James [14] have carried out a detailed analysis of the nucleation rate (I) versus temperature ($T(\text{K})$) data of James [11] for lithium disilicate, which were determined directly by means of optical microscopy. Using the viscosity (η) data of Matusita and Tashiro [10], a plot of $\ln(I\eta/T)$ vs. $1/\Delta G^2 T$, gave a straight line for higher temperatures, above the nucleation maximum T_{\max} . The slope yielded a crystal/liquid interfacial energy (σ) of 190 mJ.m^{-2} in reasonable agreement with the value calculated from the empirical formula of Matusita and Tashiro [10] (based on a relation due to Turnbull). The temperature variation of I was well described by theory from 445 to 527°C but poorly described at lower temperatures (425 to 440°C). Furthermore, the experimental value of the pre-exponential factor (A) in the expression for I , determined from the intercept of the plot, was about 20 orders of magnitude higher than the theoretical value $10^{41} \text{ m}^{-3} \text{ s}^{-1}$ for the $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass. Rowlands and James [14] discussed various possible reasons for the above discrepancy, but showed that the possibility of heterogeneous nucleation could not explain it. However, the discrepancy could be explained by postulating a temperature dependent interfacial free energy with a small negative interfacial entropy. In this case, it was necessary to express σ in the form $\sigma = 64.0 + 0.109T (\text{mJ.m}^{-2})$ where T is in K.

Neilson and Weinberg [15] have independently carried out a very similar analysis for lithium disilicate (using the same experimental data as Rowlands and James) and have reached almost identical conclusions. It should be emphasised, however, that in both these studies [14,15] the viscosity data and the nucleation data used were obtained from different melts (of the same nominal composition, $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$) and differences in “water” levels or other impurities may have had significant effects.

Steady-state nucleation rates have been analysed in the $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ (NC_2S_3) composition by Gonzalez-Oliver [16] and Gonzalez-Oliver and James [17], using measured viscosity and thermodynamic data. A $\ln(I\eta/T)$ versus

$1/\Delta G^2 T$ gave a good straight line in accordance with theory, the slope indicating an interfacial energy σ of 180 mJm^{-2} in reasonable agreement with the value of 193 mJm^{-2} obtained from the empirical formula given in [10]. However, as found for lithium disilicate, the experimentally determined pre-exponential factor (A) was much higher than the theoretical value. The authors viewed this discrepancy as tentative, since ΔG for NC_2S_3 was obtained using an average ΔC_p (the difference in specific heats between crystal and liquid) over the temperature range studied. Even a small error in ΔG could produce a large change in A , although the value of σ would be altered only slightly.

Klein et al. [18] studied $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glass. Crystal nucleation rates were deduced indirectly by means of the Johnson–Mehl–Avrami (JMA) equation using the times required to reach a given volume fraction of crystallinity (10^{-4}) and the known crystal growth rates. With the values of viscosity and assuming the validity of Hoffman's expression [19] for the thermodynamic driving force (ΔG) a test of the nucleation theory could be carried out. The results indicated agreement between the experimental data and the predictions of the classical theory of homogeneous nucleation, both in the temperature dependence of I and in the pre-exponential factor.

Although Klein et al. [18] have used an interesting approach, a number of points must be considered. First, in the analysis nucleation in the volume of the glass was assumed. However, Matusita and Tashiro [10] and Scott and Pask [20] have observed only surface (heterogeneous) crystal nucleation in $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glasses. Second, Takahashi and Yoshio [12] have shown that ΔG values calculated by Hoffman's formula do *not* agree with the experimental values for this glass. Finally, as mentioned by the authors, the pre-exponential factor (A) determined experimentally using the JMA equation was dependent on the particular volume fraction of crystallization chosen.

Recently Cranmer et al. [21] determined the nucleation kinetics in a glass of the anorthite composition by means of the JMA equation using the same approach as Klein et al. To obtain I , the times required to reach a volume fraction of crystallized material of 10^{-3} were used together with previously measured crystal growth rates. Again, a test of theory was made using these I values, the known viscosities and using ΔG calculated from the Hoffman expression. Once more the temperature dependence of I was apparently in good agreement with theory. Also the pre-exponential factor (A) determined experimentally was only three orders of magnitude less than the value expected from theory.

The results of Cranmer et al. are, however, subject to similar comments to those made on the results of Klein et al. There is a large uncertainty in the use of the Hoffman equation. It is not a good approximation for sodium or lithium disilicates [12]. Again, the experimental value of A is dependent on the limiting volume fraction chosen [21]. Furthermore, no supporting evidence was presented for volume nucleation in the samples. In independent work [22] no volume nucleation was detected in a glass of the anorthite composition, only surface nucleation being observed.

Cranmer et al. [21] based on the results obtained for the anorthite glass and those on the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ glass [18] suggested (tentatively) that problems may exist with the nucleation data on the $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass used by Rowlands and James [14], and that these data should be re-examined.

In this paper new data are presented for viscosity and nucleation frequencies in $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (LS_2) and $\text{BaO} \cdot 2\text{SiO}_2$ (BS_2) glasses. Experimental tests of the nucleation theory are carried out showing large discrepancies between calculated and experimental values of nucleation frequencies (I). The temperature dependence of I , however, is satisfactorily described by theory.

3. Theory

The nucleation rate I in condensed systems is given [1,23] by

$$I = n_v \nu (n_s^*/n^*) (W^*/3\pi kT)^{1/2} \exp[-(\Delta G_D + W^*)/kT], \quad (1)$$

where:

- n_v = the number of "molecules" or "formula units" of nucleating phase per unit volume of parent phase (typically 10^{28} – 10^{29} m^{-3});
- ν = vibration frequency $\sim 10^{13} \text{ s}^{-1}$;
- n_s^* = number of molecules on the surface of a critical nucleus;
- n^* = number of molecules in the critical nucleus;
- W^* = Thermodynamic barrier for nucleation;
- ΔG_D = Activation energy for transport across the nucleus/matrix interface;
- k = Boltzmann's constant;

The quantity $(n_s^*/n^*) (W^*/3\pi kT)^{1/2}$ is within one or two powers of ten for all nucleation problems of interest. Therefore, eq. (1) may be written with sufficient accuracy as

$$I = n_v \nu \exp[-(\Delta G_D + W^*)/kT], \quad (2)$$

where the pre-exponential factor $A = (n_v \nu)$ is typically 10^{41} – $10^{42} \text{ m}^{-3} \text{ s}^{-1}$.

Assuming that the molecular re-arrangement for the nucleation process can be described by an effective diffusion coefficient, D , we have

$$D = \nu \lambda^2 \exp(-\Delta G_D/kT) \quad (3)$$

where λ is the jump distance, of the order of atomic dimensions. D can be related to the viscosity (η) by means of the Stokes–Einstein equation:

$$D = kT/3\pi\lambda\eta. \quad (4)$$

Combining eqs. (2), (3) and (4) we have

$$I = (n_v kT/3\pi\lambda^3\eta) \exp(-W^*/kT). \quad (5)$$

For spherical nuclei

$$W^* = 16\pi\sigma^3 V_m^2/3\Delta G^2,$$

where V_m is the molar volume of the crystallizing phase. Therefore, eq. (5) can be rewritten in the form

$$\ln(I\eta/T) = (n_v k / 3\pi \lambda^3) - (16\pi\sigma^3 V_m^2 / 3\Delta G^2 T). \quad (6)$$

Hence, a plot of $\ln(I\eta/T)$ versus $1/\Delta G^2 T$ should yield a straight line, with σ and the pre-exponential factor A given by the slope and intercept, respectively.

To test the classical theory accurate data for the thermodynamic driving force for the glass to crystal transformation (ΔG) are required. ΔG for a single component system at temperature T below the melting point T_m is given by

$$\Delta G = -\Delta H_f(T_m - T)/T_m - \int_T^{T_m} \Delta C_p dT + T \int_T^{T_m} (\Delta C_p/T) dT, \quad (7)$$

where ΔH_f is the heat of fusion per mole and $\Delta C_p (< 0)$ is the difference in specific heats between the crystalline and liquid phases at constant pressure at temperature T .

If ΔC_p can be taken as independent of temperature from T_m to the temperature of interest (T) eq. (7) can be integrated to give

$$\Delta G = -\Delta H_f(T_m - T)/T_m - \Delta C_p [(T_m - T) - T \ln(T_m/T)]. \quad (8)$$

If ΔC_p is zero, ΔG is given by the well-known approximate expression

$$\Delta G = -\Delta H_f(T_m - T)/T_m. \quad (9)$$

Hoffman [9] derived the following equation assuming ΔC_p to be an unknown constant:

$$\Delta G = -\Delta H_f(T_m - T)T/T_m^2. \quad (10)$$

This equation was referred to previously.

4. Experimental

A $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ ('LS₂) and three $\text{BaO} \cdot 2\text{SiO}_2$ ('BS₂) glasses were prepared. Efforts were made to minimise impurity levels in the glasses by careful choice of starting materials because of the possible effects these might have on the nucleation rates. The lithium disilicate glass (code 33.2B) was prepared from Optipur SiO_2 (Merck) and 99.999 wt% Li_2CO_3 (Aldrich). Two of the barium disilicate glasses (33.3A and 33.2C) were prepared from Silquartz (99.99 wt% SiO_2) and BaCO_3 (Fisons A.R. grade). The BaCO_3 contained approximately 0.5 wt% impurities, the major impurity being SrO (0.4 wt%). For comparison a third barium glass (33.3P) was prepared from Optipur SiO_2 (Merck) and Puratronic BaCO_3 (Ventron). From analysis this source of BaCO_3 contained only 72 ppm of SrO and approximately 0.03 wt% total impurities.

100 to 250g batches were melted in new Pt-Rh crucibles in electric furnaces at 1350°C (lithium glass) and 1550°C (barium glasses). Each glass was homogenized by crushing and remelting five times. The melts were finally cast

Table 1

Chemical analysis (wt.%) of glasses used in the present study. Electron probe microanalysis unless otherwise stated

	$\text{BaO} \cdot 2\text{SiO}_2$			$\text{Li}_2\text{O} \cdot 2\text{SiO}_2$	
	Nominal	Analysis	Analysis	Nominal	Analysis
SiO_2	43.60	33.3A (43.12 ^a)	33.2C —	80.09	33.2B 80.19
BaO	56.05	56.15(56.07 ^a)	55.80		
Li_2O	—	—	—	19.91	—
SrO	0.33	0.33(0.29 ^c)	—		—
Na_2O		0.12(0.007 ^d)	—		0.015 ^d
Fe_2O_3		< 0.04(0.001 ^d)	—		< 0.0004 ^d
Al_2O_3		0.06 —	—		< 0.05 ^d
K_2O		0.02(0.026 ^d)	—		—
CaO		0.03(0.038 ^c)	—		—
H_2O		—	—		0.02 ^b

^a Gravimetric analysis; ^b infra-red spectroscopy; ^c flame emission spectroscopy; ^d atomic absorption spectroscopy.

and pressed between steel plates. Clear samples 1–2 mm in thickness were obtained. The chemical analysis of the glasses is given in table 1. All the glasses were close to the nominal compositions. The code number of each glass (e.g. 33.3A) gives the analysed baria (or lithia) content in mol%. The lithium disilicate glass was quite pure, the main impurity being Na_2O (0.015 wt%) and the levels of other impurities such as iron and aluminium were very low. The water content of this glass was determined by infra-red spectroscopy as described elsewhere [24]. The main impurity in the barium glasses was strontium. However, the purest barium disilicate glass (33.3P, not shown in table 1) contained 56.02 wt% BaO (33.3 mole % BaO) and only 0.004 wt% SrO . A detailed account of the analysis of these glasses is given elsewhere [25].

Glass specimens of about $3 \times 3 \times 1\text{mm}^3$ were nucleated at 685–765°C ($\text{BaO} \cdot 2\text{SiO}_2$) and at 440–497°C ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$) for different periods, air quenched and subsequently given a crystal growth or ‘development’ treatment at 800–830°C for 10–30 min ($\text{BaO} \cdot 2\text{SiO}_2$) and at 570–600°C for 30–70 min ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$), respectively. The electric tubular furnaces were maintained to within 0.5°C with proportional controllers. The furnaces were found to have a “plateau” around the hot spot, in which the temperature varied by less than 1°C over 2 cm. The glass specimens were kept inside a small mullite boat, being touched by the tip of a Pt/13 Rh thermocouple during the treatment. The thermocouple readings were found to be within 1°C of a standard thermocouple. The furnaces usually attained the equilibrium temperatures about 10 min after the insertion of the specimens, the maximum variation being 7°C in the first minutes (depending on how fast and careful the operation was performed). Therefore, some uncertainty in the heat treatments is expected for samples treated for short periods ($t < 30$ min).

The heat treated specimens were mounted on glass plates with Canada

balsam, ground with SiC (400 and 600 grit) and polished with colloidal Ce₂O₃. An etching of 10–15 s in a 0.6% HF 0.2% HCl (volume %) solution was enough to reveal the microstructure of the BS₂ glasses. The LS₂ glass required 2 min to reveal the microstructure. Photographs were taken with a Zeiss Ultraphot 2 microscope, with 16x or 40x objectives depending on the sizes of the crystals. The total magnification on the final prints was obtained by means of a calibrated graticule which was photographed in the same microscope. From 200 to 800 crystalline particles were counted and measured in each sample. The number of crystals per unit volume (N_v) was then obtained by the equation of De Hoff and Rhines [26]. The method is discussed in detail by James [11].

The statistical error in N_v was $\pm 10\text{--}20\%$ within 95% confidence limits, depending on the size distribution and number of crystals counted and measured. There is, however, another source of error, which has not been considered in the past and can be quite appreciable. The resolution of optical microscopes is usually in practice around 1 μm , the sectioning of the particles always producing a certain percentage of intersections below the resolution limit, which will not be taken into account in the calculation of N_v . This will cause N_v to be underestimated by a value which depends on the resolution of the microscope, the size distribution of particles and the maximum size and shape of particles. A complete mathematical derivation of these errors for several size distributions and resolutions is given in [25]. For usual cases, i.e., a size distribution due to a double stage heat treatment, an underestimation of 3 to 14% can be expected for the measured values of N_v and nucleation rates I . If the crystals are too small on the prints (< 2–3 mm) measurement errors can be significant also and increase the uncertainty in N_v and I . Hence only print magnifications giving a large majority of crystals greater than 3 mm in size were used in the analysis. It was found experimentally that nucleation densities up to 10^6 mm^{-3} could be measured with relative ease on optical micrographs, electron microscope techniques being required for larger densities. Other complications arise when electron microscopy is used.

Viscosity temperature curves were obtained by the penetration method described in detail in [25,27]. The apparatus was calibrated using samples of NBS 710 and NBS 711 standard glasses.

5. Results

5.1. Crystal nucleation rates

Optical micrographs of the Li₂O · 2SiO₂ and BaO · 2SiO₂ spherulites have been given elsewhere [7,11,28] and will not be shown again here.

Fig. 1 shows the number of crystal spherulites per unit volume N_v (density of volume nuclei) versus time curves of the BS₂ glasses 33.2C and 33.3A from 685°C to 765°C. Evidence for induction periods was observed at lower temperatures, particularly at 685°C, steady state conditions being rapidly established at higher temperatures.

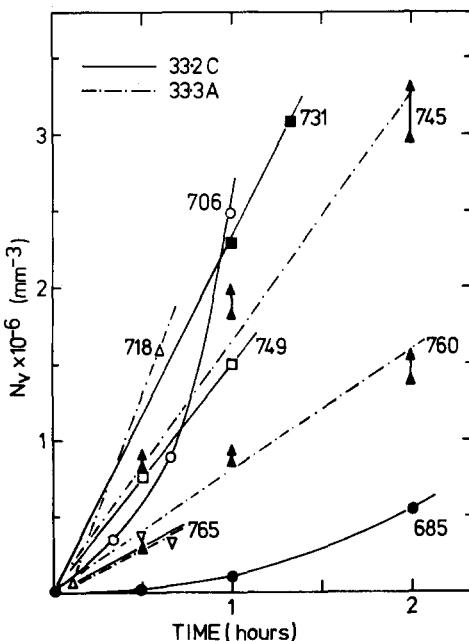


Fig. 1. Number of crystal particles per unit volume (N_v) versus time for glasses close to the $\text{BaO} \cdot 2\text{SiO}_2$ composition (33.2C and 33.3A) at various temperatures ($^{\circ}\text{C}$). — 33.2C, - - - 33.3A; points $\Delta\Delta$ refer to 33.3A (Δ at 718°C), other points (including ∇ at 765°C) refer to 33.2C.

The crystal nucleation rates were obtained from the slope of these curves and will be used later in the analysis of nucleation kinetics. The present results are shown in table 2 together with the results of Rowlands [29] and James and Rowlands [28] for a glass (denoted B6) also close in composition to $\text{BaO} \cdot 2\text{SiO}_2$ but less pure than 33.2C and 33.3A since it contained, in addition to 0.38 wt% SrO , 0.33 wt% Al_2O_3 (a detailed analysis of this glass is given in [30]). The general agreement between the sets of data is good.

Table 2
Crystal nucleation rates in barium disilicate glasses ($\text{mm}^{-3} \cdot \text{s}^{-1}$)

B6 [28,29]		33.3A		33.2C	
$T(^{\circ}\text{C})$	I	$T(^{\circ}\text{C})$	I	$T(^{\circ}\text{C})$	I
662	42 ^a	—	—	—	—
680	206 ^a	—	—	685	125 ^a
700	1870 ^a	—	—	706	1490 ^a
718	1450	718	1042	—	—
729	798	—	—	731	644
740	459	—	—	—	—
748	280	745	461	749	415
760	134	760	222	—	—
—	—	765	163	765	163
780	27	—	—	—	—

^a Underestimated due to induction periods.

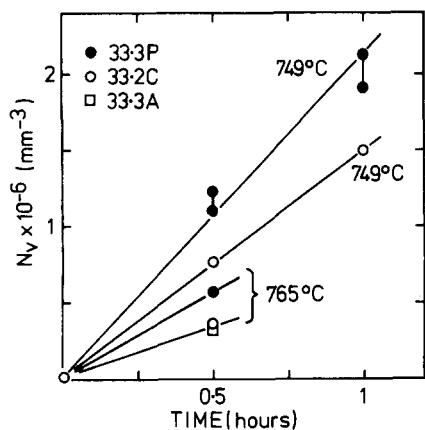


Fig. 2. Crystal nucleation (N_v versus time) plots at 749°C and 765°C for glass 33.3P (0.004 wt% SrO) and glasses 33.3A and 33.2C (0.3 wt% SrO) 33.3P (●), 33.3A (□), 33.2C (○).

As the main impurity was SrO in the BaO–SiO₂ glasses melted in this work an experiment was devised to test the effect of this oxide on the nucleation of crystals. Fig. 2 shows a comparison of glasses 33.3A and 33.2C (0.3 wt% SrO)

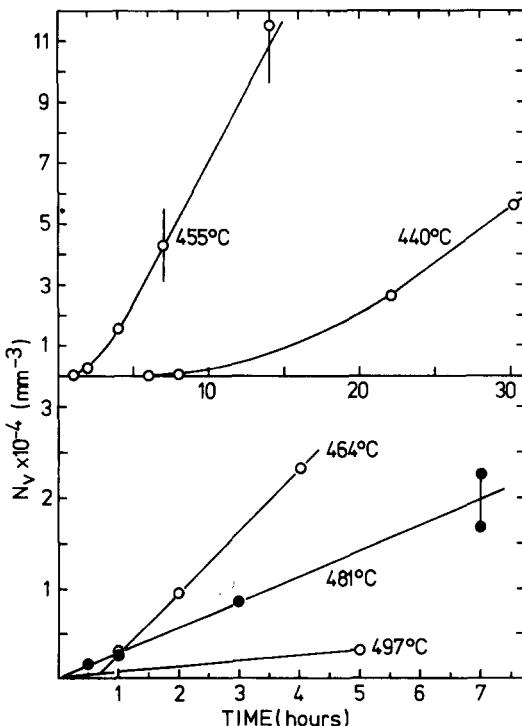


Fig. 3. Number of crystal particles per unit volume (N_v) versus time plots for glass 33.2B, close to $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ composition, at various temperatures.

Table 3

Crystal nucleation rates in $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glasses (I in $\text{mm}^{-3} \cdot \text{s}^{-1}$)

This work		James [11]	
$T(\text{°C})$	I	$T(\text{°C})$	I
440	1.05	425	0.045
		430	0.368
		435	1.041
	455	440	1.147
		445	3.761
	464	454	4.253
		465	2.863
	481	476	1.868
		489	0.639
		502	0.149
497	0.19	516	0.025
		527	0.006
Tuzzeo [33]		Fokin et al. [35]	
$T(\text{°C})$	I	$T(\text{°C})$	I
430	0.024	430	0.23
		440	0.91
446	1.263		
455	2.224		
		460	2.63
465	1.967	465	2.4
475	1.260	485	0.72
498	0.126		
523	0.009		

with glass 33.3P (0.004 wt% SrO) at 749°C and 765°C. The nucleation rate in glass 33.3P is about 1.5 times higher than in the other two glasses, and the difference may be attributed to the effect of SrO. However, since the effect is relatively small and temperature independent it does not affect the later analysis of the temperature dependence of the nucleation rates.

Fig. 3 shows the crystal nucleation density (N_v) versus time curves for the lithium disilicate glass 33.2B at various temperatures. Induction periods were observed even above T_g (about 454°C) i.e., up to 464°C, in good agreement with the results of James [11]. The nucleation rates calculated from the slopes of the curves in fig. 3 at longer times (see [11]) are given in table 3, together with the results obtained previously by several other authors.

Nucleation rates in lithium disilicate have been determined by a number of authors [9–11,31–35]. There are appreciable variations between the various sets of data, differences as great as a factor of 3 being observed for a given temperature. These variations were probably caused in part by differences in base composition or impurity contents. Also in some cases there were probably systematic errors in the stereological measurements, and errors caused by failure to achieve steady state nucleation conditions and caused by the use of too high a development temperature [7]. In spite of the differences there is

Table 4

Chemical analysis of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glasses (wt.%) used by James [11] and Tuzzeo [33]

Oxide	James, L1, [11]		Tuzzeo [33]	Nominal ($\text{Li}_2\text{O}\cdot 2\text{SiO}_2$)
	(a)	(b)	(c)	
Li_2O	19.72	(d)	20.20	19.91
SiO_2	79.84	79.50	78.66	80.09
Al_2O_3	0.04	0.07	0.79	
Fe_2O_3	0.02	0.01		
Na_2O	0.07	0.05	—	
K_2O	—	0.02	—	
CaO	—	0.07	—	
H_2O		0.02(e)	—	

(a) Electron probe microanalysis; (b) X-ray fluorescence; (c) Gravimetric analysis; (d) flame photometry; (e) Infra-red spectroscopy.

good agreement in the temperature dependence of the nucleation rates, the reported maximum being at 450–460°C.

The present results are in general agreement with the data of James [11], Tuzzeo [33], Kalinina et al. [34] and Fokin et al. [35], where a similar experimental technique was employed i.e. a double stage heat treatment followed by stereological measurements using optical microscopy. Nevertheless, some differences still exist between these data. The results of James and of Tuzzeo are compared with the present results in table 3. The data of Fokin et al. [35] are calculated by the present authors from the graphs in their paper. Chemical analyses of the glasses of James and of Tuzzeo are given in table 4 and should be compared with the analysis for glass 33.2B in table 1. Significant differences in the levels of various impurities and in the major components are observed for these glasses and are also expected in the previous studies where no detailed analyses were given. The present nucleation rates for glass 33.2B were somewhat lower than those of James for glass L1, by a fairly constant factor, independent of temperature. The water contents and Li_2O contents for 33.2B and L1 were very close but the overall level of other impurities was larger in glass L1. Since the same stereological technique was used in the two studies, the observed differences in nucleation rates are apparently due to differences in the levels of one or more impurities. The glass of Tuzzeo [33], on the other hand, had a much higher impurity content than L1 or 33.2B. Also the SiO_2 and Li_2O contents were different. The nucleation rates reported by Tuzzeo, however, are quite close to the nucleation rates of the much purer glass 33.2B in the present study.

5.2. Viscosities of BaO-SiO_2 and $\text{Li}_2\text{O-SiO}_2$ glasses

The determination of the viscosity of the BS_2 glass in the range of high viscosities is of great interest because, as far as we know there is no previous data for this range. Fig. 4 shows the viscosity curve for the 33.2C BaO glass

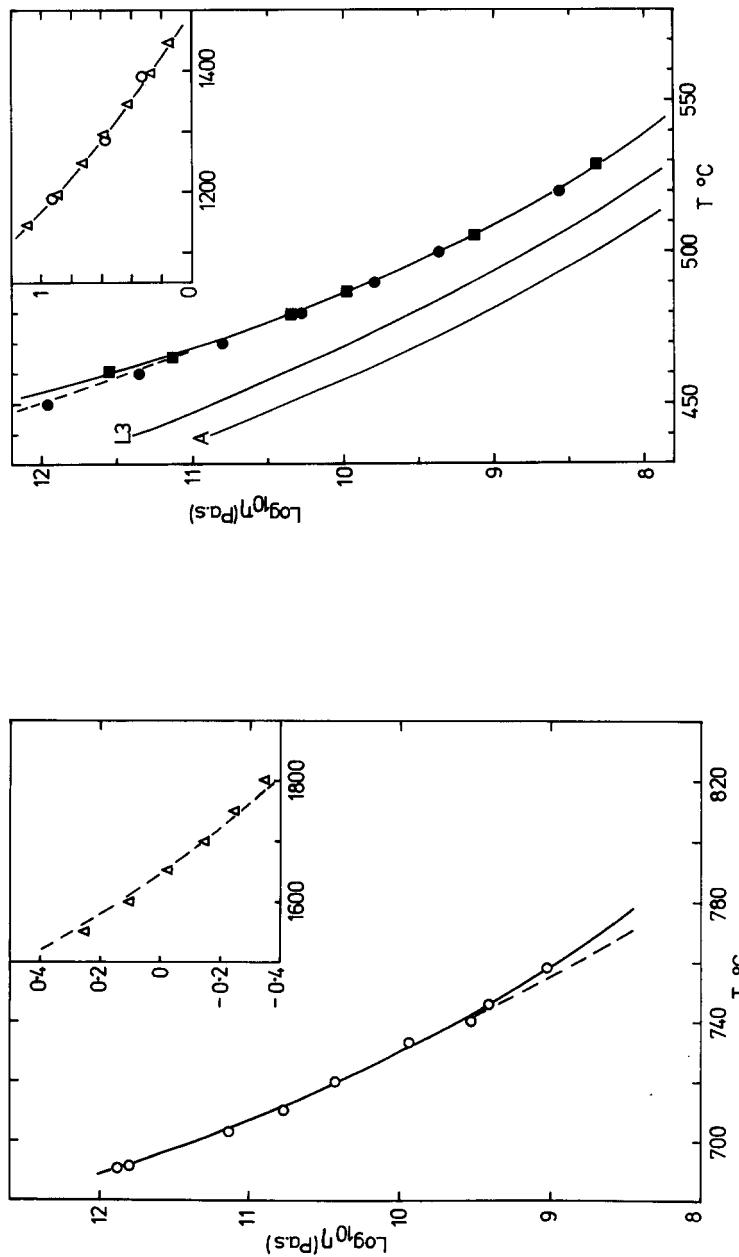


Fig. 4. Viscosity versus temperature curve for glass 33.2C, close to $\text{BaO} \cdot 2\text{SiO}_2$. The full line is the Fulcher fit to the present data only, the dashed line represents the Fulcher fit to both the present data and the data of Bockris et al. [36] at high temperatures. \circ present work; \triangle Bockris et al. [36].

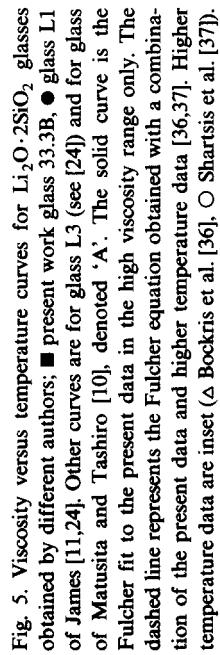


Fig. 5. Viscosity versus temperature curves for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glasses obtained by different authors: ■ present work glass 33.3B, ● glass L1 of James [11,24], ○ glass L3 (see [24]) and for glass of Matsuura and Tashiro [10], denoted 'A'. The solid curve is the Fulcher fit to the present data in the high viscosity range only. The dashed line represents the Fulcher equation obtained with a combination of the present data and higher temperature data [36,37]. Higher temperature data are inset (\triangle Bockris et al. [36], ○ Shartsis et al. [37]).

Table 5

Fulcher parameters of the glasses using viscosities from present work only. $\log_{10}\eta = A + B/(T - T_0)$; T , T_0 ($^{\circ}$ C) and η (Pas).

	Glass 33.2C BaO	Glass 33.2B Li ₂ O
<i>A</i>	1.83	1.81
<i>B</i>	1701.9	1346.6
<i>T</i> ₀	521.6	321.8

together with the viscosity curve obtained by Bockris et al. [36] for a glass with 33.5 ± 0.2 wt% BaO in the melting range. The dashed line represents the Fulcher curve obtained with a combination of the present data and that of [36]. The solid line represents the Fulcher equation for the present data in the high viscosity range only.

Fig. 5 shows the viscosity curve of glass 33.2B Li₂O together with some data from the literature. The dashed line represents the Fulcher equation obtained with a combination of the high temperature data of Bockris et al. [36] and Shartsis et al. [37] and the present data. The solid line represents the Fulcher curve through the present data only. The agreement of both curves is excellent, the solid curve being slightly higher for $\eta > 10^{11}$ PaS.

Fig. 5 also shows that the present experimental data agree well with the data of Gonzalez-Oliver et al. [24] for glass L1 which contained 0.02 wt% H₂O and was studied by James in [11]. On the other hand, glass L3 of Gonzalez-Oliver et al. [24] with a higher water content (0.136 wt% H₂O), and the glass of Matusita and Tashiro [10] have much lower viscosities. The nominal content of Li₂O was 33.3 mol% in these glasses.

The Fulcher constants for the glasses studied here are given in table 5. Only the viscosity data obtained in the present work are used.

6. Experimental tests of the classical nucleation theory

6.1. Li₂O · 2SiO₂ glasses

As discussed previously, if the thermodynamic driving force for the the glass to crystal transformation, ΔG , is available from the literature, the experimental nucleation rates and viscosity values can be used to test the classical nucleation theory. Therefore, using the viscosity results and the nucleation data (table 3) for glass 33.2B, an analysis was made according to the method described above. Thermodynamic data for the Li₂O · 2SiO₂ glass were available [12,13], although the data of [12] are probably the more accurate.

Fig. 6 shows the $\ln(I\eta/T)$ versus $(1/\Delta G^2 T)$ curves. ΔG values from both [12] and [13] were used. Good straight lines were obtained using the measured viscosities from this work. The temperature range was 440 to 497°C. This result is in agreement with the earlier work of Rowlands and James [14] who

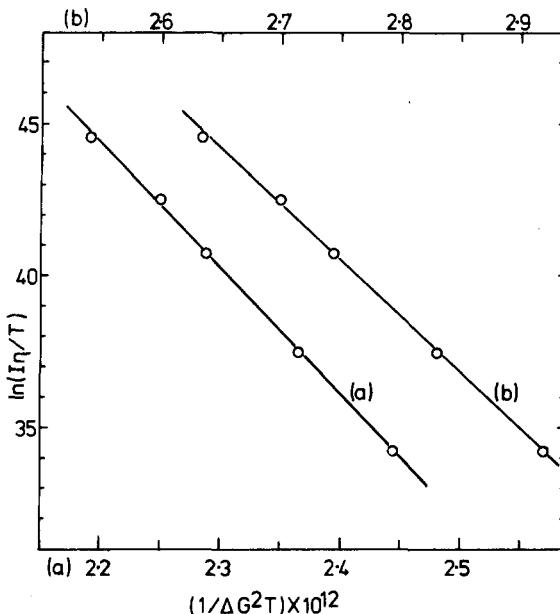


Fig. 6. $\ln(I\eta/T)$ vs. $1/\Delta G^2 T$ for glass 33.2B, close to $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$. I in $\text{m}^{-3} \cdot \text{s}^{-1}$, η in Ns m^{-2} , ΔG in J mol^{-1} , T in K . Line (a) using ΔG from [12], line (b) using ΔG from [13].

also obtained a straight line plot over a similar range (445 to 527°C) but not at lower temperatures. It should be noted that Rowlands and James [14] used the nucleation data of James [11] which extended to lower temperatures than in the present work.

Fig. 7 shows the $\ln(I\eta/T)$ versus $I/\Delta G^2 T$ curves using ΔG values calculated from eq. (8), assuming $\Delta C_p = 0, -13$ and $+13 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $\Delta H_f = 57.4 \text{ kJ} \cdot \text{mol}^{-1}$. The ΔC_p of $-13 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is an approximate value quoted for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass [29,38]. The value of $+13 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is an arbitrary (incorrect) value of ΔC_p used to test the sensitivity of the as determined parameters A and σ to the magnitude of the thermodynamic driving force ΔG used in the analysis. The ΔH_f used ($57.4 \text{ kJ} \cdot \text{mol}^{-1}$) is an average of the values given in [12] and [13]. Nucleation data obtained in this work and in other studies [11,33] together with the Fulcher fit to the experimental viscosity values for glass 33.2B were used.

The results shown in table 6 are the pre-exponential factor A , and interfacial energy σ , calculated from the intercepts and slopes of the straight lines in figs. 6 and 7. Also shown are the relationships for viscosity (η) and ΔG used in the calculations. From table 6 it is clear that the value of A is strongly dependent on which set of thermodynamic data (measured or calculated) is employed. The use of different sets of nucleation data has little influence on the value of A . The surface energy is relatively insensitive to both the nucleation data and thermodynamic values employed. Assuming a spherical

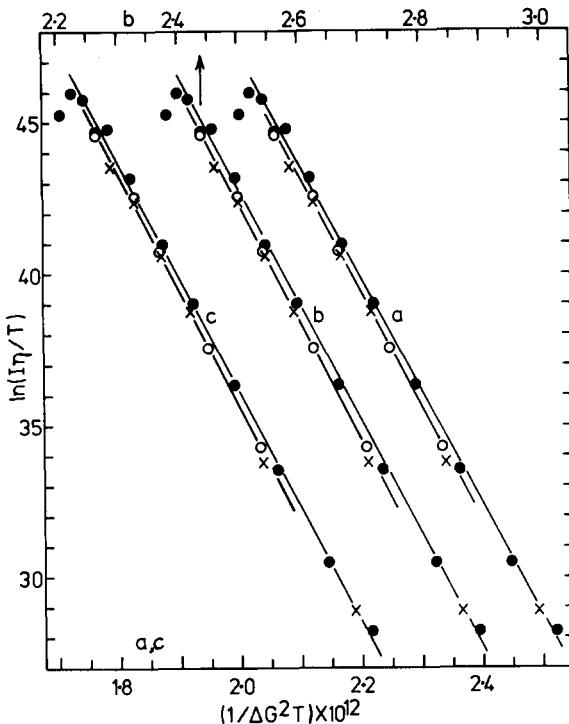


Fig. 7. $\ln(I\eta/T)$ vs. $1/\Delta G^2 T$ for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glasses using ΔG calculated from eq. (8) with $\Delta H_f = 57.4 \text{ kJ mol}^{-1}$, $T_m = 1307 \text{ K}$, and (a) $\Delta C_p = 0$, (b) $\Delta C_p = -13 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ and (c) $\Delta C_p = 13 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ (see table 6). Nucleation rates I from present work (\circ), James [11] (\bullet), and Tuzzeo [33] (\times). η in Ns m^{-2} , ΔG in J mol^{-1} , T in K .

Table 6
Experimental parameters from the analysis of nucleation rates in $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glasses.

	ΔG from eq. (8)	ΔG from		
	$\Delta C_p = 0$	-13	+13	[13]
	(a)	(b)	(c)	[12]
<i>Using nucleation data of present work</i>				
$\log_{10} A (\text{m}^{-3} \text{s}^{-1})$	63	70	58	71
$\sigma (\text{mJ m}^{-2})$	203	204	204	201
<i>Using nucleation data of James [11]</i>				
$\log_{10} A (\text{m}^{-3} \text{s}^{-1})$	62	69	58	70
$\sigma (\text{mJ m}^{-2})$	202	202	203	199
<i>Using nucleation data of Tuzzeo [33]</i>				
$\log_{10} A (\text{m}^{-3} \text{s}^{-1})$	61	67	57	69
$\sigma (\text{mJ m}^{-2})$	200	201	202	198

$$\log_{10} \eta = 1.81 + 1346.6/(T - 594.8); \quad \eta \text{ (Pas)}, \quad T \text{ (K)}.$$

(a), (b), (c) $\Delta H_f = 57.4 \text{ kJ mol}^{-1}$, $T_m = 1307 \text{ K}$, $\Delta C_p = 0, -13, +13 \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$. Eq. (8)

(d) $|\Delta G| = 47825 - (34.719)T \text{ (J mol}^{-1}\text{)}$, from [13] ($T \text{ (K)}$)

(e) $|\Delta G| = 53368 - (39.370)T \text{ (J mol}^{-1}\text{)}$ from [12] ($T \text{ (K)}$)

nucleus, the experimentally determined values of σ (198–209 mJm⁻²) are in reasonable agreement with the value of 209 mJm⁻² obtained from the empirical equation given in [10]. The values of A obtained, i.e. 10⁶¹–10⁷⁰ m⁻³·s⁻¹ for the calculated thermodynamic data (not including the results for the unrealistic $\Delta C_p = +13$) and 10⁶⁶–10⁷¹ m⁻³·s⁻¹ for the measured thermodynamic data, are many orders of magnitude *higher* than the theoretical value of 10⁴¹ m⁻³·s⁻¹.

When the arbitrary (too high) value of +13 J·mol⁻¹·K⁻¹ is used for ΔC_p , the value of log₁₀ A obtained is 57–58 for the three different sets of nucleation data, still much higher than the theoretical value.

If the Hoffman expression (eq. (10)) is used for ΔG , the ln($I\eta/T$) versus 1/ $\Delta G^2 T$ plots are *not* straight lines.

Rowlands and James [14], using the nucleation data of James [11] and the viscosity data of Matusita and Tashiro [10], obtained a value of 190 mJ·m⁻² for σ and log₁₀ $A = 62$ using the JANAF thermodynamic data, and $\sigma = 197$ mJ·m⁻² and log₁₀ $A = 60$ using Takahashi and Yoshio's thermodynamic data. Neilson and Weinberg [15] in their analysis of the same nucleation and viscosity data, obtained very similar values for σ and A . In both studies, however, a marked departure from linearity was observed in the ln($I\eta/T$) vs. 1/ $\Delta G^2 T$ plots at lower temperatures, particularly at 440°C and below. It is now clear that this effect may be explained to a large extent by the use of the viscosity data of Matusita and Tashiro [10]. When the viscosity data obtained in the present work are used in conjunction with the nucleation rates of James [11] the linearity is maintained over a wider range of temperatures. This is shown in fig. 7 and applies also to plots, which are not shown here, using the ΔG data of [12] or [13]. The presence of some experimental points lower than the straight line may be attributed to errors in the viscosities or nucleation rates at the lowest temperatures. However, this is not certain and the departure from linearity still present at the lowest temperatures may be a real effect. Further experimentation should resolve this question.

As mentioned previously, the viscosities determined by Matusita and Tashiro [10] were lower than in the present work, although nominally the glasses were both of the same lithium disilicate (LS₂) composition. The glass in the present work was close to the exact LS₂ composition and made from very pure starting materials. The glass of Matusita and Tashiro may have differed from ours in its base composition or in its impurity levels. One possibility is that it had a much higher water content.

6.2. BaO·2SiO₂ glasses

Unlike the lithium disilicate glass there are no detailed thermodynamic data available for the stoichiometric BS₂ glass, apart from the heat of fusion [38]. Eqs. (8) and (9) were used for the calculation of ΔG , in eq. (8) the specific heat difference between crystal and glass, ΔC_p , being assumed to be constant and similar to the values of ΔC_p for Na₂O·2SiO₂ and Li₂O·2SiO₂ [38]. The

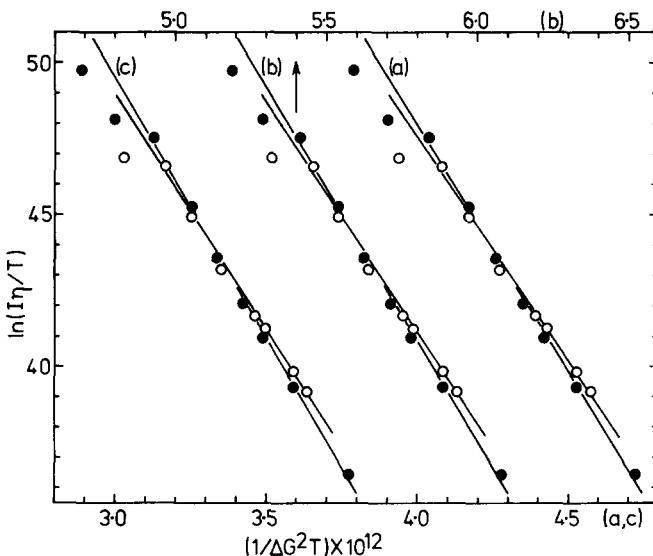


Fig. 8. $\ln(I\eta/T)$ vs. $1/\Delta G^2 T$ for $\text{BaO} \cdot 2\text{SiO}_2$ glasses, using ΔG calculated from eq. (8) with $\Delta H_f = 37.5 \text{ kJ} \cdot \text{mol}^{-1}$, $T_m = 1693 \text{ K}$ and (a) $\Delta C_p = 0$, (b) $\Delta C_p = -12 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$, and (c) $\Delta C_p = 12 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ (see table 7). Nucleation rates from present work (\circ) and from James and Rowlands [28] and Rowlands [29] (\bullet). η in $\text{Ns} \cdot \text{m}^{-2}$, ΔG in J mol^{-1} , T in K .

viscosity values, obtained from the Fulcher equation for the low temperature data, and the measured crystal nucleation rates in glasses 33.2C and 33.3A (this work) and in the glass B6 used by James and Rowlands [28], were utilized to test the classical nucleation theory.

Fig. 8 shows the $\ln(I\eta/T)$ versus $1/\Delta G^2 T$ plots of glasses 33.2C, 33.3A and B6. Table 7 shows the parameters employed in the construction of the plots of fig. 8. As in the case of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, a good linearity of the plots is obtained, only the points at the lowest temperatures, which are probably underestimated due to transient effects, departing from the straight lines. The values of interfacial energy and pre-exponential constant obtained from these plots are shown in table 7.

As for the LS_2 glasses, σ does not depend strongly on the nucleation data or on the thermodynamic values used in the analysis. The pre-exponential constant A depends strongly on ΔG but not on the nucleation data used. Using $\Delta C_p = 0$ and -12 , the experimental values of $131\text{--}137 \text{ mJ} \cdot \text{m}^{-2}$ for σ are somewhat higher than the value of $114 \text{ mJ} \cdot \text{m}^{-2}$ obtained from the empirical equation given in ref. [10]. The experimental values of A are from 15 to 28 orders of magnitude *higher* than the theoretical value of $10^{41} \text{ m}^{-3} \cdot \text{s}^{-1}$. Even when the unrealistic (too high) value of $+12 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is used for ΔC_p , the value of A obtained, $10^{51}\text{--}10^{53} \text{ m}^{-3} \cdot \text{s}^{-1}$, is 10 to 12 orders of magnitude higher than the theoretical value.

As in the case of LS_2 glasses, when the Hoffman expression (eq. (10)) is used for ΔG , the $\ln(I\eta/T)$ vs. $1/\Delta G^2 T$ plots are *not* straight lines.

Table 7

Experimental parameters obtained from the analysis of nucleation rates in $\text{BaO}\cdot 2\text{SiO}_2$ glasses

	Eq. (8) ($\Delta C_p = 0$)	Eq. (8) ($\Delta C_p = -12$)	Eq. (8) ($\Delta C_p = 12$) *
<i>Nucleation data of this work</i>			
$\log_{10} A (\text{m}^{-3} \cdot \text{s}^{-1})$	56	65	51
$\sigma (\text{mJ} \cdot \text{m}^{-2})$	131	133	134
<i>Nucleation data of James and Rowlands [28]</i>			
$\log_{10} A (\text{m}^{-3} \cdot \text{s}^{-1})$	58	69	53
$\sigma (\text{mJ} \cdot \text{m}^{-2})$	136	137	138

$$\log_{10} \eta = 1.83 + 1701.9/(T - 794.6); \eta (\text{Pas}), T(\text{K})$$

ΔG given by eq. (8) with $\Delta H_f = 37.5 \text{ kJ} \cdot \text{mol}^{-1}$,

$T_m = 1693 \text{ K}$, $\Delta C_p = 0, -12, +12, (\text{J} \cdot \text{mol}^{-1} \text{K}^{-1})$.

* The value of $+12 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$ is an arbitrary (too high) value chosen to test the sensitivity of A and σ to the magnitude of the thermodynamic driving force ΔG used in the analysis.

James and Rowlands [28] did not have viscosity data for their BS_2 glass and were not able to obtain the pre-exponential factor A . However, the experimental value of σ was $132 \text{ mJ} \cdot \text{m}^{-2}$, in good agreement with the values obtained here.

It should be emphasized that for barium disilicate more accurate thermodynamic data are required if the nucleation theory is to be tested with greater certainty. This applies in particular to the determination of the parameter A and its comparison with theory. However, it should also be pointed out that the large discrepancy in A (15–28 orders of magnitude) between theory and experiment was very similar for both the $\text{BaO}-\text{SiO}_2$ and $\text{Li}_2\text{O}-\text{SiO}_2$ systems and, in the latter system, reliable thermodynamic data were available. In the only other work where viscosity, thermodynamic and nucleation data were available for the *same* glass, carried out by Gonzalez-Oliver and James [17], an even larger discrepancy between theory and experiment was observed.

A more general problem is the uncertainty of the assumption that the atomic transport or diffusion process required for nucleation is closely related to the process of viscous flow. Turnbull and Cohen [39] suggested that for the crystallization of network liquids, interatomic bonds in the network must be broken. As interatomic bonds must be broken for viscous flow or self-diffusion, the activation energy for these processes must be of similar magnitude. One justification for the procedure of identifying the activation enthalpy for diffusion (ΔH_D) with the activation enthalpy for viscous flow (ΔH_η) is that the diffusion coefficients calculated from measured viscosity values using the Stokes–Einstein equation have been found to agree with measured values for the diffusion of oxygen in silicate glasses to within an order of magnitude [40]. Also, the apparent activation enthalpies ΔH_D for diffusion of oxygen were close to those of viscous flow for three different silicate glasses, and increased with falling temperature in the transformation range [40].

7. Discussion

Several explanations readily come to mind which might account for the large discrepancy between the theoretical and experimental pre-exponential factors.

7.1. Non-steady state nucleation

Transient effects could cause some underestimation of I at the lowest temperatures used. This would affect the linearity of the plot at these temperatures. However, transient effects were negligible at higher temperatures above the maximum in the nucleation rate versus temperature curve. So, over most of the temperature range, transient effects would not affect the slope of the $\ln(I\eta/T)$ vs. $1/\Delta G^2 T$ plots, and the value of the pre-exponential A determined from them.

7.2. Possibility of heterogeneous nucleation

It is unlikely that the disagreement can be attributed to heterogeneous nucleation. The high undercoolings below the liquidus necessary to observe internal nucleation of crystals and the experimental evidence presented by James et al. [9] strongly suggest that a homogeneous nucleation mechanism is predominant in LS_2 glasses. Furthermore, even using the experimental nucleation data of several investigators made no significant difference in the values of the pre-exponential A .

Let us now consider the possibility of a heterogeneous catalyst distributed throughout the supercooled liquid or glass. Comparison of equations describing homogeneous and heterogeneous nucleation rates shows that the pre-exponential factors are approximately in the ratio $n_v : n_h$, where n_v represents the number of formula units of the nucleating component per unit volume of liquid (homogeneous nucleation), and n_h the number of formula units of the nucleating component in contact with the catalyst surface per unit volume of liquid (heterogeneous nucleation). In most cases $n_h \ll n_v$, therefore according to theory the pre-exponential factor for heterogeneous nucleation will be many orders of magnitude less than that for homogeneous nucleation. So, there is an even greater discrepancy between the heterogeneous nucleation theory and experiment.

7.3. Experimental errors in the nucleation rates

Measurement errors do exist and probably in part account for the differences in the results obtained by several authors for nominally the same glass composition. One source of errors is the possible dissolution of nuclei during the growth (development) treatment mentioned previously. However, James [7,11] and Kalinina and coworkers [41–43] have investigated nuclei dissolution

and have shown that the effects on measured steady state nucleation rates are negligible provided the nucleation temperature is sufficiently high (i.e. usually not too far below the maximum nucleation rate temperature) and the development temperature is not too high. These conditions certainly applied in the present study. Another source of error is the stereological effect also discussed earlier. This would cause a small systematic underestimation in the nucleation rates.

It should be stressed, however, that the systematic errors introduced from these two sources are very small in relation to the large discrepancy in the pre-exponential factor A observed between theory and experiment. Furthermore, the above effects would tend to produce an underestimate in the experimental nucleation rates. Thus, if anything, disagreement with theory would be *increased* if perfectly accurate data were used.

8. Summary and conclusions

An experimental test of the classical nucleation theory was performed with $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{BaO} \cdot 2\text{SiO}_2$ glasses. New data for nucleation rates and viscosities were obtained using glasses in which special efforts were made to minimise impurity levels.

Apart from the present results, several authors have measured the crystal nucleation rates in $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glasses, and thermodynamic data were available from the literature. The test for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ was carried out with the viscosity results obtained in this work and combinations of nucleation and thermodynamic data from different sources. The experimentally determined values of interfacial energy σ were not strongly dependent on which combination of data was used. The pre-exponential factor A , however, was strongly dependent on the thermodynamic data, i.e. $10^{63} \text{ m}^{-3} \cdot \text{s}^{-1}$ and $10^{71} \text{ m}^{-3} \cdot \text{s}^{-1}$ for calculated and measured values of thermodynamic driving force, respectively, using the nucleation data of the present work. These values are much *higher* than the theoretical value of $10^{41} \text{ m}^{-3} \cdot \text{s}^{-1}$. The experimentally determined values of σ , $198\text{--}209 \text{ mJ} \cdot \text{m}^{-2}$, are in reasonable agreement with the value of $209 \text{ mJ} \cdot \text{m}^{-2}$ calculated from the empirical equation given in [10].

For the $\text{BaO} \cdot 2\text{SiO}_2$ glass crystal nucleation rates obtained in this work and those given in [28,29] were used in conjunction with the viscosity data obtained here. For this glass, no thermodynamic data are available in the literature, apart from the measured heat of fusion. Therefore, calculated free energies were used. Again, the experimental values of the pre-exponential constant depended strongly on the thermodynamic values used, and varied from 10^{56} to $10^{69} \text{ m}^{-3} \cdot \text{s}^{-1}$. The experimental values of interfacial energy, $131\text{--}137 \text{ mJ} \cdot \text{m}^{-2}$, were somewhat higher than the value of $114 \text{ mJ} \cdot \text{m}^{-2}$ calculated from the empirical equation given in [10].

For both $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{BaO} \cdot 2\text{SiO}_2$ glasses the temperature dependence of nucleation rates was satisfactorily described by the classical theory for a

wide range of temperatures. Improved agreement with theory compared with previous work was found for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ below 445°C. This was a result of using the new viscosity data in the analysis.

Several possible reasons for the discrepancy in the pre-exponential constants between theory and experiment were discussed including transient nucleation effects, experimental errors in the nucleation rates and the possibility of heterogeneous nucleation. It was concluded that none of these could account for the observed discrepancy in the values of A .

A possible explanation for the discrepancy may be the non-validity of the Stokes–Einstein relation between diffusion coefficient and viscosity, i.e., the assumption in the analysis that the kinetic barrier to nucleation is identical to that for viscosity may be incorrect. Another possible explanation is some error in the free energy (ΔG) values used in the analysis of nucleation rates. However, this seems unlikely since the discrepancy occurred even for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glasses, where apparently accurate thermodynamic data were available from direct experimental measurements.

If the thermodynamic data are accurate and the Stokes–Einstein relation is accepted then it seems that the classical theory and the assumptions therein require re-examination. One assumption usually made is that the interfacial energy σ is independent of temperature. However, a temperature dependent interfacial energy, as discussed by other authors, [14,44] is one possible way of accounting for the discrepancy in the pre-exponential factors. This possibility has recently been discussed in detail by James [45].

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