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First Measurements of Time-Dependent Nucleation as a Function of Composition

in Na$_2$O.2CaO.3SiO$_2$ Glasses

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Abstract

The first measurements in any system of the composition dependence of the time-dependent nucleation rate are presented.   Nucleation rates of the stoichiometric crystalline phase, Na$_2$O.2CaO.3SiO$_2$, from quenched glasses made with different SiO$_2$ concentrations were determined as a function of temperature and glass composition. A strong compositional dependence of the nucleation rates and a weak dependence for the induction times are observed. Using measured values of the liquidus temperatures and growth velocities as a function of glass composition, these data are shown to be consistent with predictions from the classical theory of nucleation, assuming a composition-dependent interfacial energy.

1. Introduction

For most phase transformations, the compositions of the initial and final phases differ. Though precipitate growth under these circumstances has been well-studied, compositional effects on the nucleation rate are less well understood. The few existing experimental studies on undercooled metallic liquids[1] suggest that changes in the driving free energy, ΔG_V, with composition are primarily responsible for the observed changes in the nucleation rate. A similar conclusion can be drawn from nucleation rate studies in some pseudo-binary silicate glasses. The crystal nucleation rate in $Na_2O.BaO.SiO_2$, for example, peaks at a composition near the stoichiometric composition $BaO.SiO_2$, decreasing slightly on either side of the ideal composition as the liquidus temperature decreases[2]. Similar trends were reported for $Li_2O.CaO.SiO_2$ [3] and $Li_2O.2SiO_2.BaO.2SiO_2$ [4] glasses.

It is unlikely, however, that changes in the volume free energy will dominate the nucleation behavior in all cases. Diffusion in the initial phase, species-dependent cluster interfacial attachment frequencies, and a compositional dependence of the interfacial free energy could be more important for glass devitrification and solid state precipitation in some cases. Studies of the steady state nucleation rate in $Na_2O.2CaO.3SiO_2$ glasses, for example, which crystallize polymorphically (*i.e.* with no composition change between the initial and final phases) at the stoichiometric composition, show significant changes in the nucleation rate with relatively small changes in SiO_2 concentration [5,6]. Based on measurements of the liquidus temperature, Gonzalez-Oliver and James argued that the observed changes in nucleation rate were kinetic in origin, arising from the changes in the

atomic mobility. Though measurements of the time-dependent nucleation rate provide additional information about the cluster evolution underlying nucleation behavior and reflect directly the effects of the atomic mobility [7], no studies of the time-dependent nucleation rate as a function of composition exist. To investigate the nucleation behavior more deeply, we therefore present the first measurements of the time-dependent nucleation rate as a function of composition in any system. These data demonstrate that changes in the steady state nucleation rate in $Na_2O.2CaO.3SiO_2$ glasses as a function of SiO_2 composition arise from changes in the interfacial free energy and not from changes in the atomic mobility.

2. Experimental Techniques

Glasses of composition near the stoichiometric composition $Na_2O.2CaO.3SiO_2$ were prepared with varying amounts of SiO_2. To most easily indicate the amount of silica used to produce the glass, the glass compositions will be written as $(Na_2O.2CaO)_{(1-x)}(SiO_2)_x$; in this notation, $x=0.5$ represents the stoichiometric glass. All glasses were prepared by melting mixtures of Na_2CO_3, $CaCO_3$ and SiO_2 in the appropriate amounts in a platinum crucible. The samples were well mixed and held at $1500^{\circ}C$ for 3 hours to ensure melt homogeneity. Glasses were quenched by pressing the liquid between two stainless steel plates. All glasses were prepared and stored under identical conditions to minimize water contamination.

To ensure the absence of crystallization, as-quenched glasses were examined by x-ray diffraction using a Siemens type-F goniometer in the Bragg-Bratano geometry and Cu-Kα radiation. X-ray diffraction studies were made from partially devitrified glasses to establish that nucleation measurements were made for primary crystallization to the stoichiometric phase. Transmission electron microscopy (TEM) investigations of the microstructures and compositions of the fully vitrified and partially devitrified glass samples were made using a JEOL 2000-FX TEM equipped with an energy dispersive x-ray spectrometer (EDX) for compositional studies. Scanning electron microscopy (SEM) studies were made using an Hitachi 30 kV SEM, also equipped with EDX.

The liquidus temperatures of the glasses were determined by differential thermal analysis (DTA) using a Perkin-Elmer DTA-1700 system. Platinum cups were used for the sample; the melting point of copper (chosen to be near the transformation temperatures

for the silicate glass), held in an alumina reference pan to avoid alloying, provided a calibration of the temperature scale during each scan. Small offsets in temperature arising from the use of different sample and reference pans were determined separately and were used to correct the experimental data.

Nucleation data were obtained by first annealing samples of the quenched-glass for different times at temperatures from 585°C to 631°C, the range over which the steady state nucleation rate is large. The nuclei formed were grown to a large size for observation by optical microscopy by a subsequent anneal at 700°C for 5-10 minutes. At this growth temperature the nucleation rate is sufficiently low that no new nuclei appeared during the growth treatment. The annealed samples were polished to remove the surface crystallization layer and the number of crystals in the sectioned volume was determined using a Leitz-Wetzlar-Metallux optical microscope at a magnification of 500X. The average number of nuclei per volume was obtained from the micrograph using standard statistical stereological techniques to take account of the finite crystallite sizes [8]. Estimates of the crystal growth rates as a function of temperature between 630°C and 705°C were obtained by annealing samples of the as-quenched glass for different times at a given temperature. Following each anneal, the samples were polished and examined by optical microscopy. The diameter of the largest crystallite was assumed to represent the growth of a crystallite for the total time annealed.

3. Results

Samples were prepared over a wide range of SiO_2 ($0.4 < x < 0.6$). Glass formation became noticeably difficult as the SiO_2 concentration decreased below that of the stoichiometric glass. It was not possible to obtain complete vitrification for $x < 0.47$ and quenches from melts containing less than 40% SiO_2 were entirely crystalline. In contrast, samples containing more SiO_2 than the stoichiometric glass were easily quenched to a fully amorphous phase. Within the glass forming range, nucleation rates were measured in glasses containing SiO_2 concentrations $0.494 < x < 0.53$. Due to the high density of nuclei produced, accurate measurements of the nucleation rate could not be made in glasses with SiO_2 concentrations less than 49.4%. The upper limit of 53% was chosen to ensure that the stoichiometric phase remained the primary crystallizing phase. This was verified by TEM and x-ray diffraction studies of the partially devitrified glasses.

Figure 1 shows a DTA scan from room temperature through the melting temperature for an as-quenched glass with $[SiO_2] = 0.52$ (top curve). The temperature range of the scan has not yet been corrected to the melting point of the copper standard. A subsequent scan of the same sample is shown in the lower curve. The behavior observed is representative of that found for all glasses used for the nucleation measurements. The exothermic peak at 726°C in Fig. 1 corresponds to the devitrification of the glass to the stoichiometric crystal phase. The two exothermic peaks between 1050°C and 1100°C are due to the melting of copper in the reference pan. The first peak likely corresponds to the liquidus temperature for copper containing some oxygen; based on the temperature dependence of the melting point, [O] is ≈ 0.001 at.% [14]. Some

oxygen contamination was unavoidable, even while maintaining a flow of argon through the sample and reference chambers. Fortunately, the presence of this small amount of oxygen does not effect the devitrification behavior of the glass studied. The second peak corresponds to the melting of pure copper. The small endotherm near 1250°C corresponds to the melting of the silicate glass sample. The weaker signal for melting in the as-quenched sample (top curve) is likely due to poor thermal contact between the sample and the Pt sample holder. Though sample contact can often be improved by surrounding the DTA samples with Al_2O_3 powder, this was avoided here since Al_2O_3 tends to alloy with the sample, making subsequent scans impossible. An improved resolution of this peak is observed in subsequent scans of the same sample, reflecting a better thermal contact after melting. Because of the improved signal, all estimates of the liquidus temperatures were obtained from the second DSC scans, though the values obtained from both scans often agreed to within +-1% after corrections were made to the melting temperature of the copper standard. The presence of a devitrification peak in the second scan indicates that for this sample some glass formation was possible at the cooling rate attained in the DTA. Glass formation became more difficult with decreasing SiO_2, reflecting higher nucleation rates.

Figure 2 shows x-ray diffraction patterns taken from a glass that had been prepared at the stoichiometric composition and subsequently crystallized. As indicated, the prominent peaks index well to a tetragonal phase with a=0.751 nm and c=0.740 nm, which is in disagreement with earlier suggestions that the stoichiometric phase is likely cubic[9]. Figure 3 shows the x-ray diffraction patterns for the crystallized as-quenched

glasses for all compositions studied. In all cases, the x-ray peaks can be indexed to the stoichiometric phase, indicating that the primary nucleation of this phase is measured as a function of composition.

The liquidus temperatures measured by DTA as a function of composition are shown in Fig. 4. As discussed earlier (Fig. 1), the peak breadth and small enthalpy made the determination of the melting point difficult. The estimated uncertainties are indicated by the error-bars for the data points. The data clearly show, however, that the liquidus temperature increases slightly with increasing SiO_2 concentration over the range of glass compositions studied. As will be discussed later, this cannot explain the changes observed in the nucleation rates as a function of composition.

Figure 5 shows the number of nuclei generated as a function of annealing time for three annealing temperatures, 595°C, 607°C and 620°C, and for three sample compositions, x = 0.494, 0.5 and 0.506. The behavior observed is representative of that for all compositions and annealing temperatures. The rate of nuclei production is initially low but increases with time. For long annealing times, the number of nuclei increases linearly with time, consistent with a constant nucleation rate. The slope of this linear region is the steady state nucleation rate. The induction time for nucleation is defined by the intercept of the extrapolated linear region to the time axis. As demonstrated in fig. 6, the steady-state nucleation rates and induction times for the stoichiometric glass, $Na_2O.2CaO.3SiO_2$, measured here compare well with values reported previously by Kalinina *et. al.* [10] and Deubener *et. al.* [11]. That they are in disagreement with the data reported by Gonzalez-Oliver *et al.* [5,6] is not surprising. Those data are only

estimates, based on the number of nuclei obtained after annealing for a constant time at each temperature; proper account was not taken of the time dependence of the nucleation rate.

Figure 7 shows the measured steady state nucleation rates and induction times for as-quenched glasses of different SiO_2 concentration. The lines are a fit to the classical theory assuming a compositional dependence for the interfacial energy (*c.f.* Sec. 4). A decreasing nucleation rate and an increasing induction time with increasing $[SiO_2]$ are observed. The temperatures for maximum nucleation rate are approximately independent of the SiO_2 composition of the glass. Interestingly, the change in the nucleation rate with composition is more than three orders of magnitude greater than the change in the induction time. The measured macroscopic growth velocities for glasses of different composition are shown as a function of temperature in fig 8. As for the induction time, the compositional dependence of the growth rate is small, decreasing only slightly with increasing $[SiO_2]$

4. Discussion

Changes in the nucleation rate with composition are often explained by changes in the work of cluster formation[13]. Based on the thermodynamic theory of fluctuations, the steady state nucleation rate for a partitioning system is expected to have the form:

$$I^s = A^* \exp\left(-\frac{W_{a,b}^*}{k_B T} \right) \qquad (1$$

where the pre-term A^* is a function of the interfacial atomic mobilities. k_B is Boltzmann's constant and the work of cluster formation, W_{ab}^*, is

$$W_{a,b}^* = -n\left|\Delta G_{a,b}^v\right| + \alpha\, n^{2/3}\, \sigma \qquad (2$$

Here σ is the interfacial free energy, n is the total number of atoms in the cluster and $\Delta G_{a,b}^v$ is the volume free energy change on solidification of the crystalline phase. Assuming the Turnbull approximation, $\Delta G_{a,b}^v$ should be a linear function of the melting temperature, T_m,

$$\Delta G_{a,b}^v = \frac{\Delta H_f^v}{T_m}\,(T - T_m) \qquad (3$$

where ΔH_f is the enthalpy of transformation. Since there is little change in the melting temperature with [SiO_2], the change in the driving free energy must be small, leading to only a small expected change in the nucleation rate with composition. Further, for a fixed nucleation temperature, small increases with increasing [SiO_2] are expected corresponding to the increasing liquidus and hence an increasing driving free energy for nucleation. The observed large decrease in the nucleation rate with increasing [SiO_2] is therefore unexplained.

Based on their initial studies, Gonzalez-Oliver and James [5,6] suggested that changes in the nucleation rate in these glasses arose from composition-induced changes in the bulk diffusion coefficient. Both the pre-factor for the nucleation rate, A*, and the growth velocity are proportional to the atomic mobility at the interface, which is generally taken to follow the bulk diffusion coefficient, D. Given the arguments presented against thermodynamic contributions, it is unclear how the much larger changes in the nucleation rate than for the growth velocity can be explained. Further, the induction time, which is a more direct measure of the interfacial mobility governing the nucleation rate also changes little, similar in magnitude to the changes observed in the growth velocity.

These arguments are made more clear in fig. 9. In fig. 9.a, measured steady state nucleation rates for glasses of different composition are compared with values calculated from eq. (1). Values for $\Delta G^v_{a,b}$ were estimated from the measured changes in liquidus temperature as a function of composition (Fig. 4), using eq. (3). The atomic mobility, proportional to $6D/\lambda^2$ with λ equal to the average jump distance, was estimated from the diffusion coefficient obtained from the measured growth velocity using

$$u = C\left(\frac{3\overline{v}}{4\pi}\right)^{1/3} \frac{16D}{\lambda^2} \sinh\left(\frac{\Delta G'}{2k_B T}\right) \tag{4}$$

where $\Delta G'$ is the free energy change per atom ($\Delta G^v = \Delta G / \overline{v}$) and $\overline{v}$ is the molecular volume. C is a constant (between 1 and 10) that likely reflects changes in the growth mechanism as a function of cluster size [16].

The time-dependent nucleation rate was computed numerically following a procedure that has been described elsewhere [7]. By this method, both contributions to the

measured induction time are included, *i.e.* the stochastic movement of clusters through the region near the critical size at the nucleating temperature and the growth of those clusters to the critical size at the growth temperature. The parameters used are listed in Table I. Diffusion coefficients were estimated from the measured growth velocity. These values, and those obtained earlier by James *et al.*, were fit to a Fulcher-Vogel temperature dependence [7,15]

$$D = D_o \, T \exp\left(-\frac{B}{T - T_o} \right) ,$$

(5

assuming an 80% weighting for the data obtained here. A linear temperature dependence was assumed for the interfacial energy

$$\sigma = \sigma_o + \sigma_1 T .$$

(6

Though precise measurements of the crystallization enthalpy by DTA were not possible, little change was observed. For these calculations, then, it was taken to remain unchanged with changing [SiO_2] for the glass.

While the calculated and measured values for I^s are in reasonable agreement for the stoichiometric glass, the computed values progressively rise above the measured data with increasing [SiO_2] (fig. 9.a). As shown in fig. 9.b, the agreement between the measured and calculated induction times is much better, suggesting that the assumed mobility is correct.

The classical theory of nucleation is an interface limited theory, focusing attention on the process by which monomers are incorporated into the growing cluster. For partitioning systems, however, it is possible that the rate at which monomers can diffuse to the cluster interface can become competitive with the interfacial attachment process, linking

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these two stochastic fluxes. This problem was first examined by Russell[16], who demonstrated that the steady state nucleation rate should decrease significantly due to the competitive processes of bulk diffusion and interfacial attachment. Recent computer calculations made by us for nucleation in a partitioning system[17], based on a similar model to that proposed by Russell, predict a greater change in the nucleation rate than in the induction time, in qualitative agreement with the experimental data. It is difficult, however, to understand why the measured steady state nucleation rate would continue to increase as the $[SiO_2]$ concentration fell below that of the stoichiometric glass. A symmetric behavior about $x = 0.5$ is expected instead.

Small changes in the interfacial free energy with composition are the most likely reason for the observed changes in the time-dependent nucleation rates. The nucleation rate is extremely sensitive to the interfacial energy, depending exponentially on σ^3, while the induction time depends only linearly on σ[13]. The calculated values for σ required to produce agreement with the magnitude of the steady state nucleation rate as a function of composition are listed in Table I. Calculations of I^s as a function of temperature for these values for σ are in good agreement with the experimental data (Fig. 7.a); in agreement with the data, only a small change in the temperature of the maximum rate is predicted. The agreement with the experimental data for the induction time remains good when the compositional dependence for σ are used because of the weak dependence of θ on the interfacial free energy.

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5. Conclusions

In summary, we have presented the first measurements of the composition dependence of the time-dependent nucleation rate in any system. The temperature dependencies of the nucleation rates and the induction times of the stoichiometric phase, $Na_2O \cdot 2CaO \cdot 3SiO_2$, were measured as a function of the $[SiO_2]$ for the as-quenched glasses. The growth velocities and the liquidus temperatures were also measured as a function of temperature in all glasses.

The nucleation rates decreased significantly with increasing SiO_2, while only small changes were observed in the growth velocities and induction times. These data are inconsistent with expectations from a composition dependence of the volume free energy (estimated from changes in the liquidus temperature) or a change in atomic mobility (estimated from changes in the growth velocity). An extension of the classical theory for nucleation that takes account of the linked fluxes of interfacial attachment and bulk diffusion for non-polymorphic transformations is also not adequate to describe the data quantitatively. Changes in the interfacial free energy, σ, give the best agreement with the measured nucleation and growth velocity data. To our knowledge, this is the first evidence for a composition dependence for values of σ between the liquid/glass and crystal phases.

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Table I

Parameters used for Nucleation Fits

SiO₂ Concentration	49.4%	50.0%	50.6%	52.0%	53.0%
T_m (K)	1558.9	1563	1568.1	1570.9	1573.9
ΔS (J/mole)	56.386	56.238	56.055	55.955	55.849
σ_0(Jm^{-2})[*]	0.07707	0.08891	0.07376	0.06415	0.07232
σ_T (Jm^{-2}K^{-1}) (x 10^5)[*]	5.38258	4.15444	6.12572	7.459245	6.73961
B (K)[**]	1680.27	1680.27	1680.27	1680.27	1680.27
T_0 (K)[**]	737.44	737.44	737.44	737.44	737.44
D_0 (m^{-2}s^{-1}K^{-1}) (x 10^{21})[**]	1.732	1.521	1.370	0.876	0.776
T_{peak} (K)[***]	865	867	863	860	861

[*]Interfacial free energy - $\sigma = \sigma_0 + \sigma_T T$

[**]Diffusion coefficient - $D = D_0 T \exp\left(-\dfrac{B}{T-T_0}\right)$

[***]Calculated Peak Nucleation Temperatures

Figure Captions

Fig. 1:   Typical DTA scan showing peaks corresponding to glass devitrification and melting for $(Na_2O.2CaO)_{48}(SiO_2)_{52}$. The top curve is a DTA scan on the as-quenched glass; the bottom curve is a second scan of the same sample. (1) corresponds to glass crystallization; (2) is the melting point of the copper with oxygen in solution; (3) is the melting point of pure copper and (4) is the melting point of the glass. The melting peaks of Cu and Cu-O are opposite to that of the glass because the copper is located in the reference pan of the DTA.

Fig. 2:   X-ray diffraction pattern from the crystal phase resulting from devitrification of the stoichiometric glass, $(Na_2O.2CaO)_{50}(SiO_2)_{50}$. Prominent peaks have been indexed.

Fig. 3:   X-ray diffraction patterns from devitrified glasses of composition $(Na_2O.2CaO)_{(1-x)}(SiO_2)_x$. (a) x=0.494, (b) x=0.5, (c) x=0.506 (d) x=0.52 and (e) x=0.53.

Fig. 4:   Liquidus temperatures as a function of the SiO_2.

Fig. 5: Comparison of the temperature dependence of the steady state nucleation rate, I^s, (a) and the induction time, θ, (b) for the stoichiometric glass with previously reported values: ■ - (this work); ● - ref. [10]; ▲ - ref. [11]; ▼ - ref. [5]. The solid straight lines are a fit to the classical nucleation theory. Information was insufficient to fit the data from [5]; the dotted lines are included as a guide to the eye.

Fig. 6: The measured number of nuclei/mm^3 vs. time for three different glass compositions (■ - [SiO$_2$] = 0.494; ● - [SiO$_2$] = 0.5; ▲ - [SiO$_2$] = 0.506) for three isothermal annealing temperatures: (a) T = 595°C; (b) T=607°C, and (c) T=620°C. The solid line is a fit to the linear portion of the curve.

Fig. 7: Crystal steady state nucleation rates (a) and induction times (b) as a function of temperature for glasses of different composition: ■ - [SiO$_2$] = 0.494; ● - [SiO$_2$] = 0.5 ▲ - [SiO$_2$] = 0.506; ▼ - [SiO$_2$] =0.52; ◆ - [SiO$_2$] = 0.53. The direction of increasing [SiO$_2$] is indicted by the arrows. Uncertainties in (a) are comparable to the symbol sizes. The solid lines through the points are a fit to the steady-state nucleation rates assuming a composition-dependent interfacial energy (computed data are given in Table 1).

Fig. 8: Crystal growth rate as a function of temperature in glasses of different

composition: ■ - $[SiO_2] = 0.494$; ● - $[SiO_2] = 0.5$; ▲ - $[SiO_2] = 0.506$; ▼ - $[SiO_2]$

$= 0.52$; ◆ - $[SiO_2] = 0.53$.

Fig. 9: Comparisons between calculated and measured values for the steady state

nucleation rates (a) and induction times (b) as a function of temperature.

Calculations were made by estimating the compositional dependence of the

free energy from measured changes in the liquidus temperature and the

dependence of the atomic mobility from measured changes in the growth

velocity. Glass compositions: (1) ■ - $[SiO_2] = 0.494$; (2) ● - $[SiO_2] = 0.5$; (3)

▲ - $[SiO_2] = 0.506$; (4) ▼ - $[SiO_2] = 0.52$; (5) ◆ - $[SiO_2] = 0.53$. All scales for I^s

(in $mm^{-3}s^{-1}$) are from 0.01 to 600; all scales for θ (in min) are from 5 to 100.

Peak Height (arb. units)

Temperature (°C)

Figure: Plots of Nuclei (per mm³) versus Annealing time (min) for three temperatures: (a) T = 595°C, (b) T = 607°C, and (c) T = 620°C.