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**EARLY STAGE CRYSTALLIZATION KINETICS OF LITHIUM DISILICATE
AND SODIUM SILICATE GLASSES**

by

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ABSTRACT

The formation of metastable crystalline phases in lithium disilicate glass has been a subject of controversy for decades. Here, one aspect of this problem relating to the stability of these non-equilibrium phases when glasses are heated for extended time periods in the nucleation regime is addressed. The results of a systematic experimental investigation on the persistence of metastable phases and the factors that may influence the appearance of such phases, e.g., water content, impurities, glass composition, and glass preparation procedure are presented.

Growth rates of lithium disilicate crystals in lithium disilicate glass are measured as a function water concentration in the glass and of temperature in the deeply undercooled regime. The growth rate data obtained in this work are combined with data reported in the literature and used to assess the applicability of standard models of crystal growth for the description of experimental results over a very broad temperature range.

The reduced growth rate versus undercooling graph is found to consist of three regimes. For undercoolings less than 140°C , the reduced growth rate curve is suggestive of either 2-D surface nucleation or screw dislocation growth. For undercoolings greater than 400°C , the reduced growth rate plot suggests the operative crystal growth mechanism is 2-D surface nucleation, but detailed calculations cast doubt upon this conclusion. In the intermediate undercooling range, there appears to be some sort of transitional behavior for which none of the standard models appear to be applicable. Further, it is observed that small differences in the viscosity data employed can produce enormous differences in the predicted growth rates at larger undercoolings. Results of the kinetic analyses conducted herein seem to indicate that the nature of the kinetic rate coefficient used in the standard growth models may be incorrect.

Nucleation rates of sodium metasilicate crystals in a sodium silicate glass of composition $43\text{Na}_2\text{O}-57\text{SiO}_2$ (mol%) are investigated using the development technique. The results of this study are compared with the nucleation rate results recently obtained for this composition using a novel DTA method. The two techniques are found to agree within experimental error.

INTRODUCTION

Crystallization kinetics of glasses remains an active area of inquiry due to its technological and scientific importance. In the realm of technology, knowledge of crystal nucleation and growth rates in glasses at different temperatures is essential for preparing glass-ceramics, where promoting and controlling nucleation and growth of the desired crystal phases in the desired proportions offers a means of tailoring the properties of the final material. Knowledge of crystallization kinetics is also vital for predicting glass stability in applications where crystallization must be avoided, such as optical fibers, where crystal nucleation and growth would degrade the performance of the material. Understanding transformation kinetics is also important for preparing novel glasses with unique properties, for instance, to aid in determining the quench rate necessary to obtain an amorphous form of a given substance, e.g. metallic glasses.

Glasses that appear to nucleate homogeneously within the volume are usually studied within the realm of the phenomenological theory known as Classical Nucleation Theory (CNT). It is generally presumed that CNT applies if homogeneous conditions are evident. That is, if internal nucleation is observed at relatively large undercoolings, and the equilibrium phase is produced upon transformation. Of the few glass-forming systems that appear to exhibit homogeneous nucleation, lithium disilicate (LS_2) has been the most extensively studied composition. Crystal nucleation in LS_2 glass has received particular attention since it is a pseudo-one-component system, detailed thermodynamic data necessary for quantitative analysis of crystal nucleation rates are available, and also because the lithium disilicate crystal phase is a vital component in many technologically significant glass-ceramics.

LS_2 conforms to the above mentioned criteria, and thus experimental nucleation data for this composition have traditionally been interpreted with respect to CNT. However, as observed in other systems, classical nucleation theory fails to quantitatively predict the experimentally observed nucleation rates in LS_2 glass.

The formation of metastable crystalline phases in glass compositions that appear to initiate crystallization homogeneously offers a possible explanation for the observed discrepancies between theory and experiment and is therefore an issue of considerable scientific importance. Over the past few decades, ample experimental evidence has been provided to support the claim that metastable phases do form during the initial stages of crystallization in compositions near LS_2 . However, the nature of the evidence is such that the role metastable phases play with respect to the nucleation mechanism remains unclear. There is considerable controversy over whether metastable phases form and serve as precursors for the subsequent precipitation of the stable phase, or if precipitation of the stable phase occurs independently of the formation of metastable phases. If the former were indeed the case, then present interpretations of homogeneous crystal nucleation experiments for LS_2 glass would be invalid and experimental results would have to be analyzed anew.

Very recently, a study conducted by James et al. [1] indicated that metastable phases persist in LS_2 glass for long times and could be probed via x-ray diffraction (XRD). Following the progression of the crystallization process via XRD traces, these authors observed the formation of metastable crystal phase(s), and subsequent transformation of these phases to the stable crystal phase. If this is indeed the case for LS_2 , one must consider that complex nucleation paths ubiquitously occur and all existing notions of homogeneous nucleation may have to be revised.

The remarkable findings of James provided the motivation for the first objective of the present work, namely, to determine if XRD is a viable tool for investigating the nature of metastable phases and the role that they play with respect to the nucleation mechanism. To this end, a comprehensive XRD investigation on the persistence of metastable phases in LS_2 glass was conducted.

The second objective of the present work is to assess the crystal growth behavior in LS_2 glass. For systems such as LS_2 , it is generally assumed that the kinetic coefficients for crystal growth and nucleation are identical since the expressions for the respective processes originate from the same set of differential equations. However, one can not experimentally test this assertion in a direct fashion without having nucleation and growth data at the same temperatures. Therefore, it is especially important to examine the crystal growth rates in LS_2 glass in the low temperature region where homogeneous nucleation presumably occurs, and experimental nucleation rate data are available. A second reason for studying crystal growth in this system is the availability of extensive thermodynamic and kinetic data. This feature helps facilitate quantitative comparisons between phenomenological theories of crystal growth and experimental results.

Another interesting question relates to the effect of water concentration in the glass on crystal growth rates. The results of different studies have been somewhat contradictory with respect to the influence of water on crystal growth rates, and it is another objective of this work to reconcile such apparent discrepancies.

The binary sodium silicate glass-forming system is of interest because it is one of the handful of systems which exhibit internal nucleation without the deliberate addition of constituents known as nucleating agents. Although this system is one of the simplest, nucleation rates in these glasses have received scant attention due to problems with glass formation. What makes this system particularly interesting for nucleation study is the fact that the nucleation mechanism changes with composition from internal volume nucleation to heterogeneous surface nucleation. Since it is not well understood why only certain glasses have the ability to nucleate internally, it is of interest to study the nucleation behavior of this system as a function of composition. Further, a former member of our research group proposed a novel differential thermal analysis (DTA) method for determining the temperature dependence of steady-state nucleation rates, and he demonstrated this method for a sodium silicate glass. DTA is a very attractive experimental technique for studying homogeneous nucleation rates in glasses, especially

when one considers the time consuming, labor-intensive nature of traditional methods for obtaining such information. Therefore, the final objective of this work is to test the accuracy and delimit the range of validity of this novel DTA technique.

1. EXPERIMENTAL PROCEDURE

1.1. Glass Preparation

All glasses studied herein were prepared using conventional, melt-quenching techniques.

1.1.1. Lithium Silicate Glasses

Three different batches of the stoichiometric disilicate glass composition (Glasses 1, 2, and 3), and one hyper-stoichiometric glass composition containing 34.5 mol% Li_2O (Glass 4) were prepared in Tucson at the University of Arizona (relative humidity 10-20%). In addition, a hyper-stoichiometric composition containing 33.8 mol% Li_2O (Glass 5) and a sub-stoichiometric composition containing 32.5 mol% Li_2O (Glass 6) were prepared in Brazil at the Federal University of São Carlos (relative humidity 70-80%). Glasses 1-6 were all prepared using standard reagent grade Li_2CO_3 and SiO_2 , and by employing the following general procedure. Glass precursor powders were first weighed and combined into 100-gram batches according to the desired composition. Batched precursor powders were rolled on a ball mill in a glass jar for 3 hours, then transferred into a Pt-10%Rh crucible and melted (in air) at 1350°C for 4 h in an electric furnace. To aid with homogenization, the melts were periodically stirred with a platinum rod. The melts were quenched (in air) rapidly by pressing between steel plates. The resulting glasses were transparent, bubble-free, and in the form of disks generally about 30 mm in diameter and 1 to 3 mm thick. Due to thermal stresses, the as-quenched disks invariably fractured into smaller irregularly shaped pieces upon cooling to room temperature.

The preparation procedure described above was modified slightly for Glasses 2 and 3. Glass 3 was given an additional isothermal sintering step in which the precursor powders were heated at 1000°C for 10 hours prior to melting, and Glass 2 was melted in a fused quartz (SiO_2) crucible rather than a Pt-Rh crucible. Details of the preparation procedure employed for each melt are summarized in Table 3.1.

Table 3. 1 Lithium silicate glass designation number and preparation details

Glass No.	Batch Composition (mole %)	Glass Preparation
1	33.3 Li ₂ O - 66.7 SiO ₂	Raw materials: Reagent grade Li ₂ O and SiO ₂ Melting cond.: 1350°C- 4 hours (in air) Crucible type: Pt-Rh Quench method: Pour & press between steel plates
2	33.3 Li ₂ O - 66.7 SiO ₂	Raw materials: Reagent grade Li ₂ O and SiO ₂ Melting cond.: 1350°C- 4 hours (in air) Crucible type: <i>Fused quartz</i> Quench method: Pour & press between steel plates
3	33.3 Li ₂ O - 66.7 SiO ₂	Raw materials: Reagent grade Li ₂ O and SiO ₂ Melting cond.: 1350°C- 4 hours (in air) Crucible type: Pt-Rh Quench method: Pour & press between steel plates <i>Precursor powders sintered at 1000°C for 10 hours prior to melting</i>
4	34.5 Li ₂ O - 65.5 SiO ₂	Raw materials: Reagent grade Li ₂ O and SiO ₂ Melting cond.: 1350°C- 4 hours (in air) Crucible type: Pt-Rh Quench method: Pour & press between steel plates
5	33.8 Li ₂ O - 66.2 SiO ₂	Raw materials: Reagent grade Li ₂ O and SiO ₂ Melting cond.: 1350°C- 4 hours (in air) Crucible type: Pt-Rh Quench method: Pour & press between steel plates <i>Glass prepared in Brazil at the Federal University of São Carlos (relative humidity 70-80%)</i>
6	32.5 Li ₂ O - 67.5 SiO ₂	Raw materials: Reagent grade Li ₂ O and SiO ₂ Melting cond.: 1350°C- 4 hours (in air) Crucible type: Pt-Rh Quench method: Pour & press between steel plates <i>Glass prepared in Brazil at the Federal University of São Carlos (relative humidity 70-80%)</i>

1.1.2. Sodium Silicate Glasses

Sodium silicate glasses of nominal compositions (in mol%): 49Na₂O-51SiO₂ (W-51%), 47Na₂O-53SiO₂ (W-53%), 45Na₂O-55SiO₂ (W-55%), 43Na₂O-57SiO₂ (W-57%), 41Na₂O-59SiO₂ (W-59%) were provided by a former member of our research group, Takashi Wakasugi, who prepared these glasses for an independent investigation. The sodium silicate glasses were prepared using conventional melt-quenching techniques, and following a procedure similar to that used by the present author for lithium silicate glasses. Analytical grade Na₂CO₃ and SiO₂ precursor powders were first weighed and combined according to the desired composition, then rolled on a ball mill in a glass jar for 2 hours. The batched powders were then transferred to a platinum crucible and melted (in air) at 1250°C for 1 hour in an electric furnace. The melts were periodically stirred with a platinum rod to ensure homogeneity. The melts were quenched (in air) rapidly by pressing between steel plates. The resulting glasses were transparent, bubble-free disks about 3 mm thick. The disks subsequently fractured into smaller pieces of varying sizes due to the thermal stresses incurred upon cooling. All glasses were kept carefully stored in a desiccator prior to use by the present author.

1.2. Chemical Analysis of Prepared Glasses

The chemical compositions of the as-prepared glasses were confirmed either by atomic absorption, or by the use of index of refraction measurements and published data of the index of refraction as a function of composition. As observed by Smith and Weinberg [57], the alkali content of the glass tends to be lower than expected when analyzed via atomic absorption. It has been suggested [115] that this is due to difficulties associated with adequately dissolving the glass completely in solution prior to analysis. Further, when analyzed by atomic absorption the alkali content of the glass is slightly lower, and associated errors slightly larger, than the values obtained when index of refraction measurements are utilized.

Three independent samples from each lithium silicate melt were cut into rectangles approximately 20mm x 10mm using a diamond saw. Samples were then mechanically ground and optically polished (method described in Section 3.9) on both faces. The resulting samples had parallel faces and ranged in thickness between 1.4 and 2.5 mm. For each sample, one of the short edges normal to the faces was polished by hand.

Index of refraction measurements were performed using a Zeiss Abbe-Refractometer, Model A. Since glass samples were transparent, all measurements were made in grazing transmitted light mode, which measures the index of refraction

corresponding to the sodium D line, n_D . A drop of 1-bromonaphthalene was placed on the measuring prism, and the glass sample subsequently positioned on the liquid with the polished edge facing an incandescent light source. The Abbe-Refractometer was calibrated using a standard prior to each measurement.

1.3. Water Concentration Determination

The water concentrations in the as-prepared lithium silicate glasses were measured with the aid of a Fourier Transform infrared spectrometer (Perkin-Elmer FTIR), and utilizing the procedure outlined by Davis et al. [90]. To facilitate comparison, samples from each lithium silicate melt were ground and optically polished to equal thickness (method described in Section 3.9).

Water concentrations of the lithium silicate glasses were obtained using the Lambert-Beer Law:

$$c = 10^6 \frac{A_{3500} M_w}{\epsilon \rho d} \quad (3.1)$$

where c is concentration of structurally-bound hydroxyl, SiOH, nominally taken as H_2O (ppm by weight); A_{3500} is absorbance of the $\sim 3500\text{cm}^{-1}$ peak ($\pm 10\%$) according to [90]; M_w is the molecular weight of water (18.015 g/mol); ϵ is the extinction coefficient of the 3500cm^{-1} peak, here taken as 54 l/mol-cm as per [90]; ρ is the density of the glass, and d is the sample thickness.

In studying the crystal rates of the lithium silicate glass, both the surface and internal growth rates were determined. Therefore, it was deemed unnecessary to attempt to differentiate between bulk and surface water contents.

1.4. Glass Transition Temperature Determination

Differential thermal analysis (DTA) was used to determine the glass transition temperatures, T_g , of the prepared glasses. This method was chosen for T_g determination because it is one of the most common techniques found in the lithium silicate glass literature. Since the measured T_g value of a given glass varies not only with measurement technique, but also with heating/cooling rate utilized, the frequently cited heating rate of $10^\circ\text{C}/\text{min}$. was employed in this work.

DTA was performed using a DuPont Model 1090 DTA with a platinum crucible at a heating rate of $10^\circ\text{C}/\text{min}$. For each lithium silicate melt, DTA traces were obtained from powder-form samples of the as-prepared glasses. The amount of material used varied from 40 to 50 mg. A computer recorded the data, and the glass transition temperature was determined with aid of a software program that determined the onset

point of the endotherm associated with the glass transition (T_g) to an accuracy of $\pm 2^\circ\text{C}$ by method of intersecting tangents.

1.5. Glass Density Measurements

Density measurements were made on multiple samples of each melt. The average density value obtained for each melt was used in the Lambert-Beer Equation (Section 3.3) to calculate the water concentration in the glass. The densities of the prepared glasses were determined by accurately measuring the dimensions of samples with a micrometer and caliper. The glass samples were then weighed using an electronic balance, which enabled measurement to a thousandth of a gram. The ratio of the weight to volume yielded the density (g/cm^3).

1.6. Heat-Treatment Schedule for XRD Investigation of Metastable Phase Formation

Heat-treatments were carried out (in air) in a horizontal tube furnace with a central hot zone constant to within $\pm 1.5^\circ\text{C}$. Samples were placed in a platinum boat and isothermally heated at temperatures between 440°C and 500°C for various times. Table 3.2 details the heat-treatment schedules employed for Glasses 1-6. Portions of selected heat-treated samples were removed and saved for subsequent crystal growth measurements. Heat-treated samples were prepared for XRD analysis as described below.

For Glasses 1 and 2, surface layers of all heat-treated samples were removed by mechanical grinding using the method described in Section 3.9. The remaining interior (bulk) sample materials were then ground into a fine powder using a mortar and pestle. For Glasses 3-6, the surface layer materials of the heat-treated glasses were separated from the interior material (bulk) and saved for independent analysis. This was done by cutting thin layers approximately 0.5 mm thick from (and parallel to) the faces of each sample. The surface layer materials were then mounted on a stainless steel platens, with the external surface crystalline surfaces face down, and mechanically ground using the method described in Section 3.9 until only very thin surface layers ($60 \sim 70 \mu\text{m}$) remained. Prior to XRD analysis, both the surface and bulk materials were ground into fine powders using a mortar and pestle.

Table 3. 2 Heat-treatment schedule for XRD investigation of metastable phase formation in lithium disilicate glass

	Heat-treatment Temperature ($\pm 1.5^{\circ}\text{C}$)	Heat-Treatment Time (hours)
Glass 1	440 $^{\circ}\text{C}$ 454 $^{\circ}\text{C}$ 477 $^{\circ}\text{C}$ 500 $^{\circ}\text{C}$	350, 543 120, 192, 360 120, 168, 288 24, 48
Glass 2	454 $^{\circ}\text{C}$ 477 $^{\circ}\text{C}$ 500 $^{\circ}\text{C}$	120, 360 120, 168, 24
Glass 3	454 $^{\circ}\text{C}$ 465 $^{\circ}\text{C}$	150, 328 168, 240, 288
Glass 4	454 $^{\circ}\text{C}$ 465 $^{\circ}\text{C}$	150, 328, 476 168, 240, 288, 360, 528
Glass 5	454 $^{\circ}\text{C}$ 465 $^{\circ}\text{C}$	120, 168, 240, 288, 360 168, 240, 288, 360
Glass 6	454 $^{\circ}\text{C}$	120, 168, 240, 288, 360

1.7. X-Ray Diffraction (XRD) Measurements

1.7.1. Lithium Silicate Glasses

Four different XRD instruments were used to analyze the heat-treated lithium silicate glasses; three were standard automated instruments, and one was equipped with a rotating anode x-ray source. All standard instruments used $\text{CuK}\alpha$ radiation, and all scans were performed on powdered samples with scattering angle, 2θ , values from 10° to 60° . The scan rates employed, however, differed among the three conventional XRD machines. At the University of Arizona, XRD measurements were performed using a Scintag automated diffractometer and utilizing a step-scan of $0.02^\circ/2$ min. At the Federal University of São Carlos, a step-scan of $0.015^\circ/5$ second counting time was employed. XRD measurements performed at Arizona State University were made with a Siemens (D5000) x-ray diffractometer equipped with a 7° wide position sensitive detector using a scan rate of $0.3^\circ/\text{min}$.

Additional x-ray diffraction data were also collected at ASU on a Rigaku (RU2000) diffractometer equipped with a rotating anode x-ray source using $\text{CuK}\alpha$ radiation at 50kV and 100 mA. Powder samples were scanned using a step size of 0.02° and a collection time of 3 seconds.

1.7.2. Sodium Silicate Glasses

For all sodium silicate glasses, x-ray diffraction measurements were performed at Arizona State University on a Rigaku D/Max-II B automated diffractometer using $\text{CuK}\alpha$ radiation. Powdered samples were dusted onto a 20 mm square glass slide and scanned at a rate of $2.0^\circ/\text{min}$. with scattering angle, 2θ , values from 0° to 90° .

1.8. Crystal Growth Rate Determination in Lithium Silicate Glasses

Growth rates of both internal crystals and surface crystalline layers were determined for Glasses 3, 4, and 5. Multiple samples of each glass were isothermally heated (in air) in a horizontal tube furnace with a central hot zone constant to within $\pm 1.5^\circ\text{C}$. Table 3.3 shows the heat-treatment schedules employed for each glass.

1.8.1. Internal Crystal Growth Rate Determination

All heat-treated samples were mechanically thinned and optically polished according to the method described in Section 3.9, but using different polishing slurry (a

1 μm cerium oxide powder). Optical microscopy was then performed using an Olympus BHSM polarizing microscope. Samples were examined between cross-polarizers to observe and photograph the birefringence resulting from the crystalline phases. Each heat-treated sample was extensively surveyed, and optical micrographs of the largest internal crystals observed were obtained. To enable measurement of crystal dimensions from the micrographs, photographs were also taken of a micrometer slide (smallest divisions = 0.01mm) under the appropriate objective lenses. The sizes of the largest internal crystals observed for each heat-treated sample were then measured and recorded. Multiple different samples of each glass were subjected to each heat-treatment. This provided a considerable amount of material for survey, and determination of the “largest” crystal was therefore a matter of statistics. For each glass, the crystal size data thus acquired was plotted as a function of heating time for each heat-treatment temperature. The equations of the lines through the linear regions of the kinetic curves generated were obtained by a least squares fit to each temperature data set; the least squares slopes yielding the growth rates. The errors associated with the slopes were found using standard analytical procedures [116].

1.8.2. Surface Crystal Growth Rate Determination

The samples used for internal crystal growth rate determination were also utilized to determine the growth rates of the surface crystals. By nature of the quenching method employed in the preparation of the glasses (see Section 3.1), each heat-treated sample had at least one pristine “fracture” edge surface which was perpendicular to the larger faces of the sample. Since the samples were ground and polished parallel to the faces, the crystalline layers growing into the sample from the edges were preserved. These edge fracture surfaces provided a smooth, consistent outer surface from which to measure the lengths of the surface crystalline layers. Using the same optical microscopy procedure described for acquisition of internal crystal growth rate data, the average length of the surface (edge) crystalline layers of each sample was measured and recorded. These data were plotted in the same manner as the internal crystal size data, which yielded the kinetic curves for each heat-treatment temperature. The equations of the linear regions of each kinetic curve was found using a least squares fit, the slopes of which yield the surface crystal growth rates. The errors associated with the slopes were found using standard analytical procedures [116].

Table 3. 3 Heat-treatment schedule for crystal growth rate determination in lithium silicate glasses

Heat-Treatment Temperature ($\pm 1.5^\circ\text{C}$)	Heat-Treatment Time		
	Glass 3	Glass 4	Glass 5
454°C	328*, 480, 528, 600, and 648 hours	150*, 311, 408, and 476*, hours	133, 168, 240*, 288, and 360* hours
465°C	168*, 240*, 288*, and 346 hours	168*, 240*, 288*, 360*, and 528* hours	168*, 240*, 288*, and 360* hours
477°C	90, 117.5, 163.75, 210, and 257.5 hours	90, 117.5, 163.75, 210, and 257.5 hours	90, 117.5, 163.75, 210, and 257.5 hours
490°C	51.5, 93.5, 127, and 151 hours	51.5, 93.5, 127, and 151 hours	51.5, 93.5, 127, and 151 hours
500°C	23, 32, 48, and 69.25 hours	23, 32, 48, and 69.25 hours	23, 32, 48, and 69.25 hours
575°C	5, 10, 16, and 24 hours	-	-
590°C	20, 35, 44, and 55 minutes	20, 35, 44, and 55 minutes	20, 35, 44, and 55 minutes
610°C	10, 20, 35, and 45 minutes	10, 20, 35, and 45 minutes	10, 20, 35, and 45 minutes
635°C	5, 10, 16, 20, and 30 minutes	-	5, 8, 12.5, and 18 minutes

* denotes samples from which portions were also used for XRD investigation of metastable phase formation

1.9. Nucleation Rate Determination in Sodium Silicate Glasses

Nucleation rate data were obtained by the development technique, which employs two-stage isothermal heating and optical microscopy. All samples were screened for signs of internal crystallization via optical microscopy prior to heating. All isothermal heat-treatments were carried out (in air) in horizontal tube furnaces having central hot zones constant to $\pm 1.5^\circ\text{C}$. As-prepared glass samples were first placed in a platinum boat and isothermally heated at temperatures appropriate for the promotion of crystal nucleation. After being held at the nucleation temperature, T_n , for the desired time, samples were removed from the furnace and quenched to room temperature by being placed between copper plates. Nucleated samples were subsequently transferred to a different tube furnace and isothermally heated at a higher temperature for shorter times to grow the crystals to dimensions observable by an optical microscope.

The number density, N_v , of crystals nucleated within the volume of each sample was determined as a function of heating time, t_n , for each nucleation heat-treatment temperature in the following manner. Heat-treated samples were mounted on diamond stop carrier stainless steel platens using thermoset glue. Each platen was equipped with three stop-screws and could accommodate up to three samples at a time. The desired thickness to be ground was set using the threaded diamond stop-screws, which could be set to one ten thousandth of an inch, and a Starett Vertical Displacement Gauge. The platens were placed on a R. Howard Strasbaugh Model 6BK-16" ring precision polishmaster, and the sample surfaces were ground parallel to the platen surface by grinding against a cast-iron platen using a $15\mu\text{m}$ alumina grinding slurry. After the desired sample thickness was reached, the platen was transferred to another Model 6BK-16" which was set up to optically polish the sample surfaces using a polishing slurry and a pella cloth polishing pad. When polishing was complete, the platen was re-heated; the samples flipped over, and the process repeated for the opposite surface. Resulting samples had optical quality parallel faces and were typically between 60 and $150\mu\text{m}$ thick.

Optical microscopy was performed using an Olympus BHSM polarizing microscope. The optically polished, heat-treated samples were examined between cross-polarizers to observe and photograph the birefringence resulting from the crystalline phases. Ten to twenty micrographs were obtained for samples heated at each nucleation temperature, T_n , nucleation time, t_n , combination.

The magnifications of the micrographs were determined by photographing a micrometer slide under the appropriate objective lens. The sample thickness was measured with the aid of a micrometer. Knowledge of the magnification and glass thickness allowed the volume of sample represented by each micrograph to be determined. The crystal concentrations produced in the sodium silicate glasses were relatively low, and sample thicknesses were less than the depth of field at the desired magnification. Therefore, after determining the volume represented by each micrograph, the number density data were found directly from the optical micrographs by counting the number of crystals present in each micrograph.

The number density data thus obtained were plotted as a function of nucleation heat-treatment time for each nucleation heat-treatment temperature. The equations of the linear regions of the resulting kinetic curves were found by a least squares fit; the least squares slopes yielding the steady-state nucleation rates, I^s . The error associated with each slope (and thus I^s) was found using standard error analysis procedures [116].

2. EXPERIMENTAL RESULTS

2.1. Glass Composition

2.1.1. Lithium Silicate Glasses

The chemical compositions of the prepared glasses were determined either by atomic absorption, or by index of refraction measurements according to the method described in Section 3.2. Atomic absorption was performed on lithium silicate Glasses 1 and 2 at Desert Analytics in Tucson, Arizona. The results of the chemical analysis revealed the compositions of Glasses 1 and 2 to be $33.1 \pm 0.5 \text{ Li}_2\text{O} - 66.9 \pm 0.5 \text{ SiO}_2$ and $32.7 \pm 0.5 \text{ Li}_2\text{O} - 67.3 \pm 0.5 \text{ SiO}_2$, respectively. The compositions of Glasses 5 and 6 were analyzed in Brazil, also by atomic absorption. The compositions of Glass 5 and Glass 6 were reported to be $33.8 \pm 0.5 \text{ Li}_2\text{O} - 66.2 \pm 0.5 \text{ SiO}_2$, and $32.5 \pm 0.5 \text{ Li}_2\text{O} - 67.5 \pm 0.5 \text{ SiO}_2$, respectively. Based on index of refraction measurements and the data given in refs. [117,118], the chemical composition of Glass 3 was determined to be $33.3 \pm 0.3 \text{ Li}_2\text{O} - 66.9 \pm 0.3 \text{ SiO}_2$, and that of Glass 4 was found to be $34.5 \pm 0.3 \text{ Li}_2\text{O} - 65.5 \pm 0.3 \text{ SiO}_2$. Table 4.1 gives the measured index of refraction values, along with the analyzed Li_2O contents in mole%.

Table 4. 1 Index of refraction results and analyzed compositions for lithium silicate glasses

Glass No.	Index of Refraction, n_D (± 0.0005)	Analyzed Li_2O Content (mole%)
1	-	$33.1 \pm 0.5^*$
2	-	$32.7 \pm 0.5^*$
3	1.5360	33.3 ± 0.3
4	1.5387	34.5 ± 0.3
5	-	$33.8 \pm 0.5^*$
6	-	$32.5 \pm 0.5^*$

*Compositions analyzed by atomic absorption

2.1.2. Sodium Silicate Glasses

Wakasugi using index of refraction measurements determined the chemical compositions of all sodium silicate glasses. According to the data of Morey and Merwin [119], the deviation of the prepared glass compositions from the batch was found to be within 0.2 mol%.

2.2. Water Content

The water concentration of the prepared lithium silicate glasses were determined from the peak heights of the 3500cm^{-1} water band in the FTIR spectra as described in Section 3.3. The water concentrations in Glasses 1-4 were found to be very similar in magnitude, about $70\text{ ppm} \pm 10\%$. The water concentrations in Glasses 5 and 6 were also very similar in magnitude, approximately $138\text{ ppm} \pm 10\%$, which is nearly double that of Glasses 1-4. The different concentrations of water in the two families of glasses are consistent with the relative humidity in São Carlos and Tucson where these glasses were made. Figures 4.1 and 4.2 show representative FTIR spectra showing the differences in water contents between the two families of prepared glasses. The spectra in Fig. 4.1 were obtained for samples of equal thickness (1.45 mm) from Glass 4 and Glass 6. Figure 4.2 shows the spectra obtained for samples of equal thickness (0.87 mm) from Glasses 4 and 5.

Due to the propensity of the sodium silicate glasses to absorb water on their external surfaces, no attempt was made to measure the water contents of these glasses.

2.3. Glass Transition Temperature

The glass transition temperature, T_g , of each lithium silicate melt was determined from DTA as described in Section 3.4. Multiple DTA runs were performed on each melt, and the transition in each DTA trace was readily observable. From the multiple runs, the precision of T_g measurements was determined to be $\pm 2^\circ\text{C}$. Table 4.2 shows the measured T_g value for each melt.

Table 4. 2 Glass transition temperature, T_g , of lithium silicate glasses

Glass No.	Sample Type	T_g ($\pm 2^\circ\text{C}$)
1	Powdered glass	453°C
2	Powdered glass	455°C
3	Powdered glass	454°C
4	Powdered glass	452°C
5	Powdered glass	452°C
6	Powdered glass	456°C

2.4. Experimental Density Measurements

Density measurements were performed on all lithium silicate glass samples used for index of refraction measurements. The average density for each melt was calculated, and the results are tabulated in Table 4.3.

Table 4. 3 Density values for lithium silicate glasses

Glass No.	Average density, ρ , (g/cm ³) ($\pm$ 1 standard deviation)
1	2.344 (0.005)
2	2.342 (0.010)
3	2.345 (0.018)
4	2.348 (0.007)
5	2.346 (0.020)
6	2.342 (0.020)

2.5. X-ray Diffraction Results

In reporting the XRD results it is noted that, unless stated otherwise, the diffraction patterns were obtained from heated samples that had their surfaces removed prior to pulverizing the material into a fine powder for XRD analysis (i.e. the interior of the sample). The term “surface” is used to indicate a diffraction pattern obtained from the material that was removed from the heated sample (surface crystalline layer), and which was subsequently ground to a fine powder for XRD analysis.

2.5.1. Lithium Silicate Glasses

Table 4. 4 Summary of XRD results for Glass 1

Heat-Treatment Temperature ($\pm 1.5^\circ\text{C}$)	Heat-Treatment Time (hours)	XRD Results
440°C	350	Amorphous
440°C	543	only stable LS_2 crystal phase
454°C	120	Amorphous
454°C	192	Amorphous
454°C	360	dominant peaks of LS_2 crystal phase emerged against amorphous background
477°C	120	dominant peaks of LS_2 crystal phase emerged against amorphous background
477°C	168	dominant peaks of LS_2 intensified and additional LS_2 peaks emerged
477°C	288	only stable LS_2 crystal phase
500°C	24	dominant peaks of LS_2 crystal phase emerged against amorphous background

As described above, the three different XRD instruments yielded essentially the same results. Therefore, it was deemed prudent to use only one of the XRD instruments for analysis of Glasses 3, 4, 5, and 6. XRD results subsequently reported for these glasses were obtained using the Siemens D5000 instrument described in Section 3.7. The diffraction patterns are very similar to that which was obtained using standard XRD equipment, i.e., stable LS_2 was the only crystal phase was detected. Thus, it is concluded that instrument sensitivity did not have an effect the observed crystallization.

2.5.2. Sodium Silicate Glasses

Sodium silicate glass compositions provided by Takashi Wakasugi: 49Na₂O-51SiO₂ (W51%), 47Na₂O-53SiO₂ (W53%), 45Na₂O-55SiO₂ (W55%), 43Na₂O-57SiO₂ (W57%), and 41Na₂O-59SiO₂ (W59%) were given two-stage isothermal heat-treatments in horizontal tube furnaces and then analyzed by XRD. The objectives of the XRD measurements were: (1) to determine the crystal phases precipitated by the different nucleation mechanisms, i.e., external surface and internal volume nucleation, and (2) to glean insight into the crystallization process occurring during non-isothermal (DTA) heating of glasses which had been given prior isothermal nucleation heat-treatments (see Wakasugi's investigation ref. [88]). Appropriate heat-treatment schedules were designed and implemented for each purpose.

To mimic as closely as possible the crystallization process which occurred during the DTA runs performed by Wakasugi on samples of the W51% glass composition which had been given prior isothermal nucleation heat-treatments, samples of W51% were heated at 435°C for 1, 3, and 6 hours then developed at 610°C for 2-5 minutes after the furnace had re-equilibrated to 610°C, which generally took just a few minutes (samples were very thin and thus it is reasonable to presume that they reached the desired temperature during this time period). Each as-heated sample was crushed into a fine powder and subjected to XRD. The XRD patterns for all three samples were virtually identical. Figure 4.13 shows the XRD pattern of the W51% composition heat-treated at 435°C for 6 hours and at then 610°C for 2 minutes. All observable peaks correspond to the sodium metasilicate crystal phase.

Samples of the W53% composition were nucleated at 440°C for 1, 3, and 6 hours then developed at 610°C for 3-5 minutes. The XRD patterns of these samples were also virtually identical. The predominant crystal phase detected in these samples was also sodium metasilicate.

For glass compositions W55%, W57%, and W59%, samples were heat-treated and prepared for XRD in each of following three different ways: (1) surface layers were removed (method described in Section 3.9); (2) the bulk of the sample was mechanically ground away leaving only a thin surface layer (method described in Section 3.6), and (3) samples were ground down on one side to 1/2 their original thickness (method described in Section 3.9).

The XRD patterns of the W55% composition heated at 435°C for 3 hours then at 610°C for 5 minutes and prepared according to procedures 1, 2, and 3 revealed only the presence of sodium metasilicate. When a sample of the W55% composition was given the same nucleation treatment, but developed at 610°C for 10 minutes and prepared according to procedure 2, peaks corresponding to the sodium disilicate crystal phase began to appear. Sodium metasilicate was the only crystal phase present in the XRD trace of a sample of W55% nucleated at 435°C for 13.6 hours then developed at 610°C for 3 minutes and prepared according to method 1.

Glasses of the W57% composition were nucleated at 425°C for 2 and 3 hours and developed at 610°C for 0.5 - 2 hours. The XRD patterns of these samples which had the surface layers removed prior to analysis only showed diffraction peaks corresponding to

the sodium metasilicate crystal phase. The diffraction pattern of the W57% composition heat-treated at 425°C for 2 hours then 610°C for 1 hour, which was analyzed by XRD after surface materials were removed. When a sample of this composition was given the same heat-treatment, but analyzed with the surface layers intact, both sodium metasilicate and sodium disilicate crystal phases are detected.

The diffraction peaks in all sodium silicate XRD traces were identified using JCPDS cards: #16-818 (Na_2OSiO_3), #23-529 ($\text{Na}_2\text{Si}_2\text{O}_5$), and #22-1396 ($\text{Na}_2\text{Si}_2\text{O}_5$).

2.6. Experimental Growth Rates in Lithium Silicate Glasses

2.6.1. Crystal Morphology

Optical microscopy was performed using a polarizing microscope. After being mechanically thinned and optically polished as described in Section 3.9, heat-treated samples were examined between cross-polarizers to observe and photograph the birefringence resulting from the crystalline phases.

Optical microscopy was performed on all heat-treated samples (see Table 3.3) of Glasses 3, 4, and 5, and a change in internal crystal morphology with temperature was observed for all compositions. At 454°C, 465°C, and 477°C the crystals of Glass 3 and Glass 5 were predominantly needle-shaped with faceted ends and slightly curved sides. The shape of these crystals remained the same with increasing time at each temperature until impingement with other crystals occurred. Some acicular sections were also observed at these temperatures, but they were far fewer in number. Crystals of the same general form, but with larger aspect ratios, were observed for Glasses 3 and 5 at 490°C. At this temperature, many of the crystals exhibited branching at various stages of development, and crystalline aggregates were also observed. At 500°C, the internal crystals of Glasses 3 and 5 appeared much the same as those at 490°C. However, the aspect ratio for crystals not exhibiting branching was larger than at 490°C, giving these crystals the appearance of prolate ellipsoids. For Glass 4, the same change in morphology with temperature pattern described above was observed. At 454°C and 465°C, the internal crystals of Glass 4 looked the same as in Fig 4.20. However, branching and crystalline aggregates were first observed for Glass 4 at 477°C rather than 490°C. At higher temperatures (575, 590, 610, and 635°C) spherulitic sections were generally observed for all compositions.

The interface of the surface crystalline layers of Glasses 3, 4 and 5 were faceted at all temperatures and times investigated.

2.6.2. Internal Crystal Growth Rates

Table 4. 5 Linear growth rates (fast-axis) of internal crystals for Glasses 3,4, and 5

T (°C)	U (m/s)		
	Glass 3	Glass 4	Glass 5
454	3.10×10^{-12} ($\pm 4.7 \times 10^{-13}$)	3.40×10^{-12} ($\pm 5.4 \times 10^{-13}$)	3.63×10^{-12} ($\pm 5.2 \times 10^{-13}$)
465	8.01×10^{-12} ($\pm 1.2 \times 10^{-12}$)	7.31×10^{-12} ($\pm 1.1 \times 10^{-12}$)	7.05×10^{-12} ($\pm 0.9 \times 10^{-12}$)
477	1.50×10^{-11} ($\pm 2.3 \times 10^{-12}$)	1.40×10^{-11} ($\pm 1.9 \times 10^{-12}$)	1.93×10^{-11} ($\pm 2.9 \times 10^{-12}$)
490	3.46×10^{-11} ($\pm 5.2 \times 10^{-12}$)	4.41×10^{-11} ($\pm 6.7 \times 10^{-12}$)	4.58×10^{-11} ($\pm 4.6 \times 10^{-12}$)
500	8.06×10^{-11} ($\pm 1.2 \times 10^{-11}$)	1.01×10^{-10} ($\pm 1.2 \times 10^{-11}$)	8.07×10^{-11} ($\pm 1.5 \times 10^{-11}$)
575	1.43×10^{-9} ($\pm 1.9 \times 10^{-10}$)	—	—
590	2.00×10^{-8} ($\pm 2.6 \times 10^{-9}$)	2.31×10^{-8} ($\pm 3.2 \times 10^{-9}$)	1.91×10^{-8} ($\pm 3.0 \times 10^{-9}$)
610	6.41×10^{-8} ($\pm 8.3 \times 10^{-9}$)	6.55×10^{-8} ($\pm 8.5 \times 10^{-9}$)	6.30×10^{-8} ($\pm 7.6 \times 10^{-9}$)
635	1.51×10^{-7} ($\pm 2.0 \times 10^{-8}$)	—	1.38×10^{-7} ($\pm 1.5 \times 10^{-8}$)

Table 4. 6 Linear growth rates (short-axis) of internal crystals for Glasses 3,4, and 5

T (°C)	U (m/s)		
	Glass 3	Glass 4	Glass 5
454	8.13×10^{-13} ($\pm 2.3 \times 10^{-13}$)	6.61×10^{-13} ($\pm 2.0 \times 10^{-13}$)	8.68×10^{-13} ($\pm 1.3 \times 10^{-13}$)
465	1.44×10^{-12} ($\pm 2.2 \times 10^{-13}$)	1.37×10^{-12} ($\pm 1.9 \times 10^{-13}$)	1.90×10^{-12} ($\pm 2.5 \times 10^{-13}$)
477	3.20×10^{-12} ($\pm 4.9 \times 10^{-13}$)	5.57×10^{-12} ($\pm 6.0 \times 10^{-13}$)	3.31×10^{-12} ($\pm 4.1 \times 10^{-13}$)
490	2.36×10^{-11} ($\pm 3.1 \times 10^{-12}$)	3.75×10^{-11} ($\pm 5.5 \times 10^{-12}$)	2.08×10^{-11} ($\pm 4.3 \times 10^{-12}$)
500	6.94×10^{-11}	9.72×10^{-11}	5.56×10^{-11}

	$(\pm 9.0 \times 10^{-12})$	$(\pm 2.3 \times 10^{-11})$	$(\pm 7.8 \times 10^{-12})$
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Table 4. 7 Aspect ratios of internal crystals for Glasses 3,4, and 5

Temperature °C	Glass 3 Aspect Ratio (± 1 std. deviation)	Glass 4 Aspect Ratio (± 1 std. deviation)	Glass 5 Aspect Ratio (± 1 std. deviation)
454	0.28 (± 0.02)	0.25 (± 0.02)	0.30 (± 0.02)
465	0.29 (± 0.04)	0.27 (± 0.04)	0.26 (± 0.03)
477	0.31 (± 0.03)	0.33 (± 0.04)	0.27 (± 0.05)
490	0.50 (± 0.10)	0.61 (± 0.10)	0.45 (± 0.15)
500	0.57 (± 0.15)	0.70 (± 0.10)	0.58 (± 0.12)

Table 4. 8 Surface crystalline layer growth rates for Glasses 3,4, and 5

T (°C)	Glass 3	Glass 4	Glass 5
490	5.00×10^{-11} ($\pm 7.5 \times 10^{-12}$)	—	4.67×10^{-11} ($\pm 7.0 \times 10^{-12}$)
500	1.14×10^{-10} ($\pm 1.7 \times 10^{-11}$)	1.35×10^{-10} ($\pm 4.7 \times 10^{-13}$)	1.10×10^{-10} ($\pm 1.5 \times 10^{-11}$)
575	1.70×10^{-9} ($\pm 2.6 \times 10^{-10}$)	—	—
590	2.50×10^{-8} ($\pm 3.5 \times 10^{-9}$)	2.70×10^{-8} ($\pm 3.8 \times 10^{-9}$)	2.64×10^{-8} ($\pm 4.7 \times 10^{-9}$)
610	6.81×10^{-8} ($\pm 1.1 \times 10^{-8}$)	8.16×10^{-8} ($\pm 1.0 \times 10^{-8}$)	6.60×10^{-8} ($\pm 9.2 \times 10^{-9}$)
635	1.50×10^{-7} ($\pm 2.1 \times 10^{-8}$)	—	1.32×10^{-7} ($\pm 1.8 \times 10^{-8}$)

2.7. Experimental Crystal Nucleation in Sodium Silicate Glasses

2.7.1. Steady-State Nucleation Rates

For the W57% composition, the number density data obtained by optical microscopy were plotted as a function of nucleation heat-treatment time for each nucleation heat-treatment temperature: 390, 400, 410, 415, 425, 440 and 455°C. Data collected indicated the presence of transient effects for nucleation temperatures $\leq 425^\circ\text{C}$. However, since there was very little as-prepared glass remaining after the steady-state nucleation rate investigation, the transient behavior for this composition was not analyzed in detail. The slopes of the linear regions of the kinetic curves, which yield the magnitudes of the steady-state nucleation rates, I^s , were found by a least squares fit. The error associated with each slope (and thus I^s) was calculated using standard error analysis procedures.

Table 4.9 shows the magnitudes of steady-state nucleation rates and associated errors for each nucleation temperature, T_n , as determined from the aforementioned procedures. Figure 4.54, which shows the magnitude and temperature dependence of the steady-state nucleation rate, I^s , for the glass composition W57%, was generated from the data in Table 4.9. The steady-state nucleation rate curve has the form of an asymmetric peak with a maximum rate, I_{max} , of $6.2 \times 10^3 \text{ (cm}^{-3} \text{ min}^{-1}\text{)}$ occurring at a temperature, T_{max} , of about 410°C . It appears that the nucleation range for this glass composition is approximately 385°C to 465°C .

Table 4. 9 Steady-state nucleation rates of sodium metasilicate crystals in W57% composition glass

$T_n \text{ (}^\circ\text{C)}$	$I^s \times 10^{-2} \text{ (cm}^{-3} \text{ min}^{-1}\text{)}$	Error ($\pm$) $\times 10^{-2} \text{ (cm}^{-3} \text{ min}^{-1}\text{)}$
390	0.13	0.02
400	3.22	0.58
410	61.84	5.00
415	56.17	4.67
425	35.39	1.50
440	19.64	3.33
455	10.88	1.80

2.7.2. Relative Crystal Number Densities

In order to obtain estimates of the relative internal crystal number densities in the W59% and W55% glasses, these glasses were heated and analyzed with the aid of optical microscopy. The W59% composition was nucleated at 440°C for 48 hours and developed at 610°C for 1/2 hour, and the W-55% composition was nucleated at 410°C for 1/2 hour and developed at 590°C for 20 minutes. Using the method described in Section 3.9, the crystal number density, N_v , for the W55% was found to be 325 mm⁻³ and that of the W59% was determined to be 90 mm⁻³.

2.7.3. Crystal Morphology

The internal crystals of all sodium silicate glasses given two-stage isothermal heat-treatments were observed to grow as rhomboid needles. Optical micrographs showing the morphology of sodium metasilicate crystals in Figs. 4.57 and 4.58 were obtained from the W55% composition that was nucleated at 455°C for 1 hour and then developed at 590°C for 20 minutes. The shapes of the crystals shown in these figures are representative of the morphology observed in all heat-treated sodium silicate compositions.

3. DISCUSSION

3.1. XRD Investigation of Metastable Phase Formation in LS₂ Glass

The x-ray diffraction results regarding the formation and persistence of metastable phases in lithium disilicate glass presented in this work are in sharp contrast to the results reported James et al. [1] and Iqbal et al. [74]. These authors performed XRD on lithium disilicate glasses that had been heated at 454°C for various times. A summary of their findings is given below. It is noted that in the study conducted by James and Iqbal, all heat-treated samples reportedly had their surface materials removed prior to XRD analysis.

The XRD trace obtained in ref. [74] for a glass sample which had been heated at 454° for 120 hours revealed the presence of a crystal phase that could not be identified with any previously known phase in the binary Li₂O-SiO₂ system. The authors referred to this phase as metastable α' -LS₂. After heating a glass sample for 312 hours, Iqbal found that most of the α' -LS₂ peaks remained, but a number of additional peaks also emerged which could indicate the appearance of stable LS₂. However, based on subsequent TEM results the authors suggested that the additional peaks were associated with another metastable phase, intermediate between the α' - and stable LS₂ phases. This intermediate metastable phase was denoted as β' -LS₂. The XRD results for a glass sample, which had been heated for 480 hours, showed the presence of stable LS₂ and a

decrease in the intensities of the peaks due to phase(s) other than stable LS_2 . Some time between 480 and 551 hours, the metastable phase(s) peaks disappeared entirely. After 551 hours, apart from stable LS_2 , James and Iqbal also observed the presence of several major lithium metasilicate (LS) peaks, but the LS peak intensities were much lower than those of the stable LS_2 phase were.

The XRD results of the initial investigation conducted in this work, for which lithium disilicate Glasses 1 and 2 were prepared and heated for prolonged periods at 454°C , are quite different from those described above. First, in no instance was crystalline material detected in either Glass 1 or Glass 2 after heating for 120 hours. Further, no crystalline material was detected in these glasses even after heating for 192 hours. When diffraction peaks did emerge against the amorphous background, which occurred after heating for 360 hours, they were positively identified with the stable LS_2 crystal phase. Also, upon comparison of the XRD traces for Glasses 1 and 2 heated at 454°C for 360 hours with the 454°C -312 hour XRD trace in ref. [74] it is apparent that the extent of crystallization is markedly lower in Glasses 1 and 2 than in the glass studied by James and Iqbal, even though Glasses 1 and 2 had been heated for a longer time period.

Several potential reasons for the apparent discrepancies between the XRD results obtained by James and Iqbal and those obtained for Glasses 1 and 2 were considered. First, the disparate results could have been due to the differences in glass composition. Glasses 1 and 2 utilized for the initial investigation herein were sub-stoichiometric (33.1 and 32.7 mol% Li_2O), while the glass studied by James and Iqbal was hyper-stoichiometric (33.9 mol% Li_2O). Another possibility resides in the glass preparation procedures. Although the procedure reported in ref. [74] was followed closely, James and Iqbal employed one step which was not incorporated in the preparation of Glass 1 or Glass 2; namely, sintering of precursor powders at 1000°C for 10 hours prior to melting. It is conceivable that some type of solid state reaction occurred during the sintering process which produced a species in the melt used by James and Iqbal that would not have been present in the melts studied herein. As noted earlier, the surface crystalline layers of heat-treated samples were removed prior to XRD analysis in the study conducted by James and Iqbal. However, it is still possible that surface materials were present in the powdered XRD samples used by James and Iqbal. Lastly, differences in water content of the glasses used in the respective investigations could also be responsible for the observed differences.

The above four possible causes for the disparate XRD results: (1) slight differences in composition, (2) intermediate sintering step prior to melting, (3) surface material contamination, and (4) differences in water content, were subsequently addressed in this work by preparing and analyzing Glasses 3, 4, 5, and 6. Upon comparison of the XRD results of Glass 3 with those of Glass 1 (Table 4.4), it is apparent that the intermediate sintering step had no effect on the observed crystallization. As described in Section 4.5, the crystalline phase precipitated on the surface was identical to that formed within the bulk. Hence, surface crystal contamination was apparently not responsible for the discrepancies. As described in Section 4.2, Glasses 5 and 6 were

prepared in Brazil and were found to have approximately double the water content of those prepared in Arizona (Glasses 1, 2, 3 and 4). Although the water content of the glass used in refs. [1,74] was not reported, since the glass preparation procedures used were nearly identical it is reasonable to assume that the water content was not unusually large, and was probably within the range of the glasses used in the present study. The XRD traces presented in Section 4.5 show that the extent of internal crystallization was larger in the glasses with higher water contents (Glasses 5 and 6) than in the drier glasses (Glasses 1, 2, 3, and 4) for a given heat-treatment. However, it is clear from the XRD traces presented in Section 4.5 that regardless of water concentration only the stable LS_2 crystal phase formed.

The relative differences in degrees of crystallinity between the two families of glasses (Glasses 5 and 6, and Glasses 1,2,3, and 4) were estimated from the XRD traces in the following manner. First, a baseline joining the regions of the curve on opposite sides of the amorphous hump was constructed. Then, the areas under the crystal peaks and amorphous hump were measured. The mass fraction of crystals, x_c , was then evaluated to a first approximation by the following expression:

$$x_c = \frac{A_c}{(A_a + A_c)} \quad (5.1)$$

where A_c is the area under the crystalline peaks and A_a is the area under the amorphous hump. It is stressed that this method only yields approximate results. Disorder in the crystalline regions can give rise to a reduction in area of the sharp peaks, and the size of the amorphous hump can be affected by interaction of the x-ray probe with the sample holder. This technique, however, is adequate for comparative purposes and was employed for samples of Glasses 3 and 5 heated at 454°C and 465°C, which had their surfaces removed prior to XRD analysis. It was found that the mass fraction of crystals in Glass 5 was nearly 15 times larger than in Glass 3 for $T = 454^\circ\text{C}$. At $T = 465^\circ\text{C}$, the mass fraction of crystals in Glass 5 was about 6 times larger than that in Glass 3. These results are discussed in more detail in Section 5.2.4.

As evidenced by the XRD results presented in Section 4.5, it is apparent that compositional variations also did not affect the observed crystallization. Thus, it does not appear that glass preparation procedure, composition variations, surface crystal contamination, or water concentration were responsible for the disparate results between the initial XRD investigation conducted herein, and the results reported by James and Iqbal. In view of this finding it will be useful to consider other experimental evidence that bears upon this issue.

James and Keown [124] examined the crystallization of a lithium silicate glass, which contained 33.1 mol% Li_2O , using transmission electron microscopy (TEM). Glasses were heated for 65 and 94 hours at a temperature of 490°C. Selected area diffraction (SAD) was used to determine the crystal phase of observed crystals. Stable LS_2 was the only crystalline phase detected.

In a study by Barker et al. [53], nucleation and growth as a function of heating time in lithium silicate glasses containing 33.3 mol% Li_2O (composition by batch) was investigated. In their study, samples of these glasses were heated at the maximum nucleation temperature, 455°C , until crystallization was detected by x-ray diffraction. For both glasses, after 10 days only lithium disilicate solid solution was detected.

Very recently, Mastelaro and Zanotto [125] obtained additional XRD results. These authors heated an LS_2 glass for 86 and 100 hours at a temperature of 460°C , and the only crystalline phase detected was stable LS_2 . Further, Fokin (private communication) heat-treated LS_2 glass at 440°C for 350, 543, and 642 hours. The XRD pattern of the glass heated for 350 hours had only an amorphous peak, while the scans of the glasses heated for longer times showed only stable LS_2 .

It is also important to note that TEM and NMR were also employed in the investigation of Iqbal et al. [74], and the following results were found. The TEM selected area diffraction (SAD) investigation of a glass heated at 454°C for 93 hours revealed stable LS_2 as the only crystalline phase present. Also, there were no signs (from SAD) of a metastable phase for glasses heated up to 217 hours. However, a small amount of a crystalline phase that could not be identified as stable LS_2 was observed via SAD when the glass was heated for 331 hours. In addition, the authors stated that the NMR results obtained from glasses that were heated for less than 228 hours were consistent with the formation of stable LS_2 .

Hence, there seems to be substantial experimental evidence to indicate that metastable crystalline phases do not persist in lithium disilicate glasses that have been heated for extended time periods in the nucleation region.

3.2. Experimental Crystal Growth Rates in Lithium Disilicate Glasses

3.2.1. Comparison Between Theory and Experimental Results

Presently, there are three phenomenological models used to describe the process of crystal growth controlled by interface kinetics: normal growth, screw dislocation growth, and 2-D surface nucleated growth [100]. According to the normal growth model, the interface is viewed as atomically rough with a considerable fraction of the interface sites being step sites where the growth takes place. Assuming this fraction remains essentially constant with temperature, and that motion on the scale of a molecular diameter is involved in the interface jump process, the growth rate may be expressed:

$$u = v\lambda[1 - \exp(-\Delta G/RT)] \quad (5.2)$$

In Equation (5.2) u is the growth rate, v is a jump frequency, λ is the distance advanced by the interface (taken as the molecular diameter), ΔG is bulk free energy change upon crystallization, R is the gas constant, and T is the measurement temperature in Kelvin.

According to the screw dislocation growth model, the interface is smooth but imperfect on an atomic scale. Growth takes place at step sites provided by screw dislocations intersecting the interface, and the growth rate may be expressed:

$$u = fv\lambda[1 - \exp(-\Delta G/RT)] \quad (5.3)$$

where f is the interface site factor (fraction of preferred growth sites on the interface). This fraction is given by

$$f = \frac{\lambda\Delta G}{4\pi\sigma V_m} \quad (5.4)$$

where σ is the specific surface energy of the melt-crystal interface, and V_m is the molar volume.

In the 2-D surface nucleated growth model, the surface is considered atomically smooth and free from defects. Growth occurs by the formation and lateral growth of two-dimensional nuclei on the interface. The crystal growth rate is expressed by

$$u = Cv\exp(-B/T\Delta G) \quad (5.5)$$

The quantity B in the above equation is given by

$$B = \frac{\pi \lambda V_m \sigma_E^2}{3k_B} \quad (5.6)$$

In Equation (5.6) k_B is Boltzmann's constant, and σ_E is the edge surface energy of the nucleus. For the small crystal case, where the propagation time of the surface cluster across the interface is negligible compared with the time needed to nucleate a cluster, the quantity C in Equation (5.5) is given by

$$C = \lambda N_s A_o \quad (5.7)$$

where N_s is the number of atoms (or formula units) per unit area at the interface, and A_o is the cross sectional area of the interface. For the more generally applicable case (large crystal case) [126] where the lateral propagation rate of the surface nucleus must be considered, then the quantity C is given by

$$C = \frac{(\pi/3)^{1/3} N_s^{1/3} \lambda^{5/3}}{\Gamma(4/3)} [1 - \exp(-\Delta G/RT)]^{2/3} \quad (5.8)$$

where Γ is the gamma function and N_s is the number of molecules (formula units) per unit area of the interface.

According to Jackson's treatment of the interface [92,93], substances with low entropies of fusion ($\Delta S_f < 2R\zeta^{-1}$) should have even their most closely packed interface planes rough on an atomic scale. For such materials, the growth rate anisotropy as a function of orientation should be small, and defects unimportant to growth. The crystal-liquid interface for such substances should be non-faceted, and kinetics of the form predicted by the normal growth model are expected. For materials with large entropies of fusion ($\Delta S_f > 4R\zeta^{-1}$), the most closely packed interface planes should be smooth on an atomic scale, and the more loosely packed planes should be rough resulting in a large growth rate anisotropy. Faceted interfaces are expected for at least some growth directions in these materials. Further, defects are important to growth for high entropy of fusion materials, and kinetics of the form predicted by either the screw dislocation or the 2-D surface nucleated model are expected.

To interpret experimental data with respect to the kinetic models described above, it is necessary to evaluate the jump frequency factor, v . This is generally done by assuming that the molecular motions involved are similar to those involved in transport in the bulk liquid. Thus, the temperature dependence of the interface process is assumed to be represented by that of the liquid viscosity through the Stokes-Einstein equation

$$v = \frac{k_B T}{3\pi\lambda^3 \eta} \equiv \frac{b}{\eta} \quad (5.9)$$

In Equation (5.9) η is the shear viscosity. Assuming the above type of relation between v and η , Jackson, Uhlmann, and Hunt [105] have shown that information regarding the operative growth mechanism can be more easily inferred from a plot of the reduced growth rate, U_R , which is proportional to f , versus the undercooling, ΔT . U_R is given by

$$U_R = \frac{U\eta}{\left[1 - \exp\left(\frac{-\Delta G}{RT}\right)\right]} \quad (5.10)$$

In Equation (5.10), U is the measured growth rate. The operative growth mechanism is thus reflected by the reduced growth rate defined by Equation (5.10) through the temperature dependence of the interface site factor. Hence, for normal growth where the interface site factor is essentially independent of temperature, the reduced growth rate versus undercooling plot is expected to be a horizontal line. This relation should yield a straight line of positive slope passing through the origin for screw dislocation growth, and a curve of increasing positive slope passing through the origin for 2-D surface nucleated growth.

It is clear from the above discussion that one needs to know the viscosity as a function of temperature to compute the reduced growth rates, and thus to compare theoretical predictions with experimental results. There have been several measurements made by different authors of the viscosity of lithium disilicate glasses for the temperature range of interest in this study. Figure 5.1 shows viscosity data reported by different authors for LS_2 glasses prepared under normal melting conditions, i.e. without deliberate manipulation of the melting atmosphere. As observed in Fig. 5.1, the viscosity data of Fokin et al.[127], Gonzalez-Oliver et al. [89], and Zanotto [128] agree well in both magnitude and temperature dependence. The experimental viscosity data reported by Matusita and Tashiro in ref.[44] are lower in magnitudes and slightly shallower in temperature dependence than the other three sets of data in the same temperature range. We note that the glass used by Matusita and Tashiro for viscosity measurements was a completely different melt than that used by these authors for growth rate measurements in ref. [123].

It seems reasonable to regard the Zanotto and Matusita & Tashiro data as representative of the extremes in the possible low temperature viscosity behavior of Glasses 3, 4 and 5 studied herein. Thus, these data are invoked in subsequent analyses requiring viscosity data. Figure 5.2 shows the experimental viscosity data reported in the literature plotted as $\ln \eta$ vs. $1/T$. Over the temperature range 440°C - 520°C, the experimental data of Zanotto and Matusita & Tashiro exhibit Arrhenius behavior with activation enthalpy values of about 125 kcal/mol and 97 kcal/mol, respectively.

At temperatures intermediate to those where experimental viscosity data, crystallization is relatively rapid and precludes experimental viscosity determination. Because of this experimentally inaccessible region, the temperature dependence of the viscosity between high and low temperatures is open to several interpolations. To

facilitate subsequent analyses, the temperature dependence over the entire temperature range is assumed to follow either the VFT equation derived by Zanutto [128], or the VFT equation as given by Matusita and Tashiro in ref. [123].

The above observations suggest that for $400^{\circ}\text{C} \leq \Delta T \leq 580^{\circ}\text{C}$ the 2-D surface nucleation mechanism is operative, and that for $\Delta T < 140^{\circ}\text{C}$ either the 2-D surface nucleation or screw dislocation mechanism operates. Therefore, the experimental growth rate data in both of these undercoolings regions is first analyzed below with respect to the 2-D surface nucleation model. Subsequently, the growth rate data in the region of small undercooling ($\Delta T < 140^{\circ}\text{C}$) are analyzed with respect to the screw dislocation model.

Using Equation (5.9), the equation for 2-D nucleated growth, Equation (5.5), may be rewritten as

$$\ln u\eta = \ln C_b - \frac{B}{T\Delta G} \quad (5.11)$$

Hence, the model of surface nucleation can be tested in more detail for the undercooling regions where ΔT ranges from 0 to 140°C and 400°C to 580°C by plotting $\ln U\eta$ versus $(T\Delta G)^{-1}$. This plot should yield a straight line of negative slope equal to the quantity B as given by Equation (5.6) (assuming that B , and in particular σ_E , is constant), and a y-intercept equal to $\ln C_b$. The product C_b as given by Equations (5.8) and (5.9) is a very weak function of temperature changing from a value of 1.48×10^{-3} at $T = 1020^{\circ}\text{C}$ to a value of 5.46×10^{-3} at $T = 454^{\circ}\text{C}$, and therefore can be taken as constant.

A single straight line cannot be used to describe the data. However, over the restricted temperature range $T = 500^{\circ}\text{C} - 454^{\circ}\text{C}$ each data set can be fit by a straight line of negative slope. The equation of each line was found using a least squares fit. The slope and intercept values of these lines are given in Table 5.1.

Table 5. 1 Slope, B, values, and extrapolated and computed y-intercept values

Temperature Interval	Slope, B (J K/mol) <i>VFT equation from ref.[128]</i>	Slope, B (J K/mol) <i>VFT equation from ref. [123]</i>	y-intercept <i>VFT equation from ref. [128]</i>	y-intercept <i>VFT equation from ref. [123]</i>	lnCb*
1020°C - 995°C	1.39×10^6	1.36×10^6	-5.87	-6.06	-5.99
983°C - 897°C	9.81×10^6	9.27×10^6	-2.91	-3.27	-5.46
500°C - 454°C	26.50×10^8	13.06×10^6	147.69	69.43	-5.18

*average value computed for temperature interval

Quantitative evaluation of the surface nucleated growth model for each temperature region where the data were fit by a straight line of negative slope was performed using Equations (5.8), (5.9) and (5.5). The quantity B appearing in Equation (5.5) is given by the slopes of the lines in Figs. 5.4 and 5.5 (see Table 5.1). The quantities C and b were computed from Equations (5.8) and (5.9), respectively. The parameters employed for these computations are shown in Table 5.2.

The computed y-intercept values (lnCb) are given in the last column of Table 5.1. Comparisons between the measured and calculated values of the growth rates are presented in Table 5.3. For temperatures in the interval 500°C - 454°C, the averages of the experimental growth rates obtained in this work are given in Table 5.3.

Table 5. 2 Parameters utilized for growth rate calculations

N_s^* (units/m ²)	λ (m)	V_m (m ³ /mol)	ΔG (J/mol; T in K)
4.57×10^{18}	4.68×10^{-10}	6.15×10^{-5}	$53399 - 42.015T + 0.00713T^2 - 4.79 \times 10^{-6}T^3$

$$*N_s = (n_v)^{2/3}; n_v = 9.78 \times 10^{27} \text{ (formula units/m}^3\text{)}$$

Table 5. 3 Experimental and calculated growth rate values: 2-D surface nucleation

T (°C)	$U_{\text{calc}} \text{ (ms}^{-1}\text{)}$ <i>VFT equation from</i> <i>ref.[128]</i>	$U_{\text{calc}} \text{ (ms}^{-1}\text{)}$ <i>VFT equation from</i> <i>ref.[123]</i>	$U_{\text{experimental}} \text{ (ms}^{-1}\text{)}$
1020	6.61×10^{-6}	8.00×10^{-6}	1.2×10^{-5}
1016	9.44×10^{-6}	1.15×10^{-5}	1.5×10^{-5}
1006	1.78×10^{-5}	2.15×10^{-5}	2.0×10^{-5}
1004	1.92×10^{-5}	2.31×10^{-5}	2.2×10^{-5}
996	2.35×10^{-5}	2.86×10^{-5}	2.1×10^{-5}
995	2.40×10^{-5}	2.91×10^{-5}	2.5×10^{-5}
983	1.64×10^{-6}	2.39×10^{-6}	3.4×10^{-5}
966	3.37×10^{-6}	4.78×10^{-6}	3.4×10^{-5}
963	3.65×10^{-6}	5.17×10^{-6}	4.9×10^{-5}
957	4.17×10^{-6}	5.89×10^{-6}	5.3×10^{-5}
952	4.55×10^{-6}	6.42×10^{-6}	5.4×10^{-5}
930	5.55×10^{-6}	7.86×10^{-6}	5.7×10^{-5}
918	5.65×10^{-6}	8.07×10^{-6}	6.8×10^{-5}
897	5.28×10^{-6}	7.69×10^{-6}	5.4×10^{-5}
500	4.00×10^{-77}	3.11×10^{-43}	8.1×10^{-11}
490	2.36×10^{-77}	1.84×10^{-43}	4.5×10^{-11}

477	9.70×10^{-78}	7.99×10^{-44}	1.9×10^{-11}
465	2.97×10^{-78}	3.22×10^{-44}	7.1×10^{-12}
454	7.09×10^{-79}	1.26×10^{-44}	3.6×10^{-12}

As observed in Table 5.3, regardless of which VFT equation is used the magnitudes and temperature dependence of the calculated growth rates are in excellent agreement with the experimental growth rate data for undercoolings less than about 40°C ($T \geq 995^{\circ}\text{C}$). Further, as shown in Table 5.1 the computed values of the y-intercept ($\ln C_b$) are in accord with the extrapolated values in this undercooling range.

For undercoolings from about 40°C to 140°C ($T = 983^{\circ}\text{C} - 897^{\circ}\text{C}$), the extrapolated values of the y-intercept are smaller in magnitude by about a factor of 2 than the computed values, and the calculated growth rates are one order of magnitude smaller than the experimental growth rates. However, the temperature dependence of the calculated growth rates is in accord with experimental results.

Over the undercooling range 534°C to 580°C ($T = 500^{\circ}\text{C} - 454^{\circ}\text{C}$), it is apparent from Tables 5.1 and 5.3 that quantitative agreement is poor in all aspects. What is striking about the data in Table 5.3 for this undercooling range is that the computed growth rates differ by over 30 orders of magnitude when one uses the two different VFT equations. It is noted that using polynomial fits to the viscosity just in the temperature region where experimental data are available, rather than the VFT equations, does not significantly alter the results in Table 5.3 or Table 5.1.

For each undercooling region quantitatively analyzed above, the edge surface energy of the nucleus, σ_E , was computed from Equation (5.6) using the B values from Table 5.1, i.e., slopes of the lines. The results are presented in the second column of Table 5.4. As mentioned earlier, σ_E should be equivalent to the crystal-liquid interfacial energy. The Turnbull-Steveley equation, which is a semi-empirical relationship derived from homogeneous nucleation experiments in small droplets, is commonly used for estimates of crystal-melt interfacial energies. This equation is given by

$$\sigma_h = \frac{\alpha \Delta H_f}{N^{1/3} V_m^{2/3}} \quad (5.12)$$

where N is Avogadro's number, and α is a numerical constant ranging in value from 0.25 to 0.40 for non-metallic substances. The values of α required to obtain the σ_E values given in Table 5.4 were evaluated from Equation (5.12) using $V_m = 6.15 \times 10^{-5} \text{ m}^3/\text{mol}$ and $\Delta H_f = 57400 \text{ J/mol}$. These results are shown in the last column of Table 5.4.

Table 5. 4 σ_E and α values

Temperature Interval	σ_E (J/m ²)	α
1020°C – 995°C	0.0237 ^{a,b}	0.054 ^{a,b}
983°C - 897°C	0.0634 ^{a,b}	0.150 ^{a,b}
500°C - 454°C	0.973 ^a 0.645 ^b	2.230 ^a 1.480 ^b

^aVFT equation from ref. [128]

^bVFT equation from ref. [123]

As noted earlier, the product Cb appearing in Equation (5.11) does not change significantly over the 580°C of undercooling investigated and was therefore be taken as constant in the preceding analysis. To substantiate this approach, the data were also analyzed taking the weak temperature dependence of the quantities C and b into account.

This was done by constructing $\ln \{U\eta/T[1-\exp(-\Delta G/RT)]^{2/3}\}$ vs. $(T\Delta G)^{-1}$ plots for the undercooling ranges of interest. The results obtained from these plots were not significantly different (either qualitatively or quantitatively) from the results presented above, and the same conclusions are drawn.

The experimental growth rate data in the region of small undercooling ($\Delta T < 140^\circ\text{C}$) are now analyzed with respect to the screw dislocation model. Using Equations (5.3), (5.4) and (5.9), the expression for screw dislocation growth may be written

$$u = A \frac{T \Delta G}{\eta} [1 - \exp(-\Delta G/RT)] \quad (5.13)$$

where the quantity A is given by

$$A = \frac{k_B}{12\pi^2 \lambda \sigma V_m} \quad (5.14)$$

Recalling the definition of the reduced growth rate and rearranging Equation (5.13) leads to the following expression

$$\frac{U_R}{T} = A \Delta G \quad (5.15)$$

A plot of $U_R T^{-1}$ vs. ΔG should thus yield a straight line intersecting the origin with a slope equal to the quantity A (assuming σ constant). Further, based on the above equations and Equation (5.4), it is clear that the interface site factor, f , may also be written

$$f = \frac{A 3 \pi \lambda^2}{k_B} \Delta G \quad (5.16)$$

and that the surface energy, σ , may be expressed

$$\sigma = \frac{k_B}{A12\pi^2\lambda V_m} \quad (5.17)$$

Therefore, the screw dislocation model can be tested in more detail for the small undercooling range ($\Delta T < 140^\circ\text{C}$) by constructing an $U_R T^{-1}$ vs. ΔG plot to determine the quantity A . Then, using the parameters given in Table 5.2 and Equations (5.13), (5.16), and (5.17) the growth rate, interface site factor, and surface energy, respectively, may be computed.

Using Equation (5.17) and the slope of the line shown in Fig. 5.8 (A value), the surface energy, σ , was determined to be 0.001 J/m^2 . To obtain this σ value from the Turnbull-Staveley relation (Equation 5.12), a value of $\alpha = 2.3 \times 10^{-3}$ is required.

Comparisons between the measured and calculated values of the growth rate for the screw dislocation model are presented in Table 5.5. Also shown in Table 5.5 are the computed values of the interface site factor, f . As observed in Table 5.5, the magnitude and temperature dependence of the calculated growth rates agree well with the experimental data in this temperature region. However, the calculated values of the interface site factor, f , are generally larger than one.

Table 5. 5 Experimental and calculated growth rates: screw dislocation model

T ($^\circ\text{C}$)	$U_{\text{calc}} (\text{ms}^{-1})$ Screw dislocation <i>VFT Eq. from ref.[128]</i>	f_{calc}	$U_{\text{experimental}} (\text{ms}^{-1})$
1020	4.54×10^{-6}	0.41	1.2×10^{-5}
1016	6.48×10^{-6}	0.50	1.5×10^{-5}
1006	1.38×10^{-5}	0.79	2.0×10^{-5}
1004	1.54×10^{-5}	0.84	2.2×10^{-5}
996	2.21×10^{-5}	1.06	2.1×10^{-5}
995	2.29×10^{-5}	1.10	2.5×10^{-5}
983	3.27×10^{-5}	1.45	3.4×10^{-5}
966	4.44×10^{-5}	1.91	3.4×10^{-5}
963	4.61×10^{-5}	1.99	4.9×10^{-5}
957	4.90×10^{-5}	2.16	5.3×10^{-5}
952	5.11×10^{-5}	2.30	5.4×10^{-5}
930	5.59×10^{-5}	2.91	5.7×10^{-5}
918	5.58×10^{-5}	3.24	6.8×10^{-5}

897	5.22×10^{-5}	3.81	5.4×10^{-5}
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3.2.2. Crystal Growth Behavior in Lithium Disilicate Glass

Lithium disilicate glass is a high entropy of fusion material ($\Delta S_f = 5.6R$), and is thus expected to have crystallization kinetics of the form given by either the 2-D surface nucleation model or screw dislocation model. A high entropy of fusion material such as this is also predicted to have a large growth rate anisotropy, and should exhibit crystal faceting in at least some growth directions. The morphological observations reported for the temperatures investigated in this work (see Section 4.6.1) support these latter predictions, and our kinetic analysis indicates that the 2-D nucleated or screw dislocation growth mechanism operates in lithium disilicate glass at small undercoolings.

Here, for lithium disilicate glass it has been shown that the reduced growth rate curve appears to consist of three regimes over the 580°C of undercooling investigated. For ΔT values less than about 140°C the curve is suggestive of either 2-D surface nucleation or screw dislocation growth. For undercoolings greater than about 400°C, the curve is suggestive of 2-D surface nucleation. In between these two regimes, there seems to be some type of transitional behavior in the temperature dependence of the interface site factor. Although the interface site factor seems to be relatively independent of temperature in this intermediate regime, it is highly unlikely that this region corresponds to a transition to the normal growth model. This conclusion is based on morphological observations at temperatures extending into this apparent transitional regime, i.e., spherulites and faceted surface crystalline layers at $T = 635^\circ\text{C}$.

First, the kinetic analysis of the experimental growth rate data with respect to the 2-D surface nucleation model is discussed. When the two regimes suggestive of 2-D surface nucleation as indicated by the reduced growth rate graphs ($\Delta T < 140^\circ\text{C}$ and $400^\circ\text{C} \leq \Delta T \leq 580^\circ\text{C}$) are plotted separately as $\ln U\eta$ vs. $(T\Delta G)^{-1}$, neither data set can be fit by a single straight line. For undercoolings less than about 140°C, the data are best fit by two straight lines with different slopes. Others [101,106,108-113] have made similar observations regarding the behavior of such plots for various different systems studied over comparable undercooling ranges. Here, upon quantitative analysis in terms of the 2-D surface nucleation model it was found that for $\Delta T < 40^\circ\text{C}$ calculated growth rates were in excellent agreement with experimental results with respect to both magnitude and temperature dependence for both VFT equations considered. Also, calculated values of the y-intercept were in accord with extrapolated values. Thus it appears that theory and experiment are in excellent agreement in the region of small undercooling. Results of quantitative analyses for the more deeply undercooled region ($\Delta T = 40^\circ\text{C} - 140^\circ\text{C}$) in this

regime were also essentially the same for both VFT equations considered. In this region, the calculated growth rates agree with experimental results with respect to temperature dependence, but they are found to be one order of magnitude lower than experimental growth rates, and the extrapolated y-intercept values are smaller in magnitude by about a factor of 2 than the computed values. Although these results in and of themselves do not necessarily render theory inconsistent with experiment, the fact remains that with respect to the less deeply undercooled region ($\Delta T \leq 40^\circ\text{C}$), there is an observable change in agreement between theory and experiment. This region is discussed in more detail later.

Over the restricted temperature range $T = 500^\circ\text{C} - 454^\circ\text{C}$ ($\Delta T = 534^\circ\text{C} - 580^\circ\text{C}$) of the very deeply undercooled regime, the data again appear to be fit by a straight line of negative slope. However, as revealed by quantitative analysis, the calculated growth rates are off by many orders of magnitude and the extrapolated values of the y-intercepts are unreasonably high. Smith and Weinberg [131] investigated crystal growth at comparable undercoolings in lithium diborate glass and obtained similar results. These authors found the calculated growth rates to be some 60 orders of magnitude smaller than those determined experimentally, and they also observed a large discrepancy between calculated and extrapolated y-intercept values.

What is very interesting about the results shown in Table 5.3 for the very deeply undercooled temperature range ($T = 500^\circ\text{C} - 454^\circ\text{C}$) is the extreme sensitivity of the calculated growth rates to the temperature dependence of the viscosity. Using the Matusita & Tashiro viscosity data yields a slope, B , of the $\ln U\eta$ vs. $(T\Delta G)^{-1}$ plot which is about 2 times smaller in magnitude than the slope which results when the Zanutto viscosity data are utilized. Because the calculated growth rates are exponentially dependent upon the slope, this factor of 2 translates into a difference of over 30 orders of magnitude between the growth rates calculated using the respective viscosity data. The growth rates calculated for this temperature range using the more strongly temperature dependent viscosity data of Zanutto are about 65 orders of magnitude smaller than the experimentally determined growth rates, while the growth rates calculated using the Matusita & Tashiro viscosity data are about 31 orders of magnitude smaller than experimental data. Hence, despite the sensitivity of the growth rates to the viscosity, crystal growth rate values calculated using any reported viscosity data are many orders of magnitude smaller than experimental values. Therefore, it appears that the 2-D surface nucleated growth model as given by Equation (5.11) is not a valid description of crystal growth in the very deeply undercooled regime.

To help elucidate causes for the disparity between the experimental and calculated results in the very deeply undercooled region $\Delta T = 534^\circ\text{C} - 580^\circ\text{C}$, and to compare the description of growth in the latter region with that in the region of small undercooling ($\Delta T < 40^\circ\text{C}$), the effect of the viscosity on the computed growth is now examined. The viscosity can influence the values of the computed growth rates in two ways: (1) through its temperature dependence, which is reflected in the fitting of B , and (2) by its

magnitude. If one uses Equation (5.11) with $A' = \ln C_b$, and assuming the following for the undercooling ranges of interest:

$$\eta = \eta_o \exp\left(\frac{Q}{T}\right) \quad (5.18)$$

then

$$\ln U + \frac{Q}{T} = (A' - \ln \eta_o) - \frac{B}{T \Delta G} \quad (5.19)$$

Therefore, the activation energy, Q , will strongly influence the determination of B if it is sizable, and B will be sensitive to the temperature dependence of the viscosity if the theory is correct. If the theory is incorrect at low temperatures, then depending upon the temperature dependence of the “true” kinetic factor, the error in B will follow. If the “true” kinetic factor has weak temperature dependence, then one would expect a large error in B and thus a large error in the computed growth rate since the latter is very dependent upon B . At high temperatures, it appears that Q is much smaller than at low temperatures. Hence, if the theory is correct, then the computed growth rates are much less sensitive to the temperature dependence of the viscosity at high temperatures than at low temperatures. If the theory is correct at small undercoolings, then the error in B will again depend upon the “true” kinetic factor. If the “true” kinetic factor has weak temperature dependence, then the error in B would be small. However, if the “true” kinetic factor has strong temperature dependence, then the error in B would be large.

Now examining the experimental results of this work, one sees that in regions where $\ln U \eta$ vs. $(T \Delta G)^{-1}$ are linear, the agreement between theory and experiment worsens as ΔT increases. One might speculate then that this is consistent with the failure of η^{-1} as the kinetic factor for all T . However, then it would be hard to explain why experiment and theory agree so well at high T . Thus it is concluded as follows. (1) Theory in its unmodified form fits the experimental data well at smallest ΔT and gets worse (in the linear regions) as ΔT increases. This could indicate that theory is correct at high T , but breaks down at large ΔT due to failure of the Stokes-Einstein relation, or it could indicate that theory is incorrect due to the kinetic factor at all temperatures and that agreement at small ΔT is fortuitous. (2) It is a bit trickier to determine the growth mechanism from the reduced growth rate than presumed.

In light of the above, it is possible that the change in behavior observed for $\Delta T \leq 140^\circ\text{C}$ (Fig. 5.4) may be due to the increasing temperature dependence of the viscosity. However, this is not the only possible explanation for the observed change in behavior in

this temperature regime. Crystalline lithium disilicate is known to undergo a polymorphic phase transformation near 936°C [132,133], and this could influence the processes occurring at the interface. We note that the parameters used herein (Table 5.2) for quantitative analyses are for the low temperature form of LS₂. However, these parameters do not differ significantly from those of the high temperature form; $V_m = 6.15 \times 10^{-5} \text{ m}^3/\text{mol}$ for the low temperature form, and $V_m = 6.02 \times 10^{-5} \text{ m}^3/\text{mol}$ for the high temperature form according to the lattice parameters given in ref. [133]. Therefore, quantitative results for temperatures above the transformation temperature are valid as given. Another possibility for the observed change in behavior is that for undercoolings $> 40^\circ\text{C}$ crystal growth is occurring in a dynamically rough regime. That is, there may be a critical surface roughening, i.e., change in the nature of the interface site factor, at a temperature near 995°C. However, no detailed experimental morphological (or crystallographic) information is available for this composition at high temperatures to support this claim.

In 1974, James et al. [124] performed a TEM investigation on lithium disilicate glasses that had been heat-treated at 490°C for times up to 95 hours. Figure 2a of ref. [124] shows an electron micrograph of a lithium disilicate crystal that is very similar in appearance to the crystals shown in Fig. 4.20 of the present work. Using selected area diffraction (SAD), James identified crystals of this shape as single crystals with the long axis being along the [001] direction (c-axis). Therefore, it is concluded that the direction of fastest growth, and thus that measured for $T \leq 500^\circ\text{C}$ in the present work, is along the c-axis. At 490°C, James also observed crystals exhibiting branching at various stages of development, along with crystalline aggregates. These observations too are in consonance with the morphological observations reported in Section 4.2.1 of this work.

Based on the morphological observations in this work and the above discussion, it seems that the apparent deviation from linearity in the undercooling regime $\Delta T = 400^\circ\text{C} - 580^\circ$ ($T = 635^\circ\text{C} - 454^\circ\text{C}$) observed in Fig. 5.5 correlates with a change from a single crystal habit to a spherulitic crystal morphology. At present, there is no adequate theory for the description of spherulitic growth in inorganic glasses such as LS₂. Therefore, this deviation from linearity for $T = 590^\circ\text{C} - 635^\circ\text{C}$, where the crystals are observed to grow as spherulites, is not surprising. In ref. [124], James suggests that the branching of internal crystals observed at 490°C are formed through a twinning process. He goes on to suggest that regular branching via this twinning mechanism may explain the morphology observed at higher temperatures, i.e., spherulites. If this twinning mechanism is indeed responsible for the observed change in morphology, then it seems possible that at some critical growth velocity the stresses resulting from volume contraction produce a significant number of growth faults which in turn may affect the temperature dependence of the interface site factor, and consequently the operative growth mechanism.

Next, the data given in Table 5.4 are considered. In the second column of Table 5.4, the values of the surface energy, σ_E , as computed from the slopes, B , and Equation (5.6) are presented. As mentioned earlier, by assuming α values ranging from 0.25 – 0.40 the Turnbull-Staveley relation, Equation (5.12), is commonly invoked for making estimates of the crystal-liquid interface energy. In the third column of Table 5.4 the

values of α required in Equation (5.12) to yield the aforementioned surface energy values, σ_E , are given. Alternatively, using the α values derived for non-metallic substances (0.25-0.40), the crystal-liquid interface energy is estimated from the Turnbull-Staveley equation to be between 0.109 -0.175 J/m² for LS₂. As observed in Table 5.4, for the very deeply undercooled range $\Delta T = 534^\circ\text{-}580^\circ\text{C}$ ($T = 500^\circ\text{C} - 454^\circ\text{C}$), the α values (and σ_E values) are much higher than those estimated for LS₂ by Equation (5.12). For the undercooling range $\Delta T = 40^\circ\text{-}140^\circ\text{C}$ ($T = 983^\circ\text{C} - 897^\circ\text{C}$), the σ_E and α values given in Table 5.4 approach those estimated from Equation (5.12). However, for the undercooling range where theory and experiment are found to be in excellent agreement ($T = 1020^\circ\text{C} - 995^\circ\text{C}$), the values of σ_E and α are much lower than those predicted using the Turnbull-Staveley relation.

Now the kinetic analysis with respect to the screw dislocation model is discussed. Based on the agreement between calculated and experimental growth rates, it seems that the screw dislocation model provides an equally adequate description of experimental data in the region of small undercooling. However, as noted earlier the values of the interface site factor obtained for this model are not physically meaningful. Further, the surface energy value, and thus the α value in the Turnbull-Staveley equation, obtained by interpreting the experimental data with respect to the screw dislocation model are unduly small.

3.2.3. Effect of Water Concentration on Crystal Growth Rates

The influence of water in the glass on the observed growth rates is now discussed. Here, the growth rates of glasses having disparate water contents by virtue of being prepared in different geographical regions having very different humidity levels were investigated. As noted in Section 4.2, no attempt was made to differentiate between bound OH⁻ present within the bulk of the prepared glasses and OH⁻ absorbed on the surfaces. Based on the agreement among the glasses with respect to internal and surface crystal growth rates, omission of this differentiation has been justified. The glass prepared in São Carlos (Glass 5) contained nearly twice the amount of water as the glasses prepared in Tucson (Glasses 3 and 4). As observed in the present study, this difference in water concentration does not prove to significantly affect the crystal growth rates (see Figs. 4.28, 4.36, and Table 4.8). This assertion is bolstered by the observed consistency among the data reported in various studies by different investigators (Fig. 4.31). These observations are also consistent with the results reported by Scherer and Uhlmann [104], and Meiling and Uhlmann [102]. In refs. [104,102], the authors investigated sodium silicate glasses heated under various atmospheric conditions and found no observable differences in crystal growth rates. Gonzalez-Oliver et al. [89] came to a very different conclusion in their investigation of the influence of water on the growth rates in lithium disilicate glass. These authors found that growth rates markedly increased with increased water content. It is important to note that this conclusion is based on comparison between a glass prepared under normal melting conditions (denoted

L1 in ref. [89]) and a glass prepared by bubbling the melt with steam (denoted L5 in ref. [89]). The water contents in these glasses differed by nearly a factor of 7, and the growth rates were found to differ by a factor of 2. If one considers the variation in water contents typically encountered under normal conditions, as exemplified by the glasses studied in this work, then the results of Gonzalez-Oliver et al. [89] are not necessarily inconsistent with our assertions. That is, if a difference of a factor of 7 in water concentration translates into a difference of a factor of 2 in the growth rates, then it seems reasonable that a difference of a factor of 2 in water content would not yield an observable difference in growth rates.

In contrast to the above conclusion that water does not have an observable effect on the growth rates for the alkali silicates considered, it has been reported that water significantly affects the growth rates in network materials SiO_2 and GeO_2 [134,135]. Scherer and Uhlmann [104] effectively argue that this difference in behavior is associated with structural differences with respect to the degree of disruption of the network. As suggested by Scherer and Uhlmann, the presence of OH would be expected to have a pronounced effect in increasing the growth rate of well-formed network materials, but little effect on materials whose structures are already highly disrupted by the presence of the modifying oxide in sizable concentrations.

3.3. Analysis of Crystal Nucleation in Sodium Silicate Glasses

The DTA method presented by Wakasugi [88] for determining relative steady-state nucleation rates (described in Section 2.1.3.g.) relies on producing identical number densities for different thermal histories. The parameter of interest in the DTA method is the peak shift, ΔT_p , defined as the difference between peak temperatures of maximum crystallization of as-quenched and previously isothermally nucleated glass. If the same peak shift is produced for two different nucleation temperatures for two different nucleation times, using the same scan rate, the number densities must be identical (provided that the data are outside the transient nucleation regime and that there is no significant overlap of nucleation and growth). Therefore, the inverse ratio of the two nucleation times will give the ratio of nucleation rates at the two temperatures. Thus, the DTA technique yields the relative nucleation rates as a function of temperature, but not the magnitudes of the nucleation rates.

As evidenced from XRD data (Section 4.5.2), the only crystal phases, which formed in the compositions studied, were sodium metasilicate and sodium disilicate. As expected, for all compositions the crystal phase precipitated by internal nucleation was sodium metasilicate. The sodium disilicate crystal phase was apparently precipitated by external surface nucleation. Upon examination of relative amounts of each phase present in the XRD patterns of the W51% and W53% compositions, it is apparent that the majority of crystalline material is sodium metasilicate. The predominant crystal phase in W-55% and W-57% compositions is also sodium metasilicate. The XRD results as described in Section 4.5.2 support the assumption that Wakasugi was indeed observing internal volume nucleation during the DTA runs for compositions W51%, W53%, W55%, and W57%.

According to Wakasugi, the DTA results appeared to indicate the absence of internal nucleation for the W59% composition since there were no observable peak shifts between the as-quenched and previously heated samples for this composition. However, evidence of internal nucleation was provided in the present work by observation of heat-treated samples of this composition via optical microscopy and XRD analysis. This discrepancy is most likely due to low number densities and small growth rates of internal crystals in these glasses. To support this explanation, the number density, N_v , and ΔT_p vs. nucleation heat-treatment data for the W55% composition given in ref. [88] were considered. The number density of homogeneously nucleated crystals for the W55% composition, which was heat-treated at 410°C- 1/2 hour, was determined to be 325 mm⁻³ (Section 4.7.2). Upon extrapolation of the ΔT_p values in Fig. 5 of ref. [88] corresponding to this same nucleation temperature to a nucleation heat-treatment time of 1/2 hour, one finds the expected peak shift value to be less than 7°C. After heat-treatment at 440°C for 48 hours, the number density of crystals in the W59% composition was found to be only 90 mm⁻³ (Section 4.7.2). Therefore, if a number density of 325 mm⁻³ would only be expected to produce a peak shift of about 7°C, it seems reasonable to conclude that the number densities produced in the W59% composition are insufficient to yield observable peak shifts. This shows that small number densities limit the utility of the DTA method presented by Wakasugi.

4. CONCLUSION

From the results presented herein and from previously published studies, the following conclusions are drawn regarding the persistence of metastable crystalline phases in lithium disilicate glass. (1) It is most unlikely that metastable crystalline phases exist in LS₂ glasses that have been heated for long time periods in the temperature regime where internal nucleation occurs. (2) If some amount of metastable crystalline phases do persist to long times, they can not be detected via the use of XRD.

The growth rates of lithium disilicate crystals as a function of temperature and water concentration in the glass have been measured in the deeply undercooled temperature regime. Combining the results of this research with the data of others for different temperature regions, a global assessment of the crystal growth features of LS₂ glass was formulated. The analyses performed in this research have led to the following conclusions. (1) Crystal growth over a broad ΔT range is complex with many possible mechanism changes due to phase transitions, compound crystal growth, and other morphological changes. (2) Hence, one would not anticipate the usual phenomenological laws to be applicable over the entire temperature range of measurable growth, but only over limited temperature regimes. (3) In order to test the validity of any of the standard theories, it is important not only to check that the experimental and theoretical temperature dependencies are in agreement, but also whether there is accord with regard to the magnitudes of growth. (4) In the usual version of the 2-D nucleated growth equation in which the Stokes-Einstein relationship is used, relatively small differences in

the viscosity data employed can produce enormous differences in the predicted growth rates at large undercoolings. (5) For the system studied herein, the 2-D nucleated growth model is in excellent agreement with experiment for small ΔT , but is very poor at large ΔT . It is believed that these results could indicate the incorrect nature of the kinetic rate coefficient used in the standard growth models. (6) Although the screw dislocation growth model appears to agree well with experiment for small undercoolings, the experimentally determined interface site factor is not physically meaningful. (7) Water appears to have only a small influence in enhancing crystal growth rates if the water concentration of the glass is not excessively large. That is, unless one intentionally adds water to the glass during preparation, the growth rates of prepared glasses having dissimilar water contents are the same within experimental error.

For sodium silicate glasses it was found that all compositions studied exhibited homogeneous nucleation. XRD results revealed that the crystal phase precipitated by homogeneous nucleation was sodium metasilicate, and the crystal phase precipitated by surface nucleation was sodium disilicate.

The nucleation of sodium metasilicate crystals in a binary sodium silicate glass of composition $43\text{Na}_2\text{O}-57\text{SiO}_2$ (W57%) was investigated over the temperature range 390°C to 455°C . The magnitude and temperature dependence of the steady-state nucleation rate was determined by the development technique. The magnitude of the maximum nucleation rate was found to be $6.2 \times 10^3 \text{ (cm}^{-3} \text{ min}^{-1})$. The temperature at which the maximum nucleation rate occurred was 410°C , which is near T_g for this glass. Experimental steady-state nucleation rates obtained in this research were compared to the results obtained for the temperature dependence of the steady-state nucleation rate via Wakasugi's DTA technique. The results of the two different techniques agree within experimental error. These results validate the DTA technique for determining the temperature dependence of steady-state nucleation rates, provided the number densities are sufficiently large.

Calculations of the reduced temperature as a function of composition were performed for compositions between NS and NS₂. In accord with the empirical predictions regarding the reduced temperature and ability for a composition to nucleate internally, the calculations performed in this work showed that all sodium silicate compositions studied in this investigation have T_{rg} values below 0.58.

5. REFERENCES

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