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283

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UMI
CRYSTALLIZATION KINETICS OF LITHIUM DISILICATE 
AND SODIUM SILICATE GLASSES 

by 

Lori Lynn Burgner 

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A Dissertation Submitted to the Faculty of the 
DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING 
In Partial Fulfillment of the Requirements 
For the Degree of 
DOCTOR OF PHILOSOPHY 
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THE UNIVERSITY OF ARIZONA 

2000
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by LORI LYNN BURGNER entitled CRYSTALLIZATION KINETICS OF LITHIUM DISILICATE AND SODIUM SILICATE GLASSES and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

Michael C. Weinberg

Kenneth Jackson

Dunbar Birnie

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

Dissertation Director Michael C. Weinberg
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# TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................... 8

LIST OF FIGURES ......................................................................................................... 9

ABSTRACT .................................................................................................................... 13

1. INTRODUCTION ...................................................................................................... 15

2. LITERATURE REVIEW ............................................................................................ 20

   2.1 Nucleation in Supercooled Liquids and Glasses .............................................. 20
      2.1.1. Steady-State Nucleation ............................................................................. 22
      2.1.1.a. Homogeneous Nucleation ..................................................................... 22
      2.1.1.b. Heterogeneous Nucleation ................................................................. 42
      2.1.1.c. Determination of the Thermodynamic Driving Force .......................... 46
      2.1.1.d. Determination of the Interfacial Energy ............................................. 48
      2.1.2. Time-Dependent (Transient) Nucleation .............................................. 50
      2.1.2.a. Classical Theory: Time-Dependent Nucleation ............................... 56
      2.1.2.b. Analytical Solutions .......................................................................... 58
      2.1.2.c. Numerical Solutions .......................................................................... 64
      2.1.3. Experimental Studies of Homogeneous Nucleation in Supercooled
            Liquids and Glasses ...................................................................................... 66
      2.1.3.a. Polymorphically Crystallizing Liquids .............................................. 66
      2.1.3.b. Metallic Glasses .................................................................................. 70
      2.1.3.c. Simple Oxide Glasses ........................................................................... 71
      2.1.3.d. Evidence of Metastable Phase Formation in Lithium Disilicate
            Glass ................................................................................................................ 79
      2.1.3.e. Nucleation Studies in Sodium Silicate Glasses ................................... 84
      2.1.3.f. Non-Isothermal Heating Techniques for Studying Nucleation Rates
            in Glasses .......................................................................................................... 86
      2.1.3.g. Wakasugi's DTA Method .................................................................... 91
      2.1.3.h. Factors that Influence Nucleation in Glass Systems ......................... 94

   2.2 Crystal Growth in Supercooled Liquids and Glasses ........................................ 99
      2.2.1. Interface Controlled Growth .................................................................... 100
      2.2.2. Comparison of Experimental Data with Kinetic Models ....................... 102
      2.2.2.a. Low Entropy of Fusion Materials ...................................................... 102
      2.2.2.b. High Entropy of Fusion Materials ...................................................... 103

3. EXPERIMENTAL PROCEDURE .............................................................................. 105
TABLE OF CONTENTS - Continued

3.1 Glass Preparation ........................................................................................................... 105
  3.1.1. Lithium Silicate Glasses ......................................................................................... 105
  3.1.2. Sodium Silicate Glasses ....................................................................................... 108

3.2 Chemical Analysis of Prepared Glasses ........................................................................ 109

3.3 Water Concentration Determination ............................................................................. 110

3.4 Glass Transition Temperature Determination .............................................................. 111

3.5 Glass Density Measurements ......................................................................................... 112

3.6 Heat-Treatment Schedule for XRD Investigation of Metastable Phase
  Formulation ...................................................................................................................... 112

3.7 X-ray Diffraction (XRD) Measurements ....................................................................... 115
  3.7.1. Lithium Silicate Glasses ......................................................................................... 115
  3.7.2. Sodium Silicate Glasses ....................................................................................... 116

3.8 Crystal Growth Rate Determination in Lithium Silicate Glasses ................................. 116
  3.8.1. Internal Crystal Growth Rate Determination ......................................................... 116
  3.8.2. Surface Crystal Growth Rate Determination ......................................................... 117

3.9 Nucleation Rate Determination in Sodium Silicate Glasses ........................................ 120

4. EXPERIMENTAL RESULTS ............................................................................................. 123

4.1 Glass Composition ......................................................................................................... 123
  4.1.1. Lithium Silicate Glasses ......................................................................................... 123
  4.1.2. Sodium Silicate Glasses ....................................................................................... 124

4.2 Water Content .............................................................................................................. 125

4.3 Glass Transition Temperature ....................................................................................... 128

4.4 Experimental Density Measurements .......................................................................... 129

4.5 X-ray Diffraction Results ............................................................................................ 130
  4.5.1. Lithium Silicate Glasses ......................................................................................... 130
  4.5.2. Sodium Silicate Glasses ....................................................................................... 146
TABLE OF CONTENTS - Continued

4.6 Experimental Growth Rates in Lithium Silicate Glasses ........................................... 156
  4.6.1. Crystal Morphology ......................................................................................... 156
  4.6.2. Internal Crystal Growth Rates ....................................................................... 162
    4.6.2.a. Fast-Axis (Major-Axis) Growth Rates ..................................................... 162
    4.6.2.b. Short-Axis (Minor-Axis) Growth Rates .................................................. 175
    4.6.2.c. Surface Crystal Growth Rates .................................................................. 184

4.7 Experimental Crystal Nucleation in Sodium Silicate Glasses ................................. 197
  4.7.1. Steady-State Nucleation Rates .................................................................... 197
  4.7.2. Relative Crystal Number Densities ............................................................... 208
  4.7.3. Crystal Morphology ..................................................................................... 210

5. DISCUSSION ........................................................................................................... 213

  5.1 XRD Investigation of Metastable Phase Formation in Lithium Disilicate Glass .......................... 213

  5.2 Crystal Growth Rates in Lithium Disilicate Glasses ........................................... 219
    5.2.1. Comparison Between Theory and Experimental Results ........................... 219
    5.2.2. Crystal Growth Behavior in Lithium Disilicate Glass ............................... 249
    5.2.3. Effect of Water Concentration on Crystal Growth Rates ......................... 257
    5.2.4. Analysis of XRD Results for Lithium Silicate Glasses with Respect to Crystal Growth Rate Results ................................................................. 259

  5.3 Analysis of Crystal Nucleation in Sodium Silicate Glasses .................................. 266

6. CONCLUSION ........................................................................................................... 279

7. REFERENCES .......................................................................................................... 282
**LIST OF TABLES**

<table>
<thead>
<tr>
<th>TABLE</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Lithium silicate glass designation number and preparation details</td>
<td>107</td>
</tr>
<tr>
<td>3.2</td>
<td>Heat-treatment schedule for XRD investigation of metastable phase formation in lithium disilicate glass</td>
<td>114</td>
</tr>
<tr>
<td>3.3</td>
<td>Heat-treatment schedule for crystal growth rate determination in lithium silicate glasses</td>
<td>119</td>
</tr>
<tr>
<td>4.1</td>
<td>Index of refraction results and analyzed compositions for lithium silicate glasses</td>
<td>124</td>
</tr>
<tr>
<td>4.2</td>
<td>Glass transition temperature, $T_g$, of lithium silicate glasses</td>
<td>128</td>
</tr>
<tr>
<td>4.3</td>
<td>Density values for lithium silicate glasses</td>
<td>129</td>
</tr>
<tr>
<td>4.4</td>
<td>Summary of XRD results for Glass 1</td>
<td>132</td>
</tr>
<tr>
<td>4.5</td>
<td>Linear growth rates (fast-axis) of internal crystals for Glasses 3, 4, and 5</td>
<td>169</td>
</tr>
<tr>
<td>4.6</td>
<td>Linear growth rates (short-axis) of internal crystals for Glasses 3, 4, and 5</td>
<td>181</td>
</tr>
<tr>
<td>4.7</td>
<td>Aspect ratios of internal crystals for Glasses 3, 4, and 5</td>
<td>182</td>
</tr>
<tr>
<td>4.8</td>
<td>Surface crystalline layer growth rates for Glasses 3, 4, and 5</td>
<td>194</td>
</tr>
<tr>
<td>4.9</td>
<td>Steady-state nucleation rates of sodium metasilicate crystals in W57% composition glass</td>
<td>206</td>
</tr>
<tr>
<td>5.1</td>
<td>Slope, B, values, and extrapolated and computed y-intercept values</td>
<td>234</td>
</tr>
<tr>
<td>5.2</td>
<td>Parameters utilized for growth rate calculations</td>
<td>235</td>
</tr>
<tr>
<td>5.3</td>
<td>Experimental and calculated growth rate values: 2-D surface model</td>
<td>236</td>
</tr>
<tr>
<td>5.4</td>
<td>$\sigma_E$ and $\alpha$ values</td>
<td>241</td>
</tr>
<tr>
<td>5.5</td>
<td>Experimental and calculated growth rates: screw dislocation model</td>
<td>248</td>
</tr>
<tr>
<td>5.6</td>
<td>Summary of nucleation rate results from present and prior works</td>
<td>272</td>
</tr>
<tr>
<td>5.7</td>
<td>Reduced temperature values for sodium silicate glass compositions</td>
<td>277</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

FIGURE 2.1, Bulk Gibbs energy change, $\Delta G$, for homogeneous nucleation of sphere of radius $r$ ............................................................................................................................................ 27
FIGURE 2.2, Typical experimental number density ($N_v$) vs. time plot .......................................................................................................................... 52
FIGURE 2.3, Illustration of the separation between nucleation (I) and growth (U) temperature regimes ........................................................................................................ 73
FIGURE 2.4, Schematic representation of the Gibbs energy vs. composition for a simple binary A-B system ........................................................................................................ 96
FIGURE 4.1, FTIR spectra of Glass 4 and Glass 6 obtained from samples of equal thickness ($d = 1.45$ mm) .......................................................................................... 126
FIGURE 4.2, FTIR spectra of Glass 4 and Glass 5 obtained from samples of equal thickness ($d = 0.87$ mm) .......................................................................................... 127
FIGURE 4.3, XRD traces of Glass 1 .......................................................................................................................................................................................... 133
FIGURE 4.4, XRD traces of Glass 1 and Glass 2 heated at 454°C for 360 hours .................................................................................................................................. 134
FIGURE 4.5, XRD traces of Glass 4 heated at 454°C ......................................................................................................................................................... 138
FIGURE 4.6, XRD traces of Glass 4 heated at 465°C ......................................................................................................................................................... 139
FIGURE 4.7, XRD traces of Glass 3 heated at 454°C ......................................................................................................................................................... 140
FIGURE 4.8, XRD traces of Glass 3 heated at 465°C ......................................................................................................................................................... 141
FIGURE 4.9, XRD traces of Glass 6 heated at 454°C ......................................................................................................................................................... 142
FIGURE 4.10, XRD traces of Glass 5 heated at 454°C ......................................................................................................................................................... 143
FIGURE 4.11, XRD traces of Glass 5 heated at 465°C ......................................................................................................................................................... 144
FIGURE 4.12, Rotating anode XRD trace of Glass 5 heated at 454°C for 360 h ........................................................................................................... 145
FIGURE 4.13, XRD trace of W51% heated at 435°C for 6 hours then at 610°C for 2 minutes. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d) .................................................................................. 149
FIGURE 4.14, XRD trace of W55% heated at 435°C for 3 hours then at 610°C for 5 minutes. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d) .................................................................................. 150
FIGURE 4.15, XRD trace of W55% heated at 435°C for 3 hours then at 610°C for 10 minutes. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d) .................................................................................. 151
FIGURE 4.16, XRD trace of W57% heated at 425°C for 2 hours then at 610°C for 1 hour. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d) .................................................................................. 152
FIGURE 4.17, XRD trace of W57% heated at 425°C for 2 hours then at 610°C for 1 hour. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d) .................................................................................. 153
FIGURE 4.18, XRD trace W59% heated at 440°C for 48 hours then at 610°C for 0.5 hour. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d) .................................................................................. 154
LIST OF FIGURES - Continued

FIGURE 4.19, XRD trace of W59% heated at 440°C for 48 h then at 610°C for 2.5 hours. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d).................. 155

FIGURE 4.20, Optical micrograph showing morphology of internal crystals. Glass 3 heated at 477°C for 257 hours................................................. 158

FIGURE 4.21, Optical micrograph showing morphology of internal crystals. Glass 5 heated at 500°C for 69.25 hours................................. 159

FIGURE 4.22, Optical micrograph showing morphology of internal crystals. Glass 4 heated at 610°C for 10 minutes............................... 160

FIGURE 4.23, Optical micrographs showing surface crystal interface: (a) Glass 3 heated at 490°C for 127 hours, and (b) Glass 5 heated at 590°C for 35 minutes ............................................................. 161

FIGURE 4.24, Variation of internal crystal size with time for Glass 3 .......................................................... 164

FIGURE 4.25, Variation of internal crystal size with time for Glass 3 at T = 575°C .................................................. 165

FIGURE 4.26, Variation of internal crystal size with time for Glass 4 ................................................................. 166

FIGURE 4.27, Variation of internal crystal size with time for Glass 5 ................................................................. 167

FIGURE 4.28, Crystal growth rates as a function of temperature for Glasses 3, 4, and 5......................................................... 168

FIGURE 4.29, Comparison of growth rate measurement techniques for Glass 4 at T = 465°C................................................................. 170

FIGURE 4.30, Growth rate data as a function of temperature for Glasses 3, 4, and 5 along with data reported by other investigators......................... 172

FIGURE 4.31, Growth rate data shown in Fig. 4.30 (log scale) as a function of temperature ................................................................. 173

FIGURE 4.32, lnU vs. 1/T using data shown in Figure 4.30................................. 174

FIGURE 4.33, Variation of short-axes size with time for Glass 3......................... 177

FIGURE 4.34, Variation of short-axes size with time for Glass 4......................... 178

FIGURE 4.35, Variation of short-axes size with time for Glass 5......................... 179

FIGURE 4.36, Short-axis crystal growth rates as a function of temperature for Glasses 3, 4, and 5.......................................................... 180

FIGURE 4.37, Aspect ratios of Glasses 3, 4, and 5 as a function of temperature ...... 183

FIGURE 4.38, Surface crystal layer thickness and half-axis length of internal crystals as a function of time at T = 490°C and 500°C for Glass 3..... 187

FIGURE 4.39, Surface crystal layer thickness and radius of internal crystals as a function of time at T = 575°C for Glass 3................................. 188

FIGURE 4.40, Surface crystal layer thickness and radius of internal crystals as a function of time at T = 635°C for Glass 3................................. 189

FIGURE 4.41, Surface crystal layer thickness and half-length of long axis of internal crystals as a function of time at T = 500°C for Glass 4......................... 190

FIGURE 4.42, Surface crystal layer thickness and radius of internal crystals as a function of time at T = 610°C for Glass 4......................................... 191
LIST OF FIGURES - Continued

FIGURE 4.43, Surface crystal layer thickness and half-length of long axis of internal crystals as a function of time at T = 490°C and 500°C for Glass 5 .......................................................... 192
FIGURE 4.44, Surface crystal layer thickness and radius of internal crystals as a function of time at T = 590°C, 610°C, and 635°C for Glass 5 .............................................. 193
FIGURE 4.45, Comparison of surface crystal growth data between Glass 3 and Glass 5 at T = 490°C and T = 500°C .......................................................... 195
FIGURE 4.46, Comparison of surface crystal growth data between Glass 3 and Glass 5 at T = 635°C .......................................................... 196
FIGURE 4.47, W57% kinetic curve for Tn = 390°C ................................................ 199
FIGURE 4.48, W57% kinetic curve for Tn = 400°C ................................................ 200
FIGURE 4.49, W57% kinetic curve for Tn = 410°C ................................................ 201
FIGURE 4.50, W57% kinetic curve for Tn = 415°C ................................................ 202
FIGURE 4.51, W57% kinetic curve for Tn = 425°C ................................................ 203
FIGURE 4.52, W57% kinetic curve for Tn = 440°C ................................................ 204
FIGURE 4.53, W57% kinetic curve for Tn = 455°C ................................................ 205
FIGURE 4.54, Magnitude and temperature dependence of the steady state nucleation rate for W57% glass composition ........................................... 207
FIGURE 4.55, Optical micrograph of W59% nucleated at 440 for 48 hours then developed at 610°C for 0.5 hours .................................................. 209
FIGURE 4.56, Optical micrograph of W55% nucleated at 410°C for 0.5 hours then developed at 590°C for 20 minutes .................................................. 209
FIGURE 4.57, Optical micrograph showing morphology of sodium metasilicate crystals .................................................. 211
FIGURE 4.58, Optical micrograph showing morphology of sodium metasilicate crystals .................................................. 212
FIGURE 5.1, Viscosity data reported in the literature for LS2 glass; curve (a) VFT from ref. [123] and curve (b) VFT from ref. [128] .................................................. 226
FIGURE 5.2, Data in Fig. 5.1 plotted as ln η vs. T⁻¹ ........................................... 227
FIGURE 5.3, Reduced growth rate, UR, as a function of undercooling, ΔT ........ 229
FIGURE 5.4, ln UR vs. (TΔG)⁻¹ for ΔT < 140°C ........................................... 232
FIGURE 5.5, ln UR vs. (TΔG)⁻¹ for 400°C ≤ ΔT ≤ 580°C ........................................ 233
FIGURE 5.6, Calculated and experimental growth rates as a function of temperature for ΔT < 40°C .......................................................... 238
FIGURE 5.7, Calculated and experimental growth rates as a function of temperature for 40°C < ΔT < 140°C .......................................................... 239
FIGURE 5.8, Plot corresponding to Fig. 5.4 (ref. [128] VFT) with temperature dependence of C and b taken into account ........................................... 243
FIGURE 5.9, UR⁻¹ vs. ΔG for ΔT < 140°C .......................................................... 247
LIST OF FIGURES - Continued

FIGURE 5. 10, Variation of long-axis crystal length with time for Glasses 3 and 5 at T = 454°C ................................................................. 260
FIGURE 5. 11, Variation of long-axis crystal length with time for Glasses 3 and 5 at T = 465°C ................................................................. 261
FIGURE 5. 12, Variation of short-axis crystal length with time for Glasses 3 and 5 at T = 454°C ................................................................. 262
FIGURE 5. 13, Variation of short-axis crystal length with time for Glasses 3 and 5 at T = 465°C ................................................................. 263
FIGURE 5. 14, Temperature dependence of the relative nucleation rate for the W57% as derived from DTA data ............................................. 269
FIGURE 5. 15, Comparison of results from optical microscopy and DTA methods ...................................................................................... 271
FIGURE 5. 16, Summary of nucleation rate results from present and prior works ..... 273
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 43Na₂O-57SiO₂ (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.
1. 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.

To the scientific community, glasses provide an ideal media for studying nucleation and growth phenomena in condensed systems. Because of their high viscosities and relatively slow crystal growth rates (in comparison to freezing of a liquid), glasses transform on a longer time scale than undercooled liquids. This allows for “freezing-in” of the crystallization process and convenient determination of kinetics. Therefore, studying crystal nucleation in glasses provides an excellent means of quantitatively testing standard nucleation theories.

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 (LS₂) has been the most extensively studied composition. Crystal nucleation in LS₂ 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.

LS₂ 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 LS₂ 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 LS₂. 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.

The subject of metastable crystal nucleation could be of technical importance, too. If the process of formation of metastable crystalline phases were thoroughly understood, then the appearance of such phases could potentially be promoted and regulated. This capability could lead to the production of new glass-ceramic materials.

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.
2. LITERATURE REVIEW

2.1. Nucleation in Supercooled Liquids and Glasses

A liquid cooled below its melting (or liquidus) temperature has a higher Gibbs energy than the corresponding crystal phase. The supercooled liquid is therefore thermodynamically less stable and should undergo a spontaneous phase transformation to the crystalline state. The fact that supercooled liquids can be maintained out of equilibrium without crystallizing indicates the existence of a kinetic barrier to the phase transformation.

It is generally assumed that crystallization of supercooled liquids and glasses are initiated by large-amplitude, randomly distributed localized density fluctuations, which result in small regions (clusters) of the transformation product. If the region of transformation product is smaller than some critical value, the crystalline phase (called an embryo) redissolves. However, if the regions of transformation products are larger than some critical value, the crystalline regions (now called nuclei) are stable and will continue to grow until the material has completely crystallized. The fluctuation process leading to the production of clusters larger than the critical size is called nucleation, and the rate at which such clusters appear is called the nucleation rate.

The first theory of nucleation was put forth in 1926, by Volmer and Weber [2]. This theory, which describes nucleation of a condensed phase from a vapor phase, was formulated based on the assertion that metastability of a supersaturated phase was
primarily a question of kinetics. The reaction-rate model of nucleation constructed by Volmer and Weber invoked Gibbs' formulation of the reversible work for the formation of a static cluster of the new phase to calculate the equilibrium cluster density distribution. The nucleation rate was taken as being proportional to the rate of formation of critical-sized clusters in equilibrium.

In 1935, Becker and Döring [3] proposed that a steady-state distribution of clusters was more realistic than the equilibrium distribution used by Volmer and Weber, and they derived an expression for the steady-state nucleation rate. Ten years later, Turnbull and Fisher [4] extended the formalism of Becker and Döring to nucleation in a condensed system (crystal nucleation in a liquid). Collectively, the theories of Volmer and Weber, Becker and Döring, Turnbull and Fisher, Zeldovich, and others, constitute the general scientific paradigm known as Classical Nucleation Theory (CNT). CNT is the phenomenological theory commonly invoked to describe crystal nucleation in glasses.

Within the realm of CNT, two different nucleation mechanisms are distinguished: homogeneous nucleation, and heterogeneous nucleation. In the case of homogeneous nucleation, clusters of atoms or molecules in the form of the transformation product (crystal nuclei) arise spontaneously within the parent material, and are of the same chemical constitution as the crystals which grow upon them. In heterogeneous nucleation, the nuclei can be quite different chemically from the crystals that grow upon them. Heterogeneous nucleation frequently occurs on container walls, or on foreign particles introduced into the liquid (or glass) either intentionally or accidentally.
2.1.1. Steady-State Nucleation

2.1.1.a. Homogeneous Nucleation

The following thermodynamic discussion is applicable for homogeneous nucleation in one and pseudo-one-component liquids and glasses, i.e. polymorphic liquid-to-crystal and glass-to-crystal transformations. Unlike the case of nucleation from a vapor phase, the motion of the cluster may be neglected for nucleation in such condensed phases. Also, these systems are often treated as being free from the strain and coherency effects associated with crystal nucleation from a crystalline phase.

The formation of a new phase within a parent phase is accompanied by a change in the Gibbs energy of the system, \( \Delta G \). To develop a mathematical expression for the change in Gibbs energy of the system associated with the phase transformation, it is necessary to describe the energy of the system before and after the new phase is formed. Since a glass can be viewed as a supercooled liquid of very high viscosity, one can glean insight into the thermodynamics of glass devitrification by considering the simpler case of crystallization of a liquid.

The Gibbs energy of the initial system, one that is completely liquid, will be denoted as \( G_1 \). When some of the atoms or molecules in the liquid spontaneously cluster together in the form of the transformation product (crystal), the Gibbs energy of the
system will change to \( G_2 \). In addition to the Gibbs energy associated with the crystal and liquid phases, there will be an energy contribution to \( G_2 \) arising from the creation of the interface between the two phases. Assuming a sharp interface between the cluster and the parent phase (capillarity approximation), \( G_2 \) can be expressed as the sum of the volume and interfacial energy contributions:

\[
G_2 = V_S G_s + V_L G_L + A_{SL} \sigma_{SL} \tag{2.1}
\]

where \( V_S \) is the volume of the solid (crystal), \( V_L \) is the volume of the liquid, \( A_{SL} \) is the area of the crystal/liquid interface, \( G_S \) and \( G_L \) are the Gibbs energy per unit volume of the crystal and liquid, respectively, and \( \sigma_{SL} \) is the crystal/liquid interfacial energy. The Gibbs energy of the system prior to formation of the crystalline phase, \( G_1 \), may then be expressed

\[
G_1 = (V_s + V_L) G_L \tag{2.2}
\]

The change in Gibbs energy of the system, \( \Delta G \), where \( \Delta G = G_2 - G_1 \), due to formation of the crystal phase within the liquid is given by

\[
\Delta G = V_S (G_S - G_L) + A_{SL} \sigma_{SL} \tag{2.3}
\]
or

\[ \Delta G = V_s \Delta G_v + A_{sl} \sigma_{sl} \]  \hspace{1cm} (2.4)

where

\[ \Delta G_v = G_s - G_L. \]  \hspace{1cm} (2.5)

\( \Delta G_v \) is the change in Gibbs energy per unit volume. Assuming that \( \sigma_{sl} \) is isotropic, the shape of the new phase that will minimize the excess free energy is a sphere of radius \( r \). Incorporating this assumption into the expression for the change in Gibbs energy of the system yields the following expression

\[ \Delta G = \Delta G_r = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \sigma_{sl} \]  \hspace{1cm} (2.6)

Within classical nucleation theory the macroscopic values of \( \Delta G_v \) and \( \sigma_{sl} \) are used, even for very small clusters. The interfacial energy of a small cluster is suspected to be dependent upon curvature and/or temperature. However, at the present time it is not experimentally possible to independently determine the functional form of this relationship even if it does exist. Notwithstanding temperature or curvature dependence,
the interfacial energy term will always be positive, and the sign of $\Delta G_r$ will depend solely on the sign of $\Delta G_v$.

At temperatures above the equilibrium melting temperature, $T_m$, $\Delta G_v$ is always positive, and formation of the new phase is thermodynamically unfavorable. As the temperature is raised above $T_m$, $\Delta G_r$ monotonically increases.

When the liquid is cooled below the equilibrium melting point, $T_m$, i.e., supercooled by a small amount $\Delta T$ ($\Delta T = T_m - T$), $\Delta G_v$ in the expression for $\Delta G_r$ is proportional to $\Delta T$ and commonly approximated by the following relation

$$\Delta G_v = \frac{\Delta H_m \Delta T}{T_m}$$

where $\Delta H_m$ is the latent heat of fusion per unit volume. At temperatures below $T_m$, $\Delta H_m$ (and hence $\Delta G_v$) is almost always negative, i.e., heat is evolved upon the transformation reaction. The origin of Equation (2.7) is discussed in more detail in Section 2.1.1.c.

Upon nucleation of a spherical crystal phase in a supercooled liquid, there are two competing contributions to $\Delta G_r$: a positive contribution due to the interfacial energy term which increases as $r^2$ (assuming $\sigma_{st}$ is a constant), and a negative volume contribution which increases as $r^3$. The resulting graph of $\Delta G_r$ vs. radius for a given $\Delta T$ is shown in Fig. 2.1. As observed in Fig. 2.1, at sufficiently low values of $r$ the positive interfacial energy term dominates and $\Delta G_r$ is positive and increases with increasing $r$ values. As
some critical value of r is approached, the negative r^3 term starts getting larger faster than
the positive r^2 term, and at some critical r, r_c, dominance is handed over from the r^2 term
to the negative r^3 term. At r_c, ΔG_r is at its maximum value, ΔG_c. For values greater than
the r_c, ΔG_r monotonically decreases as the cluster size is further increased.
Figure 2.1  Bulk Gibbs energy change, $\Delta G$, for homogeneous nucleation of sphere of radius $r$. 

The diagram shows a graph with $\Delta G$ on the y-axis and $r$ on the x-axis. 

- At $T < T_m$, the interfacial energy is $\alpha r^2$.
- The volume free energy is $\alpha r^3$.

The graph illustrates the change in Gibbs energy ($\Delta G_c$) as a function of the radius ($r_c$).
The behavior described above is explained as follows. For a given undercooling $\Delta T$, formation of crystal regions with radii less than some critical value, $r_c$, will have too large a surface to volume ratio and will result in a positive net change in the Gibbs energy of the system. The crystal regions (embryos) will thus tend to shrink in order to lower the Gibbs energy of the system. For crystal regions with $r > r_c$, the Gibbs energy of the system is reduced by continued growth of the nuclei. At the critical radius, $r_c$, $\Delta G_r$ is at a maximum ($\Delta G_c$) and the crystal is in unstable equilibrium with the surrounding phase. At this point, the system can lower its energy by either dissolution or growth of the crystal.

By setting the derivative of $\Delta G_r$ (Equation 2.6) with respect to $r$ equal to zero, it is easily shown that the value of the critical radius for a given undercooling, $\Delta T$, is given by

$$r_c = \frac{2\sigma_{SL}}{\Delta G_v} \quad (2.8)$$

Since $\Delta G_v$ is proportional to undercooling, $\Delta T$, the size of critical radius will decrease with increasing $\Delta T$. Substituting Equation (2.8) into the expression for $\Delta G_r$ (Equation 2.6) yields the expression for the maximum value, $\Delta G_c$, and denoting this maximum value as $W^*$ leads to the following

$$\Delta G_c = W^* = \frac{16\pi\sigma^3}{3(\Delta G_v)^2} \quad (2.9)$$
Equation (2.9) gives the minimum reversible work required to form a mole of nuclei of critical size; the thermodynamic barrier to nucleation. It is apparent from Equation (2.9) that the thermodynamic barrier to nucleation decreases with increased undercooling.

Within the realm of thermodynamics, the probability of obtaining a fluctuation of a given size in an equilibrium system can be computed from the theory of thermodynamic fluctuations [5] if the homogeneous medium is equilibrated more rapidly than the formation time of the fluctuation. For this computation, it is useful to reformulate the change in Gibbs energy upon the appearance of a new phase in terms of the number of atoms or molecules, n, of the new phase rather than the radius. Making the same capillarity approximation wherein a sharp interface is assumed, the change in Gibbs energy due to the formation of cluster containing n atoms or molecules is again expressed as the sum of the volume and interfacial energy contributions

$$\Delta G_n = n \Delta G' + \frac{1}{2} (36\pi)^{1/3} v'^{2/3} \cdot n^{2/3} \sigma$$

(2.10)

where $\Delta G'$ is the difference in Gibbs energy between the final and initial phase per molecule, and $v'$ is the molecular volume. The dependence of $\Delta G_n$ on n is analogous to that of $\Delta G_r$ on r, and the resulting plot of $\Delta G_n$ vs. n is qualitatively identical to that shown in Fig. 2.1.

The critical cluster size, $n_c$, is found in the same manner as $r_c$, i.e., by taking the derivative of Equation (2.10) with respect to n, setting it equal to zero and solving for the critical value, $n_c$. This leads to the following expression for $n_c$:  

\[ n_c = \frac{32\pi}{3\nu} \left( \frac{\sigma^3}{|\Delta G^\nu|^\nu} \right) \]  

(2.11)

The minimum reversible work to form a cluster of new phase of critical size \( n_c \) is found to be identical to the minimum work required to form a cluster of critical radius \( r_c \):

\[ \Delta G_{n_c} = \Delta G_c = W^* = \frac{16\pi \sigma^3}{3(|\Delta G^\nu|^\nu)} \]  

(2.12)

By substituting the quantity \( \Delta G/V_m \) for \( \Delta G^\nu \), where \( V_m \) is the molar volume of the crystalline phase, the thermodynamic barrier to nucleation for a spherical nucleus may also be written

\[ \Delta G_{n_c} = \Delta G_c = W^* = \frac{16\pi \sigma^3 V_m^2}{3\Delta G^2} \]  

(2.13)

Returning to the theory of thermodynamic fluctuations, the probability of obtaining a cluster of a new phase containing \( n \) atoms or molecules, \( P_n \), depends on the minimum reversible work for cluster formation and is given by

\[ P_n \propto \exp \left( -\frac{\Delta G_n}{k_B T} \right) \]  

(2.14)
where $k_B$ is Boltzmann's constant. From this equation, the equilibrium cluster size distribution per mole, $N_n^e$, is readily obtained:

$$\frac{N_n^e}{N_a} = \exp \left( \frac{-\Delta G_n}{k_B T} \right)$$

(2.15)

where $N_a$ is Avogadro's number.

It is at this point that Classical Nucleation Theory began to evolve. As mentioned previously, Vohner and Weber [2] were the first to realize that the kinetics of cluster growth, not just the cluster size distribution, $N_n^e$, were important to nucleation-initiated phase transformations. Volmer and Weber constructed their kinetic model for nucleation of a condensed phase from a vapor phase based on reaction-rate theory where clusters of the new phase are assumed to evolve slowly by a series of reactions of the type:

$$Q_{n-1} + Q_{1:} \xrightarrow{k_n} Q_n$$

(2.16a)

$$Q_n + Q_{1:} \xrightarrow{k_{n+1}} Q_{n+1}$$

(2.16b)

where a single molecule (or formula unit) is represented by $Q_1$ and a cluster containing $n$ molecules by $Q_n$. The rate of addition or removal of molecules (or formula units) to a
cluster of size \( n \) is denoted by \( k_n^+ \) and \( k_n^- \), respectively. In order to determine the time-dependent cluster density, \( N_{n,t} \), a system of coupled differential equations having the following form must be solved:

\[
\frac{dN_{n,t}}{dt} = N_{n+1,t} k_{n+1}^+ - \left[ N_{n,t} k_n^- + N_{n,t} k_n^+ \right] + N_{n+1,t} k_{n+1}^-
\]  \( (2.17) \)

which has the form of a master equation.

Volmer and Weber made the assumption that the back flux in reaction (2.16b) was zero for clusters larger than the critical size, \( n_c \), and thus set the time dependent cluster population, \( N_{n,t} \), to zero for \( n > n_c \). For \( n \leq n_c \), they assumed that \( N_{n,t} \) would be equal to \( N_n^e \) (Equation 2.15). Volmer and Weber proposed that the nucleation rate per mole, \( I \), is equal to the rate of monomer addition to clusters equal to or larger than the critical size, \( k_n^+ \), multiplied by the equilibrium distribution of clusters. The nucleation rate, \( I \), being thus given by

\[
I = k_n^+ \times N_n^e = k_n^+ \times N_n \exp \left( \frac{-\Delta G_{n_c}}{k_B T} \right)
\]  \( (2.18) \)

Becker and Döring [3] subsequently argued that a discontinuity in populations of clusters at the critical size was unreasonable, and that a steady-state distribution of clusters, \( N_n \), giving rise to a constant nucleation rate was physically more realistic than an
equilibrium distribution. In general, the forward rate of reaction \( I_n \) as in Equation (2.16b) is a function of time and of size \( n \):

\[
I_n = N_n k_n^+ - N_{n+1} k_{n+1}^-
\]  

(2.19)

At equilibrium, \( N_{n,t} = N^*_n \) and the net rate is zero:

\[
I_{n,t} = N_n^* k_n^+ - N_{n+1}^* k_{n+1}^- = 0
\]  

(2.20)

Becker and Döring pointed out that when nucleation is taking place, such equilibrium would not be established. Instead, they argued that a steady-state distribution would be established such that the net forward rate of reaction as in Equation (2.16b) is constant, independent of time and \( n \). Becker and Döring recognized that due to the rapid growth of nuclei larger than \( n_c \), the number of critical size nuclei would be smaller than the equilibrium number. Since the Gibbs energy of a critical size embryo can be reduced by losing a crystallizing unit as well as gaining one, it is equally likely that a critical size embryo will grow or dissolve (see Fig. 2.1). Allowing for the reverse bimolecular reaction, i.e., removal of monomer from a critical size cluster, and by adding a number of crystallizing units equal to one more than the critical number \( n_c + 1 \) to the initial phase for every nucleus which is removed by growth (following Volmer and Weber), the steady-state condition is maintained. The net forward rate is the steady-state nucleation rate, \( I^s \), and is given by
where $N_\text{ss}$ is the number of clusters containing $n$ molecules in the steady state. The resulting mathematical equation of Becker and Döring turned out to differ from the expression of Volmer and Weber only by a multiplicative factor, $Z$. That is, when the effects neglected by Volmer and Weber, namely: (1) for $n > n_c$, the values of $k^-_n$ are still larger than zero, and (2) that $N_{n^c} < N_{n^e}$, are taken into account the nucleation rate is reduced by the factor $Z$. $I^s$ as formulated by Becker and Döring is given by

$$I^s = N_{n_c^e}k^+_{n_c^e} \times Z$$

(2.22)

where $Z$ is known as the Zeldovich factor, which may be expressed

$$Z = \left( \frac{W^*}{3\pi k_B T (n_c^2)} \right)^{1/2}$$

(2.23)

For the case of cluster nucleation from a vapor phase, the collision flux and reaction rate constants (rate of monomer addition and removal) $k^+$ and $k^-$ are readily defined in terms of molecular velocity in the vapor, the attachment probability to a developing cluster, and the evaporation rate. However, the appropriate reaction-rate
coefficients are not easily defined for cluster nucleation from a condensed phase because mobilities and sticking probabilities are not obvious.

In 1949, nearly 10 years after the work of Becker and Döring, Turnbull and Fisher [4] formulated the definitions for the reaction-rate constants and collision flux for nucleation of a cluster from a condensed phase. Turnbull and Fisher calculated the reaction-rate constants and the collision flux of molecules for a condensed phase on the basis of the theory of absolute reaction rates. That is, they assumed that when a monomer was added or removed from a cluster, the system passed through a configurational (activated complex) state, which was higher in energy than either the initial or final state. The forward rate coefficient, $k_n^+$ as derived from Turnbull and Fisher's treatment of nucleation in a condensed system is given by the product of the number of active sites available for attachment, $O_n$, and the molecular jump rate of the forward reaction, $\gamma_n^+$:

$$k_n^+ = O_n \gamma_n^+ \quad (2.24)$$

The backward rate constant is given by

$$k_n^- = O_{n-1} \gamma_n^- \quad (2.25)$$

At $n = n_c$, $\gamma^+ \approx \gamma^- \approx \gamma$ since the derivative of $\Delta G_n$ is zero at $n_c$, and $\gamma$ may be expressed
and the forward rate coefficient may be expressed

\[ k^+_n = O_{ne} \left( \frac{k_B T}{h} \right) \exp \left( \frac{-\Delta g}{k_B T} \right) \]  

(2.27)

where \( O_{ne} \) is the surface area of a critical cluster, \( h \) is Planck’s constant, and \( \Delta g \) is the free energy of activation for atoms (or molecules) to cross the liquid-crystal interface. The term \( k_B T/h \) is a frequency factor. Turnbull and Fisher incorporated their expressions for the reaction rate coefficients into the formalism of Becker and Döring, and arrived at an expression of the following form for the steady-state homogeneous nucleation rate from a condensed phase

\[ I^s = Z \times N_n^e \times k^+_n = Z N_n^e O_{ne} \gamma \]  

(2.28)

which may be written as

\[ I^s = A \exp \left( \frac{-\Delta g}{k_B T} \right) \exp \left( \frac{-\Delta G_{ne}}{k_B T} \right) \]  

(2.29)
where $\Delta G_{\epsilon}$ is the thermodynamic barrier to nucleation, and $\Delta g$ is the activation free energy for transport across the matrix/nucleus interface; the kinetic barrier to nucleation. The pre-exponential factor, $A$, for nucleation from the condensed phase is given by

$$A = 2n_v V^{1/3} \left( \frac{k_B T}{h} \right)^{\frac{1}{2}} \left( \frac{\sigma}{k_B T} \right)^{1/2}$$

(2.30)

where $n_v$ is the number of formula units of the crystallizing component per unit volume, $V$ is the volume per crystallizing unit, and $\sigma$ is the liquid-crystal interfacial energy.

Since the quantity $\Delta g$ in Equation (2.29) is not known, when applying CNT to crystal nucleation in glasses and supercooled liquids it has become common practice to introduce two separate assumptions in order to relate the kinetic barrier to nucleation to an easily measured experimental parameter, namely, the viscosity. First, it is assumed that $\Delta g$ can be replaced with the Gibbs activation energy for ordinary self-diffusion, $\Delta G_D$, where the diffusion coefficient, $D$, is given by

$$D = D_0 \exp \left( \frac{-\Delta G_D}{k_B T} \right)$$

(2.31)

The diffusion constant, $D_0$, in Equation (2.31) is given by
where $\lambda$ is called the "jump distance" and is taken here as the atomic (or molecular) diameter.

Second, the Stokes-Einstein hydrodynamical theory for self-diffusion in a liquid is invoked. It is useful to explain the derivation of the Stokes-Einstein relation in more detail before incorporating it into the working version of CNT as it is usually applied to interpret nucleation rate data in glasses. According to Stokes Law, the force, $F$, on a sphere moving at steady state in laminar flow is expressed

$$ F = 6\pi R \eta V_{\infty} $$

(2.33)

where $R$ is the radius of spherical particle, $\eta$ is viscosity of the fluid medium, and $V_{\infty}$ is the steady-state velocity with which the particle is moving.

Independently, Einstein showed that the mobility, $B$, of a particle under the influence of an external force is related to the diffusion coefficient, $D$, by the relationship

$$ D = B k_B T. $$

(2.34)

The mobility, $B$, is equal to the mean velocity divided by the force acting on the particle
Substituting Equation (2.33) into Equation (2.35) results in the following expression for \( B \):

\[
B = \frac{V_{\infty}}{F} = \frac{1}{6\pi R\eta} .
\]  

(2.36)

It should be noted that in using the Einstein equation it is assumed that \( B \), and hence \( D \), are independent of composition and associated energy gradients. Combining Equations (2.34) and (2.36) yields the Stokes-Einstein relation

\[
D = \frac{k_B T}{6\pi R\eta} 
\]  

(2.37)

Assuming the diffusing species to be spherical with dimensions on the order of atomic (or molecular) diameter \( \lambda \), the Stokes-Einstein relation commonly appears in glass literature as

\[
D = \frac{k_B T}{3\pi \lambda \eta} 
\]  

(2.38)
It is noted that invoking the Stokes-Einstein relation has no firm theoretical sanction for the case of crystal nucleation in a glass, and is a strong point of controversy in the field of glass science.

Combining the above two assumptions, i.e., Equations (2.31), (2.32), and (2.38), it is easily shown that

\[
\frac{h}{3\pi \lambda^2 \eta} = \exp \left( -\frac{\Delta G_D}{k_B T} \right) \tag{2.39}
\]

Hence, the steady state nucleation rate for nucleation in a condensed phase may be written as

\[
I^s = A \exp \left( -\frac{\Delta G_D}{k_B T} \right) \exp \left( -\frac{\Delta G_{nc}}{k_B T} \right). \tag{2.40}
\]

Since \(\Delta G_{nc}\) decreases with increased undercooling below the melting temperature, Equation (2.40) predicts a correspondingly sharp rise in the steady-state nucleation rate with undercooling. That is, the thermodynamic driving force for the phase transformation gets larger with increasing \(\Delta T\). However, as the undercooling is further increased, \(I^s\) begins to drop off rapidly as the kinetic barrier to nucleation increases sharply at lower temperatures due to decreased atomic (or molecular) mobility. This bell-shaped temperature dependence for \(I^s\) is in accord with experimental observations.
It is typically found that the prefactor, $A$, in Equation (2.40) is essentially a constant (typically $10^{41}-10^{42}$ m$^{-3}$s$^{-1}$) and can effectively be expressed over the temperature range where nucleation occurs by

$$A = n_v \left( \frac{k_B T}{\hbar} \right)$$  \hspace{1cm} (2.41)

Then, by assuming a spherical cluster and substituting Equations (2.12), (2.39), and (2.41) into Equation (2.40), one obtains the form of the steady-state homogeneous nucleation rate commonly used to interpret experimental nucleation rate data

$$I^s = \left( \frac{n_v k_B T}{3 \pi \lambda^3 \eta} \right) \exp \left( \frac{-16 \pi \sigma^3}{3 (\Delta G_v)^2 k_B T} \right)$$  \hspace{1cm} (2.42)

which may be written

$$I^s = \frac{A'}{\eta} \exp \left( \frac{-16 \pi \sigma^3}{3 (\Delta G_v)^2 k_B T} \right).$$  \hspace{1cm} (2.43)
2.1.1.b. Heterogeneous Nucleation

The second nucleation mechanism considered in Classical Nucleation Theory is heterogeneous nucleation. This is one of the mechanisms by which nucleating agents promote or enhance volume nucleation in glasses for the production of glass-ceramics. This is also the mechanism by which such things as dust particles and container walls affect nucleation. This mechanism will be demonstrated by once again considering the simpler case of a solid (crystal) nucleating in a liquid. It is first assumed that the surface of the heterogeneity (foreign surface) is large compared to the size of the nucleating particle, and that \( \sigma_{sl} \) is isotropic. Subject to these constraints, the total interfacial energy is minimized if the transformation product has the shape of a spherical cap on the heterogeneity surface. The wetting angle, \( \theta \), is then given by the condition that the interfacial tensions between the heterogeneity/liquid (\( \gamma_{hl} \)), crystal/heterogeneity (\( \gamma_{sh} \)), and crystal/liquid (\( \gamma_{sl} \)), balance in the plane of the heterogeneous surface. This condition is expressed mathematically by

\[
\gamma_{hl} = \gamma_{sh} + \gamma_{sl} \cos \theta
\]  

(2.44)

The change in Gibbs energy associated with the formation of such a nucleus is once again given by the sum of the volume and interfacial energy contributions, which for this case is
\[
\Delta G_{\text{het}} = V_s \Delta G_v + A_{SL} \gamma_{SL} + A_{SH} \gamma_{SH} - A_{SH} \gamma_{HL}
\]  \hspace{1cm} (2.45)

where

\[
V_s = \frac{1}{3} \pi r^2 (2 + \cos \theta)(1 - \cos \theta)^2
\]  \hspace{1cm} (2.46)

\[
A_{SL} = 2\pi r^2 (1 - \cos \theta)
\]  \hspace{1cm} (2.47)

\[
A_{SH} = \pi r^2 \sin^2 \theta
\]  \hspace{1cm} (2.48)

\[
\cos \theta = \frac{\gamma_{HL} - \gamma_{SH}}{\gamma_{SL}}
\]  \hspace{1cm} (2.49)

By substituting Equations (2.46)-(2.49) into Equation (2.45), and denoting \( \gamma_{SL} \) as \( \sigma_{SL} \), it is easily shown that \( \Delta G_{\text{het}} \) may be expressed by

\[
\Delta G_{\text{het}} = \left\{ \frac{4}{3} \pi r^4 \Delta G_v + 4\pi r^2 \sigma_{SL} \right\} f(\theta)
\]  \hspace{1cm} (2.50)

where

\[
f(\theta) = \frac{1}{4} (2 + \cos \theta)(1 - \cos \theta)^2
\]  \hspace{1cm} (2.51)
Thus, the thermodynamic barrier for heterogeneous nucleation is smaller than that of homogeneous nucleation by shape factor $f(\theta)$:

$$W_{\text{het}}^* = W^* f(\theta) \quad (2.52)$$

Therefore, for any wetting angle $\theta < 180^\circ$, the thermodynamic barrier to nucleation will be lower for nucleus formation on the surface of the heterogeneity than for homogeneous nucleation. The kinetic barrier to nucleation, however, is comparatively unaffected by the presence of heterogeneous nucleation sites. Thus, whenever suitable heterogeneous sites are available, heterogeneous nucleation will generally occur in preference to homogeneous nucleation. The steady-state heterogeneous nucleation rate on a flat substrate in a supercooled liquid is given by [6]:

$$I_{\text{het}}^* = n_s \frac{k_B T}{h} \exp \left[ -\frac{\left(W_{\text{het}}^* + \Delta G_D\right)}{k_B T} \right] \quad (2.53)$$

where $n_s$ is the number of atoms or formula units of the liquid (or glass) in contact with the heterogeneity surface per unit area.

As noted, the above expressions are based on the assumption that the heterogeneous surface is large compared to the nucleus, and are valid when the surface is effectively flat e.g. container walls and relatively large impurity particles. In general, the thermodynamic energy barrier for heterogeneous nucleation will be greater or smaller for...
convex and concave (to the liquid or glass) heterogeneous surfaces respectively, than the corresponding value for a flat substrate [7]. If the heterogeneity is in the form of a spherical particle in the liquid, Fletcher [8] has shown that the heterogeneous activation energy is given by

\[ W_{\text{het}}^* = W^* g(\theta, x) \]  

(2.54)

where \( g(\theta, x) \) is function given by Fletcher where; \( x = R/r_c \), \( r_c \) is the critical radius for homogeneous nucleation, and \( R \) is the radius of the heterogeneous substrate. Based on the work of Fletcher, it has been suggested [7] that incorporation of the heterogeneous substrate curvature only has a large effect on \( W_{\text{het}}^* \) and hence on the heterogeneous nucleation rate, when \( x \) is less than about 10. For example, it has been experimentally determined that \( r_c \) for silicate glasses is approximately 1nm at temperatures where the nucleation rate is appreciable. Thus, for spherical particles with radii values less than about 10nm, the heterogeneous nucleation rate for a convex surface is expected to sharply decrease relative to \( I_{\text{het}} \) for a flat heterogeneous substrate. As a result, very fine convex particles below a certain size are not expected to act as efficient nucleation sites.
2.1.1.c. Determination of the Thermodynamic Driving Force, $\Delta G$

The thermodynamic driving force for transformation from the supercooled liquid (or glassy) state to the crystalline state at temperatures away from the equilibrium melting temperature is given by the magnitude of the change in Gibbs energy, $\Delta G$, where

$$\Delta G = \Delta H - T \Delta S$$  \hspace{1cm} (2.55)

In Equation (2.55), $\Delta H$ is the change in enthalpy of the system upon going from the initial state (supercooled liquid or glass) to the final (crystalline) state, $\Delta S$ is the corresponding change in entropy of the system, and $T$ is the temperature in Kelvin. At the melting (or liquidus) temperature, $T_m$, the system is in thermodynamic equilibrium and $\Delta G = 0$, i.e., the Gibbs energy of the crystal and liquid phases are equal. Therefore, at this temperature

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$  \hspace{1cm} (2.56)

where the quantity $\Delta S_m$ is the entropy of fusion, and $\Delta H_m$ is the enthalpy of fusion (also called the latent heat of fusion) at the melting point. If the heat capacities at constant pressure, $C_p$, of the two phases are known as a function of temperature, then $\Delta G$ can be
readily computed as a function of temperature from Equation (2.55) using the measured enthalpy at the melting point, $\Delta H_m$, and the following equations

$$\Delta H = \Delta H_m - \int_{T'}^{T_m} \Delta C_p \, dT' \quad (2.57)$$

$$\Delta S = \Delta S_m - \int_{T'}^{T_m} \frac{\Delta C_p}{T'} \, dT' \quad (2.58)$$

where $\Delta C_p$ is the difference in heat capacities between the two phases. Substituting Equations (2.57) and (2.58) into Equation (2.55) and using Equation (2.56), the change in Gibbs energy is given by

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \int_{T'}^{T_m} \Delta C_p \, dT' + T \int_{T'}^{T_m} \frac{\Delta C_p}{T'} \, dT' \quad (2.59)$$

where $\Delta T$ is the undercooling, $T_m - T$. At large undercoolings, accurate experimental determinations of $\Delta C_p$ are difficult, and several approximate expressions for $\Delta G$ have thus been developed based on different assumptions regarding the temperature dependence of $\Delta C_p$. Of these approximate expressions, the simplest is the one suggested by Turnbull [9], who argued that if no data are available the best approximation is attained by setting $\Delta C_p$ equal to zero. This yields the following linear relation between $\Delta G_v$ and $\Delta T$: 
\[ \Delta G = \frac{\Delta H_m \Delta T}{T_m}. \]  \hspace{1cm} (2.60)

If \( \Delta C_p \) is not a function of temperature and is non-zero, integration of Equation (2.59) gives

\[ \Delta G = \frac{\Delta H_m \Delta T}{T_m} - \Delta C_p \left[ \Delta T - T \ln \left( \frac{T_m}{T} \right) \right] \]  \hspace{1cm} (2.61)

By assuming \( \Delta C_p \) to be an unknown constant, Hoffman [10] arrived at the following equation for approximating \( \Delta G \):

\[ \Delta G \approx \frac{\Delta H_m \Delta T T}{T_m^2}. \]  \hspace{1cm} (2.62)

2.1.1.d. Determination of the Interfacial Energy

As mentioned in Section 2.1.1.a, CNT in its standard form uses macroscopic values for the interfacial surface energy, \( \sigma \), even for very small clusters. Various experimental methods for determining solid-liquid interfacial energies exist and
are described in ref. [11]. However, measurements are difficult and there are no direct methods available to measure the interfacial surface energy between a crystal and its liquid (or glass) of the same composition. Therefore, \( \sigma \) values are commonly inferred from nucleation measurements. For example, when the classical expression for \( \Gamma^* \) is written as

\[
\Gamma^* = \frac{A'}{\eta} \exp \left[ -\frac{16\pi}{3k_B T} \frac{\sigma^3}{\Delta G_v} \right]
\]  

(2.63)

it is clear that a plot of \( \ln \Gamma^* \eta \) vs. \( 1/T(\Delta G_v)^2 \) should give a straight line of negative slope proportional to \( \sigma^3 \), and an intercept equal to the prefactor for the nucleation rate.

However, this procedure does not allow for an independent test of the theoretical models.

The \( \sigma \) values obtained by the above procedure are commonly compared to the values estimated using a semi-empirical relationship originally derived by Turnbull [12] based on values of crystal-liquid interfacial energies, \( \sigma_h \), obtained from maximum undercooling experiments on small droplets of various elemental liquids (described in Section 2.1.3.a). Turnbull defined a surface one atom thick containing Avogadro's number of atoms and calculated the interfacial energy of this surface, which he called the "gram-atomic free surface energy," \( \sigma_s \), defined by

\[
\sigma_s = \sigma_h V_m^{2/3} N_a^{1/3}
\]  

(2.64)
where $V_m$ is the molar volume and $N_a$ is Avogadro’s number. By plotting $\sigma_g$ vs. the molar quantity $\Delta H_m$, a linear relation is observed for both metals and non-metallic substances with average slopes, $\alpha$, of about 0.45 and 0.32, respectively.

Using the numerical constants given above ($\alpha$ values), the following equation, known as the Turnbull-Stavely relation, is commonly invoked for making estimates of the interfacial energy (taken here as being equal to $\sigma_h$):

$$\sigma_h = \frac{\alpha \Delta H_m}{N_a^{1/3} V_m^{2/3}}$$

(2.65)

An approximate theoretical estimate of $\sigma$, based on a model of the solid-liquid interface developed by Skapsi [13] for metals, is also sometimes invoked for comparison with $\sigma$ values obtained from steady-state nucleation rate measurements. In this model, $\sigma$ is related to the densities of the liquid and solid, $\Delta H_m$, the surface energy of the liquid, $\sigma_L$, and the entropies of the two phases.

2.1.2. Time-Dependent (Transient) Nucleation

In many silicate glasses, the nucleation rate can be measured directly by counting the number of nuclei per unit volume, $N_v$, produced at a given temperature for
various different heating times. The number density of nuclei is related to the nucleation rate, \( I \), by

\[
N_v = \int_0^t I(t) \, dt .
\]  

(2.66)

If the nucleation rate is independent of time, i.e., in the steady-state regime, then

\[
N_v = \int_0^t I(t) \, dt = I^* t
\]  

(2.67)

and a plot of \( N_v \) vs. time should yield a straight line which intersects the time axis at \( t = 0 \); the slope of the line being equal to the steady-state nucleation rate, \( I^* \), at the measurement temperature. In nucleation rate studies, however, non-linear behavior of \( N_v \) vs. time plots is often observed at shorter times. Such plots generally indicate an initially low nucleation rate that approaches the steady-state value at longer times. Figure 2.2 depicts a typical \( N_v \) vs. time curve representing this situation. The non-linear region in Fig. 2.2 is called the transient nucleation regime. In addition to silicate glasses, transient nucleation has been reported for other materials including metallic glasses, enamel, glass-ceramics, and non-silicate based glasses.
Figure 2.2  Typical experimental number density \( (N_v) \) vs. time plot
As illustrated in Fig. 2.2, by extrapolating the linear region of the kinetic curve back to the time axis, one can obtain what is known as the experimental induction time, $t_{ind}$ (also called the effective lag time), for the temperature at which the data were obtained. The time necessary to reach a constant (steady-state) nucleation rate is denoted in Fig. 2.2 by $t^\ddot{\circ}$. Experimentally, curves of the type depicted in Fig. 2.2 are usually generated from number density data, $N_v$, obtained via a two-step isothermal annealing method. In this technique, the glass is first isothermally heated at the nucleation temperature, $T_N$, for the desired time, then quenched to room temperature and subsequently reheated at a higher "development" temperature, $T_{dev}$, to grow the nuclei to dimensions observable by an optical microscope. Assuming spherical clusters, the time $t^0$ shown in Fig. 2.2 is considered to be nearly equal to the time of exposure required for a nucleus of critical radius $r_c(T_N)$ to reach, at temperature $T_N$, the critical size $r_c(T_{dev})$ at temperature $T_{dev}$; only crystals larger than the critical size at the development temperature can grow at $T_{dev}$. Therefore, $t^0$ may be expressed by

$$t^0 = \int_{r_c(T_N)}^{r_c(T_{dev})} \frac{dr}{U(T,r)}, \quad r_c = \frac{2\sigma}{\Delta G_v}$$

(2.68)

where $U(T,r)$ is the growth rate of the crystals with radius $r$ at the nucleation temperature $T_N$; $\sigma$ is the crystal nucleus-glass interfacial energy, and $\Delta G_v$ is the difference in Gibbs energy between the glass and the crystal per unit volume. From Equation (2.68), it
follows that the value of $t^o$ increases with increasing $T\text{dev}$, and the curve in Fig. 2.2 is correspondingly shifted toward larger $t$. The value of this shift along the $t$ axis can be used to estimate $\sigma$ if $\Delta G_v$ and $U(T,r)$ are known.

The time-dependent nucleation rate, $I(t)$, is given by the local slope of the $N_v$ curve shown in Fig. 2.2. For sufficiently long heating times, $N_v$ can be approximated by

$$ N_v = I^o \left( t - t_{\text{ind}} \right) \quad t >> t_{\text{ind}} \quad (2.69) $$

where $t_{\text{ind}}$ is the induction time. Of the times identified in Fig 2.2, the induction time is most related to the transient time, $\tau$, that appears in the analytical expressions for transient nucleation. The physical meaning of the measured induction time, $t_{\text{ind}}$, is clarified in Section 2.1.2.b.

Transient nucleation is important not only for crystallization of supercooled liquids and glasses, but also for a variety of nucleation initiated first-order phase transformations including liquid phase separation, condensation from a vapor, and crystal-to-crystal phase transformations. Transient nucleation can play a crucial role in glass formation. From a kinetic standpoint, glass formation occurs when crystallization is avoided upon cooling a liquid. Unlike other approaches to glass formation (e.g. structural, electronic, or thermodynamic), the implication of the kinetic approach is that any material can be obtained in an amorphous form if cooled at a sufficient rate. As suggested by Uhlmann (e.g. ref. [14]), a material may be considered glassy if the crystalline volume fraction is less than some arbitrary value after quenching. The just-
detectable degree of crystallinity is typically chosen to be $10^{-6}$. The cooling rate necessary to avoid just-detectable crystallization is called the critical cooling rate. Ordinary silicate glasses can be produced by cooling at about 1-10 K s$^{-1}$. In contrast, cooling rates on the order of $10^6$ K s$^{-1}$ are required for amorphization of some metallic alloy systems. Using a novel experimental technique, iron has been obtained in the amorphous state [15] by quenching at a rate near $10^9$ K s$^{-1}$. Hence, even very short transient times of about a 1µs (or less) can play a decisive role in facilitating glass formation for such rapid quenches. Neglecting transient effects can lead to erroneous, excessively large predictions of the necessary cooling rate for glass formation. Therefore, understanding and modeling transient effects during the quench is of significant technological interest for the production of novel amorphous materials. Further, as described above, transient effects can suppress nucleation in the quenched glass leading to enhanced stability of the glass.

Transient nucleation times in silicate glasses can be quite long and are thus amenable to experimental study. For example, near the glass transition temperature, $T_g$, transient times can be as long as one day in some silicate glasses. Measurements of the magnitude and temperature dependence of the experimentally accessible parameters: $t^0$, $t_{\text{ind}}$, and $t^s$, offers an alternative means for testing the applicability of standard nucleation theories in high-viscosity condensed systems.
2.1.2.a. Classical Theory: Time-Dependent Nucleation

According to the theory of non-stationary nucleation, a steady-state rate of formation of stable nuclei is not achieved immediately but requires a certain period of time. This time-interval is required to create a steady-state size distribution of embryos (or clusters) of the new phase by transport in the parent phase and incorporation of the atomic (or molecular) species into the embryos. As the temperature decreases towards the glass transition temperature, $T_g$, and diffusion rates diminish, transient effects become increasingly important.

In 1942, Zeldovich [16] first showed that both the time-dependent and time-independent nucleation rates could be computed by constructing a Fokker-Planck form of a master equation. Zeldovich [17] and Frenkel [18] described the nucleation equation as a diffusion equation for particles (embryos and nuclei) moving in a force field (drift) set up by a potential, $\Delta G$. At present, there are two accepted forms of the general nucleation equation, one of which is a Fokker-Planck form known as the Zeldovich-Frenkel equation (Equation 2.73), and the other form is the finite-difference analog of Equation (2.73). Although both forms of the general nucleation equation lead to the same values in the steady-state regime, they predict different values in the time-dependent regime. A brief explanation of how one may arrive at the Zeldovich-Frenkel equation is outlined below.

The following discussion deals with the transient behavior which results subject to the condition that at there are no existing clusters at $t = 0$, i.e.,
where \( N \) in Equation (2.70a) is the total number of molecules in the system. As embryos form, the cluster distribution, \( N_{n,t} \), tends toward the steady-state distribution and the nucleation rate \( I(t) \) rises from zero to its steady-state value, \( I^* \). In the transient regime, the net forward rate, \( I_{n,t} \), at any point can be shown from Equations (2.19) and (2.20) to be

\[
I_{n,t} = N^e_n k^e_n \left\{ \frac{N_{n,t}}{N_n^e} - \frac{N_{n+1,t}}{N_{n+1}^e} \right\}
\]

(2.71)

The values of \( N_{n,t} \) change according to

\[
\frac{\partial N_{n,t}}{\partial t} = I_{n-1,t} - I_{n,t}
\]

(2.72)

Making the continuum approximation, i.e., taking \( n \) to be continuous, the coupled set of linear differential equations described in Section 2.1.1 can be written as a single partial differential equation. Based on this assumption, combination of Equations (2.71) and (2.72) (see ref. [19]) leads to the Zeldovich-Frenkel equation:
By substituting Equation (2.15) for \( N_n^e \) in the above equation, Equation (2.73) may be written

\[
\frac{\partial N_{n,t}}{\partial t} = \frac{\partial}{\partial n} \left( k_n^+ N_n^e \frac{\partial}{\partial n} \left( \frac{N_{n,t}}{N_n^e} \right) \right).
\] (2.73)

This equation has the form of a diffusion equation where \( k_n^+ \) is the analog of the concentration and \( N_{n,t} \) is the analog to the diffusion coefficient. In this analogy, \( k_n^+ (\delta N_{n,t}/\delta n) \) in Equation (2.74) is the 1-D diffusional flux in a concentration gradient, and \( (k_n^+/k_B T)(\delta \Delta G_n/\delta n) \) is the drift velocity in a gradient of the potential \( \Delta G_n \).

2.1.2.b. Analytical Solutions

Most treatments of transient nucleation are based on approximate analytical solutions to the Zeldovich-Frenkel equation. Here, only a few representative forms of such solutions are given.

The first analytical treatment of the Zeldovich-Frenkel equation was performed by Zeldovich [17]. Zeldovich assumed that the clusters act as particles that are harmonically
bound to \( n=0; \) \( \Delta G_n \) thus being proportional to \( n^2 \). Then, by taking \( k_a^+ = k_{n_c}^- \), Zeldovich

found the time-dependent nucleation rate at the critical size, \( I_{n_c,t} \) to be

\[
I_{n_c,t} \approx I^s \exp\left(\frac{-\tau_z}{t}\right)
\]

(2.75)

where \( I^s \) is the steady-state nucleation rate, and \( \tau_z \) is the transient time given by

\[
\tau_z = \frac{n_c^3}{4k_{n_c}^+}
\]

(2.76)

A more thorough analytical treatment is due to Kashchiev [20], who derived an

approximate solution in the form of an infinite series by approximating the free energy of

cluster formation \( \Delta G_n \) by the first two nonzero terms in a Taylor expansion about \( n_c \). By

setting \( k_a^+ = k_{n_c}^- \) for all \( n \), Kashchiev arrived at the following expression:

\[
I_{n_c,t} = I^s \left[ 1 + 2 \sum_{m=1}^{\infty} (-1)^m \exp\left( -\frac{m^2 t}{\tau_k} \right) \right]
\]

(2.77)

where \( m \) is an integer, and the transient time, \( \tau_k \), is given by
In Equation (2.78), $Z$ is the Zeldovich factor given by Equation (2.23). In Kashchiev’s treatment, the values of $N_{n,t}$ are different from the corresponding values of $N_{n}^s$ only in the region known as the critical region. The critical region is defined as being a range of $n$ about $n_c$ for which $(\Delta G_{n_c} - \Delta G_n) \leq k_B T$. Although the time dependence of small clusters is not modeled accurately, since the nucleation rate evaluated at the critical size is dominated by the behavior of clusters in the critical region Equation (2.77) should still model $I_{n_{c,t}}$ well.

Equation (2.77), which may be evaluated numerically, is a more accurate approximate solution to the Zeldovich-Frenkel equation than Equation (2.75). However, Equation (2.77) is not in a convenient form for comparison with experiment since it is the total number of nuclei that is more easily measured than the transient nucleation rate. Equation (2.77) can be integrated to obtain the number of nuclei which have reached a supercritical size, $N(t)$, at time $t$ for a given temperature. The resulting equation is given by

$$\tau_k = \frac{4}{\pi^3 k_{n_c}^2 Z^2} \quad (2.78)$$

$$N(t) = I^s \left[ t - \frac{\pi^2 \tau}{6} - 2\tau \sum_{m=1}^{\infty} \frac{(-1)^m}{m^2} \exp \left( -\frac{m^2 t}{\tau} \right) \right] \quad (2.79)$$
Kashchiev related the measured induction time to the transient time in the following manner. First he used the integrated form of Equation (2.77) to obtain the number of clusters passing the critical size, $\chi_{n_{c,t}}$, at long times ($t > 5\tau$):

$$\chi_{n_{c,t}} = \ln \left( \frac{t - \frac{\pi^2 \tau}{6}}{t^0} \right). \quad (2.80)$$

Then by assuming that all clusters larger than the critical size eventually appear as nuclei, Kashchiev set $\chi_{n_{c,t}}$ equal to $N(t)$:

$$N(t) = \ln \left( \frac{t - \frac{\pi^2 \tau}{6}}{t^0} \right) \quad (2.81)$$

which is the asymptote of the curve $N(t)$ given by Equation (2.77). According to Equation (2.81), a plot of $N(t)$ vs. time should yield a straight line that intersects the time axis at time $t = (\pi^2 \tau/6)$.

At a given temperature, the number $N(t)$ coincides with number $N_v$ given in Fig. 2.2 shifted along the t axis by $t^0$:

$$N(t) = N_v \left( t + t^0 \right) \quad (2.82)$$
Therefore, it follows from the preceding equations and Fig. 2.2 that the measured induction time, $t_{\text{ind}}$, is related to the transient time, $\tau$, by

$$t_{\text{ind}} - t^0 = \frac{\pi^2 \tau}{6}. \quad (2.83)$$

Another analytical form of the time-dependent nucleation rate, arrived at in a different fashion than those described above, is due to Wakeshima [21]:

$$I_{n,t} = I^0 \left[ 1 - \exp \left( -t \frac{1}{\tau_w} \right) \right] \quad (2.84)$$

where the transient time, $\tau_w$, is given by

$$\tau_w = \frac{1}{8\pi k_n^2 Z^2}. \quad (2.85)$$

Due to the nature of the assumptions made by Wakeshima in his treatment, it turns out that Equation (2.84) is only valid if there is a significant population of clusters, and therefore is not valid for small $t$. Equation (2.84) may, however, be a good approximation for $t \geq \tau$. 
An expression similar to Equation (2.84) was obtained by Chakraverty [22] who assumed that the solution for N_{n,t} was separable in n and t. The transient time obtained by Chakraverty, \tau_c, differs from Equation (2.85) by a constant term in the denominator.

Schneidman [23] arrived at the analytical dependence of I(t) by performing an asymptotically exact analysis of the Zeldovich equation in the limit of a high nucleation barrier. Through his analysis, Schneidman was able to unambiguously single out the diffusion and drift regions in the initial kinetic equation and obtained the following analytical relation

\[ I_{n,t} = I^* \exp\{-\exp(-x)\}, \quad x = \frac{t - t_{i(0)}}{\tau} \]  

(2.86)

where \( t_i \) is the "incubation" time. Schneidman arrived at the following relation between the incubation time and the experimentally determined induction time \( t_{\text{ind}} \):

\[ t_{\text{ind}} = t_i + \gamma \tau \]  

(2.87)

where \( \gamma \) is Euler's constant (0.577...). The transient time, \( \tau \), is given by Shneidman as

\[ \tau \equiv \frac{2N_{v,\text{ind}}}{I^*} \]  

(2.88)

where \( N_{v,\text{ind}} \) is the measured number density at the induction time, \( t_{\text{ind}} \).
2.1.2.c. Numerical Solutions

Analytical solutions to the differential equations are based on the continuum approximation along with other unverifiable assumptions and approximations; hence, the different forms of solution presented in Section 2.1.2.b. Numerical solutions to the differential equations describing cluster evolution, however, avoid the usual restrictive assumptions and are free to simulate directly the discrete steps for cluster growth that are at the core of classical theory. Numerical calculations are also more flexible and are easily extended to include such things as arbitrary cluster distributions, heterogeneous nucleation, compositional effects, and nucleation under non-isothermal conditions. Moreover, analytical solutions are usually tested by comparison with numerical results.

Although numerical solutions for the time evolution of cluster sizes offer many advantages, these models are subject to uncertainty. These uncertainties arise from differences in the approximations used for the rate coefficients, limited knowledge of size or temperature effects of the interfacial energy (and hence of the Gibbs energy of sub- and near critical clusters), and from choice of boundary conditions.

The first numerical solution for time-dependent nucleation was obtained by Turnbull [24] to explain the recrystallization rates observed in cold-worked aluminum. Turnbull considered two systems for which \( n_c \) (also taken as the maximum cluster size) was equal to 4 and 25. Ignoring the back flux to \( I_{n,t} \), it was shown by Turnbull that for each cluster size, the time dependent cluster density \( (N_{n,t}) \) rose sigmoidally with time from zero to the steady-state distribution \( (N_n^*) \), and that \( dN_{n,t} / dt \) went through a
maximum. The time to reach the maximum increased with n. These results were later quantitatively confirmed by Christiansen [25] who considered condensation from a vapor and obtained an exact solution for a system of four cluster sizes. Christiansen assumed that \( k_n^+ \) and \( k_n^- \) were independent of \( n \) and that \( k_n^+ \gg k_n^- \).

Courtney [26], Kelton et al. [27] and Volterra [28] used finite difference methods to solve the coupled differential equations without making restrictive assumptions, such as those above, about the rate constants. In the finite difference calculation, the time is divided into a large number of small intervals, \( \delta t \), and the number of clusters of size \( n \) at the end of the interval, \( N_{n,t+\delta t} \), is calculated from

\[
N_{n,t+\delta t} = N_{n,t} + \delta t \frac{dN_{n,t}}{dt}
\]  

(2.89)

where \( dN_{n,t}/dt \) is given by Equation (2.17). Expressions for the rate constants (\( k_n^+ \) and \( k_n^- \)) and material parameters are required for numerical solutions. Two nucleation models are commonly assumed for the rate constant expressions. (1) The Turnbull-Fisher model (described in Section 2.1.1.a), which is most relevant for the description of nucleation in a condensed phase, and (2) the ballistic model where \( k_n^+ \) is taken as being proportional to the surface area of the nucleus, which is more likely for condensation from the vapor.

Kelton et al. [27] computed their numerical solution based on the Turnbull-Fisher model using materials parameters which closely approximated those of lithium disilicate glass, and compared their numerical results with the predictions of the analytical...
expressions of Zeldovich, Kashchiev, Wakeshima, Chakraverty, and others. The authors found that the shape of the curve and transient time predicted by the Zeldovich equation to be in poor agreement with the numerical solution. These authors found the Kashchiev expression to agree best with the numerical calculations.

2.1.3. Experimental Studies of Homogeneous Nucleation in Supercooled Liquids and Glasses

2.1.3.a. Polymorphically Crystallizing Liquids

As mentioned earlier, many liquids can be cooled below their equilibrium melting temperature without solidifying. The maximum amount by which a liquid can be undercooled (maintained out of equilibrium) is denoted $\Delta T_{\text{max}}$. This parameter can be experimentally determined by cooling the liquid below its equilibrium melting temperature until the onset of crystallization is detected from some macroscopic property change such as the volume (diatometry), electrical resistivity, or heat evolution (calorimetry). It is often the case that attainment of the undercooling limit imposed by homogeneous nucleation is obstructed by heterogeneous nucleation on container walls, foreign particles in the liquid, or the surface of the liquid. As described in Section 2.1.1.b, heterogeneous nucleation occurs at smaller undercoolings than homogeneous nucleation, and thus to obtain the true $\Delta T_{\text{max}}$ of a liquid care must be taken to eliminate heterogeneous sites. Various experimental methods have been developed and utilized to
eliminate heterogeneous sites. The more common techniques that have been used are fluxing, the emulsion technique, the substrate technique, and containerless solidification (e.g. levitation and drop-tower techniques). Nearly all techniques for eliminating heterogeneous sites for $\Delta T_{\text{max}}$ determination require the liquid being in the form of very small droplets. Droplet contamination by heterogeneities is more probable for emulsion, fluxing and substrate techniques and hence maximum undercooling values obtained from these techniques can vary considerably. The droplets used in the drop-tower experiments are less susceptible to surface contamination, and for a given liquid these droplets show the largest undercooling. An excellent overview of these techniques is given in ref. [29].

When comparing undercooling data, the droplet size, $v$ (in moles), and cooling rate, $Q$, must be taken into account. The maximum undercooling results from droplets that are least susceptible to nucleation. For uniformly sized droplets, $v$, the volume fraction of droplets containing no nuclei, $x$, given $N$ nuclei per mole (or equivalently the probability of having no nuclei in a droplet) is

$$x = \exp(-vN). \quad (2.90)$$

If the cooling rate from the melting temperature to the temperature of maximum undercooling, $T_u$, is constant, and assuming steady-state homogeneous nucleation:

$$x = \exp\left[-\frac{v}{Q} \int_{T_u}^{T_m} I'(T) \, dT \right]. \quad (2.91)$$
For liquid metals, the growth rates in the nucleation regime are generally quite large so that the time scale for crystallization is dominated by the time to form nuclei. Due to the large growth rates, just one nucleation event is sufficient to crystallize the droplet. Assuming the preceding assertions, and taking \( x \approx 0.05 \) (if a sensitive enough technique is not available for experimental determination of \( x \)), the nucleation rate at the maximum undercooling may be calculated from Equation (2.91) if the ratio of droplet volume to quench rate is known. The following discussion explains how such maximum undercooling experiments are used to determine the crystal-liquid interfacial energy in metallic and non-metallic substances.

The classical theory for homogeneous nucleation may be expressed

\[
\Gamma^n = A^* \exp \left( \frac{-16\pi \sigma^3}{3(\Delta G)^2 k_B T} \right)
\]

(2.92)

where the prefactor \( A^* \), which is explicitly given in Equation (2.42), contains the viscosity, \( \eta \). Measurements of the viscosity of undercooled liquid metals are rare. However, experimental studies indicate that the viscosity is not strongly dependent upon temperature over the range sampled by maximum undercooling measurements. Therefore, by extrapolating the measured viscosity at the melting point back to the maximum undercooling temperature, \( A^* \) may be calculated. For metallic systems, the heat capacity of the liquid is nearly equal to the heat capacity of the crystal for the
temperatures involved in maximum undercooling experiments, and the Gibbs energy difference per unit volume, $\Delta G_v$, is well approximated by Equation (2.60). If the heat of fusion at the melting point is known, $\Delta G_v$ can be calculated for $T = T_u$ and the liquid-crystal interfacial energy, $\sigma$, can be estimated using Equation (2.91) for $I^*$ determination and Equation (2.92). As described in Section 2.1.1.d, the results of such experiments for metallic and non-metallic substances led to the so-called Turnbull-Stavely relation (Equation 2.65), which is commonly used to estimate crystal-glass interfacial energy values.

Equation (2.91) can also be used to determine the steady-state nucleation rate as a function of undercooling temperature for liquid metals. Experimental results from homogeneous nucleation experiments in supercooled metallic liquids show that $I^*$ rises sharply with undercooling, which is in accord with the predictions of classical theory. Substituting Equation (2.60) for $\Delta G_v$ in Equation (2.92) yields the following:

$$I^* = A^* \exp \left[ -\frac{16 \pi T_m^2}{3k_B \Delta H_m} \frac{\sigma^3}{T \Delta T^2} \right]. \tag{2.93}$$

A plot of $\ln I^*$ vs. $(T(\Delta T)^2)^{-1}$ should give a straight line with a slope proportional to $\sigma^3$ and $y$-intercept equal to $\ln A^*$. This type of behavior was observed for liquid Hg by Turnbull [9] who used dialatometry to measure the volume fraction $x$ (and hence $I^*$). The measured value of the prefactor $A^*$ was found to be about $10^7$ times larger than the value predicted from classical nucleation theory. Turnbull [9] was the first to note that if $\sigma$ was
assumed to increase linearly with temperature, then theoretical and experimental values for the prefactor could be reconciled. It has been argued [30-32] that such a linear temperature dependence for metallic systems is due to a sizable negative entropy arising from ordering in the liquid near the interface. Nucleation data for water [33] also gives a prefactor that is about seven orders of magnitude larger than predicted by theory. Experimentally obtained nucleation rates for several n-alkane liquids [34], however, indicate agreement between theory and experiment with regard to temperature dependence and prefactor values.

2.1.3.b. Metallic Glasses

For metallic glasses, the growth rates are sufficiently large in the nucleation regime so that crystal nuclei can be both formed and developed at a single annealing temperature. The number of crystals can be directly counted from prepared sections of the heat-treated glass sample via optical microscopy or scanning electron microscopy (SEM), and using standard stereological methods [35,36].

Devitrification studies in Fe$_{40}$Ni$_{40}$P$_{14}$B$_{6}$ [37,38] have provided the best evidence for homogeneous nucleation in a metallic glass that transforms by a eutectic mechanism. In ref. [37], Morris used transmission electron microscopy (TEM) to determine the number and size of crystals that nucleated and grew during isothermal annealing. Morris showed that the crystallite size distribution increased with annealing time with no evidence of site saturation, which is indicative of homogeneous nucleation. No evidence
of transient effects was reported in ref. [37]. The nucleation rates were determined using the JMAK equation (see Section 2.1.3.f.). Tiwari [38] fit measured nucleation data for this system to classical theory. Experimental data were plotted as \( \ln \eta \) vs. \( (T(\Delta G_v)^3)^{-1} \), which according to CNT should yield a straight line with a slope proportional to \( \sigma^3 \) and intercept equal to the prefactor in Equation (2.63). However, as shown in Fig. 17 of ref. [29], the curve is only linear at higher temperatures. From the data in the linear region, the experimentally determined value of the prefactor was found to be about ten orders of magnitude larger than predicted by theory. The observed disparity in prefactor values could, however, be rectified by assuming a linear temperature dependence for the interfacial energy.

2.1.3.c. Simple Oxide Glasses

Without the deliberate addition of constituents known as nucleating agents to promote nucleation within the volume, most oxide glasses tend to initiate crystallization on external surfaces. Only a handful of glass forming systems including \( \text{Li}_2\text{O-SiO}_2 \), \( \text{BaO-SiO}_2 \), \( \text{Na}_2\text{O-SiO}_2 \), \( \text{Li}_2\text{O-B}_2\text{O}_3 \), \( \text{Na}_2\text{O-CaO-SiO}_2 \), and \( \text{CaO-SiO}_2 \) are known to exhibit volume nucleation without the aid of nucleation catalysts.

In this section, only the more pertinent results of experimental nucleation rate studies of "simple" stoichiometric glass compositions that presumably nucleate homogeneously are discussed. Among such compositions are the following: \( \text{Li}_2\text{O-2SiO}_2 \) (LS2), \( \text{BaO-2SiO}_2 \) (BS2), \( 3\text{BaO-5SiO}_2 \) (B3S5), \( \text{Na}_2\text{O-2CaO-3SiO}_2 \) (NC2S3), \( 2\text{Na}_2\text{O-CaO-}- \)
$3\text{SiO}_2 (N_2\text{CS}_3)$, $\text{Na}_2\text{O-SiO}_2$ (NS) and $\text{CaO-SiO}_2$ (CS) and $\text{Li}_2\text{O-2B}_2\text{O}_3$ (LB$_2$). For these compositions the crystallizing phase has the same composition as the parent glass, and therefore they can effectively be treated as one-component systems. Hence, nucleation rate data for these compositions are most readily compared with the predictions of Classical Nucleation Theory.

Experimental procedures commonly employed by investigators to obtain the nucleation rate data, along with methods of interpretation with respect to CNT, are now discussed. For glass compositions that initiate nucleation within the volume, it is commonly found that the temperature range where nucleation rates are appreciable lies well below the temperature range where growth rates are significant. This is illustrated in Fig. 2.3
Figure 2.3 Illustration of the separation between nucleation (I) and growth (U) temperature regimes
The method known as the “development technique,” which was outlined in Section 2.1.2, takes advantage of the characteristic behavior shown in Fig. 2.3. For lower temperatures near the temperature of the maximum nucleation rate, glass samples are first isothermally heated at a temperature $T_N$ for the desired time to promote nucleation. Then, the samples are quenched to room temperature and subsequently heated at a higher “development” temperature $T_{dev}$ for shorter times to grow the crystals to dimensions observable by an optical microscope or SEM. For higher nucleation temperatures, a single stage heat treatment can be used. There are two basic assumptions of two-stage isothermal heating technique. (1) After nucleation treatment, the glass contains an assembly of nuclei some of which will have grown into small crystals, the large majority of which do not redissolve on heating to the second stage, and (2) the nucleation rate at the growth temperature is negligible. The basis of this method has been investigated in detail and justified by Kalinnina and co-workers [39,40]. The number density data, $N_v$, that are used to determine the steady-state nucleation rate at $T_N$ are typically obtained via optical microscopy, and the methods for making such measurements are discussed fully in ref. [41]. The linear region of the $N_v$ vs. time curves generated, as exemplified in Fig.2.2, gives the steady-state nucleation rate at $T_N$.

If the temperature dependence of the viscosity is known, the measured steady-state nucleation rate data are typically compared with the predictions of CNT (as given by Equation 2.43) by constructing a $\ln \Gamma^2 \eta$ vs. $1/T(\Delta G_v)^2$ or a $\ln (\Gamma^2 \eta T^{-1})$ vs. $1/T\Delta T^2$ graph.
Either plot should yield a straight line with a slope proportional to \(\sigma^3\) and the y-intercept equal to the natural log of the prefactor.

Of the few simple compositions given above, nucleation rates have been most extensively studied for the LS\(_2\) composition [39,41-53]. One of the reasons LS\(_2\) has received so much attention is because the detailed thermodynamic data [54-55] necessary for quantitative evaluation, and thus comparison with theory, are available.

Rowlands and James [48] carried out a detailed analysis of experimental nucleation rates in LS\(_2\) using various methods, including the one described above, for interpreting experimental data with respect to CNT. In ref. [48], a plot of \(\ln (I^r T^{-1})\) vs. \(1/T (\Delta G_v)^2\) was found to give a straight line (as predicted by CNT) only for higher temperatures, those above the temperature of the maximum nucleation rate. From this linear region, the authors determined the crystal/liquid interfacial energy, \(\sigma\), to be 190 mJm\(^{-2}\). At lower temperatures, significant deviation from linearity was observed. Furthermore, the pre-exponential factor, \(A\), in the expression for \(I^r\) as determined from the intercept of the plot was about 20 orders of magnitude higher than the theoretical value \(10^{41} \text{ m}^{-3} \text{s}^{-1}\) for LS\(_2\) glass. It was demonstrated in [48] that the possibility of heterogeneous nucleation could not explain the observed discrepancies. In fact, the discrepancy between theory and experiment was even larger if one assumed heterogeneous nucleation theory.

Neilson and Weinberg [56] also made detailed comparisons between theoretical predictions of CNT and experimental results for crystal nucleation in LS\(_2\) glass. The conclusions reached by these authors were essentially the same as the conclusions of
Rowlands and James. The authors considered several explanations for these results (e.g. water contents, heterogeneous nucleation), but all were shown to be either inadequate or unlikely causes of the observed discrepancies.

Zanotto and James [51] later performed additional nucleation rate experiments on LS₂ glass. Using their new data, nucleation rate data which had been collected by others, and new viscosity data, Zanotto and James conducted an extensive analysis in terms of CNT. Again, the same types of discrepancies originally found to exist between CNT and experimental results were observed, i.e., experimental nucleation rates were much larger than predicted by theory. In ref. [51], it was also observed that the experimentally determined interfacial energy values were not strongly dependent on which combination of nucleation rate data and viscosity data were used. The values of σ were found to range from about 198 - 210 mJm⁻². The pre-exponential factor, A, was found to be strongly dependent upon thermodynamic data. There was a difference of nearly ten orders of magnitude between the value of A obtained through use of ΔGᵥ as calculated from the expressions given in Section 2.1.1.c (using different assumptions regarding ΔCₚ), and the value obtained using the measured values of the thermodynamic driving force [54,55].

Using their new nucleation rate and viscosity data, Zanotto and James found the experimentally determined values of the pre-exponential factor to be 10⁶³ m⁻³ s⁻¹ and 10⁷¹ m⁻³ s⁻¹ for the calculated and measured values of ΔGᵥ, respectively. As found in earlier studies, these values are many orders of magnitude larger than the theoretical value.

Smith et al. [57] studied homogeneous nucleation in the LB₂ glass composition and compared their experimental results with the predictions of CNT. These authors
concluded that neither the magnitude nor the temperature dependence of measured nucleation rates could be adequately described by CNT.

Other comparisons between CNT and nucleation measurements in pseudo-one-component silicate glasses have been performed [51,58-61]. In refs. [51,58,59], experimental nucleation rate data for the BS$_2$ composition were collected and interpreted with respect to CNT in the same manner as described above for LS$_2$. Conclusions regarding agreement between theory and experiment were essentially the same as those for LS$_2$; the experimentally determined value of the prefactor was found to be many orders of magnitude too large. However, it is noted that accurate thermodynamic data for the BS$_2$ system were not available and $\Delta G_v$ had to be calculated using the measured value of $\Delta H_m$ and Equation (2.60).

Comparison of experimental nucleation rates and CNT were made in refs. [60,61] for the NC$_2$S$_3$ composition using measured viscosity and thermodynamic data. In these analyses, $\Delta G_v$ was calculated from the more accurate Equation (2.61) using the average (constant) measured value of $\Delta C_p$ over the temperature range of interest. From a plot of $\ln (\Gamma \eta T^{-1})$ vs. $1/T(\Delta G_v)^2$, the value of experimentally determined prefactor was about $10^{90}$ m$^{-3}$s$^{-1}$, which is much larger than predicted by theory.

Although the predicted nucleation rates for LS$_2$, BS$_2$ and NC$_2$S$_3$ are many orders of magnitude too small, CNT did adequately describe the temperature dependence (at least above the maximum nucleation rate temperature) of the nucleation rate in all cases.

Several modified versions of CNT have been shown to give good agreement with experimental results. For example, James [62] showed that using a temperature...
dependent liquid-crystal surface tension could reconcile theoretical predictions and experimental results without destroying the accord in temperature dependence. Kelton and Greer [63], and Greer and Kelton [64] employed a temperature dependent liquid-crystal surface tension and reached similar conclusions via numerical simulations. Weinberg et al. [65] showed that disparate results between theory and experiment could be reconciled by modifying CNT to include a curvature dependent, rather than a temperature dependent, surface tension.

Thus, it might appear that the disagreements between theory and experiment have been resolved. However, that is not the case. In the first place, although plausible, the temperature and curvature dependent surface tension hypotheses are completely unverifiable. Further, even if surface tension were dependent on curvature or temperature, the correct functional form of the dependence would still have to be demonstrated. Moreover, it has been demonstrated that even with a temperature dependent surface tension CNT fails when applied to the LB$_2$ glass composition.

Aside from $\sigma$, there are other factors that may contribute to the observed discrepancies between theory and experiment. For example, cluster sizes relevant to nucleation are very small and effects associated with finite width of the crystal-liquid interface may be important. However, at present there is no way of experimentally assessing the influence of such effects even if they do exist. The assumptions regarding the activation energy for jumps at the interface between the nucleus and parent phase may be in error and could also contribute to the observed discrepancies. As discussed in Section 2.1.2.a, the kinetic part of the classical expression is normally associated with
that of ordinary diffusion and is replaced by the viscosity via the Stokes-Einstein relation.

It has been demonstrated [66], however, that using a more rigorous approach, which makes use of the induction times for nucleation rather than the viscosity, yields discrepancies similar to those observed when viscosity is utilized. Lastly, and most importantly for this research, the possibility exists that metastable crystalline phases form and serve as precursors for subsequent precipitation of the stable phase. The implication of this notion is that the nuclei which form are not of the same chemical constitution as the crystals which form upon them, and thus what is measured experimentally is not homogeneous nucleation.

2.1.3.d. Evidence of Metastable Phase Formation in Lithium Disilicate Glass

The issue of metastable crystal phase formation is of considerable scientific importance because it offers a possible explanation for the observed discrepancies between theoretically predicted and experimentally determined nucleation rates in glasses. As described in Section 2.1.3.c, the value of $\Delta G_v$ markedly affects the value of the experimentally determined prefactor. The $\Delta G_v$ value associated with the formation of a metastable phase in the glass matrix should be smaller than the $\Delta G_v$ associated with formation of the stable phase in the matrix. One also expects the surface energy associated with formation of a metastable phase to be smaller than that associated with the stable phase. Thus, according to the classical expression for homogeneous
nucleation as given by Equation (2.42), if a metastable crystalline phase formed as the nucleus, then the observed discrepancies can be explained.

As described in Section 2.1.3.c, LS$_2$ has served as the model system for testing nucleation theories, and most observations of metastable phase formation have been for glasses near this composition. The notion of metastable phases forming prior to crystallization of equilibrium phases in lithium silicate glasses was initially proposed back in 1968, by Kinser and Hench [67]. Using XRD, dielectric relaxation measurements, and TEM, Kinser and Hench observed that a metastable lithium metasilicate (LS) crystal phase formed prior to the precipitation of stable LS$_2$ in a 30 mol% glass composition which had been heat-treated at 500°C. In 1971, Hench et al. [68] compared lithium silicate glasses containing 30 and 33 mol% Li$_2$O. Hench performed small angle x-ray scattering (SAXS) and electrical conductivity experiments on samples of both compositions that had been heat treated at 500°C for various times between 2 and 10 hours. The results of the SAXS experiments for both compositions were very similar and are as follows. The scattering intensities initially increased with time, went through a maximum at about 5 hours, then decreased back to the initial value after about 10 hours; indicating the formation and subsequent dissolution of particles with electron densities different from the glass matrix. Because the results for both compositions were the same, and since it had been determined earlier [67] that a metastable LS crystal phase formed in the 30 mol% composition, Hench concluded that a metastable LS crystal phase also formed in the 33 mol% composition.
In 1986, Joseph and Pye [69] performed Raman spectroscopy experiments on LS$_2$ glass samples that had been heat-treated at 450°C and 500°C for various times between 0 and 15 hours. Joseph and Pye determined the ratio of peak intensities of the bands associated with Si-O stretching vibration in SiO$_4$ tetrahedra with 2 non-bridging oxygens (2 NBO) and 1 non-bridging oxygen (1 NBO) as a function of heating time. For both 450°C and 500°C, the ratio (2 NBO/1 NBO) initially increased with heating time, went through a maximum, then decreased toward the initial value. Joseph and Pye interpreted these observations as the formation of a metastable LS-like phase during the initial stages of nucleation and offered these results as supporting evidence for the proposition of Hench.

Subsequent nucleation rate and XRD experiments performed by Barker et al. [53] indicated that nucleation in LS$_2$ glass was indeed homogeneous in nature. The results of this study cast considerable doubt on the proposal of metastable phase formation in LS$_2$, and the proposition was generally dismissed.

In 1993, Deubener et al. [70] conducted a TEM investigation on heat-treated LS$_2$ glass and produced provocative electron diffraction patterns that provided direct evidence for the presence of a metastable LS-like crystalline phase during the early stages of nucleation. Sparked by the work of Deubener, the scientific community has turned its attention back to the original proposition of Hench, and there has since been a resurgence of investigations into metastable phase formation in LS$_2$ glass.

Adams and DeJong [71] attempted to determine the constitution of the nascent nuclei in LS$_2$ glass via x-ray photoelectron spectroscopy (XPS). Spectra were obtained
from glass samples that had been heated at 450°C for various times between 0.5 and 200 hours. The sequence of spectra as a function of heating time showed significant changes in Li 1s binding energy, presumably corresponding to a change from being predominantly 4-fold to 5-fold, then back to 4 fold. Although these results indicate some type of transient effects, the nature of this behavior is unclear.

Schmidt and Frischat [72] studied the early stages of crystallization in LS$_2$ glass using high-resolution atomic force microscopy (AFM). By examining the glass fracture surfaces of heat-treated samples, these authors observed an anomalous topography that could not be attributed to the stable LS$_2$ crystal structure.

Zanotto [73] recently repeated the TEM experiments performed by Deubener et al. [70] and obtained results similar to those reported in ref. [70] regarding the presence of metastable crystalline phases in LS$_2$ glass. Zanotto also performed SAXS experiments and analysis of the measurements revealed a maximum when the integrated scattering intensity was plotted as a function of time. Zanotto interpreted the SAXS results as further proof of metastable phase formation. It is important to note that metastable phases were detected by TEM and SAXS only in the very early stages of crystallization, when the crystallized volume fractions were smaller that ~ 2%, i.e., for short treatments at 454°C (t < 20 hours). For higher volume fractions (longer treatments) only the stable LS$_2$ phase was observed by TEM. Zanotto also conducted crystal growth measurements and computed the volume fraction crystallized as a function of time using the JMAK equation as corrected for transient behavior, and assuming homogeneous nucleation. Zanotto found that the measured and calculated volume fractions agreed well and thus
concluded that nucleation of the disilicate phase occurs homogeneously. Zanotto's position is that even though metastable phase formation occurs, it does not affect the nucleation process of the stable disilicate crystal phase.

An entirely different point of view regarding the nucleation mechanism in LS₂ glass has been provided by the most recent results of James et al. [1] and Iqbal et al. [74]. Refs. [1] and [74] report the results of the same experimental work by the same authors, but ref. [74] describes the results in more detail. The work of James and Iqbal concerning metastable phase formation in lithium disilicate glass is quite striking in that they found the metastable phases to persist for very long times. The authors utilized XRD to follow the early stages of the crystallization in LS₂ glass. Samples of LS₂ glass (analyzed composition 33.9 mol% Li₂O) were given single stage heat-treatments at 454°C for extensive time periods. Employing scanning speeds of 0.25 and 0.125°/min., XRD traces were obtained from samples that were heated for 50, 120, 312, 331, 480, and 551 hours. Following the progression of the crystallization process via XRD traces, James and Iqbal observed the formation of metastable phase(s), and subsequent transformation of these phases to stable LS₂. The x-ray diffraction patterns of glasses heated for 120, 312, and 480 hours revealed the presence of two crystal phases, denoted by the authors as α-LS₂ and β-LS₂, which could not be identified with any of the known phases in the Li₂O-SiO₂ system. The XRD pattern of the glass heated for 551 hours, however, showed only the stable LS₂ crystal phase to be present. As a result of their investigation, James and Iqbal proposed the following nucleation path for LS₂ glass: (1) initial formation of a metastable
phase (α-LS₂); (2) transformation of the α-LS₂ to the β-LS₂ metastable phase, and (3) final transformation to the equilibrium LS₂ phase.

2.1.3.e. Nucleation Studies in Sodium Silicate Glasses

Although the Na₂O-SiO₂ glass forming system is one of simplest systems which exhibits internal nucleation, this system has received very little attention with respect to nucleation rate studies due to problems with glass formation. What makes this system particularly interesting for nucleation rate study is that the nucleation mechanism changes with composition from homogeneous internal nucleation to heterogeneous external surface nucleation.

In 1961, Scott and Pask [75] employed the development technique to study the crystallization kinetics of sodium disilicate (NS₂) glasses. These authors studied 20 different glass samples during the course of 200 melting and crystallization cycles and reported, "no homogeneous nucleation was observed; i.e., in no instance did a crystal form spontaneously within the melt. In no instance did a bubble act as a nucleating site." The only nucleation observed was initiated either at the glass-atmosphere interface or the glass-platinum interface.

Prior to the work of Scott and Pask, Wiehr [76] studied the surface crystallization of NS₂ glasses for various surface conditions in different atmospheric environments. Wiehr found that a fire-polished surface developed fewer nuclei than did a fracture
surface. He also found that samples exposed in a vacuum developed a lower number of nuclei than samples exposed to dry air, dry nitrogen, and moist air.

Filipovich et al. [77] observed homogeneous nucleation in binary sodium silicate glasses of composition 46Na₂O-54SiO₂ (mol%). From x-ray diffraction analysis, they determined the crystal phase of the internally nucleated crystals to be sodium metasilicate. The sodium metasilicate crystals grew as rhomboid needles rather than spherulites, and Filopovich presented a modified method for making stereological corrections to obtain the necessary number density data for such shapes. The magnitudes and temperature dependence of the steady-state nucleation rates were experimentally determined using two-stage heat-treatment and optical microscopy techniques. The magnitude of the maximum nucleation rate for this composition was \(3.6 \times 10^4 \text{ mm}^{-3} \text{ min}^{-1}\), which occurred at about \(T = 460^\circ\text{C}\). The temperature range of internal nucleation was from \(T = 410^\circ\text{C}\) to \(T = 490^\circ\text{C}\). Transient effects were reportedly observed, but no details were given.

Fokin and Yuritsyn [78] observed and studied homogeneous nucleation in a sodium silicate glass of composition 44Na₂O-56SiO₂ (mole%). The magnitudes and temperature dependence of the steady state nucleation rates were determined using the development technique and optical microscopy. The magnitude of the maximum nucleation rate was found to be \(183 \text{ mm}^{-3} \text{ min}^{-1}\), which occurred at about \(T = 427^\circ\text{C}\). The range of internal nucleation spanned from about \(T = 400^\circ\text{C}\) to about \(T = 470^\circ\text{C}\). Transient effects were observed for temperatures near the maximum nucleation rate temperature.
2.1.3.f. Non-Isothermal Heating Techniques for Studying Nucleation Rates in Glasses

Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) are commonly used in the field of glass science for investigating such things as glass forming ability and crystallization kinetics. DTA is an appealing experimental technique because it is quick and easy, thus providing a method for the rapid survey of phase transformations under both isothermal and non-isothermal conditions. Further, because DTA requires only a very small amount of sample even hard-to-form glasses may be analyzed.

DTA experimental techniques are particularly attractive for studying homogeneous nucleation rates in glasses, especially when one considers the time-consuming labor-intensive nature of traditional (e.g. development technique) methods for obtaining such information. Ray and Day [79] and Xu et al [80] have used DTA to determine the temperature dependence of the nucleation rates in LS$_2$ and NC$_2$S$_3$ glasses, respectively. The procedure employed by these authors is essentially the following. First, a glass sample is heated isothermally in the DTA apparatus for a given time period at a temperature appropriate for the promotion of nucleation. Then, the glass is subjected to non-isothermal heating (at a uniform rate) to crystallize the sample. The non-isothermal DTA trace is recorded. This procedure is subsequently repeated using different isothermal nucleation temperatures. The result of this process is a family of
DTA traces. The parameters of interest in the DTA traces are the peak temperature of maximum crystallization, \( T_p \), and peak height, \( \delta T_p \). The variation of either parameter with nucleation temperature can be employed for the computation of the temperature dependence of the nucleation rate, \( I^*(T) \). These methods rely upon the observation that the number of particles nucleated for a given time period is inversely proportional to \( T_p \) and directly proportional to \( (\delta T)_p \). The mathematical analyses of such DTA data are typically based on the JMAK equation. Before proceeding further, it is useful to briefly explain the JMAK expression since it is one of the fundamental equations of materials science.

The Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory [81-85] of phase transformations that occur by nucleation and growth was developed about the same time as classical theory. JMAK theory provides an expression for the fraction of material transformed as a function of time, \( X(t) \), in terms of the nucleation and growth rates. The significance of JMAK theory stems from its universality (e.g. can be applied to both isothermal and non-isothermal transformation) and its applicability to any type of material. Here, only a simple explanation and relevant results of JMAK theory are presented. An excellent explanation of the nature of the equations, their restrictions, and full derivations are given in ref. [86].

For isothermal transformations, the JMAK equation can be written as:

\[
X(t) = 1 - \exp(-X_e(t))
\]

(2.94)
where \( X_e(t) \) is the extended volume transformed. The extended volume transformed is typically given by

\[
X_e(t) = kt^n
\]

(2.95)

where \( k \) is dependent on the nucleation and growth rates, and \( n \) is an integer or half integer from \( \sim 1 \) to 4. The exponent, \( n \), is termed the Avrami exponent and from Equation (2.94) it follows that this quantity is the slope of a \( \ln \ln(1-X(t))^t \) vs. \( \ln t \) plot, which is known as an Avrami plot. The parameter \( n \) is related to the mechanism of the process (e.g. \( n = 1 \), surface crystallization; \( n = 3 \), bulk crystallization), and is independent of temperature if there is no mechanism change.

For short times (i.e., small \( X \)); \( X(t) = X_e(t) \) since \( 1- \exp(-z) \approx z \) when \( z \ll 1 \).

The following considers this simple case, and assumes that the crystals grow as spheres. For this case, the volume of a crystal nucleated at time \( t=0 \) will be given by

\[
V = \frac{4}{3} \pi r^3
\]

(2.96)

For the simple case where the nucleation and growth rates are independent of time, i.e. steady-state rates, then \( r \) is simply given by the product of the growth rate, \( U \), and time \( t \):

\[
r = Ut
\]

(2.97)
and $V$ may be expressed

$$V = \frac{4}{3} \pi (Ut)^3. \quad (2.98)$$

A crystal that does not nucleate until time $t = \tau$ will have a volume

$$V' = \frac{4}{3} \pi U^3 (t - \tau)^3. \quad (2.99)$$

The number of nuclei formed in a time increment $dt$ per unit volume of untransformed phase is $I^d dt$. If the particles do not impinge upon one another, then the extended volume transformed for this case may be written

$$X_e = \sum V' = \frac{4}{3} \pi U^3 \int_0^t (t - \tau)^3 d\tau$$

or

$$X_e = \frac{\pi}{3} I^d U^3 t^4 \quad (2.101)$$
For longer times, yet prior to impingement, $X(t) \neq X_e(t)$ and Equation (2.94) may be used, which for this case gives

$$X(t) = 1 - \exp\left(-\frac{\pi}{3} I^* U^3 t^4\right)$$

(2.102)

where $k = \pi I^* U^3/3$ and $n = 4$ in Equation (2.95).

Returning to the aforementioned DTA methods, mathematical analysis of non-isothermal data usually begins with Equations (2.94) and (2.95). However, in the case of non-isothermal heating, a functional form of $k$ must be assumed. Typically, $k$ is assumed to be related to the absolute temperature, $T$, by an Arrhenius type equation

$$k = AN \exp\left(-\frac{E_c}{RT}\right)$$

(2.103)

where $N$ is the number of nuclei, $E_c$ is the activation energy for the crystal’s growth, and $A$ is a constant. When a glass crystallizes during a DTA run, heat is evolved and an exothermic crystallization peak is observed in the DTA trace. The shape of this peak is related to the Avrami exponent in the following manner; the higher the $n$ value the narrower the peak. In ref. [87], Weinberg describes and analyzes traditional schemes, which employ JMAK theory and assume the functional form of $k$ given by Equation (2.103), for relating DTA data to the temperature dependence of homogeneous nucleation rates.
2.1.3.g. Wakasugi’s DTA Method

As described in [87], traditional schemes for extracting nucleation rate data from DTA measurements generally rely upon unverified assumptions, e.g. the functional form of the rate constant, and it is not clear how sensitive the results obtained are to these assumptions. A novel DTA method for determining the temperature dependence of homogeneous steady-state nucleation rates, which does not rely upon any of the standard assumptions used in other methods, was developed by a former member of our research group, Takashi Wakasugi. Wakasugi presented and demonstrated this method for a sodium silicate glass of composition 43Na₂O-57SiO₂ (mol%) [88]. An outline of Wakasugi’s method is given below.

In Wakasugi’s DTA method, as-quenched glass samples are isothermally heated to promote nucleation prior to being subjected to DTA. The nucleated sample (in bulk-form) is subsequently subjected to DTA, and the peak temperature of maximum crystallization is recorded from the DTA trace. The parameter of interest in this method is the peak shift, \( \Delta T_p \). The peak shift is defined as the difference between the peak temperature of maximum crystallization of a bulk-form glass given a nucleation treatment prior DTA and the peak temperature of maximum crystallization of an as-quenched bulk-form glass sample.

Wakasugi’s method is based on the following reasoning. If the same peak shift, \( \Delta T_p \), can be produced at two different nucleation temperatures for two different
nucleation times, using the same scan rate, then the number density of nuclei must be identical. Therefore, the inverse ratio of the two nucleation times will give the ratio of nucleation rates at the two temperatures. Two assumptions are made to reach these conclusions: (1) data is outside the transient nucleation regime, and (2) there is no significant overlap of growth and nucleation. The second assumption is required to ensure that the number densities be identical, and the first assumption is needed to obtain the temperature dependence of the nucleation rate from the relative nucleation times.

The above assertions may be demonstrated by using the following form of the JMAK expression for the fraction transformed as a function of time, $X(t)$:

$$\ln(1 - X) = -\frac{4\pi}{3} \int_0^t \left[ \int I(\tau) d\tau \right] \left[ \int U(t') dt' \right]^3$$

(2.104)

where $I$ and $U$ are the nucleation and growth rates, respectively. Equation (2.104) may be rewritten as

$$F \equiv -\frac{3}{4\pi} \ln(1 - X) = \int_0^t \tau I(\tau) \left[ \int U(t') dt' \right]^3 + \int_{t_1}^t \tau I(\tau) \left[ \int U(t') dt' \right]^3$$

(2.105)

In Equation (2.105), $t_1$ is the duration of the isothermal heating. If nucleation and growth curves do not overlap, then $I(\tau) = 0$ in the second term of Equation (2.105) and
where $T_j$ is the temperature of the isothermal heating. However, once again, if the nucleation and growth curves do not overlap, $U(T_j) = 0$ and

$$F = \int_0^{t_j} d\tau I(\tau) \left[ \int_{t_1}^{t_j} U(t') dt' + U(T_j)(t_j - \tau) \right]^3$$

(2.106)

where $N(t_j)$ is the total particle number density after isothermal heating for time $t_j$. Since the growth integral is the same in all cases, i.e., the only difference in conditions for DTA scans are time and temperature of isothermal hold, scans producing the same $F$ value for all times must correspond to the same $N(t_j)$. It is easy to see, however, that if nucleation and growth occurred in the same temperature regime, then this simple result would not be obtained.

If the nucleation is occurring in steady-state, then $N(t_i) = I(t_i)$. Then, if $N(t_i) = N(t_2)$:

$$\frac{I'(T_2)}{I'(T_1)} = \frac{t_1}{t_2}$$

(2.108)

Figure 19 of ref.[88] shows the temperature dependence of the relative nucleation rate of a 43Na2O-57SiO2 (mol%) composition as derived by this method. The
temperature at which the nucleation rate is a maximum, $T_{\text{MAX}}$, occurs near or below 410°C. For temperatures $T > 410^\circ\text{C}$, the nucleation rate decreases continuously and appears to tend towards zero near 465°C.

2.1.3.h. Factors that Influence Nucleation in Glass Systems

Among the factors that can influence the nucleation process occurring in a glass are electric fields, oxidizing and reducing atmospheres, ultrasound, phase separation, compositional differences, water content and impurities. Only the latter three factors are relevant to the present research, and hence the following discussion will be limited to these factors.

When the nucleating crystal phase has a different chemical composition than the glass matrix from which it precipitates (as is the case for the sodium silicate compositions discussed in Section 2.1.3.e.), interpretation of the experimental results with respect to nucleation theories is much more complex than for "simple" compositions. First it is necessary to understand the compositional dependence of the thermodynamic driving force. For the glass systems known to exhibit internal (presumably homogeneous) nucleation, this type of data is rare and for most systems nonexistent. A general understanding of how the Gibbs energy (thermodynamic driving force) is affected by composition may be gained by consideration of Fig. 2.4, which shows a Gibbs energy vs. composition diagram for a simply binary eutectic system with two crystallizing phases $\alpha$ and $\beta$. It is important to note that this figure neglects the effects of $\Delta G_D$ and the interfacial energy, $\sigma$. The thermodynamic driving force, $\Delta G$, for nucleation of the $\alpha$
phase in a liquid phase of composition $X$, which is different than the composition of $\alpha$, is determined as follows. First, a tangent to the point on the liquid Gibbs energy curve corresponding to the composition $X$ of the parent (liquid) phase is constructed. Then, a tangent line to the point corresponding to the composition of the $\alpha$ phase is drawn. The vertical distance between these two tangents is the thermodynamic driving force $\Delta G$ for nucleation of the $\alpha$ phase in the liquid of composition $X$. As observed from Fig. 2.4, as the liquid composition $X$ approaches the composition of $\alpha$, the thermodynamic driving force increases, and the thermodynamic barrier to nucleation correspondingly decreases. Therefore, as the parent phase composition nears the $\alpha$ phase composition, the magnitudes of the steady state nucleation rate ($I^s$) should steadily increase and reach a maximum when the compositions of the nucleating and parent phase are the same.
Figure 2.4 Schematic representation of the Gibbs energy vs. composition for a simple binary A-B system.
Compositional differences can also influence the nucleation rates by affecting the kinetic barrier to nucleation, $\Delta G_D$. Since the kinetic barrier is commonly related to the viscosity in nucleation rate studies, insight as to the effects of compositional changes can be gained by considering how the viscosity is affected by such changes. In oxide glasses, increasing the ratio of network modifier (e.g. alkali content) to network former (e.g. SiO$_2$) generally decreases the viscosity of the glass. Decreased viscosity is assumed to correspond directly to increased diffusion rates. Thus one would expect the kinetic barrier to decrease, and hence nucleation rates to increase, as the alkali content is increased. Further, a decreased kinetic barrier would be expected to shift the temperature of the maximum nucleation towards lower temperatures.

Water content acts to decrease the viscosity in the same manner as alkali content i.e., through breaking up of the network. Hence, one would expect that for a given composition, nucleation rates would be larger in a higher water content glass than in a lower water content glass. Further, for a given composition one would expect the temperature of the maximum nucleation rate to be shifted towards lower temperatures for a higher water content glass due to the decreased kinetic barrier. Gonzalez-Oliver et al. [89] investigated the influence of water on the nucleation rates in LS$_2$ and NC$_2$S$_3$ glasses, and they found that crystal nucleation rates significantly increased, whereas viscosities of the glasses decreased, as the water content increased. Also, the temperature of the maximum nucleation rate was shifted to lower temperatures for the higher water content glasses. It was concluded in ref. [89] that the main effect of water was to lower
the kinetic barrier to nucleation, $\Delta G_D$, rather than to influence the thermodynamic barrier to nucleation, $\Delta G_v$. Davis et al. [90] conducted an extensive study into the influence of water on nucleation rates in LS$_2$ glasses. Davis found steady-state nucleation rates and induction times for crystal nucleation to depend exponentially on water content. Davis further observed that the time-dependent crystal number densities exhibited self-similar behavior as a function of water content, and the authors were therefore able to construct a universal curve for the description of all data. Based on this feature, the authors concluded that mechanisms involved with nucleation are accelerated by water, but that no new reaction pathways are created by the presence of water. In contrast to the conclusions of Gonzalez-Oliver, however, Davis concluded that the influence of water on crystal nucleation was not solely attributable to the effect of water on the viscosity, but that the thermodynamic barrier to nucleation was also reduced by the addition of water.

Impurity particles present in the glass melt can provide sites for heterogeneous nucleation in an otherwise homogeneously nucleating glass-forming system. If such impurities are of sufficient size and number, then artificially high nucleation rates are expected to be observed. James et al. [47] considered the possibility that the discrepancies between theory and experiment observed for nucleation in LS$_2$ glass were due to either impurities in the raw materials, or platinum contamination from the crucibles in which the raw materials were melted. After a thorough investigation, James concluded that neither type of impurity significantly affected the nucleation kinetics in LS$_2$ glass.
2.2. Crystal Growth in Supercooled Liquids and Glasses

Although the processes of nucleation and growth are intimately related, they are often studied separately. Theories of crystal growth from the melt are mainly concerned with elucidating the relationship between the growth rate and the undercooling at the crystal-liquid interface. In general, crystallization is a complex process that involves the interaction of many variables such as the thermodynamic driving force for growth, transport mechanisms for both material and heat, and the nature of the crystal-liquid interface. The interplay of all these variables determines the temperature dependence of the growth rate for a given substance.

In low viscosity (high fluidity) liquids, such as liquid metals, growth velocities are usually quite large and crystal growth rates are often limited by the rate at which the heat evolved upon crystallization can be removed from the growth front. Even if heat transfer away from the crystallizing front is not the limiting variable, the rapid growth rates in such materials precludes study over a broad enough undercooling range to unambiguously clarify the nature of the relationship between the growth rate and undercooling.

Growth rate studies in polymorphically crystallizing (stoichiometric) glass-forming systems have proved invaluable in illuminating the kinetics and mechanisms of crystal growth from the melt. Such materials are generally highly viscous, and consequently the growth rates sufficiently small so that the rate at which heat is evolved is negligible even for large undercoolings. For these materials, the crystal-glass interface temperature can well be taken as the surrounding temperature (furnace temperature).
These features allow for growth rate determination over a wide range of undercooling temperatures. The above characteristics also allow the morphology of the crystallizing front to be directly observed. Further, growth rates in stoichiometric glass-forming systems are not limited by mass transfer, as is the case when the composition of the crystallizing phase is significantly different than the parent phase. The mode of growth in polymorphically crystallizing liquids and glasses is therefore considered to be limited by the matrix-crystal interface kinetics. Since this is the only mode of growth relevant to the present research, the following discussion is limited to interface controlled growth.

2.2.1. Interface Controlled Growth

Presently, there are three standard models used to describe crystal growth in systems that crystallize without a change in composition: normal growth, screw dislocation growth, and 2-D surface nucleated growth. These models and their respective predictions of kinetic behavior, along with Jackson's treatment of the interface, are elaborated upon in Section 5.2.1, and only a brief overview of interface controlled growth is given below.

The temperature dependence of the growth rate of a crystal growing in a supersaturated phase (e.g. supercooled liquid or glass) may be written in the general form [91]:
\[ u = B z \left[ 1 - \exp \left( \frac{-\Delta G}{kT} \right) \right] \Omega \]  

(2.109)

where \( B \) is a constant, \( z \) is the impingement rate of the molecules of the surrounding phase, \( \Delta G \) is the thermodynamic driving force of the process, and \( \Omega \) is a function of the thermodynamic driving force (\( \Delta G \)) and depends on the growth mechanism. In the normal growth model (continuous growth), a sizable fraction of the interface sites are considered to be viable sites for growth to take place and this fraction is assumed to remain essentially constant with temperature. In this case, \( \Omega \) in Equation (2.109) is approximately a constant near unity. According to Jackson's treatment of the interface (for example refs. [92,93]), this is the case envisaged for substances in which the melts are structurally similar to the corresponding crystal. That is, for substances with a low entropy of fusion (\( \Delta S_m < 2R \)).

In the screw dislocation model, spiral growth occurs on crystal faces containing emergent points of screw dislocations, which serve as a constant source of growth sites. In this case [94,95], \( \Omega \) is proportional to the thermodynamic driving force \( \Delta G \). According to Jackson, this is one of the types of growth mechanisms expected to operate in materials with large entropies of fusion (\( \Delta S_m > 4R \)).

The other type of growth mechanism anticipated for high entropy of fusion materials is 2-D surface nucleation. In the 2-D surface nucleated model, two-dimensional nuclei are assumed to fluctuatively form upon, and latterly propagate across, an atomically smooth interface. The two possible models of surface nucleation are the layer
by layer growth model proposed by Kasichew and Stransi [96], and the multinuclear growth model developed by Hillig [97]. For the case of 2-D surface nucleation, the dependence of $\Omega$ on $\Delta G$ is of the form

$$
\Omega \propto \exp\left(\frac{-K}{k_B T \Delta G}\right)
$$

where $K$ is a constant proportional to the square of the interfacial energy, $\sigma^2$ (assuming $\sigma$ is a constant).

2.2.2. Comparison of Experimental Data with Kinetic Models

2.2.2.a. Low Entropy of Fusion Materials

As mentioned, the normal or continuous growth mechanism is expected to operate in low entropy of fusion ($\Delta S_m < 2R$) materials. Kinetic data are available for two such glass-forming systems: SiO$_2$ [98] and GeO$_2$ [99]. In accord with Jackson's predictions, both these materials exhibit non-faceted interface morphologies. As described in Section 5.2.1, experimental data are often compared with theoretical predictions by constructing a reduced growth rate, $U_R$, which is proportional to the interface site factor, versus undercooling ($\Delta T$) plot. Since the fraction of interface sites is essentially constant for normal growth, this plot should yield a horizontal line for low
entropy of fusion materials. In accord with these predictions, this type of behavior has been observed for both SiO\textsubscript{2} and GeO\textsubscript{2} (see ref. [100]).

### 2.2.2.b. High Entropy of Fusion Materials

Glass-forming materials with large entropies of fusion (\(\Delta S > 4R\)) are expected to exhibit kinetics of the form predicted by either the screw dislocation or 2-D surface nucleated growth models. The growth rate anisotropy is expected to be large, and a faceted interface morphology should be observed for these materials. High entropy of fusion glass-forming systems have been extensively studied experimentally (see for example, review articles [100,101]). Experimental studies have provided overwhelming support for the predictions of Jackson, which emphasize the importance of the entropy of fusion in characterizing the crystallization process. In all experimental studies where interface morphology was reported, with the exception of one data set for Na\textsubscript{2}O-2B\textsubscript{2}O\textsubscript{3}, they were observed to be faceted.

For materials in which the screw dislocation mechanism operates, the interface site factor increases continually with undercooling and the \(U_R\) vs. \(\Delta T\) plot should yield a straight line of positive slope which intersects the undercooling axis at the origin. This type of behavior has been observed in high entropy materials such as Na\textsubscript{2}O-2SiO\textsubscript{2} [102], Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} [103], and Na\textsubscript{2}O-3SiO\textsubscript{2} [104].
If 2-D surface nucleation is the operative growth mechanism, the reduced growth rate vs. $\Delta T$ plot is anticipated to be a curve of positive slope and positive curvature. Glass-forming materials in which the 2-D surface mechanism is suspected to operate often exhibit curious behavior in their reduced growth rate plots over some part of the undercooling range sampled. Such anomalous behavior has been observed materials including salol and glycerine (see Fig. 11b and 14b of ref. [105]), 1,2,5-Tri-$\alpha$-Naphthylbenzenene [106], Pb$_2$SiO$_4$ [107], and K$_2$B$_9$O$_{13}$ [108]. As detailed in Section 5.2.1, a plot of $\ln U_T$ vs. $1/T\Delta G$ should yield a straight line of negative slope if the 2-D mechanism is indeed operative. This plot generally appears in the literature as $\ln U_T$ vs. $1/T\Delta T$ wherein $\Delta G$ has been taken to be directly proportional to $\Delta T$. However, it is often observed [101,106,109-113] that two straight lines with different (negative) slopes better describe such plots than a single straight line. Computer simulations (for example, ref [114]) have indicated that below some critical undercooling, surface roughening (an increase in the number of available growth sites) is possible and may correspond to the observed change in slope. However, no convincing verifiable explanation of these experimental findings has been produced.
3. EXPERIMENTAL PROCEDURE

3.1. Glass Preparation

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

3.1.1. 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$_2$O (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$_2$O (Glass 5) and a sub-stoichiometric composition containing 32.5 mol% Li$_2$O (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$_2$CO$_3$ 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 (SiO₂) crucible rather than a Pt-Rh crucible. Details of the preparation procedure employed for each melt are summarized in Table 3.1.
<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Batch Composition (mole %)</th>
<th>Glass Preparation</th>
</tr>
</thead>
</table>
| 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: Fused quartz  
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  
*Precursor powders sintered at 1000°C for 10 hours prior to melting* |
| 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  
*Glass prepared in Brazil at the Federal University of São Carlos (relative humidity 70-80%)* |
| 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  
*Glass prepared in Brazil at the Federal University of São Carlos (relative humidity 70-80%)* |
3.1.2. 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.
3.2. 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, \(n_0\). 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.

3.3. 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:

\[
c = 10^6 \frac{A_{3500} M_w}{\varepsilon \rho d}
\]

where \( c \) is concentration of structurally-bound hydroxyl, SiOH, nominally taken as H\( \text{H}_2\text{O} \) (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); \( \varepsilon \) is the extinction coefficient of the 3500\( \text{cm}^{-1} \) peak, here taken as 54 l/mol-cm as per [90]; \( \rho \) 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.

3.4. 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°C/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°C/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 \( \pm 2^\circ C \) by method of intersecting tangents.
3.5. 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$^3$).

3.6. 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 ±1.5°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 ~ 70 μm) 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

<table>
<thead>
<tr>
<th>Glass</th>
<th>Heat-treatment Temperature (±1.5°C)</th>
<th>Heat-Treatment Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass 1</td>
<td>440°C</td>
<td>350, 543</td>
</tr>
<tr>
<td></td>
<td>454°C</td>
<td>120, 192, 360</td>
</tr>
<tr>
<td></td>
<td>477°C</td>
<td>120, 168, 288</td>
</tr>
<tr>
<td></td>
<td>500°C</td>
<td>24, 48</td>
</tr>
<tr>
<td>Glass 2</td>
<td>454°C</td>
<td>120, 360</td>
</tr>
<tr>
<td></td>
<td>477°C</td>
<td>120, 168, 288</td>
</tr>
<tr>
<td></td>
<td>500°C</td>
<td>24</td>
</tr>
<tr>
<td>Glass 3</td>
<td>454°C</td>
<td>150, 328</td>
</tr>
<tr>
<td></td>
<td>465°C</td>
<td>168, 240, 288</td>
</tr>
<tr>
<td>Glass 4</td>
<td>454°C</td>
<td>150, 328, 476</td>
</tr>
<tr>
<td></td>
<td>465°C</td>
<td>168, 240, 288, 360, 528</td>
</tr>
<tr>
<td>Glass 5</td>
<td>454°C</td>
<td>120, 168, 240, 288, 360</td>
</tr>
<tr>
<td></td>
<td>465°C</td>
<td>168, 240, 288, 360</td>
</tr>
<tr>
<td>Glass 6</td>
<td>454°C</td>
<td>120, 168, 240, 288, 360</td>
</tr>
</tbody>
</table>
3.7. X-Ray Diffraction (XRD) Measurements

3.7.1. 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 CuKα 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°/2 min. At the Federal University of São Carlos, a step-scan of 0.015°/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°/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 CuKα radiation at 50kV and 100 mA. Powder samples were scanned using a step size of 0.02° and a collection time of 3 seconds.
3.7.2. Sodium Silicate Glasses

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

3.8. 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 ±1.5°C. Table 3.3 shows the heat-treatment schedules employed for each glass.

3.8.1. 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 1µm 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].

3.8.2. 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

<table>
<thead>
<tr>
<th>Heat-Treatment Temperature (±1.5°C)</th>
<th>Glass 3</th>
<th>Heat-Treatment Time</th>
<th>Glass 4</th>
<th>Heat-Treatment Time</th>
<th>Glass 5</th>
<th>Heat-Treatment Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>454°C</td>
<td>328°, 480, 528, 600, and 648 hours</td>
<td>150°, 311, 408, and 476°, hours</td>
<td>133, 168, 240°, 288, and 360° hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>465°C</td>
<td>168°, 240°, 288°, and 346 hours</td>
<td>168°, 240°, 288°, 360°, and 528°, hours</td>
<td>168°, 240°, 288°, and 360° hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>477°C</td>
<td>90, 117.5, 163.75, 210, and 257.5 hours</td>
<td>90, 117.5, 163.75, 210, and 257.5 hours</td>
<td>90, 117.5, 163.75, 210, and 257.5 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>490°C</td>
<td>51.5, 93.5, 127, and 151 hours</td>
<td>51.5, 93.5, 127, and 151 hours</td>
<td>51.5, 93.5, 127, and 151 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500°C</td>
<td>23, 32, 48, and 69.25 hours</td>
<td>23, 32, 48, and 69.25 hours</td>
<td>23, 32, 48, and 69.25 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>575°C</td>
<td>5, 10, 16, and 24 hours</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>590°C</td>
<td>20, 35, 44, and 55 minutes</td>
<td>20, 35, 44, and 55 minutes</td>
<td>20, 35, 44, and 55 minutes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>610°C</td>
<td>10, 20, 35, and 45 minutes</td>
<td>10, 20, 35, and 45 minutes</td>
<td>10, 20, 35, and 45 minutes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>635°C</td>
<td>5, 10, 16, 20, and 30 minutes</td>
<td>-</td>
<td>5, 8, 12.5, and 18 minutes</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* denotes samples from which portions were also used for XRD investigation of metastable phase formation
3.9. 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 ±1.5°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 μm 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 pellon 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 μm 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].
4. EXPERIMENTAL RESULTS

4.1. Glass Composition

4.1.1. 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 Glasses 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 $\text{Li}_2\text{O}$ contents in mole%.
Table 4.1  Index of refraction results and analyzed compositions for lithium silicate glasses

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Index of Refraction, n_D (±0.0005)</th>
<th>Analyzed Li_2O Content (mole%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>33.1 ± 0.5*</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>32.7 ± 0.5*</td>
</tr>
<tr>
<td>3</td>
<td>1.5360</td>
<td>33.3 ± 0.3</td>
</tr>
<tr>
<td>4</td>
<td>1.5387</td>
<td>34.5 ± 0.3</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>33.8 ± 0.5*</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>32.5 ± 0.5*</td>
</tr>
</tbody>
</table>

*Compositions analyzed by atomic absorption

4.1.2. 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%
4.2. 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 ppm ± 10%. The water concentrations in Glasses 5 and 6 were also very similar in magnitude, approximately 138 ppm ± 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.
Figure 4.1  FTIR spectra of Glass 4 and Glass 6 obtained from samples of equal thickness (d =1.45 mm)
Figure 4.2 FTIR spectra of Glass 4 and Glass 5 obtained from samples of equal thickness ($d = 0.87\text{mm}$)
4.3. 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 $\pm 2^\circ$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

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Sample Type</th>
<th>$T_g$ ($\pm 2^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Powdered glass</td>
<td>453°C</td>
</tr>
<tr>
<td>2</td>
<td>Powdered glass</td>
<td>455°C</td>
</tr>
<tr>
<td>3</td>
<td>Powdered glass</td>
<td>454°C</td>
</tr>
<tr>
<td>4</td>
<td>Powdered glass</td>
<td>452°C</td>
</tr>
<tr>
<td>5</td>
<td>Powdered glass</td>
<td>452°C</td>
</tr>
<tr>
<td>6</td>
<td>Powdered glass</td>
<td>456°C</td>
</tr>
</tbody>
</table>
4.4. 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

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Average density, $\rho$, (g/cm$^3$) (± 1 standard deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.344 (0.005)</td>
</tr>
<tr>
<td>2</td>
<td>2.342 (0.010)</td>
</tr>
<tr>
<td>3</td>
<td>2.345 (0.018)</td>
</tr>
<tr>
<td>4</td>
<td>2.348 (0.007)</td>
</tr>
<tr>
<td>5</td>
<td>2.346 (0.020)</td>
</tr>
<tr>
<td>6</td>
<td>2.342 (0.020)</td>
</tr>
</tbody>
</table>
4.5. 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.

4.5.1. Lithium Silicate Glasses

For Glass 1, measurements were made using each of the three different conventional XRD instruments described in Section 3.7. The results obtained from each instrument were essentially the same and are described in the last column of Table 4.4. Samples of Glass 1 heated at 440°C for 350 hours were amorphous. After heating for 543 hours at 440°C, the only crystal phase detected was stable LS$_2$. Samples heated at 454°C remained x-ray amorphous for at least up to 192 hours. After 360 hours at 454°C, the dominant diffraction peaks of the stable LS$_2$ crystal phase emerged. These same peaks emerged for samples heated at 477°C for 120 hours. After 168 hours at 477°C, the dominant LS$_2$ peaks grew in intensity and several other LS$_2$ peaks emerged. The amorphous background had almost completely disappeared for samples heated at 477°C
for 288 hours, and the only crystal phase detected was stable LS$_2$. For samples heated at 500°C for 24 hours, the dominant LS$_2$ diffraction peaks emerged.

The x-ray diffraction patterns illustrated in Fig. 4.3 are representative of the results obtained from the different XRD instruments. The vertical lines along the abscissa in Fig. 4.3 (and in all subsequent lithium silicate XRD figures) denote the positions and relative intensities of diffraction peaks corresponding to the stable LS$_2$ crystal phase as per JCPDS card #40-0376. As observed in Fig. 4.3, the extent of crystallization is relatively small, and stable LS$_2$ is clearly the only crystal phase present.

For Glass 2, XRD data were collected at the University of Arizona and Arizona State University. The results from the different XRD equipment for Glass 2 were essentially the same, and very similar to the results reported above for Glass 1. Samples heated at 454°C for 120 h were amorphous. After heating for 360 h at 454°C, the dominant peaks of the stable LS$_2$ crystal phase emerged. The same peaks emerged for the sample heated at 477°C for 120 hours. After heating for 168 h at 477°C, these peaks intensified and several other of the stable LS$_2$ peaks emerged. For samples heated at 500°C for 24 h, the dominant LS$_2$ peaks emerged. The similarity between the XRD results of Glass 1 and Glass 2 are exemplified in Fig. 4.4, which shows the diffraction patterns obtained for each glass after heating at 454°C for 360 hours.
Table 4.4 Summary of XRD results for Glass 1

<table>
<thead>
<tr>
<th>Heat-Treatment Temperature (± 1.5°C)</th>
<th>Heat-Treatment Time (hours)</th>
<th>XRD Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>440°C</td>
<td>350</td>
<td>Amorphous</td>
</tr>
<tr>
<td>440°C</td>
<td>543</td>
<td>only stable LS₂ crystal phase</td>
</tr>
<tr>
<td>454°C</td>
<td>120</td>
<td>Amorphous</td>
</tr>
<tr>
<td>454°C</td>
<td>192</td>
<td>Amorphous</td>
</tr>
<tr>
<td>454°C</td>
<td>360</td>
<td>dominant peaks of LS₂ crystal phase emerged against amorphous background</td>
</tr>
<tr>
<td>477°C</td>
<td>120</td>
<td>dominant peaks of LS₂ crystal phase emerged against amorphous background</td>
</tr>
<tr>
<td>477°C</td>
<td>168</td>
<td>dominant peaks of LS₂ intensified and additional LS₂ peaks emerged</td>
</tr>
<tr>
<td>477°C</td>
<td>288</td>
<td>only stable LS₂ crystal phase</td>
</tr>
<tr>
<td>500°C</td>
<td>24</td>
<td>dominant peaks of LS₂ crystal phase emerged against amorphous background</td>
</tr>
</tbody>
</table>
Figure 4.3  XRD traces of Glass 1
Figure 4.4  XRD traces of Glass 1 and Glass 2 heated at 454°C for 360 hours
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.

Figure 4.5 shows the XRD traces of samples of Glass 4 that had been heated at 454°C for 150, 328, and 476 hours. The top-most diffraction pattern shown was obtained from the surface material of the sample heated at 454°C for 476 hours. As observed in Fig. 4.5, Glass 4 remained x-ray amorphous after heating for 150 hours. After heating for 328 h, the dominant peaks of the stable LS2 phase emerged against the amorphous background. Upon further heating, these LS2 peaks intensified and other peaks corresponding to the stable phase appeared. Consistent with our observations for all heat-treated lithium silicate glasses, and as exemplified by Fig. 4.5, there were no apparent differences between the XRD traces obtained from surface and interior materials of heated samples, save the fact that diffraction peaks of surface materials had greater intensities.

The XRD traces obtained for samples of Glass 4 that were heated at 465°C are shown as a function of heating time in Fig. 4.6. As shown in Fig. 4.6, and as observed for all other lithium silicate glasses heated at 465°C, the only diffraction peaks detectable are the dominant peaks of stable LS2. These LS2 peaks intensified and additional peaks associated with the stable LS2 phase appeared with increased heating time.
The XRD traces of samples from Glass 3 that had been heated at 454°C are shown in Fig. 4.7. As observed in Fig. 4.7, the glass remained x-ray amorphous after heating for 150 hours. After heating for 328 hours, the dominant peaks of the stable LS$_2$ phase emerged against an amorphous background. Fig. 4.8 shows the XRD traces for Glass 3 heated at 465°C for 168, 240 and 288 hours. Although the extents of crystallization are larger for samples heated at 465°C, the crystallization pattern is the same as described for 454°C.

Crystallization of Glass 6 that had been heated at 454°C for 120, 168, 240, 288 and 360 hours is similar to that observed for Glasses 3 and 4 at 454°C. Glass 6 also remained x-ray amorphous after heating for 120 hours. The dominant LS$_2$ peaks, although barely detectable, emerged after 168 hours. After 240 hours, these LS$_2$ peaks were clearly resolvable. Upon further heating, these peaks intensified and additional LS$_2$ peaks appeared. These results are shown in Fig. 4.9.

Figure 4.10 shows the series of diffraction patterns obtained from samples of Glass 5 heated at 454°C for 120, 168, 240, and 360 hours. Crystallization of Glass 5 is consistent with that observed for all other lithium silicate glasses. However, for Glass 5 the more intense LS$_2$ diffraction peaks began to emerge after heating for 120 hours. As shown in Fig. 4.10, upon further heating these peaks intensified and additional stable phase peaks appeared. The XRD traces obtained for samples of Glass 5 heated at 465°C exhibit similar behavior and are shown in Fig. 4.11.

To ensure that our observations described above were not limited by instrument sensitivity; XRD measurements were also performed on an instrument equipped with a
rotating anode x-ray lamp. This larger intensity x-ray beam allows for greater penetration depth in the material and provides a better signal to noise ratio, thus enabling greater resolution of small peaks, and hence detection of even small volume fractions of crystalline material which may not be resolvable via standard XRD equipment. Figure 4.12 shows the diffraction pattern obtained via the rotating anode XRD instrument for a sample of Glass 5 that had been heated at 454°C for 360 hours. The diffraction pattern shown in Fig. 4.12 is very similar to that which was obtained using standard XRD equipment, i.e., stable LS₂ was the only crystal phase was detected. Thus, it is concluded that instrument sensitivity did not have an effect the observed crystallization.
Figure 4.5  XRD traces of Glass 4 heated at 454°C
Figure 4.6  XRD traces of Glass 4 heated at 465°C
Figure 4.7  XRD traces of Glass 3 heated at 454°C
Figure 4.8  XRD traces of Glass 3 heated at 465°C
Figure 4.9  XRD traces of Glass 6 heated at 454°C
Figure 4.10  XRD traces of Glass 5 heated at 454°C
Figure 4.11  XRD traces of Glass 5 heated at 465°C
Figure 4.12  Rotating anode XRD trace of Glass 5 heated at 454°C for 360 hours
4.5.2. 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. Figure 4.14 shows the XRD trace obtained from W55% heated at 435°C for 3 h then at 610°C for 5 minutes and prepared for XRD analysis using method 3. However, as shown in Fig. 4.15, 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, is depicted in Fig. 4.16. As shown in Fig. 4.17, 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.

Figure 4.18 shows the XRD pattern of the W59% composition which was heat-treated at 440°C for 48 hours and then at 610°C for 0.5 hour. This sample had a very low surface to volume ratio, and all except one of the peaks corresponded to sodium metasilicate crystal phase. For a similarly prepared sample of this composition, which had been subjected to the same nucleation treatment, but heated at 610°C for 2 hours, both sodium disilicate and sodium metasilicate crystal phases were present in the diffraction pattern. The XRD pattern of this sample is shown in Fig. 4.19.

The diffraction peaks in all sodium silicate XRD traces were identified using JCPDS cards: #16-818 (Na2OSiO3), #23-529 (Na2Si2O5), and #22-1396 (Na2Si2O5).
Figure 4.13 XRD trace of W51% heated at 435°C for 6 hours then at 610°C for 2 minutes. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d).
Figure 4.14 XRD trace of W55% heated at 435°C for 3 hours then at 610°C for 5 minutes. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d).
Figure 4.15  XRD trace of W55% heated at 435°C for 3 hours then at 610°C for 10 minutes. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d).
Figure 4. 16 XRD trace of W57% heated at 425°C for 2 hours then at 610°C for 1 hour. Peaks corresponding to sodium metasilicate denoted by (m), and peaks corresponding to sodium disilicate denoted by (d).
Figure 4.17  XRD trace of W57% heated at 425°C for 2 hours then at 610°C for 1 hour. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d).
Figure 4.18 XRD trace W59% heated at 440°C for 48 hours then at 610°C for 0.5 hour. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d).
Figure 4. 19  XRD trace of W59% heated at 440°C for 48 h then at 610°C for 2.5 hours. Peaks corresponding to sodium metasilicate denoted by (m) and peaks corresponding to sodium disilicate denoted by (d).
4.6. Experimental Growth Rates in Lithium Silicate Glasses

4.6.1. 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 as in Fig. 4.20. 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 as in Fig. 4.20, 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 as in Fig. 4.21. 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 500°C, the crystals in Glass 4 looked like those in Fig. 4.21. At higher temperatures (575, 590, 610, and 635°C) spherulitic sections as in Fig. 4.22 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. Optical micrographs representative of the surface crystalline interface observed at all temperatures are shown in Figs. 4.23a and 4.23b.
Figure 4. 20  Optical micrograph showing morphology of internal crystals. Glass 3 heated at 477°C for 257 hours
Figure 4.21  Optical micrograph showing morphology of internal crystals. Glass 5 heated at 500°C for 69.25 hours.
Figure 4.22  Optical micrograph showing morphology of internal crystals. Glass 4 heated at 610°C for 10 minutes.
Figure 4.23  Optical micrographs showing surface crystal interface: (a) Glass 3 heated at 490°C for 127 hours, and (b) Glass 5 heated at 590°C for 35 minutes
4.6.2. Internal Crystal Growth Rates

4.6.2.a. Fast-Axis (Major-Axis) Growth Rates

For all compositions studied (Glasses 3, 4, and 5), the length of the long axes and radii of spherulitic sections were found to increase linearly with time at each temperature. This type of behavior is characteristic of crystal growth controlled by interface kinetics.

The lengths of the long axes and radii of spherulites for Glass 3 are shown as a function of heating time at each temperature in Fig. 4.24. The kinetic curve for Glass 3 heated at 575°C does not conveniently fit within the axes of Fig. 4.24, and is therefore shown separately in Fig. 4.25. Similar plots were constructed for Glasses 4 and 5 and are shown in Figs. 4.26 and 4.27, respectively. The equations of the resulting kinetic curves for all compositions 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 (and thus the growth rates) were found using standard analytical procedures. The slopes of all curves generated for T ≤ 500°C were then divided by a factor of two for consistency with radii measurements.

The linear growth rates thus obtained are plotted as a function of temperature in Fig. 4.28. The vertical error bars in Fig. 4.28 represent the aforementioned errors associated with the slopes. These growth rates are tabulated in Table 4.5. One observes from Fig. 4.28 that to within experimental error, the growth rates of all three
compositions are the same. Based on this figure, it is apparent that the amount of water introduced into the melts by virtue of different ambient conditions (i.e., different humidity levels) does not have a significant effect on crystal growth rates. Also, one observes that the growth rate is only weakly dependent upon temperature until about 600°C where it appears to rise steeply with increasing temperature.

To verify the accuracy of the technique used to obtain the internal crystal growth rate data described in Section 3.8, i.e., using different as-prepared glass samples for each heat-treatment time, a single sample of Glass 4 was heated at 465°C for 168 h. The sizes of the largest internal crystals in the sample were measured and recorded as described in Section 3.8.1. The sample was subsequently returned to the furnace and heated at 465°C for an additional 72 hours, then removed and re-examined via optical microscopy and the sizes of the largest internal crystals were measured and recorded. This process was repeated for various additional heating times. The results from this technique, denoted “method b,” are shown in Fig. 4.29 along with the results from Fig. 4.26 for 465°C. It is apparent from Fig. 4.29 that the data from the two techniques agree well with respect to both magnitude and temperature dependence, thus confirming the accuracy of the growth rate measurement technique employed herein.
Figure 4.24 Variation of internal crystal size with time for Class 3
Figure 4.25  Variation of internal crystal size with time for Glass 3 at $T = 575^\circ C$
Figure 4.26 Variation of internal crystal size with time for Glass 4.
Figure 4.27 Variation of internal crystal size with time for Glass 5
Figure 4.28 Crystal growth rates as a function of temperature for Glasses 3, 4, and 5.
Table 4.5  Linear growth rates (fast-axis) of internal crystals for Glasses 3, 4, and 5

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Glass 3</th>
<th>U (m/s)</th>
<th>Glass 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.10 x 10^{-12} (± 4.7 x 10^{-13})</td>
<td>3.40 x 10^{-12} (± 5.4 x 10^{-13})</td>
<td>3.63 x 10^{-12} (± 5.2 x 10^{-13})</td>
</tr>
<tr>
<td>454</td>
<td>8.01 x 10^{-12} (± 1.2 x 10^{-12})</td>
<td>7.31 x 10^{-12} (± 1.1 x 10^{-12})</td>
<td>7.05 x 10^{-12} (± 0.9 x 10^{-12})</td>
</tr>
<tr>
<td>465</td>
<td>1.50 x 10^{-11} (± 2.3 x 10^{-12})</td>
<td>1.40 x 10^{-11} (± 1.9 x 10^{-12})</td>
<td>1.93 x 10^{-11} (± 2.9 x 10^{-12})</td>
</tr>
<tr>
<td>477</td>
<td>3.46 x 10^{-11} (± 5.2 x 10^{-12})</td>
<td>4.41 x 10^{-11} (± 6.7 x 10^{-12})</td>
<td>4.58 x 10^{-11} (± 4.6 x 10^{-12})</td>
</tr>
<tr>
<td>490</td>
<td>8.06 x 10^{-11} (± 1.2 x 10^{-11})</td>
<td>1.01 x 10^{-10} (± 1.2 x 10^{-11})</td>
<td>8.07 x 10^{-11} (± 1.5 x 10^{-11})</td>
</tr>
<tr>
<td>500</td>
<td>1.43 x 10^{-9} (± 1.9 x 10^{-10})</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>575</td>
<td>2.00 x 10^{-8} (± 2.6 x 10^{-9})</td>
<td>2.31 x 10^{-8} (± 3.2 x 10^{-9})</td>
<td>1.91 x 10^{-8} (± 3.0 x 10^{-9})</td>
</tr>
<tr>
<td>590</td>
<td>6.41 x 10^{-8} (± 8.3 x 10^{-9})</td>
<td>6.55 x 10^{-8} (± 8.5 x 10^{-9})</td>
<td>6.30 x 10^{-8} (± 7.6 x 10^{-9})</td>
</tr>
<tr>
<td>610</td>
<td>1.51 x 10^{-7} (± 2.0 x 10^{-8})</td>
<td>–</td>
<td>1.38 x 10^{-7} (± 1.5 x 10^{-8})</td>
</tr>
</tbody>
</table>
Figure 4.29  Comparison of growth rate measurement techniques for Glass 4 at $T = 465^\circ C$
The growth rate data in Fig. 4.28, along with various growth rate data reported in the literature for lithium disilicate glasses prepared under normal melting conditions [42,53,70,89,120-123], are shown as a function of temperature in Fig. 4.30. Since the growth rates vary by many orders of magnitude over the temperature range of interest, the data in Fig. 4.30 are more readily compared when plotted on a log scale as in Figure 4.31. It is noted that growth rate data reported as diameters or lengths in the literature were divided by a factor of 2 before being incorporated into Fig. 4.30 and subsequent figures. Despite the disparity of glass preparation procedures and/or crystal growth measurement methods employed by the various investigators, one observes from Fig. 4.31 that all of the data seem to be in accord with respect to magnitude and temperature dependence for T ≤ 640°C, save the data of Ito et al.[42]. When the data are viewed collectively as in Fig. 4.31, it is apparent that a smoother overall curve is generated by using the high temperature growth rate data of Matusita and Tashiro [123], rather than the data of Leontjewa [122]. In light of the seemingly anomalous results of Ito et al. and Leontjewa, these two data sets are excluded from subsequent figures and analyses invoking data from the literature.

The data in Figure 4.30 (excluding the data of Ito and Leontjewa) are plotted as ln U vs. 1/T in Fig. 4.32. Arrhenius behavior is observed for temperatures less than about 560°C. The activation enthalpy for crystal growth obtained from a least squares fit through the data in this temperature regime was found to be approximately 79 kcal/mol.
Figure 4.30  Growth rate data as a function of temperature for Glasses 3, 4, and 5 along with data reported by other investigators
Figure 4.31 Growth rate data shown in Fig. 4.30 (log scale) as a function of temperature.
Figure 4.32  ln U vs. 1/T using data shown in Figure 4.30
4.6.2.b. Short-Axis (Minor-Axis) Growth Rates

The lengths of the short axes of internal crystals were measured for temperatures $T \leq 500^\circ$C for Glasses 3, 4, and 5. As described in Section 4.6.1, the internal crystals of Glasses 3 and 5 heated at 454, 465, and 477$^\circ$C, and those of Glass 4 heated at $T = 454$ and 465$^\circ$C, were generally uniform in shape and of the form shown in Fig. 4.20. For these heat-treatment temperatures, the widths of the largest crystals observed for each glass at each heat-treatment time were measured and used to determine the short-axis growth rates. At temperatures 490 and 500$^\circ$C, there was considerable variation in crystal shape for Glasses 3 and 5. For Glass 4, this non-uniformity in crystal shape was observed at temperatures 477, 490, and 500$^\circ$C. The widths (length of the short-axes) of the largest crystals having the general form shown in Fig. 4.21 were measured for each heat-treatment time and used to determine the short-axes growth rates at these temperatures.

For all three glasses, the lengths of the short-axes were found to increase linearly with time at each temperature $T \leq 500^\circ$C. Figures 4.33, 4.34, and 4.35 show the lengths of the short-axes (widths) of internal crystals as a function of heating time for Glass 3, Glass 4, and Glass 5, respectively. The equations of the lines in these figures were found by a least squares fit to each temperature data set, and the errors associated with the slopes (and hence the growth rates) were determined using standard analytical procedures. The values of the slopes were then divided by a factor of two, thus yielding the linear growth rates of the short-axes.
The linear growth rates thus obtained are shown as a function of temperature for Glasses 3, 4, and 5 in Fig. 4.36. As observed in Fig. 4.36, the magnitudes and temperature dependence of the short-axes growth rates are to within experimental error for Glasses 3 and 5 for all temperatures \( T \leq 500^\circ\text{C} \). For \( T \geq 477^\circ\text{C} \), the magnitudes and temperature dependence of the short-axes growth rates for Glass 4 are slightly larger than those of Glasses 3 and 5. For all glasses, the temperature dependence of the growth rates is observed to rise (relatively) sharply as the temperature increases above \( 477^\circ\text{C} \). The growth rate data shown in Fig 4.36 are tabulated in Table 4.6.

As mentioned in Section 4.6.1, the shapes of the internal crystals remained essentially constant with time at each temperature until impingement with other crystals occurred. This qualitative observation was quantified by evaluating the aspect ratio (ratio of short- to long-axis lengths) of the crystals at each heating time for each heat-treatment temperature. The results of these calculations are shown in Table 4.7, which gives the average value of the aspect ratios for all heating times at the given temperature, along with the standard deviations from the average values. The data in Table 4.7 are plotted as a function of temperature in Figure 4.37. The data points in Fig. 4.37 represent the average aspect ratio values, and the vertical error bars represent the standard deviation from the average value. From Fig. 4.37, it appears that the aspect ratios for each glass remain relatively constant up to about \( 477^\circ\text{C} \), at which point they appear to increase linearly with temperature. Assuming this linear relationship holds for \( T \geq 477^\circ\text{C} \), then by extrapolation of the data it appears that an aspect ratio value of 1 is approached as the temperature nears about \( 530-540^\circ\text{C} \).
Figure 4.33 Variation of short-axis size with time for Glass 3.
Figure 4.34 Variation of short-axis size with time for Glass 4.
Figure 4.35 Variation of short-axes size with time for Glass 5
Figure 4.36 Short-axis crystal growth rates as a function of temperature for Glasses 3, 4, and 5
Table 4.6  Linear growth rates (short-axis) of internal crystals for Glasses 3, 4, and 5

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Glass 3</th>
<th>Glass 4</th>
<th>Glass 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>454</td>
<td>$8.13 \times 10^{-13}$</td>
<td>$6.61 \times 10^{-13}$</td>
<td>$8.68 \times 10^{-13}$</td>
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<td>($\pm 2.3 \times 10^{-13}$)</td>
<td>($\pm 2.0 \times 10^{-13}$)</td>
<td>($\pm 1.3 \times 10^{-13}$)</td>
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<tr>
<td>465</td>
<td>$1.44 \times 10^{-12}$</td>
<td>$1.37 \times 10^{-12}$</td>
<td>$1.90 \times 10^{-12}$</td>
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<td>($\pm 2.2 \times 10^{-13}$)</td>
<td>($\pm 1.9 \times 10^{-13}$)</td>
<td>($\pm 2.5 \times 10^{-13}$)</td>
</tr>
<tr>
<td>477</td>
<td>$3.20 \times 10^{-12}$</td>
<td>$5.57 \times 10^{-12}$</td>
<td>$3.31 \times 10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>($\pm 4.9 \times 10^{-13}$)</td>
<td>($\pm 6.0 \times 10^{-13}$)</td>
<td>($\pm 4.1 \times 10^{-13}$)</td>
</tr>
<tr>
<td>490</td>
<td>$2.36 \times 10^{-11}$</td>
<td>$3.75 \times 10^{-11}$</td>
<td>$2.08 \times 10^{-11}$</td>
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<tr>
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<td>($\pm 3.1 \times 10^{-12}$)</td>
<td>($\pm 5.5 \times 10^{-12}$)</td>
<td>($\pm 4.3 \times 10^{-12}$)</td>
</tr>
<tr>
<td>500</td>
<td>$6.94 \times 10^{-11}$</td>
<td>$9.72 \times 10^{-11}$</td>
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<tr>
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<td>($\pm 9.0 \times 10^{-12}$)</td>
<td>($\pm 2.3 \times 10^{-11}$)</td>
<td>($\pm 7.8 \times 10^{-12}$)</td>
</tr>
</tbody>
</table>
Table 4.7  Aspect ratios of internal crystals for Glasses 3, 4, and 5

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Glass 3 Aspect Ratio (± 1 std. deviation)</th>
<th>Glass 4 Aspect Ratio (± 1 std. deviation)</th>
<th>Glass 5 Aspect Ratio (± 1 std. deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>454</td>
<td>0.28 (±0.02)</td>
<td>0.25 (±0.02)</td>
<td>0.30 (±0.02)</td>
</tr>
<tr>
<td>465</td>
<td>0.29 (±0.04)</td>
<td>0.27 (±0.04)</td>
<td>0.26 (±0.03)</td>
</tr>
<tr>
<td>477</td>
<td>0.31 (±0.03)</td>
<td>0.33 (±0.04)</td>
<td>0.27 (±0.05)</td>
</tr>
<tr>
<td>490</td>
<td>0.50 (±0.10)</td>
<td>0.61 (±0.10)</td>
<td>0.45 (±0.15)</td>
</tr>
<tr>
<td>500</td>
<td>0.57 (±0.15)</td>
<td>0.70 (±0.10)</td>
<td>0.58 (±0.12)</td>
</tr>
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</table>
Figure 4.37 Aspect ratios of Glasses 3, 4, and 5 as a function of temperature
4.6.2.c. Surface Crystal Growth Rates

For temperatures in the range 490°C - 635°C, the linear growth rates of surface crystalline layers were found to be within experimental error of the fast-axes (long-axes) linear growth rates of internal crystals as reported in Section 4.6.2 for Glasses 3, 4, and 5. At lower temperatures (T < 490°C), the number density of internal crystals is very high, and impingement of the surface layer with internal crystals at longer times tended to obscure the interface. Hence, the surface layer growth rate data obtained are less reliable at these lower temperatures and are not reported. In subsequent figures, the data points give the average value of the surface crystalline thickness, and the vertical error bars represent the standard deviation from the average value.

To facilitate comparison between surface crystal thickness and long-axes (fast-axes) crystal size data for 490°C and 500°C, the internal crystal size data given in Section 4.6.2 were divided by a factor of 2 to yield the half-axes size data. For T > 500°C, the radii data as given in Section 4.6.2 are utilized for comparative purposes.

Figure 4.38 shows the surface crystalline layer thickness as a function of heating time at 490°C and 500°C (solid markers), along with the half-length of the major axis data (open markers) for Glass 3. Figure 4.39 shows the surface crystal layer thickness and radii of spherulites for Glass 3 at 575°C using the same marker notation. Figure 4.40 shows these data (using the same marker notation) for 635°C.
The surface layer thickness as function time for 500°C is shown along with the half-axis size data for Glass 4 in Fig. 4.41. The surface layer thickness and radii of spherulites as a function of time at 610°C are shown for Glass 4 in Fig. 4.42. As in Figs 4.38-4.40, closed markers correspond to surface layer thickness.

Figure 4.43 shows the surface crystal layer thickness (closed markers) and half-axis size (open markers) data at 490°C and 500°C for Glass 5. The surface layer thickness and radii of spherulites at 590, 610, and 635°C are shown as a function of time in Fig. 4.44 using the same marker notation.

The equations of the lines shown through the surface crystal data in figs. 4.38-4.44 were found using a least squares fit; the least squares slopes yielding the linear growth rates of the surface crystalline layers. These results are given in Table 4.8. As observed in Figs. 4.38 – 4.44, and as noted above, the growth rates of surface crystalline layers are the same as the linear growth rates (reported in Table 4.5) of the fast-axes of internal crystals to within experimental error. Although the growth rates (slopes) agree well between the surface and internal crystals, the size (length) of the surface crystal layers is generally larger than the size (half-length or radius) of the corresponding internal crystals for all heat treatment time-temperature combinations.

In Section 4.6.2, it was shown that the disparate water concentration between Glass 5 and Glasses 3 and 4 did not significantly influence the observed internal crystal growth rates. Figure 4.45 shows the surface crystal data of Glass 3 and Glass 5 for 490°C and 500°C. Figure 4.46 shows the surface crystal data of Glass 3 and Glass 5 at 635°C. Figures 4.45 and 4.46 illustrate that the difference in water concentration between these
two families of glasses does not significantly affect the observed surface crystal growth rates.
Figure 4.38 Surface crystal layer thickness and half-axis length of internal crystals as a function of time at $T = 490^\circ C$ and $500^\circ C$ for Glass 3.
Figure 4.39  Surface crystal layer thickness and radius of internal crystals as a function of time at $T = 575^\circ C$ for Glass 3
Figure 4.40 Surface crystal layer thickness and radius of internal crystals as a function of time at $T = 635^\circ\text{C}$ for Glass 3
Figure 4.41  Surface crystal layer thickness and half-length of long axis of internal crystals as a function of time at $T = 500^\circ$C for Glass 4
Figure 4.42  Surface crystal layer thickness and radius of internal crystals as a function of time at $T = 610^\circ$C for Glass 4
Figure 4.43  Surface crystal layer thickness and half-length of long axis of internal crystals as a function of time at $T = 490^\circ\text{C}$ and $500^\circ\text{C}$ for Glass 5
Figure 4.44  Surface crystal layer thickness and radius of internal crystals as a function of time at $T = 590^\circ C$, $610^\circ C$, and $635^\circ C$ for Glass 5
Table 4. 8 Surface crystalline layer growth rates for Glasses 3, 4, and 5

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Glass 3</th>
<th>U (m/s)</th>
<th>Glass 4</th>
<th>Glass 5</th>
</tr>
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<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>490</td>
<td>5.00 x 10^{-11}</td>
<td>(± 7.5 x 10^{-12})</td>
<td>-</td>
<td>4.67 x 10^{-11}</td>
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<td>(± 1.7 x 10^{-11})</td>
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<td>(± 4.7 x 10^{-13})</td>
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<tr>
<td>575</td>
<td>1.70 x 10^{-9}</td>
<td>(± 2.6 x 10^{-10})</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>590</td>
<td>2.50 x 10^{-8}</td>
<td>(± 3.5 x 10^{-9})</td>
<td>2.70 x 10^{-8}</td>
<td>(± 3.8 x 10^{-9})</td>
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<tr>
<td>610</td>
<td>6.81 x 10^{-8}</td>
<td>(± 1.1 x 10^{-8})</td>
<td>8.16 x 10^{-8}</td>
<td>(± 1.0 x 10^{-8})</td>
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<tr>
<td>635</td>
<td>1.50 x 10^{-7}</td>
<td>(± 2.1 x 10^{-8})</td>
<td>-</td>
<td>1.32 x 10^{-7}</td>
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</table>
Figure 4.45 Comparison of surface crystal growth data between Glass 3 and Glass 5 at $T = 490^\circ C$ and $T = 500^\circ C$
Figure 4.46  Comparison of surface crystal growth data between Glass 3 and Glass 5 at $T = 635^\circ$C
4.7. Experimental Crystal Nucleation in Sodium Silicate Glasses

4.7.1. 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 ≤ 425°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, \( \Gamma^s \), were found by a least squares fit. The error associated with each slope (and thus \( \Gamma^s \)) was calculated using standard error analysis procedures.

The kinetic curves for nucleation temperatures 390°C, 400°C, 410°C, 415°C, 425°C, 440°C and 455°C are shown in Figs. 4.47, 4.48, 4.49, 4.50, 4.51, 4.52, and 4.53, respectively. As noted in Section 3.9, multiple micrographs were obtained for each heat-treatment, and the data points in Figs. 4.47-4.53 represent the average \( N_v \) values. The vertical error bars represent the standard deviations from the average values. For \( T \leq 425°C \), the lines through the steady-state regions are extrapolated back to the x-intercepts to show the estimated induction times, \( t_{\text{ind}} \). As observed from Figs. 4.47-4.53, the induction time appears to decrease with increasing temperature from 390°C to 425°C.
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, \( I_n \), for the glass composition W57%, was generated from the data in Table 4.9. As depicted in Fig. 4.54, the steady-state nucleation rate curve has the form of an asymmetric peak with a maximum rate, \( I_{\text{max}} \), of \( 6.2 \times 10^3 \) (cm\(^{-3}\) min\(^{-1}\)) occurring at a temperature, \( T_{\text{max}} \), of about 410°C. Also, from Fig. 4.54 it appears that the nucleation range for this glass composition is approximately 385°C to 465°C. It should be noted that the line connecting the experimental data points in Fig. 4.54 has no theoretical significance and is only present for the purpose of providing a guide for the eye of the reader.
Figure 4.47  W57% kinetic curve for $T_n = 390^\circ C$
Figure 4.48  W57% kinetic curve for $T_n = 400^\circ C$
Figure 4. 49  W57% kinetic curve for $T_n = 410^\circ C$
Figure 4.50 W57% kinetic curve for $T_n = 415^\circ C$
Figure 4.51  W57% kinetic curve for $T_n = 425^\circ$C
Figure 4.52  W57% kinetic curve for $T_n = 440^\circ$C
Figure 4.53  W57% kinetic curve for $T_n = 455^\circ$C
Table 4.9 Steady-state nucleation rates of sodium metasilicate crystals in W57% composition glass

<table>
<thead>
<tr>
<th>$T_n$ (°C)</th>
<th>$\bar{n} \times 10^{-2}$ (cm$^3$ min$^{-1}$)</th>
<th>Error (±) $\times 10^{-2}$ (cm$^3$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>390</td>
<td>0.13</td>
<td>0.02</td>
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<tr>
<td>400</td>
<td>3.22</td>
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<tr>
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<td>4.67</td>
</tr>
<tr>
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<td>1.50</td>
</tr>
<tr>
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<td>3.33</td>
</tr>
<tr>
<td>455</td>
<td>10.88</td>
<td>1.80</td>
</tr>
</tbody>
</table>
Figure 4.54 Magnitude and temperature dependence of the steady state nucleation rate for W57% glass composition
4.7.2. 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. Optical micrographs showing internal nucleation for the W59% and W55% compositions are shown in Fig. 4.55 and Fig. 4.56, respectively. 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\(^{-3}\).
Figure 4.55 Optical micrograph of W59% nucleated at 440°C for 48 hours then developed at 610°C for 0.5 hours.

Figure 4.56 Optical micrograph of W55% nucleated at 410°C for 0.5 hours then developed at 590°C for 20 minutes.
4.7.3. 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.
Figure 4.57 Optical micrograph showing morphology of sodium metasilicate crystals.
Figure 4.58  Optical micrograph showing morphology of sodium metasilicate crystals
5. DISCUSSION

5.1. XRD Investigation of Metastable Phase Formation in LS$_2$ 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°C for 120 hours revealed the presence of a crystal phase that could not be identified with any previously known phase in the binary Li$_2$O-SiO$_2$ system. The authors referred to this phase as metastable $\alpha'$-LS$_2$. After heating a glass sample for 312 hours, Iqbal found that most of the $\alpha'$-LS$_2$ peaks remained, but a number of additional peaks also emerged which could indicate the appearance of stable LS$_2$. However, based on subsequent TEM results the authors suggested that the additional peaks were associated with another metastable phase, intermediate between the $\alpha'$- and stable LS$_2$ phases. This intermediate metastable phase was denoted as $\beta'$-LS$_2$. The XRD results for a glass sample, which had been heated for 480 hours, showed the presence of stable LS$_2$ 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 (Fig. 4.4) 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$_2$O), while the glass studied by James and Iqbal was hyper-stoichiometric (33.9 mol% Li$_2$O). 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 (Fig. 4.7) with those of Glass 1 (Figs 4.3 and 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 (see for example, Fig. 4.5). 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.
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 $T = 454°C$. At $T = 465°C$, 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$_2$O, 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$_2$O (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 LS2 glass for 86 and 100 hours at a temperature of 460°C, and the only crystalline phase detected was stable LS2. Further, Fokin (private communication) heat-treated LS2 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 LS2.

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 LS2 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 LS2 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 LS2.

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.
5.2. Experimental Crystal Growth Rates in Lithium Disilicate Glasses

5.2.1. 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:

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

(5.2)

In Equation (5.2) \( u \) is the growth rate, \( v \) is a jump frequency, \( \lambda \) is the distance advanced by the interface (taken as the molecular diameter), \( \Delta G \) 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:
where \( f \) is the interface site factor (fraction of preferred growth sites on the interface). This fraction is given by

\[
f = \frac{\lambda \Delta G}{4 \pi \sigma V_m}
\]

where \( \sigma \) 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

\[
u = C \exp\left(-\frac{B}{T \Delta G}\right)
\]

The quantity \( B \) in the above equation is given by

\[
B = \frac{\pi \lambda V_m \sigma_E^2}{3k_B}
\]
In Equation (5.6) $k_b$ is Boltzmann's constant, and $\sigma_e$ 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

$$C = \lambda N_s A_o$$  \hspace{1cm} (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

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

where $\Gamma$ 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 (ΔS_f > 4R ζ^-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

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

(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
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 LS2 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].

Based on Fig. 5.1, 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.

Also shown in Fig. 5.1 are the viscosity data for LS2 reported by Shartsis [129] and Bockris [130] for temperatures near the melting temperature, which is about 1034°C for this composition. These high temperature data are in accord in both magnitude and temperature dependence.

At temperatures intermediate to those where experimental viscosity data are shown in Fig. 5.1, 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 shown in Fig. 5.1 is assumed to follow either the VFT equation derived by Zanotto [128], or the VFT equation as given by Matusita and Tashiro in ref.
[123]. The curves corresponding to these equations are shown along with the experimental data in Fig. 5.1.
Figure 5.1 Viscosity data reported in the literature for LS$_2$ glass; curve (a) VFT from ref. [123] and curve (b) VFT from ref. [128]
Figure 5.2  Data in Fig. 5.1 plotted as $\ln \eta$ vs. $T^{-1}$
The reduced growth rate plot shown in Fig. 5.3 was constructed using the experimental growth data in Fig. 4.30 (excluding the data of refs. [42,122]), Zanotto's VFT equation, and ΔG according to equation; ΔG = 53399 − 42.015T + 0.00713T^−4.790 \times 10^{-6}T^3 \text{ (J/mol; } T \text{ in K}), which was obtained by fitting the measured thermodynamic data given in ref. [55]. As observed in Fig. 5.3, the overall reduced temperature plot seems to suggest 2-D surface nucleation. However, upon examination of inset (a), which is a blow up of the ΔT region 0 to 250°C, the reduced growth rate curve only appears increase (either with positive slope or with positive slope and positive curvature) up to an undercooling of about 140°C. We note that according to ref. [123], the growth rate was found to be zero at T =1033°C, thus there is also a data point at the origin in Fig. 5.3. Over the undercooling region spanning about 140°C to 400°C, there appears to be some type of transitional behavior wherein the interface site factor is relatively independent of undercooling. For undercoolings greater than about 400°C, the reduced growth rate data again increase and appear to follow a curve of positive slope and positive curvature. When the same plot is constructed using the Matusita and Tashiro VFT equation, the qualitative behavior of the reduced growth rate is similar to that shown in Fig. 5.3, but magnitudes are smaller.
Figure 5.3 Reduced growth rate, $U_R$, as a function of undercooling, $\Delta T$. 
The above observations suggest that for $400^\circ C < \Delta T \leq 580^\circ C$ the 2-D surface nucleation mechanism is operative, and that for $\Delta T < 140^\circ C$ 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 ($\Delta T < 140^\circ C$) 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

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

Hence, the model of surface nucleation can be tested in more detail for the undercooling regions where $\Delta T$ ranges from 0 to $140^\circ C$ and $400^\circ C$ to $580^\circ C$ by plotting $\ln u_T$ 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 $\sigma_E$, 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 $1.48 \times 10^{-3}$ at $T = 1020^\circ C$ to a value of $5.46 \times 10^{-3}$ at $T = 454^\circ C$, and therefore can be taken as constant.

Figure 5.4 shows the region of $\ln u_T$ vs. $(T \Delta G)^{-1}$ plot corresponding to $\Delta T < 140^\circ C$, wherein the reduced growth rate is suggestive of 2-D surface nucleation. The filled markers in Fig. 5.4 are the results obtained using Zanotto's VFT equation. The
open markers are the results obtained when the Matusita and Tashiro VFT equation is employed. Neither data set can be fit with a single straight line over the entire temperature regime. However, as shown in Fig. 5.4 both data sets can be fit by two straight lines with different slopes. The equation of each line shown was found using a least squares fit. The resulting slope and intercept values are shown in Table 5.1.

Figure 5.5 shows the temperature region of the \( \ln U_\eta \) versus \( (T\Delta G)^{-1} \) plot corresponding to the undercooling regime \( \Delta T = 400^\circ \text{C} - 580^\circ \text{C} \), wherein the reduced growth rate is also suggestive of 2-D surface nucleation. For clarity, Fig. 5.5 was constructed using only the averages of the experimental growth rates obtained in the present study. The filled markers represent the resulting data when Zanotto's VFT equation is used, and the open markers correspond to the data obtained using the Matusita and Tashiro VFT equation. As in Fig 5.4, 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.
Figure 5.4  \( \ln \eta \) vs. \((T\Delta G)^{-1}\) for \(\Delta T < 140^\circ C\). Filled markers: VFT eq. from ref. [128], open markers: VFT eq. from ref. [123]
Figure 5.5 $\ln U_\eta$ vs. $(T\Delta G)^{-1}$ for $400^\circ C \leq \Delta T \leq 580^\circ C$. Filled markers: VFT eq. from ref. [128], open markers: VFT eq. from ref. [123]
Table 5.1  Slope, B, values, and extrapolated and computed y-intercept values

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<th>Temperature Interval</th>
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*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 ($\ln C_b$) 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 $500^\circ\text{C} - 454^\circ\text{C}$, the averages of the experimental growth rates obtained in this work are given in Table 5.3.

<table>
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<tr>
<th>$N_s^*$ (units/m$^2$)</th>
<th>$\lambda$ (m)</th>
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*N$_s = (n_v)^{2/3}$; $n_v = 9.78 \times 10^{27}$ (formula units/m$^3$)
Table 5.3  Experimental and calculated growth rate values: 2-D surface nucleation

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<th>T (°C)</th>
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<th>$U_{calc}$ (ms$^{-1}$)</th>
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<td>$6.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>897</td>
<td>$5.28 \times 10^{-6}$</td>
<td>$7.69 \times 10^{-6}$</td>
<td>$5.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>500</td>
<td>$4.00 \times 10^{-77}$</td>
<td>$3.11 \times 10^{-43}$</td>
<td>$8.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>490</td>
<td>$2.36 \times 10^{-77}$</td>
<td>$1.84 \times 10^{-43}$</td>
<td>$4.5 \times 10^{-11}$</td>
</tr>
<tr>
<td>477</td>
<td>$9.70 \times 10^{-78}$</td>
<td>$7.99 \times 10^{-44}$</td>
<td>$1.9 \times 10^{-11}$</td>
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<tr>
<td>465</td>
<td>$2.97 \times 10^{-78}$</td>
<td>$3.22 \times 10^{-44}$</td>
<td>$7.1 \times 10^{-12}$</td>
</tr>
<tr>
<td>454</td>
<td>$7.09 \times 10^{-79}$</td>
<td>$1.26 \times 10^{-44}$</td>
<td>$3.6 \times 10^{-12}$</td>
</tr>
</tbody>
</table>
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 ≥ 995°C). Further, as shown in Table 5.1 the computed values of the y-intercept (ln Cb) are in accord with the extrapolated values in this undercooling range. The calculated growth rates are shown along with the experimentally determined growth rates as a function of temperature over this undercooling range in Fig. 5.6.

For undercoolings from about 40°C to 140°C (T = 983°C - 897°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. These results are illustrated in Fig. 5.7, which shows the calculated and experimental growth rates as a function of temperature over this undercooling range.

Over the undercooling range 534°C to 580°C (T = 500°C - 454°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.
Figure 5.6 Calculated and experimental growth rates as a function of temperature for $\Delta T < 40^\circ C$
Figure 5.7  Calculated and experimental growth rates as a function of temperature for \(40^\circ\text{C} < \Delta T < 140^\circ\text{C}\)
For each undercooling region quantitatively analyzed above, the edge surface energy of the nucleus, $\sigma_e$, 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, $\sigma_e$ should be equivalent to the crystal-liquid interfacial energy. The Turnbull-Staveley 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

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

where $N$ is Avogadro's number, and $\alpha$ is a numerical constant ranging in value from 0.25 to 0.40 for non-metallic substances. The values of $\alpha$ required to obtain the $\sigma_e$ 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 \( \sigma_E \) and \( \alpha \) values

<table>
<thead>
<tr>
<th>Temperature Interval</th>
<th>( \sigma_E ) (J/m(^2))</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020°C - 995°C</td>
<td>0.0237(^{ab})</td>
<td>0.054(^{ab})</td>
</tr>
<tr>
<td>983°C - 897°C</td>
<td>0.0634(^{ab})</td>
<td>0.150(^{ab})</td>
</tr>
<tr>
<td>500°C - 454°C</td>
<td>0.973(^{a}) 0.645(^{b})</td>
<td>2.230(^{a}) 1.480(^{b})</td>
</tr>
</tbody>
</table>

\(^{a}\)VFT equation from ref. [128]
\(^{b}\)VFT equation from ref. [123]

As noted earlier, the product \( C_b \) 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 \( \ln \{U\eta/[1-\exp(-\Delta G/RT)]^{2/3}\} \) 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. This point is illustrated in Fig. 5.6, which depicts the plot corresponding to Fig. 5.4 (using Zannotto's VFT equation) resulting when the temperature dependence of the quantities \( C \) and \( b \) are incorporated. As observed in Fig. 5.6, the temperature dependence of the quantities \( C \) and \( b \) do not
introduce curvature, and two straight lines with different slopes still best describe the plot.
Figure 5.8  Plot corresponding to Fig. 5.4 (ref. [128] VFT) with temperature dependence of C and b taken into account
The experimental growth rate data in the region of small undercooling (ΔT < 140°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

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

where the quantity A is given by

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

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

\[ \frac{U_R}{T} = A \Delta G \] (5.15)
A plot of $U_RT^{-1}$ vs. $\Delta G$ should thus yield a straight line intersecting the origin with a slope equal to the quantity $A$ (assuming $\sigma$ constant). Further, based on the above equations and Equation (5.4), it is clear that the interface site factor, $f$, may also be written

$$f = \frac{A^2 \pi \lambda^2}{k_B} \Delta G$$

(5.16)

and that the surface energy, $\sigma$, may be expressed

$$\sigma = \frac{k_B}{A12\pi^2 \lambda V_m}$$

(5.17)

Therefore, the screw dislocation model can be tested in more detail for the small undercooling range ($\Delta T < 140^\circ C$) by constructing an $U_RT^{-1}$ vs. $\Delta G$ 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.
Figure 5.8 shows the $U_R T^{-1}$ vs. $\Delta G$ plot for the small undercooling region ($\Delta T < 140^\circ C$) as constructed using Zanotto's VFT equation for $\eta$ and the experimental growth rate data. The equation of the line shown in Fig. 5.8 was found using a least squares fit; the least squares slope yielding the quantity $A$. The results obtained using the Matusita and Tashiro VFT equation (not shown) are essentially the same as those obtained using the Zanotto VFT equation.
Figure 5.9  \( U_R T^{-1} \) vs. \( \Delta G \) for \( \Delta T < 140^\circ C \)

\[ U_R T^{-1} = 1.72 \times 10^{-6} + 4.03 \times 10^9 \Delta G; \quad R = 0.963 \]
Using Equation (5.17) and the slope of the line shown in Fig. 5.8 (A value), the surface energy, $\sigma$, was determined to be 0.001 J/m$^2$. To obtain this $\sigma$ 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>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$U_{\text{calc}}$ (m/s$^{-1}$)</th>
<th>$f_{\text{calc}}$</th>
<th>$U_{\text{experimental}}$ (m/s$^{-1}$)</th>
</tr>
</thead>
<tbody>
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<td>1020</td>
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</tr>
<tr>
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</tr>
<tr>
<td>1006</td>
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<td>$2.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>1004</td>
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<td>0.84</td>
<td>$2.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>996</td>
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<td>1.06</td>
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<td>$4.61 \times 10^{-5}$</td>
<td>1.99</td>
<td>$4.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>957</td>
<td>$4.90 \times 10^{-5}$</td>
<td>2.16</td>
<td>$5.3 \times 10^{-5}$</td>
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<tr>
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<td>2.30</td>
<td>$5.4 \times 10^{-5}$</td>
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</tr>
<tr>
<td>897</td>
<td>$5.22 \times 10^{-5}$</td>
<td>3.81</td>
<td>$5.4 \times 10^{-5}$</td>
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</tbody>
</table>
5.2.2. 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 $\Delta T$ 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 $T = 635^\circ C$.

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 ($\Delta T < 140^\circ C$ and $400^\circ C \leq \Delta T \leq 580^\circ C$) are plotted separately as $\ln U_\eta$ vs. $(TA)^{-1}$, neither data set can be fit by a single straight line. For undercoolings less than about $140^\circ C$, 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 $\Delta T < 40^\circ C$ 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 ($\Delta T = 40^\circ C - 140^\circ C$) 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 ($\Delta T \leq 40^\circ C$), there is an observable change in agreement between theory and experiment. This region is discussed in more detail later.

Over the restricted temperature range $T = 500^\circ C - 454^\circ C$ ($\Delta T = 534^\circ C - 580^\circ C$) 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 ($T = 500^\circ C - 454^\circ C$) 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 $\ln \eta$ vs. $(T \Delta G)^1$ plot which is about 2 times smaller in magnitude than the slope which results when the Zanotto 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 Zanotto 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 $\Delta T = 534^\circ C - 580^\circ C$, and to compare the description of growth in the latter region with that in the region of small undercooling ($\Delta T < 40^\circ C$), 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:

$$\eta = \eta_0 \exp\left(\frac{Q}{T}\right)$$

(5.18)
then

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

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 \( \Delta T \) increases. One might speculate then that this is consistent with the failure of \( \eta^{-1} \) 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 as 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 ΔT ≤ 140°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°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 ≤ 500°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 ΔT = 400°C - 580°C (T = 635°C - 454°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°C - 635°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, $\sigma_E$, as computed from the slopes, $B$, and Equation (5.6) are presented. As mentioned earlier, by assuming $\alpha$ 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 $\alpha$ required in Equation (5.12) to yield the aforementioned surface energy values, $\sigma_E$, are given. Alternatively, using the $\alpha$ 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/m$^2$ for LS$_2$. As observed in Table 5.4, for the very deeply undercooled range $\Delta T = 534°-580°C$ ($T = 500°C - 454°C$), the $\alpha$ values (and $\sigma_E$ values) are much higher than those estimated for LS$_2$ by Equation (5.12). For the undercooling range $\Delta T = 40°-140°C$ ($T = 983°C - 897°C$), the $\sigma_E$ and $\alpha$ 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 ($T = 1020°C - 995°C$), the values of $\sigma_E$ and $\alpha$ 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 and 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 $\alpha$ value in the Turnbull-Stavely equation, obtained by interpreting the experimental data with respect to the screw dislocation model are unduly small.

5.2.3. 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 $\text{OH}^-$ present within the bulk of the prepared glasses and $\text{OH}^-$ 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 SiO₂ and GeO₂ [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.

5.2.4. Analysis of XRD Results for Lithium Silicate Glasses with Respect to Crystal Growth Rate Results

As observed in the XRD traces presented in Section 4.5.1 and as discussed in Section 5.1, the extent of crystallization in the higher water content glasses (Glasses 5 and 6) was considerably larger than in the lower water content glasses (Glasses 1, 2, 3, and 4). The reasons for this difference in crystallization behavior can be more fully addressed with respect to the growth rate data given in Section 4.6.2. To help explain the observed behavior, the crystal growth data obtained for Glasses 3 and 5 are examined at the temperatures of interest in the XRD investigation of metastable phase formation (T = 454°C and T = 465°C). The variation in length of the long axis of internal crystals for Glass 3 and Glass 5 are presented as a function of heating time at T = 454°C in Figure 5.10. Figure 5.11 shows variation in long axis crystal length with time for Glasses 3 and 5 at T = 465°C. Figures 5.12 and 5.13 show the corresponding plots for the short-axes of internal crystals for these glasses at T = 454°C and T = 465°C, respectively.
Figure 5.10  Variation of long-axis crystal length with time for Glasses 3 and 5 at T = 454°C
Figure 5.11 Variation of long-axis crystal length with time for Glasses 3 and 5 at $T = 465^\circ$C
Figure 5.12 Variation of short-axis crystal length with time for Glasses 3 and 5 at $T = 454^\circ C$
Figure 5.13  Variation of short-axis crystal length with time for Glasses 3 and 5 at $T = 465\,^\circ$C
It is apparent from Figs. 5.10 – 5.13 that although the linear growth rates (given by the slopes divided by a factor of 2) are the same for Glasses 3 and 5 at T = 454°C and T = 465°C, the internal crystals in Glass 5 are larger than those of Glass 3 after heating at these temperatures for a given time. Also, upon extrapolation of the lines in these figures back to the time axis, the induction time for growth is apparently much shorter for Glass 5 than for Glass 3. The difference in internal crystal sizes after heating for a given time helps explain why the crystallinity is larger for Glass 5 than for Glass 3. However, the observed size differences are not sufficient to account for the disparate degrees of crystallinity as assessed from the XRD traces (Section 5.1). To account for the differences in relative extents of crystallization between Glass 5 and Glass 3 at 454°C and 465°C, not only must the crystals be larger, but there must also be more of them in Glass 5 than in Glass 3.

Since the crystal growth rates are known at T = 454°C and T = 465°C, the JMAK equation may be invoked to estimate the relative concentrations of internal crystals in Glasses 5 and 3 at these temperatures. Assuming that the nucleation rate, I, and growth rate, U, in these glasses to be in steady state regimes for the times investigated, then the volume fraction transformed, X(t), under isothermal conditions may be expressed by the following form of the JMAK equation

\[ X(t) = 1 - \exp\left(-\frac{gtU^3t^4}{4}\right) \]  

(5.20)
where $g$ is a shape factor, equal to $4\pi/3$ for spherical grains, and $t$ is the time period. By approximating the shape of the internal crystals as prolate ellipsoids, Equation (5.20) may be rewritten as

$$X(t) = 1 - \exp\left(\frac{\pi}{3} I U_a U_b^2 t^4\right)$$  \hspace{1cm} (5.21)

where $U_a$ and $U_b$ ($U_b \sim U_c$) are the growth rate of the major (long) and minor (short) half-axes given in Tables 4.5 and 4.6. Taking $X(t)$ to be proportional to $x_c$ (where $x_c$ was determined by the method described in Section 5.1), the relative nucleation rates, $I^*$, of Glass 3 and Glass 5 were approximated using Equation (5.21) by taking the ratio of this equation with the parameters ($x_c$, $U_a$, and $U_b$) appropriate for Glass 3 to that of this equation with parameters appropriate for Glass 5. At $T = 454^\circ$C, the nucleation rate of Glass 5 was thus determined to be about 13 times larger than the nucleation rate of Glass 3. At $T = 465^\circ$C, the nucleation rate of Glass 5 was determined to be nearly 8 times larger than that of Glass 3. Hence, it seems that the disparate extents of crystallization as described in Section 5.1 correspond to the relative nucleation rates of the glasses at these temperatures.

Further analysis of the relative nucleation rates of Glass 3 using Equation (5.21) in conjunction with XRD traces revealed that the nucleation rate for this glass was higher at $T = 465^\circ$C than at $454^\circ$C and $477^\circ$C. While for Glass 5, the same type of analysis revealed the nucleation rate to be higher at $454^\circ$C than $465^\circ$C and $477^\circ$C. Thus it seems
that the effect of water content present in the glass on the nucleation rates is to increase
the magnitudes and to decrease the temperature at which the maximum occurs. This
observation is consistent with the findings of others (see for example ref. [89]), and the
discussion regarding the effect of water on crystal nucleation rates given in Section
2.1.3.h.

5.3. 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, $\Delta T_p$, 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 in 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 \( \Delta T_p \) 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 \( \Delta T_p \) 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.

Figure 5.14 shows the temperature dependence of the relative nucleation rate for the W57% composition as derived from the data in ref. [88]. As indicated by the data in Fig. 5.14, the temperature at which the nucleation rate is a maximum, $T_{\text{MAX}}$, occurs near or below 410°C. For temperatures $T > 410°C$, the nucleation rate decreases continuously and appears to tend towards zero near 465°C.
Figure 5.14  Temperature dependence of the relative nucleation rate for the W57% as derived from DTA data
As mentioned, Wakasugi’s DTA technique yields the relative nucleation rates as a function of temperature, but not the magnitudes of the nucleation rates. Therefore, to test the accuracy of the DTA method, the nucleation rate data obtained at various T_n in the present study (Table 4.9) were normalized to the rate at 440°C, since this is the temperature to which Wakasugi normalized his data. Figure 5.15 shows the normalized data from the present investigation along with the data from ref. [88]. The absence of error bars for the DTA experimental points notwithstanding, it is apparent from Fig. 5.10 that the results from the two different techniques agree within experimental error. Data points from the DTA technique do not show error bars because it is not obvious how to calculate the errors associated with this method.

Further, as shown in Fig. 5.15, the steady-state nucleation rates for nucleation temperatures 390°C and 400°C are relatively small. Thus, as exemplified by Figs. 4.47 and 4.48, the number densities of crystals produced at these T_n remain small for long times. Although the development technique is sensitive to such small crystal number densities, the DTA technique is not. As described previously, to produce a detectable peak shift, ΔT_p, the number densities must be sufficiently large. Due to the small nucleation rates in this glass at temperatures of 390°C and 400°C, the nucleation times employed by Wakasugi (≤ 24 hours) would not produce large enough number densities to enable generation of nucleation rate data for these temperatures by the DTA method.
Figure 5.15 Comparison of $I^8$ results from optical microscopy and DTA methods
To this author's knowledge, only two other works [77,78] have investigated internal nucleation rates in binary sodium silicate glasses. The salient features of the prior works and the present work are given in Table 5.5, and are shown graphically in Figure 5.16. These data reveal an emergent trend in nucleation kinetics as a function of composition. Both the temperature of maximum nucleation, \( T_{\text{max}} \), and the magnitude of the maximum nucleation rate, \( I_{\text{max}} \), increase in value as composition tends towards stoichiometric sodium metasilicate. These findings are consistent with discussion in Section 2.1.3.h. regarding the effect of composition on nucleation rates.

Table 5.6 Summary of nucleation rate results from present and prior works

<table>
<thead>
<tr>
<th>Composition (mol%)</th>
<th>Nucleation Range (°C)</th>
<th>( T_{\text{max}} ) (°C)</th>
<th>( I_{\text{max}} ) (cm(^3) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^a)46 Na(_2)O-54 SiO(_2)</td>
<td>410 – 490</td>
<td>460</td>
<td>360 x 10(^6)</td>
</tr>
<tr>
<td>(^b)44 Na(_2)O-56 SiO(_2)</td>
<td>400 – 470</td>
<td>427</td>
<td>183 x 10(^3)</td>
</tr>
<tr>
<td>(^c)43 Na(_2)O-57 SiO(_2)</td>
<td>385 – 465</td>
<td>410</td>
<td>62 x 10(^2)</td>
</tr>
</tbody>
</table>

\(^a\) reference [77], \(^b\) reference [78], \(^c\) this work
Figure 5.16 Summary of nucleation rate results from present and prior works
Although strictly speaking the classical expression for the steady state nucleation rate is not correct for off-composition pseudo one-component internal nucleation, it is reasonable to invoke this expression for predicting qualitative trends. There are three critical factors to consider when interpreting the change in nucleation kinetics with composition, namely, the kinetic barrier, the thermodynamic barrier, and the surface energy. Not much is known about the compositional dependence of the surface energy, and no attempt will be made here to speculate about the influence of this factor on the observed trend.

According to CNT, the nucleation rate is a monotonically decreasing function of viscosity. Therefore, the above features could be a result of disparate water contents in the glasses used by the different investigators. Increased water content could decrease the viscosity of the glass. This in turn would decrease the kinetic barrier to nucleation, thus increasing $I^\ddagger$. If we assume the water contents to be similar, the same argument can be made based on compositional effects since increasing Na$_2$O content also decreases the viscosity (see discussion in Section 2.1.3.h). However, it does not seem likely that the reduction in the kinetic barrier to nucleation over this small composition range would be large enough to account for the significant variation in the nucleation rates described in Table 5.5.

The aforementioned features are more readily explained based on thermodynamic arguments. According to the binary Na$_2$O-SiO$_2$ phase diagram [136], the liquidus temperature ($T_L$) shows a sharp decrease from the metasilicate composition to about the
62SiO\(_2\) (wt. %) composition. Therefore, for a given temperature, \(T\), below the liquidus, the undercooling \(\Delta T\) (where \(\Delta T = T_L - T\)) increases as the SiO\(_2\) content decreases. Consequently, the thermodynamic driving force at temperature \(T\) increases and the thermodynamic barrier decreases as SiO\(_2\) content decreases, and \(I^s\) would increase accordingly. Based on the above, it is concluded that the thermodynamic driving force dominates the nucleation behavior over this compositional range. Barker et al. [53] found similar behavior for the composition dependence of \(I_{\text{max}}\) in a nucleation rate study conducted on the binary Li\(_2\)O-SiO\(_2\) system, and they drew a similar conclusion regarding the origin of this behavior. The data of Barker showed that \(T_{\text{max}}\) and \(I_{\text{max}}\) in a 40Li\(_2\)O-60SiO\(_2\) (mol\%) composition was higher than \(T_{\text{max}}\) and \(I_{\text{max}}\) in a 36Li\(_2\)O-64SiO\(_2\) (mol\%) composition. According to the phase diagram for the binary Li\(_2\)O-SiO\(_2\) system [137], the liquidus temperature sharply decreases with increasing SiO\(_2\) content over this composition range. Similar trends were also observed in nucleation rate studies for Na\(_2\)O-CaO-SiO\(_2\) [138], Li\(_2\)O-CaO-SiO\(_2\) [58], and Li\(_2\)O-BaO-SiO\(_2\) [139] glasses.

An empirical correlation between the reduced temperature, \(T_{\text{rg}}\), \((T_{\text{rg}} = T_g/T_m)\) where \(T_g\) is the glass transition temperature and \(T_m\) is the melting temperature (both in Kelvin), and the ability of a glass to nucleate internally has been observed [62,140]. It has been demonstrated [62,140] that glass forming systems which do not show internal nucleation have \(T_{\text{rg}}\) values greater than 0.58, and glass forming systems which do show internal nucleation have \(T_{\text{rg}}\) values less than 0.58. As described in Section 2.1.3.e, the nucleation mechanism in the binary sodium silicate system is known to shift from internal to surface nucleation over the compositional range NS to NS\(_2\). Therefore, it is of
interest to examine the reduced temperature as a function of composition over this
compositional range. To calculate $T_{rg}$ for the various compositions, the $T_g$ data reported
by Knoche et al. [141] (extrapolated values where necessary), and the liquidus
temperature data from the binary Na$_2$O-SiO$_2$ phase diagram were utilized. Table 5.7
summarizes the results of these calculations.
Table 5.7  Reduced temperature values for sodium silicate glass compositions

<table>
<thead>
<tr>
<th>SiO₂ (mole%)</th>
<th>Tₑₑₑ/ₑₑₑ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.0</td>
<td>0.50</td>
</tr>
<tr>
<td>54.0</td>
<td>0.52</td>
</tr>
<tr>
<td>55.8</td>
<td>0.54</td>
</tr>
<tr>
<td>57.0</td>
<td>0.55</td>
</tr>
<tr>
<td>60.0</td>
<td>0.58</td>
</tr>
<tr>
<td>60.8</td>
<td>0.61</td>
</tr>
<tr>
<td>61.5</td>
<td>0.62</td>
</tr>
</tbody>
</table>
As shown in Table 5.7, the values of $T_{rg}$ steadily increase from 0.50 for NS to 0.62 for the 61.5SiO$_2$ (mol%) composition. From the data in Table 5.7, it is apparent that the compositions studied in this investigation, which were observed to nucleate internally, all have $T_{rg}$ values less than 0.58 indicating that this system conforms to the above empirical relationship. Furthermore, based on these calculations the expected cut-off for internal nucleation is near 60-61mol% SiO$_2$ composition.
6. 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 LS$_2$ 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 LS$_2$ glass was formulated. The analyses performed in this research have led to the following conclusions. (1) Crystal growth over a broad $\Delta T$ 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 $\Delta T$, but is very poor at large $\Delta T$. 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 43Na$_2$O-57SiO$_2$ (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 x 10$^3$ (cm$^{-3}$ 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.
7. REFERENCES


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283

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