Effect of Pt doping on nucleation and crystallization in \( \text{Li}_2\text{O} \cdot 2\text{SiO}_2 \) glass: experimental measurements and computer modeling

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Abstract

Heterogeneous nucleation and its effects on the crystallization of lithium disilicate glass containing small amounts of Pt 
are investigated. Measurements of the nucleation frequencies and induction times with and without Pt are shown to be 
consistent with predictions based on the classical nucleation theory. A realistic computer model for the transformation is 
presented. Computed differential thermal analysis data (such as crystallization rates as a function of time and temperature) 
are shown to be in good agreement with experimental results. This modeling provides a new, more quantitative method for 
analyzing calorimetric data.

1. Introduction

For many reasons, lithium disilicate glass provides a model system for studying nucleation and 
crystallization in glasses. Good experimental data exist for steady-state and time-dependent nucleation 
rates and growth velocities [1–3]. Further, the free 
energy differences between the glass and the crystal 
are available as a function of temperature [4]. These 
data have been used extensively to test the classical 
theory for homogeneous nucleation [5,6] and its ex-
tensions to describe polymorphic growth [7]. Further, 
those kinetic models have been used to simulate 
crystallization in this glass under isothermal and 
non-isothermal conditions [8,9]. Possible extensions 
to treat crystallization that is nucleated heteroge-
nously on glass impurities have also been consid-
ered [10,11].

It is well known that the addition of noble metals 
in controlled quantities increases the tendency for 
glasses to nucleate. Rindone [12], for example, 
demonstrated the effectiveness of platinum particles 
in precipitating lithium disilicate crystals from lithium 
disilicate glass. Cronin and Pye [13] have investi-
gated the effect of Pt particle size on the crystalliza-
tion of lithium disilicate glass. Heterogeneous or  
catalyzed nucleation, however, has received less the-
etrical attention than has homogeneous nucleation. 
This is primarily due to insufficient information about 
the number, size and catalytic efficiency of the het-
erogeneous particles. By conducting quantitative in-
vestigations on metallic and silicate glasses, Kelton

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and Greer [6,14] demonstrated previously that detailed studies of the transient nucleation rates provide more information about the nucleation process than is available from the study of steady-state rates alone. Surprisingly, only a few measurements of the time-dependent heterogeneous nucleation rates in silicate glasses exist [15].

Here, we present measurements of heterogeneous nucleation rates in lithium disilicate glass as a function of Pt concentration. Both time-dependent and steady-state nucleation rates are measured at each Pt concentration, and the nucleation induction times are determined. Similar measurements were also conducted on an undoped glass to compare the quantitative effects of homogeneous and heterogeneous nucleation on the crystallization of the lithium disilicate glass. The computer model developed for homogeneous nucleation is extended to include the effect of heterogeneities [10] and is used to analyze the experimental data.

A numerical model previously developed to provide a description of polymorphic crystallization for glasses heated at a constant rate, such as is used in differential scanning calorimetry (DSC) or differential thermal analysis (DTA) experiments, is extended to include heterogeneous nucleation. Exothermic crystallization peaks were measured and were modeled as a function of dopant (Pt) concentration and the heating rate. The applicability of the Kissinger method [26] for extracting an overall activation energy for crystallization was also evaluated.

2. Theoretical background

Nucleation is normally modeled assuming the classic theory of nucleation, in which clusters of various sizes exist simultaneously, growing or shrinking as governed by a series of bimolecular rate equations, describing the addition and loss of a single monomer per step. Assuming a sharp interface, the reversible work of formation of a cluster of size \( n \) is the sum of a volume term (which is negative for the phase transformation to proceed) and a positive energetic penalty for the introduction of a surface:

\[
W_n = n \Delta G + \alpha n^{2/3} \sigma.
\]

Here \( \Delta G \) is the free energy difference per molecule between the crystal and the glass, \( \alpha \) is a geometrical factor and \( \sigma \) is the interfacial energy between the crystal and the glass. The barrier to nucleation is decreased if the nucleating cluster wets the catalyzing impurity. Within the spherical cap model for heterogeneous nucleation, the interfacial energy is decreased from its value for homogeneous nucleation, \( \sigma_0 \),

\[
\sigma_n^3 = f(\phi) \sigma_0^3,
\]

where

\[
f(\phi) = \left( \frac{(2 + \cos \phi)(1 - \cos \phi)^2}{4} \right).
\]

Here \( \phi \) is the contact angle between the growing crystal nucleus and the heterogeneous impurity. Following a sufficiently long time, the cluster distribution will approach the steady-state distribution, which is characterized by the temperature and the thermodynamic and kinetic constants but is independent of time and sample thermal history. Due to the quenching process, however, nucleation in most glasses is not initially at its steady-state value but approaches it with time as the cluster distribution approaches its constant value [8,9]. The rate of change in the cluster density is given by

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

where \( k_n^+ \) and \( k_n^- \) are the rates at which molecules join or leave clusters of \( n \) molecules, giving a time- and cluster-size-dependent nucleation rate

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

Following Turnbull and Fischer [16], the atomic attachment and detachment frequencies, respectively, are

\[
k_n^+ = O_n \gamma \exp \left( \frac{W_n - W_{n+1}}{2k_BT} \right),
\]

\[
k_n^- = O_n \gamma \exp \left( \frac{W_{n+1} - W_n}{2k_BT} \right),
\]

where \( k_B \) is the Boltzmann’s constant, \( O_n \) is the number of sites available for the attachment of a monomer and \( \gamma \) is an unbiased jump frequency that
can be expressed in terms of the diffusion coefficient, \( D \), and the average jump distance, \( \lambda \),
\[ \gamma = 6D/\lambda^2. \]  

In silicate glasses, the nucleation rate is determined by first annealing the sample at a temperature at which the nucleation rate is large and the growth velocity is small, followed by an anneal at a higher temperature at which the nucleation rate is negligible, but the growth velocity is substantial. During the growth treatment, all clusters larger than the critical size at that temperature, \( n_c \), will grow [3,15]. To compare theory with experiment, the cluster size, \( n \), in Eq. (5) is, therefore, typically chosen equal to \( n_c \). The measured quantity is the number of nuclei, \( N(T,t) \), produced as a function of time; its time derivative is the nucleation rate, \( I(t,T) \). Under steady-state conditions, the slope of \( N \) vs. \( t \) is equal to the steady-state nucleation rate, \( I_s \). Experiments on quenched glasses typically give a nucleation rate that is lower than \( I_s \); that value is approached asymptotically with time. At long times,
\[ N(T,t) = I_s(t-\theta), \]  
where \( \theta \), the effective time-lag, depends upon the particular glass system and temperature, \( T \), and \( I_s \) is the steady-state nucleation rate.

While often not discussed, heterogeneous nucleation can also display transient behavior. This can be easily seen with only minor modifications to the development for homogeneous nucleation. The work of cluster formation is changed, as already discussed. The number of surface attachment sites is decreased,
\[ O_s \rightarrow O_s[f(\theta)]^{2/3} \]  
which, according to Eq. (6), decreases the atomic attachment and detachment frequency, as well.

### 3. Computer simulation of crystallization

The details of the numerical model for crystallization under non-isothermal conditions have been discussed elsewhere [8,9]. With the changes mentioned in the previous section, the model can be directly applied to describe crystallization by heterogeneous nucleation. As before, the non-isothermal scan is divided into a series of isothermal anneals, the duration of which, \( \Delta t \), is set by the coarseness of the temperature step, \( \Delta T \), and the scan rate, \( Q \):
\[ \Delta t = \Delta T/Q. \]  

Within each isothermal interval, the clusters are allowed to evolve following the bimolecular rate kinetics of the classical theory of nucleation, using the kinetic and thermodynamic factors appropriate to the temperature of that interval. To include the effect of heterogeneous nucleation, the work of cluster formation and the rate constants are adjusted using Eqs. (2) and (9), respectively. This is accomplished by further dividing each isothermal interval into finer time steps, \( \delta t \), and using a finite difference approach to solve the coupled kinetic equations of nucleation, i.e., Eqs. (4) and (5). The cluster density as a function of time is computed by
\[ N_{n+\delta t} = N_{n,t} + \delta t(dN_{n,t}/dt). \]  
where \( dN_{n,t} \) is determined from Eq. (4). The time-dependent nucleation rate is, therefore, calculated from Eq. (5), avoiding the introduction of ad hoc assumptions regarding its behavior. At the end of each isothermal interval, the clusters generated during that isothermal anneal and those generated during the previous isothermal intervals are grown using the appropriate cluster-size-dependent growth velocity [9,17]
\[ \Delta \tau = \frac{16CD}{\lambda^2} \left( \frac{3\bar{v}}{4\pi} \right)^{1/3} \sinh \left[ \frac{\bar{v}}{2k_B T} \left( \Delta G_v - \frac{2\alpha}{r} \right) \right]. \]  

As was demonstrated previously [7], the temperature dependence of the macroscopic growth rate calculated from Eq. (12) using thermodynamic and kinetic parameters derived from nucleation data (appropriate for the growth of small clusters) is in good agreement with experimental results. The magnitudes of the calculated values, however, are too low. This is likely due to a relatively temperature-independent anisotropic growth mechanism that causes an increase in the number of attachment sites on the larger clusters (see Ref. [7] for more detail). For the computer calculations presented here, \( C \) was set to 4.77 to give good agreement with the observed macroscopic crystal growth rates. Keeping track of the number of clusters of a given size, \( r_{c,t} \), and
Table 1
Parameters for the simulation of crystallization of lithium disilicate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temperature, $T_m$</td>
<td>1300 K</td>
</tr>
<tr>
<td>Molecular volume, $V_m$</td>
<td>$9.962 \times 10^{-29}$ m$^3$</td>
</tr>
<tr>
<td>Entropy of fusion, $\Delta S_f$</td>
<td>39.08 kJ mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Interfacial energy for homogeneous nucleation, $\sigma$</td>
<td>$(0.094 + 7 \times 10^{-5} T)$ J m$^{-2}$</td>
</tr>
<tr>
<td>Jump distance, $\lambda$</td>
<td>4.6 Å</td>
</tr>
<tr>
<td>Diffusion coefficient:</td>
<td>$D = D_0 F \exp \left( \frac{b}{T_0 - T} \right)$</td>
</tr>
<tr>
<td>$D_0$</td>
<td>$3.63 \times 10^{-14}$ m$^2$ K$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$b$</td>
<td>7761 K</td>
</tr>
<tr>
<td>$T_0$</td>
<td>460 K</td>
</tr>
<tr>
<td>Gibbs free energy ($J$ mol$^{-1}$)</td>
<td>$\Delta G = a_0 + a_1 T + a_2 T^2 + a_3 T^3$</td>
</tr>
<tr>
<td>$a_0$</td>
<td>48045 J mol$^{-1}$</td>
</tr>
<tr>
<td>$a_1$</td>
<td>$-36.81$ J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$a_2$</td>
<td>$5.607 \times 10^{-2}$ J mol$^{-1}$ K$^{-2}$</td>
</tr>
<tr>
<td>$a_3$</td>
<td>$-4.3179 \times 10^{-6}$ J mol$^{-1}$ K$^{-3}$</td>
</tr>
</tbody>
</table>

assuming no overlap between the clusters, the total extended volume transformed is calculated directly as

$$x_e = \frac{4\pi}{3V_0} \sum_i N_i r_{i,j}^3$$  \(13\)

Cluster overlap is taken into account statistically using the Johnson–Mehl–Avrami equation [28] to relate the actual volume fraction transformed to the extended volume fraction transformed:

$$x = 1 - \exp(-x_e)$$  \(14\)

Assuming that the DSC signal scales with the rate of volume fraction transformed,

$$\text{DSC signal} \propto \left[ x(T_i + \delta T) - x(T_i) \right] / \delta t.$$  \(15\)

The physical parameters used in the calculations of nucleation and growth in lithium disilicate glass are given in Table 1.

4. Experimental procedure

Samples of lithium disilicate glass were prepared with differing amounts of Pt to act as heterogeneous sites. These were annealed and the rate of nuclei production was measured to determine time-dependent nucleation rates. Experimental DSC scans were made to determine the effect of these heterogeneities on the overall transformation behavior. In this section, experimental procedures are discussed.

4.1. Glass preparation

A well mixed, 50 g batch of lithium disilicate composition was melted in a platinum crucible at 1450°C for 2 h, and the melt was cast between two steel plates. Chloroplatinic acid was used in the batch to prepare glasses containing platinum. Before casting, the melt was stirred periodically (25–30 min interval) with a silica rod to ensure homogeneity. X-ray diffraction and examination by scanning electron microscopy (SEM) showed no evidence of unmelted or crystalline particles in the as-quenched glass. Glasses containing 0 (undoped), 1, 5, 10 and 50 ppm nominal concentration of Pt by weight were prepared and used in the present investigation. To avoid moisture contamination, all glasses were stored in a vacuum desiccator until used for measurements.

4.2. Nucleation rate measurements

Glasses containing 0 (undoped), 1 and 5 ppm Pt of dimensions $1 \times 1 \times 4$ mm were used for nucleation rate measurements. They were placed in a tube furnace capable of maintaining the temperature to $\pm 1$ C. To determine the nucleation kinetics, the glasses were nucleated over a temperature range from 432 to 500°C, and then grown at 700°C for 3 min, following James [15].

The annealed samples were ground and polished to remove effects due to surface crystallization. They were lightly etched for 15 s in a 3% HF, 4% HNO$_3$ solution prepared in deionized water. The samples were then analyzed in an optical microscope (Leitz–Wetzlar, type Metallux-3) at magnifications up to 1000 times. Standard stereologic corrections were applied to determine the crystal density per unit volume [18]. Assuming that each crystal grows from a single nucleus and that no nuclei larger than the critical size at the growth temperature re-dissolve in the second stage anneal, the number of visible clusters present in a unit volume of the sample corresponds to the number of nuclei per unit volume, $N_i$. 
By measuring the number of nuclei, \( N_0 \), present in a non-nucleated as-quenched glass, the number of nuclei generated per unit volume during an annealing period was determined as \( N = N_e - N_0 \).

Attempts to determine platinum concentration and cluster sizes were made using SEM (Hitachi 4000GL) and transmission electron microscopy (JEOL 2000FX).

4.3. DTA studies

All of the calorimetric data were obtained in a flowing argon atmosphere (40 cm\(^3\)/min) using a Perkin–Elmer DTA 1700 system. Samples weighing between 15 and 20 mg were ground and heated in a Pt crucible until crystallization was complete. To minimize surface crystallization effects, particles approximately 1 mm in diameter were used. Scans were made at 5, 10, 20, 40 and 80°C/min, respectively, on all samples. High purity \( Al_2O_3 \) was used as the reference material. Instrumental shifts in temperature were corrected by measuring the melting point of aluminum as a function of the scan rate. These experimental DTA exotherms were then compared with those simulated using identical sample characteristics and heating rates in the computer model.

5. Results and discussion

Direct measurements of the nucleation rates and induction times were made to obtain estimates of the contact angles and to check predictions of the theories. Data from these nucleation measurements were used to compute non-isothermal crystallization peaks for the glass, which were compared with experimental results. These studies allowed an investigation of the effect of the heterogeneities on the nucleation and crystallization behavior and a check on the validity of the computer model.

5.1. Nucleation rate measurements

Fig. 1(a)–(c) show the number of nuclei generated as a function of time at several representative temperatures for the undoped samples and samples containing 1 and 5 ppm of Pt, respectively. In all cases, the nucleation rate is very low initially and eventually reaches a steady-state value, yielding a linear rate of production of nuclei with time. The slope of the linear portion of the curve is equal to the steady-state nucleation rate, \( \dot{N} \); the intercept with the time axis defines the induction time for nucleation, \( \theta \). As is suggested from Fig. 1(a), homogeneous nucleation peaks at around 723 K, and the rate falls as the temperature is increased, giving smaller slopes. The induction times, however, decrease monotonically with temperature, giving a lower intercept. The heterogeneous nucleation rate peaks near 738 K.

Heterogeneous and homogeneous nucleation occur simultaneously in the doped glasses. To determine the heterogeneous nucleation rates alone, the number of nuclei generated by homogeneous nucleation was estimated from the measured homogeneous nucleation rate; this was subtracted from the total number of nuclei. The nucleation rates obtained by this method are shown in Fig. 2 as a function of temperature and dopant level. The homogeneous nucleation rates are also provided for comparison. As anticipated, the heterogeneous nucleation rates are two to three orders of magnitude larger than the homogeneous nucleation rates. Assuming that the Pt

![Fig. 1. Number of nuclei produced per unit volume as a function of time in \( Li_2O \cdot 2SiO_2 \) glass: (a) undoped, (b) glasses doped with 1 ppm and (c) glasses doped with 5 ppm platinum. Experimental errors are indicated by the error bars.](image-url)
nucleants are of similar sizes in all cases, the magnitude of the nucleation rates should scale with the density of dopants. Within measurement error, this appears to be the case here; the peak nucleation rate is approximately four to ten times larger for the 5 ppm doped sample than for the 1 ppm doped sample.

The size of the nucleating agents is important. If the heterogeneous particles are too small, their catalytic efficiency as nucleating agents is decreased [19–21]. The assumption of a flat interface between the particle and the nucleus also becomes questionable [23,24]. For particles of sufficient size, on the other hand, there is the possibility of a single nucleus supporting more than one nucleation event [24]. While the precise size of the nucleating impurity in our case is unknown, SEM studies indicate an upper bound of 100 Å for the particle size. Consequently, the average impurity size was taken as 50 Å.

Since we do not observe a decrease of the nucleation rate with time in Fig. 1, the particles are either of sufficient size to act as effective nucleating agents with no significant depletion of the heterogeneous sites during the time of our measurements or, if the heterogeneous particles are large enough to support several nucleation events, surface saturation is not important. Similar results were reported by Gonzalez-Oliver and James [22] in Pt-doped Na₂O·2CaO·3SiO₂ glass. In the absence of any evidence to the contrary, a single nucleation event per particle was assumed for the modeling.

By fitting the measured steady-state nucleation rates for the doped glasses to the classic theory of nucleation, the effective interfacial energy, \( \sigma \), for the crystal and dopant interface can be obtained, which can be used to calculate the contact angle, \( \phi \), using Eq. (2). Shown in Fig. 3 are the calculated contact angles for the glasses containing 1 and 5 ppm Pt at different temperatures. The figure shows that \( \phi \) is independent of both the temperature and the dopant concentration. Using the size for the catalyzing impurity, the heterogeneous nucleation rates can be described by \( \phi = 132° \pm 18° \).

### 5.2. Induction times for nucleation

Fig. 4 compares the induction times for homogeneous nucleation, \( \theta \), with those from Refs. [1,3]. The broken line shows the calculated values [7] using the viscosity data in Ref. [25]. The good agreement between our data and those of others verifies the reliability and reproducibility of our measurements. The measured values of \( \theta \) for homogeneous and heterogeneous nucleation are compared in Fig. 5. The calculated values for homogeneous nucleation are again included for comparison (solid line). Interestingly, the addition of platinum seems to have no significant effect on the induction time for nucleation.

These similarities between the measured values of \( \theta \) for homogeneous and heterogeneous nucleation...
Fig. 4. The induction times for homogeneous nucleation for different temperatures. The solid line is the calculated induction time [7] using data from Ref. [24]. The experimental induction times from Refs. [1] and [3] are also included.

Fig. 5. The induction time for heterogeneous nucleation for glasses containing 0 ppm Pt, 1 ppm Pt and 5 ppm Pt. The solid line is the calculated induction time from Ref. [7].

<table>
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<th>Table 2 (a) Homogeneous crystal nucleation rates, ( L ), and crystallization induction times, ( \theta ), for lithium disilicate</th>
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<tr>
<td>( T ) (°C)</td>
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<tr>
<th>Table 2 (b) Crystal nucleation rates, ( L ), and crystallization induction times, ( \theta ), for lithium disilicate glass with Pt dopants</th>
</tr>
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<tbody>
<tr>
<td>( T ) (°C)</td>
</tr>
<tr>
<td>432</td>
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<td>445</td>
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<td>500</td>
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</table>
1.2-
1.0-
0.8-
0.6-
0.4-

Contact Angle (degrees)

Fig. 6. Computed induction time for heterogeneous nucleation as a function of contact angle. The relative effective time-lag is defined as the ratio of $\theta(\phi)$ to $\theta(180^\circ)$. The datapoints are from a numerical simulation; the solid line is a calculation based only on the decreased cluster surface area with decreasing contact angle. Taken from Ref. [10].

are in agreement with earlier predictions. Based on the numeric algorithm presented here, Greer et al. [10] computed the time-lag as a function of contact angle using parameters similar to those given in Table 1. The results of that calculation are shown in Fig. 6; the filled circles indicate the results of computer simulations, while the solid line is a calculation based only on the decreased interfacial area with decreasing contact angle. While a significant difference between the induction times for homogeneous and heterogeneous nucleation is predicted for small contact angles, they are nearly equal for contact angles near $130^\circ$, the value obtained for these experiments.

The measured values for $\theta$ and the steady-state nucleation rates are collected in Table 2; for comparison, data obtained by James [1] and Deubener et al. [3] are also provided. The nucleation rates and the induction times for glasses doped with 1 and 5 ppm Pt (by weight) are also provided.

5.3. Differential thermal analysis

Variations in the transformation behavior can be characterized by three parameters that describe the DTA profile: the intensity, $I_p$, and temperature, $T_p$, of the peak maximum and the peak width at half-maximum, $\Delta T_p$. These parameters are shown as a function of platinum concentration for two DTA scan rates in Fig. 7. As demonstrated in Fig. 7(a), the peak temperature decreases approximately linearly with the logarithm of the Pt concentration, while the peak intensity increases (Fig. 7(b)) and the width decreases (Fig. 7(c)). These are expected effects. An increase in the platinum leads to an increase in the nuclei production, causing the phase transition to occur more rapidly (higher intensity) at a lower temperature than for the homogeneous case. Since the transformation occurs more quickly, it leads to a decreased peak width.

The simulation discussed in Section 3 was used to model the DTA data for lithium disilicate glass, taking the measured value for the contact angle, $\phi$, and the known values for the free energy, interfacial energy and the diffusion coefficient (Table 1). The DTA peak parameters determined from the computed peaks are indicated by the solid lines in Fig. 7.
Fig. 8. Kissinger analysis for samples with different dopant concentrations. (a) Typical Kissinger plots for glasses doped with 0, 5 and 50 ppm Pt. (b) Activation energies determined from the Kissinger plots of experimental (■) and computed (○) DTA peaks. The lines are straight line fits to the points.

Differential scanning calorimetry and DTA data are typically analyzed using the Kissinger method [26]. The slope of $\ln(Q/T_p^2)$ vs. $1/T_p$, at which $Q$ is the heating rate and $T_p$ is the temperature of the DTA peak maximum, is argued to give the activation energy of the transformation. Fig. 8 shows the experimental DTA data analyzed in that way. A series of straight lines are obtained with slopes roughly independent of the platinum concentration. The slopes of these lines give activation energies between 250 and 275 kJ/mol, which are in reasonable agreement with previously reported values for this glass [29–31]. The simulated DTA peaks obtained at different heating rates were also analyzed by the Kissinger method. As shown in Fig. 8(a), the activation energies calculated from the simulated data are slightly lower than the values computed from the experimental data, although the differences were within 20–40 kJ/mol. The good agreement between the model calculations and the experimental data shown in Figs. 7 and 8 demonstrates the validity of our modeling approach and justifies the usefulness of such computer calculations for analyzing DSC and DTA data.

The activation energies determined from the Kissinger method are close to the value for macroscopic growth in lithium disilicate glass (282 kJ/mol) [27]. This supports previous suggestions that the Kissinger analysis provides a reasonable estimate of the activation energy for growth [32], but should not be taken to describe the overall activation energy of the transformation. Consequently, caution should be exercised when applying the Kissinger analysis to first order phase transformations proceeding by nucleation and growth. The numerical approach presented here provides a better basis for analysis.

6. Conclusions

Our results are in good agreement with predictions based on the classic theory of nucleation and with previous computer models of heterogeneous nucleation. The induction times for homogeneous and heterogeneous nucleation are virtually identical, which agrees with previous predictions that the induction time for heterogeneous nucleation approaches that for homogeneous nucleation when the contact angle is high (120–130°), the value extracted from the measured heterogeneous nucleation rates. A computer model of non-isothermal phase transformations in heterogeneously nucleating glasses is developed and demonstrated to give good agreement with experimental data, pointing to a more quantitative approach to the analysis of such data.

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