Nonstoichiometric crystallization of lithium metasilicate–calcium metasilicate glasses. Part 1 – Crystal nucleation and growth rates

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1. Introduction

The vast majority of articles aimed at testing crystal nucleation, growth and overall crystallization models using experimental studies of the crystallization kinetics of glass-forming liquids address their stoichiometric or polymorphic crystallization, i.e., the growing crystals and supercooled liquid have the same composition. However, very few glasses satisfy the above condition [1,2], and moreover, the true nature of the critical nuclei in such stoichiometric glasses remains (mostly) unknown [3]. In other words, some research indicates that, even in the case of “polymorphic” crystallization, the composition of the critical nuclei might differ from the parent glass [2]. Most oxide glasses display more than one crystalline phase after crystallization with different composition from the parent glass, at least in the advanced stages of crystallization. Hence, a detailed study of the kinetics of non-stoichiometric crystallization is quite important from both theoretical and practical points of view.

For the present study, we have chosen glasses belonging to the Li2SiO3 (LS)–CaSiO3 (CS) pseudo-binary join that has a single eutectic between LS and CS. To the best of our knowledge, only data on the crystallization kinetics of the stoichiometric end-member compositions (Li2SiO3 and CaSiO3 glasses) exist for this system. However, the nucleation rate in LS glass is so high that it is extremely difficult to prepare such glass, whereas, according to Ref. [4], the internal nucleation rate of CS glass is very low, which is corroborated by our inability to detect internal nucleation in small (mm) pieces of this glass treated for several hours above the Tg. Therefore, a strong difference obviously exists between the nucleation kinetics in these two glasses (LS and CS). This difference correlates to the reduced glass transition temperatures (Tg = Tm; where Tm is the glass transition temperature and Tm is the melting point of the crystal). It should be stressed that, according to empirical findings [5], the higher the Tg, the lower the maximum nucleation rate, Imax. The maximum crystal nucleation rate in the stoichiometric LS glass is expected to be approximately 107−109 m−3 s−1, i.e., close to the values reported for some metals (e.g., Imax ~ 1029 m−3 s−1 for tin [6]).

The aim of this systematic study is to shed some light on the nucleation and growth processes of two stoichiometric crystalline phases (CS and LS) in non-stoichiometric glasses from the LS–CS join. The relevance of this type of research is related to the crystallization of commercial glass-ceramics, which is never stoichiometric! This paper addresses the first part of the present study, the nucleation kinetics and data on the very initial stages of crystal growth when, to a first approximation, the growth rates depend entirely upon the temperature and not on the treatment time. The forthcoming paper, part 2 [7], is devoted to the evolution of the residual melt composition during the more advanced stages of crystallization.

2. Materials and methods

The glasses were prepared from lithium and calcium carbonates and fumed silica. The solid-phase reactions of the desired mixtures of these reagents were performed at 800–900 °C. The produced material was then melted for 4 h in an electrical furnace at 1400 °C in a platinum crucible. These melts were poured on a steel (or brass) slab and pressed
by a steel (or brass) plate. The nominal composition of the batches is shown in Table 1.

The heat treatment of the glass samples was performed in a stabilized vertical electric box furnace kept within approximately 1 °C of the chosen temperature.

The characteristic temperatures for the parent glasses and residual glass matrices were estimated using a Netzsch 404 differential scanning calorimeter (Netzsch, Selb/Bavaria, Germany) with a platinum crucible at 10 °C/min.

A Leica DMRX optical microscope (Leica Microsystems, Wetzlar, Germany) coupled with a Leica DFC490 CCD camera was used to investigate the morphology, size and number density of crystals embedded within the glass interior. Both transmitted light and reflected light modes were used. Thin slab-sided plates were prepared for transmitted light optical microscopy from heat-treated pieces of glass by cutting, grinding and CeO2 polishing.

A Philips XL30 field emission gun SEM (Philips, Amsterdam, The Netherlands) was used for both secondary electron (SE) and back scattering (BS) imaging as well as EDS.

X-ray diffraction measurements were carried out on both powdered and monolithic samples using an Ultima IV X-ray diffractometer (Rigaku Corp., Japan) operating at 20 mA and 40 kV. CuKα (1.5406 Å) incident radiation was used.

The glass densities were measured with a Mettler Toledo Balance (Model AX204).

3. Results

3.1. Phase diagram, concentration dependency of the glass transition temperature, and glass densities

The phase diagram of the LS–CS join was constructed by A.R. West in 1978 [8]. We used DSC analysis of 25 – 30 mg glass samples to confirm and enhance the data in Ref. [8]. Fig. 1 shows a typical DSC heating curve performed at a rate of 10 °C/min. The first exothermic peak corresponds to the formation of LS and the second, to the crystallization of the residual glass in both LS and CS. The solidus, Tₘ, and liquidus, Tₗ, temperatures were determined by the beginning and the end of the melting peak, respectively (see also Ref. [9]).

We also measured the glass transition temperature, Tg, and the area, Aₑut/m, of the part of the endothermic peak corresponding to the eutectic melting. The values of Tg and Tₑut (points in Fig. 2a) corroborate the data in Ref. [8], which is denoted by the solid lines. It should be noted that only some of the compositions close to the eutectic were studied in Ref. [8].

By plotting the area, Aₑut/m, versus the melt composition, we were able to determine the so-called “Tammann triangles” (Fig. 2b). Because the Aₑut/m reaches a maximum at the eutectic composition, this procedure helped us detect and refine the position of the eutectic point.

Figs. 3a and b show the dependence of the glass transition temperature and glass density on the glass composition, respectively. The linear dependence of the latter provides indirect evidence for the similarities between the batch and actual glass composition. This dependence also allows us to suppose that in the framework of the “model of associated solutions” [12] the glasses belonging to the LS–CS join only contain structural units similar to the lithium and calcium metasilicate crystals. This assumption is corroborated by the fact that the LS–CS join is binary at all temperatures [8], i.e., only two crystalline phases (Li₂SiO₃ and CaSiO₃) are observed.

3.2. Crystallization

3.2.1. Volume nucleation

Only glasses containing less than 50 mol% CaO·SiO₂ revealed homogeneous internal nucleation at a reasonable laboratory time scale (hours). We measured the nucleation rates of the lithium metasilicate crystals (LS) in glasses B₅₀, B₄₇, and B₃₅ using the development method [2] in which the nucleation heat treatments were followed by crystal growth, i.e., higher-temperature development to crystal sizes that were visible with an optical microscope. Calcium metasilicate crystals (CS) only appeared during the advanced stages of the phase transition. The X-ray diffraction spectra of crystallized glass B₆₇ are shown in Fig. 4 with micrographs for different double treatments. According to the X-ray analysis, a glass sample subjected to a nucleation heat treatment at 675 °C for 1.5 min contains only LS crystals (Fig. 4a). To confirm this finding, we decreased the XRD scanning rate in the angular range corresponding to the main diffraction peaks of CS by a factor of 20. The new XRD spectrum also did not show any trace of CS crystals. But prolonging the heat treatment to 675 °C to 60 min resulted in full crystallization; at this point, the X-ray spectrum reveals both LS and CS crystal phases (Fig. 4b).

Table 1

The nominal composition of the batches.

<table>
<thead>
<tr>
<th>Glass</th>
<th>CaO·SiO₂ mol%</th>
<th>Li₂O·SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂₀</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>B₁₅</td>
<td>35</td>
<td>65</td>
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<tr>
<td>B₄₇</td>
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<tr>
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<td>50</td>
<td>50</td>
</tr>
<tr>
<td>B₆₀</td>
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<td>40</td>
</tr>
<tr>
<td>B₆₇</td>
<td>66.7</td>
<td>33.3</td>
</tr>
</tbody>
</table>

Fig. 1. DSC curves for the different glasses of this study. The insets show a zoom of the eutectic melting. A heating rate of 10 °C/min and 30 mg glass pieces were used.

Fig. 2. CS–LS phase diagram (a) and the Tammann triangle (b). The lines in the top figure were taken from Ref. [7].
Two different methods were used to estimate the crystal number density, \( N_V \), in the glass volume. Because the nucleation rates for glasses B50 and B47 are extremely low, we polished the sides of two plane-parallel plates with thickness between 80 and 200 \( \mu \text{m} \) (depending on the values of \( N_V \)) after the heat treatment. These samples were then analyzed by transmitted light microscopy to estimate the number of crystals in a given volume. Cross sections of the heat treated samples with high nucleation rates (glass B35) were prepared, and their number densities, \( N_V \), were estimated using standard stereological methods.

During the initial stages of growth, the LS crystals in glasses B50 and B47 are needle-like dendrites with a complex structure (Fig. 5), while glass B35 had spherulitic shaped crystals (Fig. 6). It should be noted that prolonging the isothermal nucleation treatment and development time of glasses B50 and B47 led to the transformation of these needle-like LS crystals into star-like LS crystals by creating new growth directions (see Fig. 7 and inset in Fig. 4b).

The number density, \( N_V \), of LS crystals (nucleated on cooling during the glass preparation and/or on heating to the development temperature) in glass B35 was very high, approximately \( 10^6 \) crystals \( \text{mm}^{-3} \), because of this material’s extremely high nucleation rate. In contrast, glasses B50 and B47 without any preliminary nucleation heat treatment primarily displayed surface crystallization. The small number (~1 mm\(^{-3}\)) of crystals in these latter two glasses could only be detected after a long development time. These crystals have spherulitic shapes and according to X-ray analysis (Fig. 8) contain LS crystals and traces of CS (wollastonite) which most likely forms within the residual glass remaining inside the spherulites. In contrast to glass B47, the spherulitic crystals in the B35 glass consisted of only lithium metasilicate (Fig. 9). This could be caused not only by the difference in the parent glass compositions but also by the large difference in the sizes of the spherulites, which have grown about 100 times

![Fig. 3. Glass transition temperature (a) and glass density, measured at room temperature, (b) versus glass composition. The dotted and dashed lines show the density of the appropriate crystalline phases [11]. The density of the Li\(_2\)SiO\(_3\) glass was taken from Ref. [10].](image)

![Fig. 4. X-ray diffraction spectra of partly and fully crystallized B\(_{50}\) glass after nucleation at \( T_n = 484 \) °C for 15 h and 35 min plus growth at \( T_d = 675 \) °C for (a) 1.5 and (b) 60 min. The photos show the corresponding transmitted (a) and reflected (b) light optical micrographs.](image)

![Fig. 5. Transmitted light optical micrograph of a plate of glass B\(_{50}\) treated at \( T_n = 494 \) °C for 12 h and then at \( T_d = 675 \) °C for 3 min. The inset shows the details of the crystal morphology.](image)

![Fig. 6. Transmitted light optical micrograph of a plate of glass B\(_{50}\) treated at \( T_n = 560 \) °C for 30 min. Cross-polarized contrast.](image)
longer in the glass B47. The residual glass within the spherulites has already started to form CS.

Thus, the first crystalline phase formed via internal homogeneous nucleation at relative low temperatures in glasses containing over 50 mol% LS was lithium metasilicate. Therefore, all measurements of the nucleation kinetics of this paper refer to LS crystals.

Fig. 10 shows the typical kinetic dependence of \( N_V \) on nucleation time, \( t \), for glasses B50, B47, and B35. The solid lines were plotted using Eq. (1) for the time-dependence of the number of super-critical nuclei, taken from Ref. [13]:

\[
N_V(t) = I_{st} \tau \left( \frac{t}{\tau} \right)^\frac{m}{2} \sum_{m=1}^{\infty} \frac{(-1)^m}{m^2} \exp \left( -m^2 \frac{t}{\tau} \right).
\]

This equation includes two fundamental parameters, the steady-state nucleation rate, \( I_{st} \), and the time-lag for nucleation, \( \tau \), which were estimated as fit parameters. The temperature dependences of \( I_{st} \) and \( \tau \) are shown in Figs. 11 and 12, respectively.

3.2.2. Crystallization at temperatures close to the liquidus, \( T_L \), and solidus, \( T_S \)

In contrast to the previous chapter, we consider the result of fast crystallization at temperatures close to the \( T_S \) and \( T_L \) in this chapter. The reflected light optical micrograph in Fig. 13 (top) shows a cross section of the sample from glass B47 treated for 10 min at \( T = 900 °C \) immediately after melting at \( T = 1250 °C \) (for this composition \( T_L = T_S = 1026 °C \)) for 10 min. A fine mixture of alternating crystals (LS and CS) is typical for eutectic crystallization as it is the case of the B47 glass (see Fig. 2). The Ca and Si concentration profiles (see Fig. 14) along the white line showed in the top SEM BS image provide direct evidence for such alternations. The chemical contrast in the BS image also corroborates the Ca profile; the bright and dark crystals are CS and LS, respectively. It should be noted that the Si concentration is the same in both crystals as the two crystalline phases are metasilicates.

A sample of glass B66 (see Fig. 13 bottom) heated for 20 min at \( T = 1100 °C \) (i.e., at a temperature between the \( T_L \) and \( T_S \)) and cooled to a temperature below the \( T_g \) at approximately 200 °C/min shows a
very different morphology. According to the phase diagram (Fig. 2), only CS crystals formed (large faceted crystals in Fig. 13, bottom) at \(T = 1100 \, ^\circ\text{C}\) (region of primary crystallization). Then, cooling to temperatures below the \(T_s\) causes the rapid crystallization of the residual glass matrix – with a composition close to the eutectic – with formation of a fine structure that is typical for eutectics. Similar results are shown in Fig. 15, which presents a DSC cooling curve for glass B66 with a photo (inset) of the sample surface taken directly after the DSC run. By accounting for the temperature of the crystallization peaks, we may attribute the first peak to the formation of CS crystals and the second one to the crystallization of the residual eutectic liquid. It should be noted that a delay was observed for the two crystallization peaks relative to \(T_s\) and \(T_L\).

### 3.2.3. Crystal growth rates

The data presented in this section relate to the growth of the LS crystals at relatively low temperatures (as for the nucleation data shown in Section 3.2.1). Once the change in the residual glass composition can no longer be neglected, the dependence of the crystal size on time begins to deviate from linear. The evolution of the residual glass composition and associated phenomena will be presented and discussed in detail in a companion paper [7]. In the present paper, we restrict our considerations to the initial stage of crystal growth, i.e., when the growth rates can be considered time-independent to a

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**Fig. 11.** Steady-state nucleation rates versus temperature of lithium metasilicate crystals in glasses B50, B47, and B35.

**Fig. 12.** Temperature dependencies of the nucleation time-lags for glasses B50, B47, and B35 in Arrhenius coordinates. The top solid line is a linear fit of data of the B50 glass. In the case of glasses B47 and B35 the solid lines are plotted parallel to the former.

**Fig. 13.** Reflected light optical micrographs of cross-sections of glasses B47 (a) and B66 (b) subjected to the following heat treatments: a – \(T = 1250 \, ^\circ\text{C}\), 10 min + \(T = 900 \, ^\circ\text{C}\), 10 min; b – \(T = 1100 \, ^\circ\text{C}\), 20 min. Full crystallization occurred during cooling of the samples at a temperature \(T < T_s\) (1026 °C).

**Fig. 14.** SEM BSE image and concentration along the cross section of a sample of glass B47 treated at 1250 °C for 10 min and then at 900 °C for 10 min.
first approximation. Such restriction allows us to study and compare the temperature dependence of the crystal growth rates in glasses B50, B47, and B35.

For glasses B50 and B47, we measured the growth rates of the crystalline surface layer, which consisted of needle-like LS crystals separated by the residual liquid, at different temperatures. Without a preliminary nucleation treatment, these glasses contain primarily surface crystallization as previously mentioned. Fig. 16 shows an example of the reflected light optical micrographs and SEM images from the cross sections of the B50 glass sample after treating at $T = 675$ °C for 10 min. These cross-sections were made in two different directions, parallel (taken from the vicinity of the sample surface) and perpendicular to the external surface of the sample, as shown by a scheme in Fig. 16. The morphology of the surface nucleated crystals is similar to that of crystals nucleated in the glass volume (please compare with Fig. 5). It should be emphasized that there is no contact between the numerous LS crystals (Fig. 16 bottom) due to the Li-depleted diffusion zones around each crystal! The study of the residual melt composition between the needle-like LS crystals that formed both on the surface, with enhanced peaks corresponding to (200) and (020). This result indicates that the crystals are highly oriented with their c axis perpendicular to the sample surface. It should be noted that the samples have different areas and crystal fractions due to sectioning, so direct comparison between the absolute intensities of peaks from different curves is not possible.

Fig. 17 presents the X-ray diffraction spectra of the cross sections shown in Fig. 16, both parallel (Fig. 17c) and perpendicular (Fig. 17b) to the external surface. The bottom curve (Fig. 17a) relates to a finely ground sample (~20 μm). A strong crystallographic orientation of the surface nucleated LS crystals was observed. The reflection (002) was greatly enhanced for the sample cut parallel to the surface (Figs. 16 bottom, and 17c) while all the other reflections have been strongly suppressed. The opposite is seen for the sample cut perpendicular to the surface, with enhanced peaks corresponding to (200) and (020). This result indicates that the crystals are highly oriented with their c axis perpendicular to the sample surface. It should be noted that the samples have different areas and crystal fractions due to sectioning, so direct comparison between the absolute intensities of peaks from different curves is not possible.

Fig. 18 shows the dependence of the crystal layer thickness, $h$, on time, $t$, for different temperatures for glasses B50 (a) and B47 (b). All of the plots were nearly linear. This feature allows us to conclude that, at least up to the values of $h$ in these experiments, the crystallization front advances towards the inner parts of the sample without changing the liquid composition inside the glass sample. In other words, only the composition of the inter-dendritic residual glass, which is trapped between the LS arms, changed. Thus, the estimated

Fig. 15. DSC cooling curve (10 °C/min) of B66 melt. The inset shows a reflected light optical micrograph of the surface of a sample after the DSC run. The arrows point to CS crystals and the crystallized residual (eutectic) melt.

Fig. 16. Reflected light optical micrographs of cross sections perpendicular and parallel to the external surface (see scheme) of a B50 glass sample treated at $T = 675$ °C for 10 min. The inset is an SEM image.

Fig. 17. a) X-ray diffraction spectrum of a powder of the B50 glass sample crystallized at $T = 675$ °C for 10 min. b) and c) X-ray diffraction spectra of different cuts of the same sample: cross section parallel (c) and perpendicular (b) to the external surface of the sample (see scheme in Fig. 16). The ratio between the areas of the diffraction peaks are shown close to the spectra. The dashed vertical lines correspond to the positions of the diffraction peaks taken from card 29-828.

Fig. 18. Thickness of the crystalline surface layer of B50 (a) and B47 (b) glass samples versus heat treatment time at different temperatures. The solid lines are linear approximations to the data.
crystal growth rate, \( U = dh/dt \), is a function of just the temperature. It should be noted that, at any given temperature, the growth rate of the surface nucleated crystals equals that of the internally nucleated crystals. Fig. 19 shows the half length and width of the needle-like crystals nucleated within the volume of glass B47 (see inset of Fig. 19) versus their growth time at 675 °C. According to this figure, 0.5dL/dt (slope of the solid line) is very close to dh/dt (slope of the dashed line). The apparent induction period, approximately 26 s, of the parent induction period, approximately 26 s, of the crystal growth rate, \( U \) (screw dislocation model, [14,15]) were used to analyze the crystal nucleation and growth kinetics:

\[
I_d = \sqrt{\frac{\alpha}{k_B T \Delta a^*}} \exp\left(\frac{-W^*}{k_B T}\right),
\]

(2)

\[
W^* = \frac{16}{3} \pi \alpha^3 \Delta G_f^0.
\]

(3)

\[
\tau = \frac{16}{3} \frac{k_B T \pi \alpha^4 \Delta G_f^0 D_l}{D_i}.
\]

(4)

\[
U = f \frac{D_i}{4d} \left[1 - \exp\left(-\frac{1}{2} \frac{\Delta G_f a^3}{k_B T}\right)\right],
\]

(5)

\[
f = \frac{1}{2\pi} \frac{(T_i - T)}{T_i},
\]

(6)

where \( k_B \) is the Boltzmann constant; \( T \) is the absolute temperature; \( \alpha \) is a characteristic size parameter (size of the building units in the melt); \( \sigma \) is the specific energy of the liquid/critical nucleus interface; \( \Delta G_f \) is the thermodynamic driving force for crystallization per unit volume of crystal; \( W \) is the work of formation for a nucleus of critical size, i.e., the so-called thermodynamic barrier; \( D_i \) and \( D_o \) are the effective diffusion coefficients for the building units in the case of nucleation and growth processes respectively; and \( f \) is the fraction of screw dislocations on the crystal surface.

Strictly speaking, Eq. (2) was derived for single-component systems. When the crystal composition is the same as that of the liquid (stoichiometric crystallization) and the possible dissociation of structural units is neglected, the liquid could be considered to only consist of building units similar to the crystalline cell. The system is often considered a single component in such situations.

Two corrections should be made when employing Eq. (2) for non-stoichiometric crystallization, i.e., for precipitation of crystalline phases with different composition from the parent liquid. First, the value of the molar fraction of the precipitating substance in the melt, \( x \), has to be introduced into the pre-exponential term. Thus, the decrease in the number of building units participating in the nucleation of the new phase relative to stoichiometric crystallization will be taken into account. However, the effect of this factor is much less than that for the change in the thermodynamic driving force for crystallization, \( \Delta G_f \). This driving force was derived for binary (metallic) melts in Ref. [16].

4. Discussion

The following equations for the steady-state nucleation rate, \( I_s \), (see e.g., [14]), the time-lag for nucleation, \( \tau \) ([13], see also Eq. (1)), and the crystal growth rate, \( U \) (screw dislocation model, [14,15]) were used to analyze the crystal nucleation and growth kinetics:

\[
I_d = \sqrt{\frac{\alpha}{k_B T \Delta a^*}} \exp\left(\frac{-W^*}{k_B T}\right),
\]

(2)
based on the regular solution model for the liquid and solid. In the limiting case involving the absence of solid solutions, i.e., when the solubility of a second component in the crystalline phase is zero, the following formula was proposed for the driving force [16]:

$$\Delta G_{\text{v}} = (T_{\text{l}} - T) \Delta S_{\text{m}} - R \ln x/\nu_{\text{m}},$$  \hspace{1cm} (7)

where $T_{\text{l}}$ is the liquidus, $\Delta S_{\text{m}}$ is the entropy of fusion per mole of pure crystal, and $\nu_{\text{m}}$ is the molar volume.

Using $\Delta S_{\text{m}} = 50 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [17] for lithium metasilicate, we calculated the thermodynamic driving force versus the crystallization temperature for LS in several glasses belonging to the LS–CS join as shown in Fig. 22. For glass $B_{50}$ the value of $T_{\text{l}}$ was taken from the extension of the liquidus to the RHS of the phase diagram. This prolongation corresponding to the metastable equilibrium between LS crystals and liquid takes place up to the formation of the CS phase and is discussed in detail in Ref. [7].

We plotted $I_{\text{st}}(T)$ and $U(T)$ for glasses $B_{50}$, $B_{47}$, and $B_{35}$ in Fig. 23, to compare the influence of the glass composition on the nucleation and growth rates. It is clear that the crystal growth rate increased no more than $1-2$ orders of magnitude due to the increase in LS content from 0.50 to 0.65 molar fraction, whereas the nucleation rate increased by seven orders of magnitude. At high undercoolings the crystal growth rate is primarily determined by the effective diffusion coefficient (see Eq. (5)). Hence, assuming $D_{\text{f}} \equiv D_{0}$, we can conclude that the strong increase in the nucleation rate is caused primarily by the decreased thermodynamic barrier for nucleation $W$. Combining Eq. (4) with Eq. (2) and correcting by using the molar fraction, $x$, of LS in the glass (see discussion above), one can rewrite the equation for the steady-state nucleation rate as:

$$I_{\text{st}} = \chi \times \frac{16 \sigma^{3/2}}{3 \times \Delta G_{\text{v}}^{*}} \frac{1}{d^{3}} \exp \left( \frac{-W^{*}}{k_{B}T} \right).$$ \hspace{1cm} (8)

Eq. (8) was employed to estimate $\sigma$ as a fit parameter. One should recall that $\sigma$ enters into the thermodynamic barrier $W$ (see Eq. (3)). In our calculations, we used $\sigma = (V_{0}N_{A})^{1/2} = 3.9 \times 10^{-11} \text{m}$, and the results are shown in Figs. 24 and 25 for 477 °C, close to the temperature of the maximum nucleation rate in glasses $B_{50}$, $B_{47}$, and $B_{35}$. As was expected, the thermodynamic barrier strongly decreases with increasing Li$_2$O content in the glass (Fig. 25).

Eq. (2) and correcting by using the molar fraction, $x$, of LS in the glass (see discussion above), one can rewrite the equation for the steady-state nucleation rate as:

$$I_{\text{st}} = \chi \times \frac{16 \sigma^{3/2}}{3 \times \Delta G_{\text{v}}^{*}} \frac{1}{d^{3}} \exp \left( \frac{-W^{*}}{k_{B}T} \right).$$ \hspace{1cm} (8)

Fig. 26 shows the maximum nucleation rates versus the reduced glass transition temperature. The large squares relate to the glasses $B_{50}$, $B_{47}$, and $B_{35}$ whereas the other points, taken from Ref. [2], relate to different silicate glasses. The $I_{\text{st}}(T_{\text{max}})$ values for glasses $B_{50}$, $B_{47}$, and $B_{35}$ confirm the strong correlation between the $I_{\text{st}}(T_{\text{max}})$ and $T_{\text{gr}} = T_{\text{gr}}/T_{\text{l}}$. Because the new data relates to the same crystal (LS) and the same glass system, the correlation between $I_{\text{st}}(T_{\text{max}})$ and $T_{\text{gr}}$.

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Fig. 22. Thermodynamic driving force for crystallization of lithium metasilicate crystals in glasses $B_{50}$, $B_{47}$, and $B_{35}$, and in the liquid with Li$_2$O-SiO$_2$ composition.

Fig. 23. Crystal nucleation and growth rates in glasses $B_{50}$, $B_{47}$, and $B_{35}$ as a function of temperature.

Fig. 24. Energy of the liquid/critical LS crystal interface versus glass composition. The empty circles refer to the present glasses. The solid line is a linear fit. The star is the expected value corresponding to the LS melt.

Fig. 25. $W^{*}/k_{B}T_{\text{max}}$ versus the molar fraction of LS in the glass.
The nucleation and growth rates of lithium metasilicate crystals were measured for several glass compositions of the Li$_2$O·SiO$_2$–CaO·SiO$_2$ pseudo-binary join with a simple eutectic at a 0.53 Li$_2$O–SiO$_2$ mole fraction. Increasing the LS content in the glass from 0.50 to 0.65 mole fractions increases the maximum steady-state nucleation rate by approximately seven orders of magnitude, whereas the growth rate only increases by one or two orders of magnitude.

This extreme increase in the nucleation rate was primarily caused by a decrease in the thermodynamic barrier for nucleation due to the increased thermodynamic driving force for crystallization and decreased nucleus/liquid interfacial energy, $\sigma$. In the studied composition range, $\sigma$ linearly decreases when the melt composition approaches the crystal composition and can be represented by two portions: the first is the surface energy of the crystal in its own melt, and the second is proportional to the difference between the crystal and melt compositions.

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References