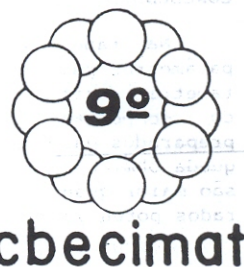


CRYSTALLIZATION MECHANISM IN A  $\text{Li}_2\text{O}-\text{SiO}_2$ 

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*The early nucleation stages in  $\text{Li}_2\text{O}:\text{SiO}_2$  ( $\text{LS}_2$ ) glasses, and compositions in its neighborhood, have been a subject of interest and controversy over the past 25 years. In this article a critical review of the relevant papers is presented with special focus on the evidence, pro and contra, of the possible nucleation of a metastable metasilicate phase (LS) prior to the appearance of equilibrium  $\text{LS}_2$  crystals. Additionally, an original SAXS study of a  $\text{Li}_2\text{O}:\text{SiO}_2$  glass heat-treated at  $500^\circ\text{C}$  was carried out using a pinhole collimated X-ray beam from a synchrotron source. The present experimental results, allied to the majority of previous research, provide strong evidence of the precipitation of the metastable LS phase which redissolves after a continuous treatment at  $500^\circ\text{C}$ .*

## INTRODUCTION

The crystallization behavior of  $\text{Li}_2\text{O}-\text{SiO}_2$  glasses has been a subject of interest for several years since these materials are the basis for many commercial glass-ceramics. A second cause is due to their volume crystallization without the aid of nucleating agents. For this reason, these glasses have been used to test the classical nucleation theory<sup>[1-3]</sup>. A possible explanation for the strong discrepancy between calculated and experimental nucleation rates is that a metastable metasilicate phase,  $\text{Li}_2\text{O}:\text{SiO}_2$  (LS), nucleates before the equilibrium  $\text{Li}_2\text{O}:\text{SiO}_2$  ( $\text{LS}_2$ ) crystal.

Kalinina et al<sup>[4]</sup> in their X-ray diffraction study found that, in addition to the equilibrium lithium disilicate phase, a small amount of nonequilibrium deposition of lithium metasilicate occurred in substoichiometric glasses containing 20.0 to 30.0 mol%  $\text{Li}_2\text{O}$  on prolonged heating ( $t > 96\text{h}$ ) at  $480^\circ\text{C}$  and also in the  $630-900^\circ\text{C}$  range. Cristobalite lines appeared after 24h in the  $800-900^\circ\text{C}$  range. After a prolonged treatment at  $960^\circ\text{C}$ , three tridymite lines also emerged, while the LS line ( $d=3.33\text{\AA}$ ) disappeared. Its dissolution was associated with the establishment of equilibrium, in accordance with the phase diagram.

Superstoichiometric glasses, with compositions close to the stoichiometric disilicate (34.2-36.0 and 37.1 mol%  $\text{Li}_2\text{O}$ ) treated at 630 and  $960^\circ\text{C}$ , also crystallized  $\text{LS}_2$  and LS, as expected from the equilibrium diagram. Special emphasis was given to glass 34.2 mol% which was heated at 480, 630, 940 and  $1000^\circ\text{C}$  for 24 h. With the exception of  $480^\circ\text{C}$ , all treatments lead to crystallization of LS in addition to  $\text{LS}_2$ . Therefore it appears that a prolonged heating is necessary to nucleate the LS phase at the lowest temperature ( $480^\circ\text{C}$ ). In any case, it is important to stress that this (nonequilibrium) phase also nucleated in the substoichiometric glasses.

Kinser and Hench<sup>[5]</sup>, based on their X-ray analysis, electron microscopy and dc/ac electrical measurements in a 30 mol%  $\text{Li}_2\text{O}$  glass treated at  $500^\circ\text{C}$ , concluded that a metastable LS phase precipitates and subsequently redissolves prior to the appearance of the  $\text{LS}_2$  crystal. The highly conducting LS phase in the silica-rich matrix gave rise to large dielectric losses. The electron micrograph and X-ray diffraction showed that LS began to redissolve after 10h at  $500^\circ\text{C}$  and the magnitude of the MWS loss was reduced.

In a further work, Hench et al<sup>[6]</sup> studied an almost stoichiometric (33 mol%  $\text{Li}_2\text{O}$ ) glass with small-angle X-ray scattering (SAXS) and dielectric measurements. They also concluded that the LS phase precipitates in this glass. The particle size of the LS crystals did not depend significantly on the heat treatment time at  $500^\circ\text{C}$ , the Guinier radius being between 230 and  $250\text{\AA}$ . The integrated SAXS intensity reached a maximum value after 5h and decreased with further treatment. It should be stressed, however, that no LS Bragg peaks were detected within the limits of sensitivity of the Guinier-De Wolf X-ray camera (0.1%).

Joseph and Pye<sup>[7]</sup> probed the structural changes of a  $33.3 \pm 0.2$  mol%  $\text{Li}_2\text{O}$  glass with time of nucleation at two heat-treatment temperatures ( $450^\circ$  and  $500^\circ\text{C}$ ) by Raman spectroscopy. The analysis of the spectra indicated an increase in the number of  $\text{SiO}_4$  units with two non-bridging oxygens ("metasilicate-like" units) during the initial stages of nucleation, up to 6h at  $450^\circ\text{C}$  and 1.5h at  $500^\circ\text{C}$ .

Kalinina et al<sup>[8]</sup> determined the crystal nucleation rates of  $\text{LS}_2$  as a function of composition in several glasses from 33.5 to 39.0 mol%  $\text{Li}_2\text{O}$ . The maximum nucleation rates  $I_{\text{max}}$  strongly increased with  $\text{Li}_2\text{O}$  content, from 0.15 for glass 33.5% to  $270\text{ mm}^{-3}\cdot\text{min}^{-1}$  for glass 39.0%. The temperature of maximum nucleation rates ( $T_{\text{max}}$ ) were  $460^\circ\text{C}$  for glasses with less than 35 mol%  $\text{Li}_2\text{O}$  and  $480^\circ\text{C}$  for glasses with compositions higher than 36 mol%  $\text{Li}_2\text{O}$ . Traces of LS were found in this last family of glasses.

In a recent work, Barker et al<sup>[9]</sup> determined the crystal nucleation rates in three glasses with 33.3, 36.0 and 40.0 mol%  $\text{Li}_2\text{O}$ . For a given temperature, compositions 33.3 and 36.0% presented similar nucleation rates (glass 36.0 had only a slightly smaller rate), in clear disagreement with the results of Kalinina et al<sup>[8]</sup>. The maximum nucleation temperature was  $450^\circ\text{C}$  for both compositions. Glass 40.0 presented a much higher rate and  $T_{\text{max}}$  was  $480^\circ\text{C}$ . Since the stoichiometric lithium metasilicate glass has the highest nucleation rate, the authors concluded that the formation of a metastable phase LS is very unlikely since that would lead to an enhanced nucleation in glass 36.0, because it is closer to the LS composition than glass 33.3.

Therefore, there is a clear discrepancy in the literature. While several authors<sup>[7-9]</sup> indicate the (improbable) pre-

cipitation of LS in lithium disilicate glass as a precursor to the equilibrium LS2 crystal, the most recent research<sup>[9]</sup> provides evidence for the opposite view.

The objective of this paper is to present an original SAXS study of an stoichiometric  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass, using a pinhole collimated X-ray beam from a synchrotron source in an attempt to clarify the polemic situation.

## EXPERIMENTAL RESULTS

### Glass preparation

The  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass was melted, quenched and remelted three times for approximately 3 hours at  $1350^\circ\text{C}$  to ensure homogeneity. The final melt was quenched between 2 steel plates, to obtain 1-2 mm thick specimens. The analysed composition agreed within 0.1 mol%  $\text{Li}_2\text{O}$  with the nominal composition.

The heat treatments were carried out in a tubular furnace at  $500 \pm 2^\circ\text{C}$ , for periods of time up to 50 hours. The specimens were ground with SiC to a thickness of about 100  $\mu\text{m}$ . Two sets of samples were prepared under similar conditions for SAXS measurements.

### SAXS experiments

The structural evolution of the  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass heat-treated at  $500^\circ\text{C}$  was studied by means of the small angle X-ray scattering technique using a SAXS work-station at LURE synchrotron radiation laboratory (Université Paris-Sud). The experimental set-up is composed of: i) a bent silicon monochromator providing a beam of wavelength  $\lambda = 1.60 \text{ \AA}$ , ii) a pin-hole collimation system for the direct beam which allows for obtaining aberration-free scattering intensity curves, iii) a sample holder and iv) a one-dimensional X-ray position sensitive detector. A vacuum pass was used to reduce the intensity of air scattering. The remaining parasitic scattering has been subtracted from the total experimental scattering intensity curves. The SAXS curves corresponding to the samples heat-treated at  $500^\circ\text{C}$  for different periods of time, have been normalized to equivalent X-ray absorption.

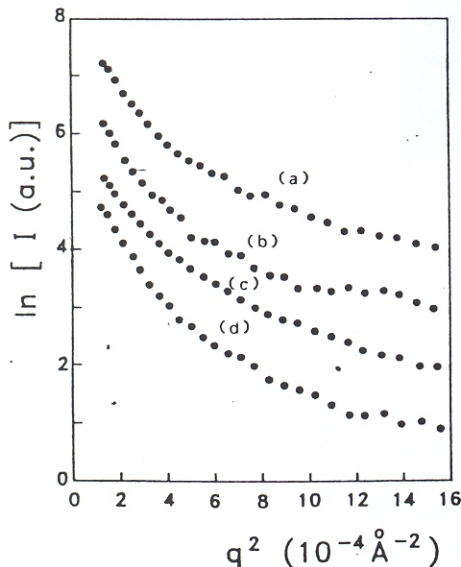


Figure 1: Guinier's plot for samples after different heat treatments: 2 (a), 4 (b), 6 (c) and 20 hours (d). The curves are displaced vertically for clarity.

The SAXS intensities were determined as functions of the modulus of the scattering vector  $q = (4\pi/\lambda)\sin(\varepsilon/2)$ ,  $\varepsilon$  being the scattering angle. The experimental intensities,  $I(q)$ , corresponding to one set of samples, were plotted in Fig. 1 as functions of  $q$  using a  $\log I$  versus  $q^2$  scale. From these plots the average radius of gyration,  $R_G$ , of the nucleated crystals has been determined by applying Guinier's law<sup>[10]</sup>:

$$I(q) = I(0)e^{-\frac{1}{3}R_G^2q^2} \quad (1)$$

where

$$I(0) \propto (\rho - \rho_o)^2 N v^2, \quad (2)$$

( $\rho - \rho_o$ ) being the difference in electronic densities between matrix and crystals,  $N$  the number of particles (crystals) per unit volume and  $v$  an average volume of the particles.

The radii of gyration obtained from the SAXS results should be considered as approximative values since no clear linear behavior on the  $\log I$  versus  $q^2$  plots has been found.

Fig. 2 shows typical Porod's plots of the scattering curves. Porod's law, including the influence of the electronic density fluctuations in the matrix, is given by<sup>[11]</sup>

$$\lim Iq^4 = \alpha + \beta q^4 \quad (q \rightarrow \infty) \quad (3)$$

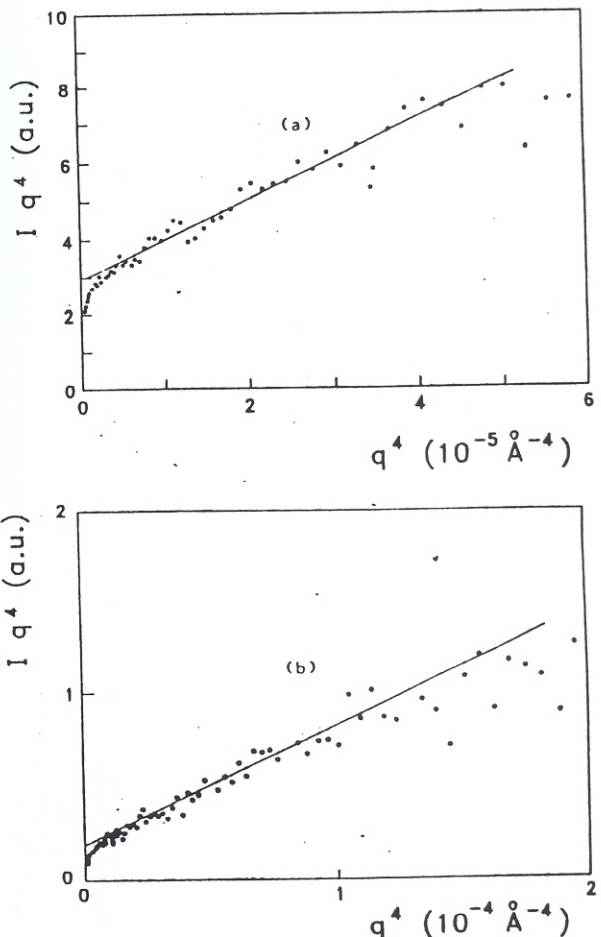


Figure 2: Porod's plots of SAXS results for glasses after heat treatments of 8 hours (a) and 54 hours (b).

where

$$\alpha \propto (\rho - \rho_0)^2 Na, \quad (4)$$

$a$  being the average interface area per particle and  $\beta$  a parameter proportional to the magnitude of density fluctuations in the vitreous phase. The plots of Fig. 2 indicate that Porod's law actually holds for the studied glass.

Another relevant parameter determined from the SAXS curves is the integral

$$Q = \int_0^\infty q^2 I(q) dq, \quad (5)$$

$Q$  being related to the structure by

$$Q \propto (\rho - \rho_0)^2 Nv. \quad (6)$$

Equation 1 and 3 were applied for determining the average radius of gyration of the crystals,  $R_G$ , and the fluctuation term,  $\beta$ , respectively. These parameters, which are plotted in Fig. 3, do not significantly vary during the crystallization process.

On the contrary, the functions  $I(0)$ ,  $\alpha$  and  $Q$  defined in equation 1, 3 and 5, respectively, exhibit apparent variations with time as can be seen in Fig. 4. The main features in Fig. 4 are the sharp maxima at about 8 hours of heat treatment, observed for the two sets of glass samples.

$I(0)$ ,  $\alpha$  and  $Q$  are proportional to  $(\rho - \rho_0)^2$ , as stated by equation 2, 4 and 6, respectively. Therefore, these functions are very sensitive to variations in electronic density contrast between the two phases. Since Guinier's plots (Fig. 1) do not exhibit a significant variation in their maximum slope with time, the average radius of gyration ( $R_G$ ) and the other geometrical parameters of the crystals ( $v$  and  $a$ ) may be considered as constants. Consequently the presence of maxima

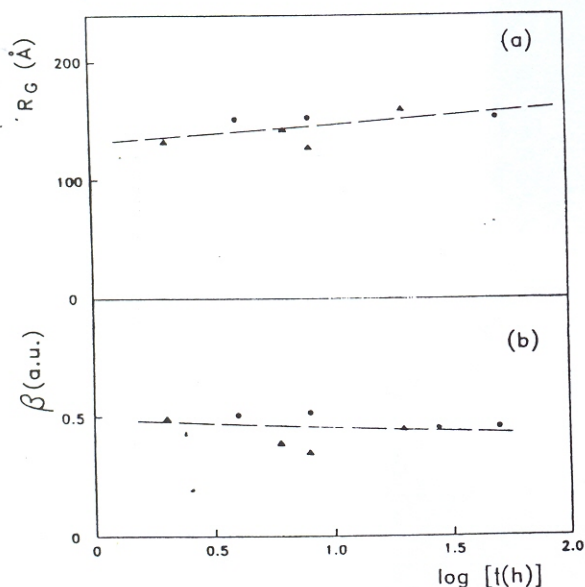


Figure 3: Variations in the average radius of gyration of the crystals (a) and in the fluctuation parameters (b) with time. The different symbols correspond to two sets of samples.

in the time evolution of  $I(0)$ ,  $\alpha$  and  $Q$  (Fig. 4) are mainly due to a variation in  $N(\rho - \rho_0)^2$ . This variation is consistent with the existence of a process of formation and later dissolution of particles having an electronic density which is appreciably different from that of the glass matrix. This result is compatible with the model of formation and redissolution of LS crystals in the LS2 glass and completely discards the possibility of having a transformation from the glass directly toward the equilibrium LS2 crystalline phase. It proves that a precursor metastable phase, having a different electronic density than that of the matrix, is actually formed and precedes the crystallization of the equilibrium LS2 phase.

## CONCLUSIONS

The presented experimental results are fully compatible with the previous studies which established the nucleation of metastable metasilicate  $\text{LiO}_2 \cdot \text{SiO}_2$  crystals prior to the appearance of the equilibrium disilicate  $\text{LiO}_2 \cdot 2\text{SiO}_2$  crystals phase.

What would be the reasons for the nucleation of the LS intermediate phase? From a purely chemical point of view, all  $\text{SiO}_4$  units in lithium disilicate glass should have one non-bridging oxygen, i.e. three corners shared per tetrahedra. However, the NMR study of Schramm et al<sup>[12]</sup> demonstrated that about 14.6% of  $\text{SiO}_4$  units, without non-bridging oxygens ( $Q_4$  units), exist in  $\text{Li}_2 \cdot 2\text{SiO}_2$  glass. This result was confirmed by Stebbins et al<sup>[13]</sup> who found 11.5% of  $Q_4$  units in a similar glass. Therefore, structural disproportionation reactions ( $2Q_3 = Q_4 + Q_2$ ) occur, leading to the formation of about 20% of  $Q_2$  or 'metasilicate like' units, with two non-bridging oxygens per tetrahedra, in the glass. Thus, it is conceivable that these special units be responsible for the nucleation of the metasilicate (LS) phase in the studied glass.

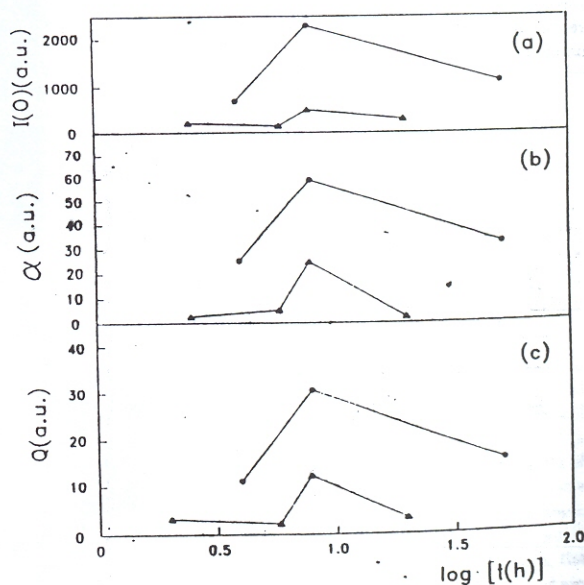


Figure 4: Variations in the  $I(0)$  (a),  $\alpha$  (b) and  $Q$  (c) parameters with time. The plots of these functions are shown for the two sets of glass samples.

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