



TEM and XRD study of early crystallization of lithium disilicate glasses

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Abstract

Numerous researchers have speculated the precipitation of metastable phase(s) in the early stages of crystallization of lithium disilicate glass to explain the large discrepancies between the predictions of the classical nucleation theory (CNT) and experimental data. Therefore, we have investigated the early and intermediate stages of crystallization of three glasses on both sides of the stoichiometric composition through direct observations by transmission electron microscopy (TEM)/selected area electron diffraction (SAED) and X-ray diffraction (XRD). In samples heat-treated at $\sim T_g = 454$ °C, two distinct crystalline phases, stable lithium disilicate (LS₂) and metastable lithium metasilicate (LS) coexist up to 120 h at 454 °C (crystalline fraction <1 vol.%). For longer treatments (240–600 h) only the stable phase (LS₂) was observed. These results suggest that in the early stages, simultaneous homogeneous nucleation of both LS and LS₂ takes place. As treatment time and crystallized fraction increase, the relative number of LS crystals decreases. Therefore, the precipitation of the LS phase does not disturb the nucleation of the stable LS₂ phase and thus cannot explain the failure of CNT in predicting the nucleation rates in this glass.

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1. Introduction

It is well established that the classical nucleation theory (CNT) underestimates the steady-state nucleation rates in glasses by many orders of magnitude [1,2]. Several assumptions in the theory may be responsible for such discrepancy [3], including its failure for the smallest nuclei for which the crystal/glass interface is not sharp [4], a possible temperature or size dependence of the surface en-

ergy [2,5] and the elastic stresses that arise on crystal nucleation [6,7]. Moreover, there is a possibility that metastable crystalline phases of small surface energy could nucleate first in the early stages inducing heterogeneous nucleation of the stable phase or transform into the stable form at later times [8].

The nucleation and crystallization kinetics of lithium silicate glasses close to Li₂O·2SiO₂ (LS₂) composition have been studied intensively for decades, because this glass can be made easily, detailed thermodynamic data are available in the literature, and internal crystal nucleation and growth kinetics can be measured conveniently.

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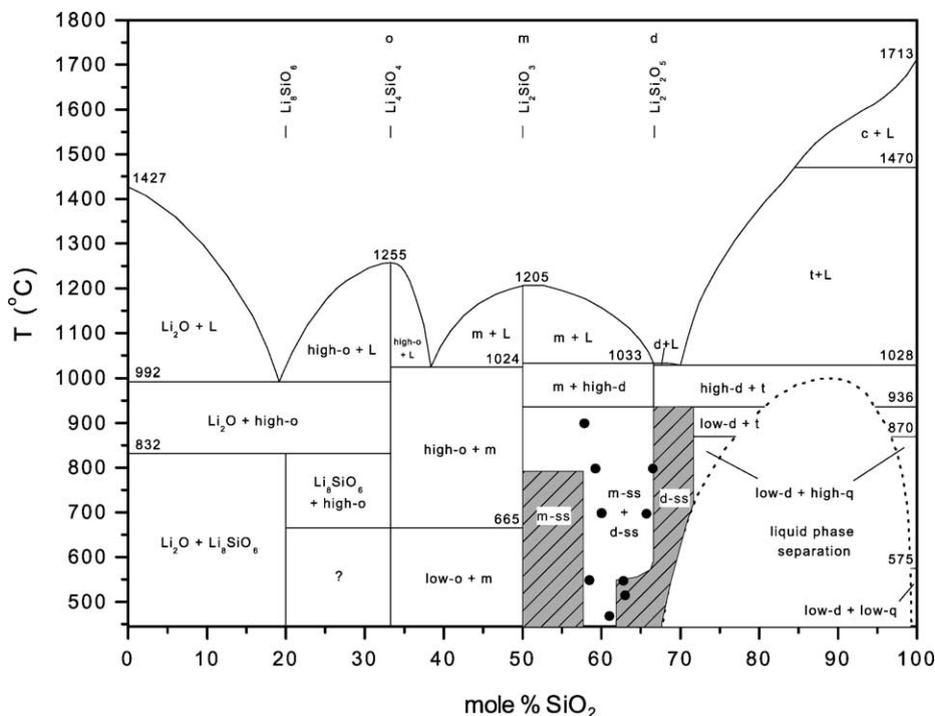


Fig. 1. Phase diagram of the Li_2O - SiO_2 system according to Migge [9], showing solid-solution regions determined by West and Glasser [10] (dashed area), and Deubener [11] (circles). The figure also shows the liquid-liquid phase separation region, according to Zanotto [12].

Fig. 1 shows a phase diagram of this system. In equilibrium at 454 °C, both slightly hypo-stoichiometric (<33.3 mol% Li_2O) and slightly hyper-stoichiometric LS_2 compositions (>33.3 mol% Li_2O) should crystallize as LS_2 -ss (solid-solution).

While several authors suggested the possibility of a metastable phase precipitation (discussed below), Zanotto and Leite [13] concluded that metastable phases, if present at all, do not have any significant impact on the overall crystallization kinetics of LS_2 glass. This is one of the major controversies concerning crystallization kinetics in this system and has not been resolved conclusively yet.

In addition, the different phases reported to precipitate in the early stages of crystallization in this system have not been clearly identified yet. Some authors, contradicting others who could not detect any phase prior to stable LS_2 , have suggested the appearance of a metastable phase for certain heat treatments. Though many techniques

have been used (SAXS, dielectric relaxation, Raman spectroscopy, XPS, e.g. [14–19]) they only give *indirect* evidence of a metastable phase formation, and hence do not resolve the controversy unambiguously. Reviews on this issue can be found in Refs. [20–23].

Towards *direct* observations, James and Keown [24] used TEM/SAED for studying the nucleation of a stoichiometric lithium disilicate glass heat-treated in the 450–490 °C temperature range, for up to 150 h. Electron diffraction patterns showed only the stable phase LS_2 . On the other hand, in another TEM study, Deubener et al. [25] observed a transient phase in a slightly hyper-stoichiometric (33.5 mol% Li_2O) sample heat-treated at 454 °C for 7 h. That phase was indexed on the basis of LS unit cell parameters, but with doubled c -lattice constant. After further heat treatment for 40 h at 454 °C, two phases, LS_2 and the transient phase, were indexed. However, Deubener [26] mentioned later that their results were subjected to some un-

certainty due to fast degradation of the crystals under the electron beam. Crystal degradation was also observed in Ref. [27].

Soares Jr. [27] also observed a phase different from LS_2 using TEM, in a hypo-stoichiometric glass (32.5 mol% Li_2O) nucleated at 454 °C for 5–20 h. Heat-treated samples were prepared by chemical thinning. Two different phases were found: LS_2 and LS, but the LS crystals were indexed only in the [001] direction. These results allowed him to identify the a and b lattice parameters only. Samples nucleated for 20 h at 454 °C were given a growth treatment at 610 °C for 10 min, yielding only the stable LS_2 phase.

Iqbal et al. [22] followed the crystallization stages in hyper-stoichiometric LS_2 glasses with 33.9 mol% Li_2O by TEM and XRD and showed that two metastable phases (different from LS) persisted to very long times at 454 °C. In their investigation, glass samples were heat-treated at 454 °C for time periods of 50–551 h. After 120 h at 454 °C, they observed by XRD only a metastable

phase, referred as α' - LS_2 . After longer heat treatment times at the same temperature, most of the peaks of this phase were present though with decreasing intensity, along with the stable LS_2 phase. This metastable phase was not observed by TEM/SAED. After 551 h, apart from LS_2 , they observed small traces of stable LS phase by XRD, which was attributed to the slight hyper-stoichiometry of the glass. According to the phase diagram (Fig. 1), only LS_2 -ss may crystallize as a stable phase in the glass with 33.9 mol% Li_2O at 454 °C. Another metastable phase, β' - LS_2 , was identified by TEM/SAED in samples nucleated for 331 and 502 h at 454 °C. In recent papers, Burgner et al. [20,21] have repeated the XRD experiments of Iqbal et al. [22] in a series of LS_2 glasses heat-treated for long times (120–600 h) at 454 and 465 °C. No phase other than the stable lithium disilicate was observed.

In summary, there is some evidence that different metastable phases may form during the early stages of crystallization in LS_2 glasses, but

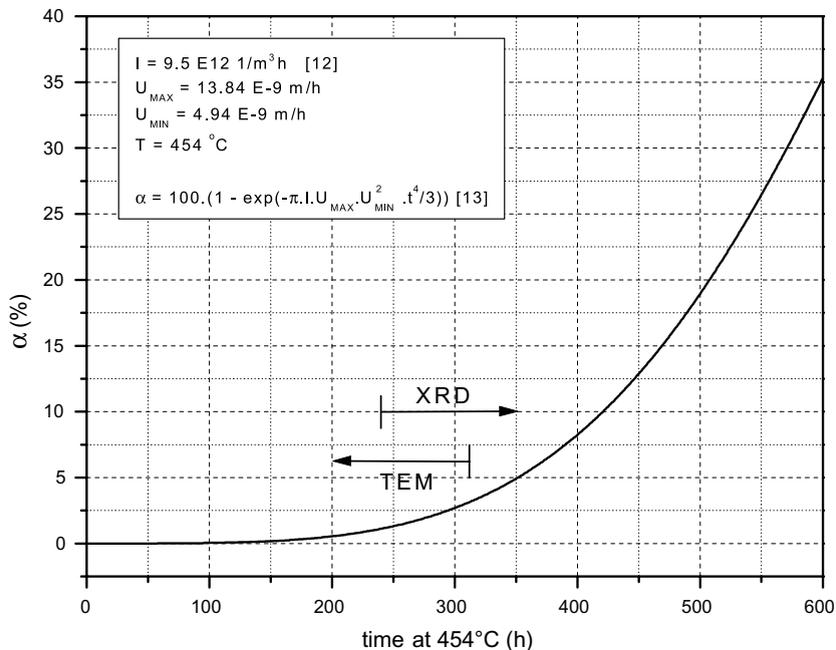


Fig. 2. Estimated volume fraction of crystals, α , in stoichiometric lithium disilicate glass heat-treated at 454 °C. Nucleation rate data from Zanotto [12] and growth rate measured from TEM sizes. The volume fraction of crystals was determined using the JMAK equation for crystals of elongated shape [13].

Table 1

Composition of *hypo*, *hyper* and *stoich* glasses obtained by DSC and by inductive plasma spectrometry (ICP)

Glass	DSC Mol% Li ₂ O (± 0.7)	ICP Mol% Li ₂ O (± 0.5)	Average composition Mol% Li ₂ O
<i>hypo</i> (1)	33.0	32.0/32.5	32.5
<i>stoich</i> (2, 3)	33.2/33.2	33.4/33.2	33.3
<i>hyper</i> (4, 5)	34.3/34.6	34.8/34.2/35.0	34.6

these were not clearly identified so far and the role metastable phases play with respect to the crystallization mechanism remains unclear. In particular, there is considerable uncertainty over whether metastable phases form and serve as precursors for subsequent precipitation of the stable LS₂ phase (which could partially explain the apparent failure of CNT), or if the precipitation of the stable phase occurs concurrently and independently of the formation of metastable phases.

In this paper we shed further light on the complex crystallization mechanism of lithium disilicate glasses. We observe the very early stages of crystallization (<1 vol.% crystallized fraction, as shown in Fig. 2) using TEM/SAED, and present XRD results for samples with higher crystalline fractions (up to 35 vol.%), thus overlapping both techniques. The main objective is to systematically identify the crystallization pathways and the possible formation of metastable phases in the glass volume, in an attempt to explain the controversies of the previous studies.

2. Experimental

Three lithium silicate glasses nearby the Li₂O·2SiO₂ composition were prepared using standard reagent grade Li₂CO₃ (Aldrich Chem. Co., 99+%) and ground Brazilian quartz, >99.9% SiO₂. The 200 g batches were melted in a Pt crucible at 1450 °C for 2 h in an electric furnace. To ensure homogeneity, the poured glasses were ground and remelted at the same temperature for one additional hour. The melts were quenched by pressing between steel plates. Subsequent chemical analysis revealed the composition of the prepared glasses to be 32.5 ± 0.5 mol% Li₂O (*hypo*), 33.3 ± 0.5 mol% Li₂O (*stoich*) and 34.6 ± 0.5 mol%

Li₂O (*hyper*) as shown in Table 1. They are hypo-stoichiometric, stoichiometric and hyper-stoichiometric, respectively. These chemical analyses were repeated twice, and to obtain more accurate results we also performed differential scanning calorimetric (DSC) experiments according to a procedure proposed by Fokin and Ugolkov [28]. Bulk pieces of glass (≈40 mg) were analyzed in a Netzsch 404 DSC, using Pt crucibles and 10 K/min heating rate. The crystallization peak temperatures were related to molar fractions of Li₂O. Results are shown in Fig. 3.

Heat treatments were carried out in a vertical tube furnace with the temperature controlled within ±1 °C. Samples were given single stage heat treatments at the temperature of maximum nucleation rate, $T_g = 454$ °C for periods of 2.5, 5, 10, 20, 50, 120 and 312 h for the TEM; and 120, 240, 360, 480 and 600 h for the XRD experiments. The crystallized surface layer of the heat-treated glass samples, which may have foreign phases, was removed before characterization.

We used two methods to prepare TEM samples. The crushing method, based on Ref. [29], where a few grams of glass were crushed into fine powder using an agate mortar. The resulting fine powder was then dispersed in pure ethyl alcohol in a 50 ml beaker by keeping the solution in an ultrasonic bath for a few minutes. A carbon coated 200-mesh TEM copper grid was placed on a wire support inside the beaker. The suspension decanted on the grid. After its removal from the beaker the alcohol evaporated, leaving the glass particles adhering to the grid surface. We also used the chemical thinning method, where ≈150 μm thick discs of 3 mm diameter were dimpled up to 10 μm, and then chemically thinned in a solution of 15HF–5HCl–75H₂O (by vol.%). Once perforation occurred, the samples were washed in ethyl alcohol and distilled water.

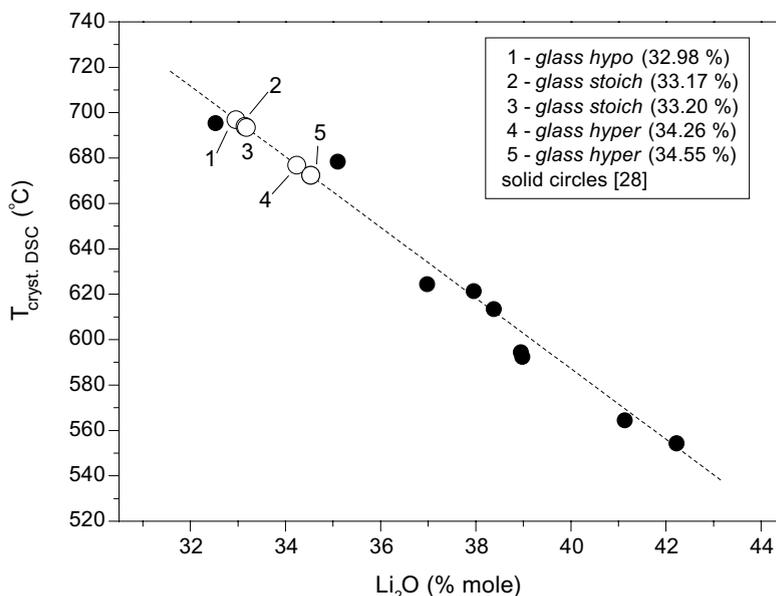


Fig. 3. DSC crystallization peak temperature as a function of glass composition: (●) Fokin's glasses [28]; (○) glasses *hypo*, *hyper* and *stoich*.

TEM analysis was carried out at 120 kV using a Philips EM-420T microscope at Lehigh University, USA and a Philips CM120 microscope at the Universidade Federal de São Carlos, Brazil.

XRD data were collected on monolithic samples on two different equipments: (i) a conventional Rigaku RU2000 diffractometer, using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at 50 kV and 100 mA, where the samples were scanned from 15° to 45° , in steps of 0.02° for 3 s; (ii) a synchrotron radiation source at LNLS, Campinas, Brazil, where the samples were scanned from 10° to 32° ($\lambda = 1.48 \text{ \AA}$).

3. Results

The selected area diffraction patterns were indexed using a commercial software [30] based on the method described by Goodhew [31] and Beeston et al. [32], with structure details from the ICSD database [33]. Gold standard samples were used for the camera length calibration. Indexing of the phases was performed using the lattice constants listed in Table 2.

Among all known phases listed in Table 2, we observed through TEM two different crystalline phases in all samples heat-treated from 2.5 to 120 h at 454°C , which were indexed as LS_2 (from Liebau [34] and De Jong et al. [35]) and LS (from Hesse [37]). According to the phase diagram, at temperatures below 550°C , the LS phase should not appear as a stable phase in the three glasses (*hypo*, *stoich* and *slightly hyper*). Hence LS is a metastable phase in these glasses.

Examples of bright field TEM micrographs of crystals and their related electron diffraction patterns are shown in Figs. 4 and 5. Fig. 4(a) shows a lithium metasilicate crystal observed in a *stoich glass* sample treated for 20 h at 454°C . The corresponding electron diffraction (Fig. 4(b)) reveals that the crystal was oriented with the $[001]$ plane parallel to the beam direction. Fig. 5(a) shows a lithium disilicate crystal observed in a sample of *hyper glass* (nucleated at 454°C for 312 h), indexed with the $[312]$ plane parallel to the beam direction. After 312 h at 454°C ($\alpha \approx 3\%$), we observed several crystals with sizes ranging from 0.5 to $7 \mu\text{m}$ in chemically thinned samples of the *hyper glass*. All the crystals observed were identified as stable LS_2 .

Table 2
Crystallographic data for lithium silicate phases

Phase	Crystalline system	Space group	a, b, c (Å), β (°)	Ref.
$\text{Li}_2\text{Si}_2\text{O}_5$ (LS_2)	Monoclinic	Cc	5.82, 14.66, 4.79, 90.08	Liebau [34]
$\text{Li}_2\text{Si}_2\text{O}_5$ (LS_2)	Orthorhombic	Ccc2	5.81, 14.58, 4.77	De Jong et al. [35]
$\text{Li}_2\text{Si}_2\text{O}_5$ (LS_2)	Monoclinic	–	5.73, 14.64, 4.79	Deubener et al. [25]
$\text{Li}_2\text{Si}_2\text{O}_5^*$ (LS_2^*)	Orthorhombic	Pbcn	5.68, 4.78, 14.65	Smith et al. [36]
Li_2SiO_3 (LS)	Orthorhombic	Cmc2 ₁	9.39, 5.4, 4.66	Hesse [37]
Li_4SiO_4 (LS_4)	Monoclinic	P2 ₁ /m	5.14, 6.1, 5.3, 90.5	Vollenkl et al. [38]
$\text{Li}_4\text{H}_2\text{Si}_2\text{O}_7$	Tetragonal	P-42 ₁ m	7.6, 7.6, 5.1	Vollenkl et al. [39]

*Metastable.

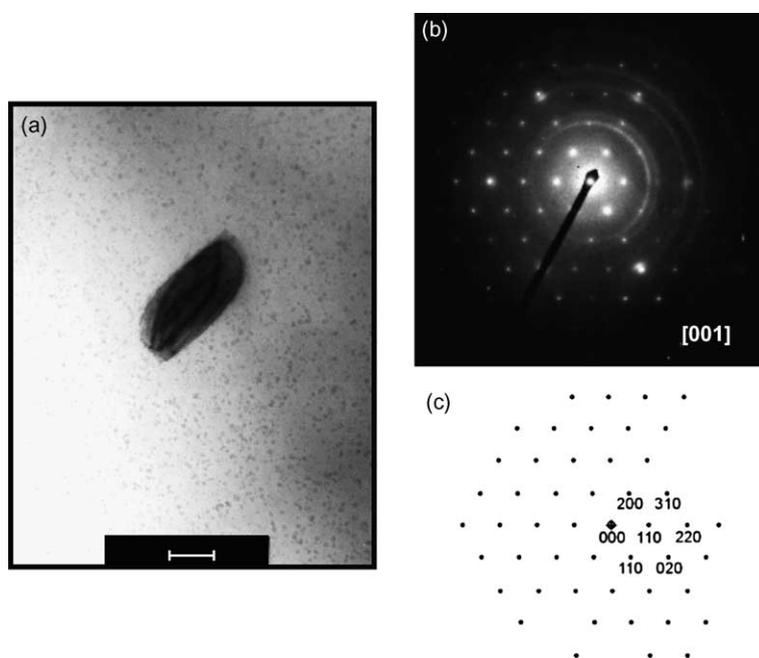


Fig. 4. TEM micrograph of the stoichiometric glass (33.3 mol% Li_2O) heat-treated for 20 h at 454 °C: (a) bright field image; (b) corresponding electron diffraction pattern; (c) indexed as LS phase in the $[001]$ direction. The bar denotes 150 nm.

One could imagine that the LS crystals were in some way dissolved chemically, but then they were observed clearly in chemically thinned samples heat-treated at 454 °C for 10 and 20 h (*hypo* and *hyper* glasses).

Fig. 6(a) shows the XRD results of the *hyper* glass samples heat-treated at 454 °C for longer periods than the TEM treatments. There is no crystalline material detected in the sample heated for 120 h ($\alpha \approx 0.07\%$). Diffraction peaks start to emerge against the amorphous background after heating for 240 h (estimated volume fraction

crystallized $\approx 1\%$). These peaks were identified as the stable LS_2 phase (JCPDS 40-0376). After further heating, at 360, 480 and 600 h (5, 16 and 35 vol.% crystalline fraction, respectively) the intensity of these peaks increased. Results from synchrotron radiation XRD showed only the LS_2 phase (Fig. 6(b)).

4. Discussion

Fig. 7 shows the observed crystal size of the largest crystals of both phases as a function of heat

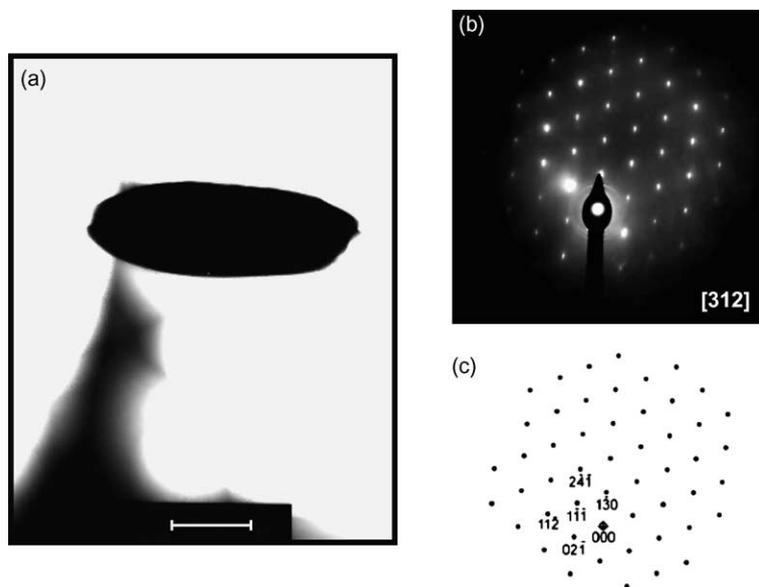


Fig. 5. TEM micrograph of the hyper-stoichiometric glass (34.6 mol% Li_2O) heat-treated for 312 h at 454 °C: (a) bright field image; (b) corresponding electron diffraction pattern; (c) indexed as the LS_2 phase in the $[3\ 1\ 2]$ direction. The bar denotes 2 μm .

treatment time at 454 °C in *hypo*, *hyper* and *stoich* glasses. From Fig. 7 we find that the metastable LS phase (open symbols) appears simultaneously with the stable LS_2 phase in all samples up to 120 h (<1 vol.% fraction crystallized). The growth rate of LS (slope of the curve) is nearly zero. On the other hand, the size of the LS_2 crystals follows reasonably well the estimated values of D_{max} (maximum diameter of crystals) using extrapolated crystal growth rate data from higher temperatures [40].

Fig. 8 shows the relative frequency of occurrence (number of crystals of each phase divided by the total number of crystals) of both phases with heat treatment time, including all indexed crystals of all samples. Despite the poor statistics (on average only a dozen crystals were detected in the TEM samples for each treatment time), we observe that up to 20 h, the relative number of LS crystals is larger than LS_2 . This number decreases with increasing treatment time and, in spite of this decreasing LS/ LS_2 ratio, LS crystals are still present at 120 h (0.07 vol.% crystallized fraction). After 312 h (3 vol.% crystallized fraction), only the stable LS_2 phase is observed. These results show that both phases coexist in the early stages of crystallization in glasses around the lithium disilicate

composition. For the three glasses LS is a metastable phase. Therefore, the following two possible situations could occur:

- (i) There is simultaneous homogeneous nucleation of LS_2 and LS phases, but LS phase disappears at some point during the heat treatment. In this case LS is a metastable phase that does not affect the nucleation path of LS_2 ;
- (ii) The LS crystals nucleate first and then the LS_2 crystals nucleate heterogeneously over the LS. This mechanism could partially explain the failure of the classical nucleation theory.

The fact that lithium metasilicate forms initially in a larger number than the disilicate phase was suggested before by Hench et al. [14]. A reasonable argument is that $[\text{-SiO}_2\text{-}]$ units (Q^2 chains, typical of LS) are more readily organized than the Q^3 layers present in the disilicate (here Q^n refers to SiO_4 units with n bridging oxygens). It has also been suggested that the formation of the lithium metasilicate phase enriches the glass matrix in SiO_2 increasing the glass viscosity in its vicinity, which presumably restricts the growth. Based on the present results, the mechanism proposed is that

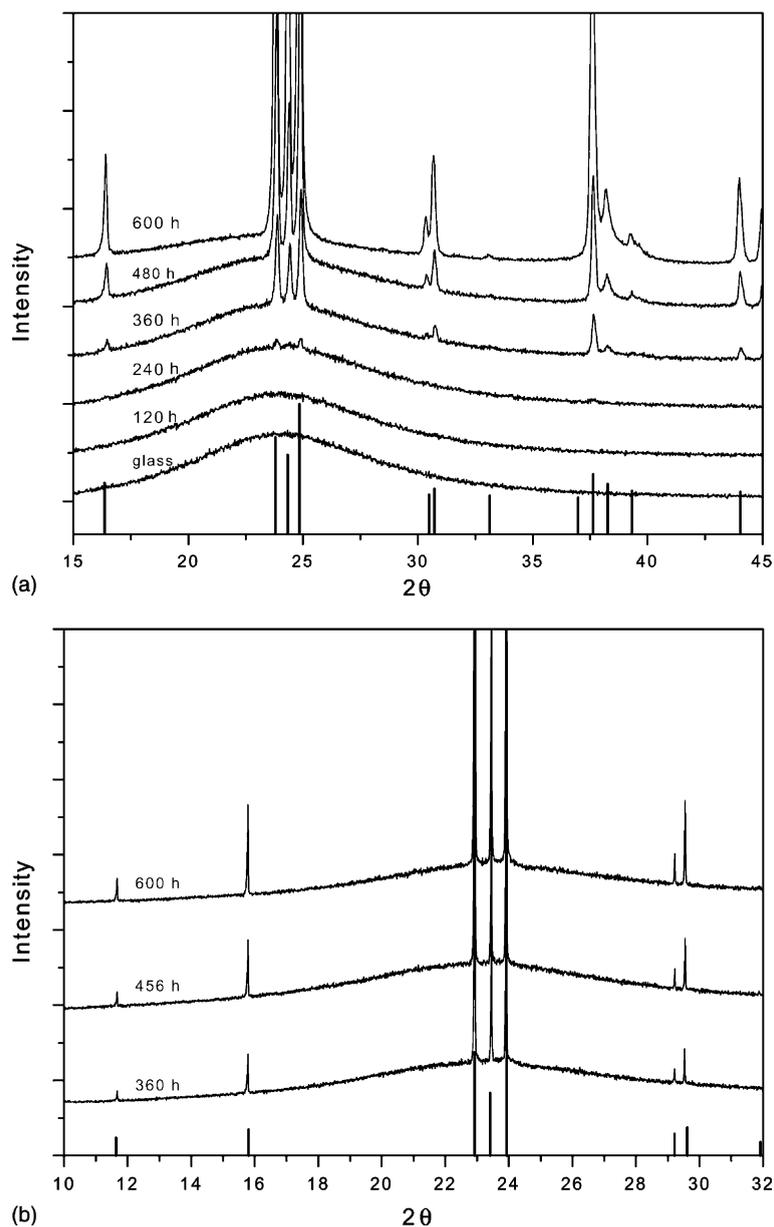


Fig. 6. XRD diffraction patterns of the *hyper glass* samples heated at 454 °C for 120–600 h. Vertical lines correspond to LS_2 pattern from JCPDS 40-0376. Using: (a) conventional diffractometer, (b) synchrotron radiation.

both phases nucleate concurrently at the very early stages of nucleation (up to 10 h at 454 °C), but LS overcomes LS_2 due to the ease of its formation. As the treatment time increases, nucleation and growth of LS becomes restricted, as shown by its almost zero growth rate (Fig. 7). The relative

number of LS crystals decreases, and they are no longer observed after 120 h at 454 °C. As significant amount of glassy phase remains after 312 h at 454 °C (97 vol.% glassy), we can thus safely state that equilibrium has not been reached and that lithium metasilicate is a metastable phase that will

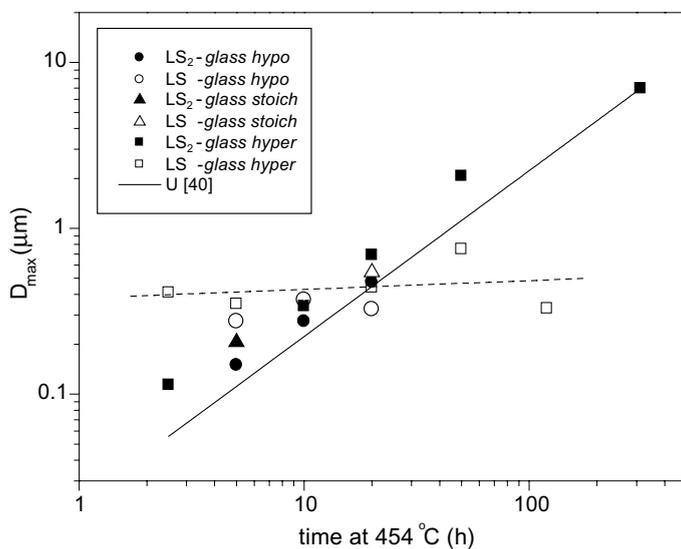


Fig. 7. Maximum dimension (D_{\max}) of the largest crystals observed by TEM in samples of *hypo*, *stoich* and *hyper* glasses as a function of heat treatment time (in hours) at 454 °C. U refers to calculated D_{\max} using extrapolated crystal growth rate data from higher temperatures [40].

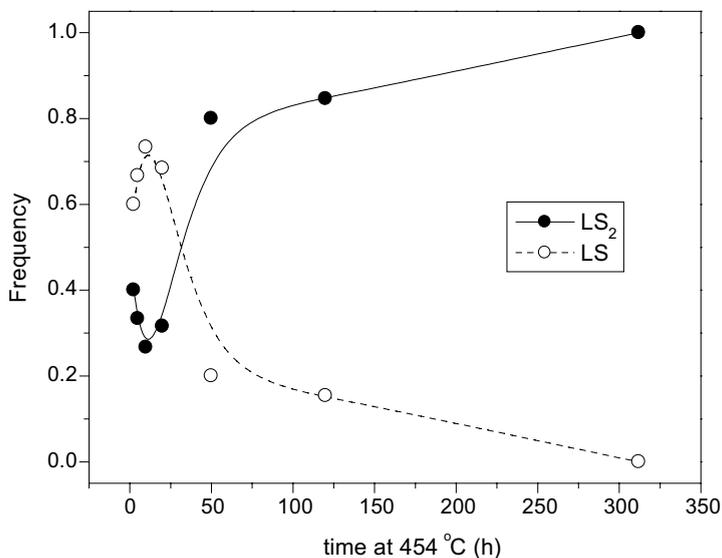


Fig. 8. Ratio of number of crystals observed for each phase by the total number of crystals found in all samples as a function of treatment time.

disappear at some stage. We thus have no evidence that the lithium metasilicate crystals induce heterogeneous nucleation of lithium disilicate.

As in general, nucleation treatments are carried out for short times, typically less than 20 h at $\approx T_g$ before the growth treatment, our results show that

up to 20 h at 454 °C the LS phase is dominant and, therefore, the measured nucleation rates often reported in the literature could, in principle, reflect the kinetics of precipitation of LS and not of LS₂. However, XRD results for double-treated samples (as in most published research) reveal only LS₂. A sample of the *stoich* glass was treated at 454 °C for 10 h (temperature with the highest LS/LS₂ ratio) and then at 600 °C for 30 min. Only the LS₂ phase was detected, showing that LS dissolves in the second heating path.

5. Conclusions

We studied the early and intermediate stages of crystallization of *hypo*, *hyper* and *stoichiometric* lithium disilicate glasses heat-treated at $T_g = 454$ °C for 2.5 to 600 h (≈ 35 vol.% crystallized fraction). TEM analyses of specimens provided clear evidence of a second phase, viz. lithium metasilicate (LS), which nucleates simultaneously with the stable LS₂ phase.

The LS/LS₂ ratio decreases with heat treatment time up to 120 h (< 0.1 vol.% crystallized fraction). These results support the following crystallization mechanism: in the early stages there is concurrent homogeneous nucleation of both phases (LS and LS₂), but LS phase disappears at some point during heat treatment. In this case, LS is a metastable phase (in all glasses in the vicinity of lithium disilicate composition) that does not play a role in the nucleation path of LS₂, and thus cannot explain the discrepancy between the theoretical and experimental crystallization kinetics.

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