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Metastable phases in lithium disilicate glasses

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Abstract

This article deals with crystal nucleation in glass, with special emphasis on new findings about metastable phase formation in lithium disilicate glass (LS_2) and its effects on crystallization of the stable LS_2 crystal phase. The early crystallization stages of slightly sub-stoichiometric LS_2 glasses were probed with SAXS and selected area diffraction (SAD). The second task was accomplished by carefully measuring the crystal nucleation rate (I), growth rate (U), the time evolution of crystallinity and the apparent induction periods (t') for crystal nucleation and growth at 500°C ($T_g \sim 450$°C). Finally, the independently determined kinetic parameters (I and U) were used in a modified form of the JMAK equation, which account for transient nucleation conditions, to test the nucleation mechanism. Depending on the heat treatment, one or more metastable phases precipitate in the early crystallization stages of LS_2 glass, however, they do not play a significant role on the crystallization mechanism of the thermodynamically stable phase. © 1997 Elsevier Science B.V.

1. Introduction

Controlled crystallization of glasses can lead to a wide range of glass-ceramics having unusual microstructures and properties. From a more fundamental point of view, the vitreous state is only attainable when crystallization can be avoided during synthesis. Hence, the scientific and technological importance of understanding and controlling the *crystallization mechanisms* of glass is crucial. Additionally, the failure of the classical nucleation theory to quantitatively describe crystal nucleation rates in glasses could be attributed to several reasons, including the fact that the nucleus/glass surface energy may be size dependent. Another possibility to explain the discrepancy is the birth of *metastable phases* in the early crystallization stages, before the appearance of the equilibrium phase [1].

Several issues on the subject, including effects of amorphous phase separation on crystal nucleation and growth, applicability of both the classical nucleation theory (CNT) and the theory of overall transformation kinetics (JMAK theory) to glass crystallization, some trends on homogeneous and heterogeneous crystal nucleation, and the status of surface nucleation and crystallization of oxide glasses [1–3] were previously reviewed.

The main questions addressed here concern the crystallization mechanism of glass (lithium disilicate is used as a significant example): (i) Does any metastable phase form in the initial crystallization stages of glasses?; (ii) if so, does it lead to heterogeneous nucleation of the stable crystal? These two points are discussed in the following way: First we probe the early nucleation stages of LS_2 by small angle X-ray scattering (SAXS) and selected area

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2. The quest for a metastable phase

Regarding the possibility of metastable phase formation, the case of lithium disilicate glass is particularly interesting because several authors have proposed the appearance of metastable phases in LS_2 or in neighbor compositions. For instance, Kalinina et al [4], based on XDR results for both sub and super-stoichiometric LS_2 glasses; and Hench et al. [5,6], based on SAXS patterns and electrical behavior of similar compositions, suggested the appearance of a metastable phase for certain heat treatments.

In a systematic study of crystal nucleation in glasses containing between 33.3 and 40.0 mol% Li_2O, Barker et al. [7] concluded that it was unlikely that the primary nucleation in the 33.3 and 36.0 mol% lithia glasses would be a metastable precursor phase upon which the lithium disilicate would nucleate heterogeneously. In a similar type of study, Kalinina et al. [8] proposed a contrasting explanation.

Interest in the subject has recently been reawakened by the report of Deubener et al [9] who observed a difference of two orders of magnitude between the apparent induction periods (t') for nucleation and crystal growth in LS_2 at 490°C, while for two soda–lime–silica glasses these periods were similar. They concluded that the difference in t' was due to previous nucleation of a metastable phase in LS_2 glass which was confirmed by electron diffraction of glasses treated at 454°C. Deubener et al. [9] thus concluded that nucleation of the stable LS_2 crystal was heterogeneous. However, Deubener [10] later mentioned that his diffraction patterns were obtained very quickly due to fast degradation of the crystals under the electron beam. Thus a long standing dispute exists concerning the nucleation mechanism of LS_2 glass.

Although the experimental evidence presented in the previous studies was not too strong, for the understandable reason that the amount of a potential metastable phase in the glass could be quite small, I was intrigued by the fact that several researchers suggested the appearance of a transient phase in LS_2. Thus, my co-authors and I have performed a series of SAXS and electron diffraction experiments.

2.1. SAXS experiments

Pioneering SAXS work of Hench et al. [6] in the early seventies, suggested the existence of a transient phase in a sub-stoichiometric 33% Li_2O glass. The integrated SAXS intensity reached a peak after about 6 h at 500°C and then decreased with further treatment, which was attributed to the birth and dissolution of a metastable phase. However, the use of an X-ray beam having a linear cross-section, obliged them to carry out a series of corrections that, in principle, could render the interpretation of the weak scattering curves quite troublesome. Hence, keeping that possibility in mind, we decided to repeat the SAXS experiments using a powerful point like X-ray beam at a synchrotron facility.

An LS_2 glass whose composition was within 0.1 mol% of the perfect stoichiometry was treated at 500 ± 2°C for periods between 2 and 50 h and studied by SAXS [11]. Weak but reproducible scattering was detected, indicating the presence of particles having a different electronic density from the LS_2 glass matrix. The gyration radius of the scattering particles, determined from Guinier plots, varied slowly with time, from about 135 to 155 Å, for 2 and 50 h of treatment, respectively. Hence an estimated average growth rate of 10^{-14} m/s is anticipated.

The integrated SAXS intensities, Q, were calculated as a function of treatment time, for two sets of specimens, treated independently. The results of Fig. 1 show a reproducible peak in both curves (■, ▲) at about 8 h. It also shows the results of Hench et al. (×) with a maximum at about 6 h.

Q is related to the specimen microstructure by [11]

$$Q = \int_0^\infty I(q)\, q^2\, \mathrm{d}q = (\rho - \rho_0)^2 N_v v, \qquad (1)$$

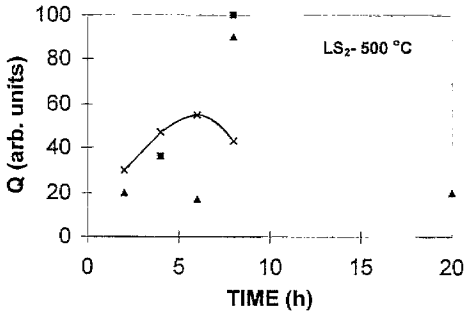

Fig. 1. Integrated SAXS intensity as a function of treatment time at 500°C for a glass with 33.2 mol% Li_2O. The different symbols (▲, ■) denote two distinct experiments using two specimen sets. The data of Hench et al. [6] for a glass with 33 mol% Li_2O are shown by the continuous line marked by crosses (×).

where q is the modulus of the scattering vector, $I(q)$ the experimental SAXS intensity, $(\rho - \rho_0)$ is the electronic density difference between the scattering particles and the vitreous matrix, N_v is the number of particles per unit volume and v the average particle volume. Since R_g (and v) increase continuously, the peak in the Q versus time curve must be related to a change in $N_v(\rho - \rho_0)^2$. That behavior indicates that X-ray scattering was not due to stable LS_2 crystals, because the number of those crystals increase continuously with treatment time, which would not lead to a peak in Q. Additionally, the observed crystal growth rate of LS_2 crystals at 500°C (10^{-10} m/s [12]) is much larger than the estimated value of 10^{-14} m/s from the SAXS plots. Hence, the time dependence of Q suggests a process of formation and coalescence or dissolution of particles having an electronic density different from the glass matrix. This suggests a simultaneous precipitation of a (unidentified) metastable phase together with the LS_2 phase.

2.2. Electron diffraction

A glass with 40 mol% Li_2O was prepared and heated to 480°C for 24 h to crystallize both lithium metasilicate, LS (a suspected metastable phase in a glass with 33.3 mol%) and LS_2. These crystal phases were used as electron diffraction standards, since we were searching for those two phases, as well as for any other (metastable) phases in the candidate glass.

Table 1
Lattice parameters of a metastable phase (MS), LS and LS_2 [9,16]

Crystal	a (Å)	b (Å)	c (Å)	Theta	Ref.
LS_2	5.82	14.66	4.79	90.08°	[16]
LS	9.36	5.40	4.68	90.00°	[16]
MS	9.16	5.43	9.08	–	[9]
LS_2	5.7	15.1	4.7	–	this work
MS^1	8.2–8.7	4.7–5.1	–	–	this work
MS^2	6.3	3.6	–	–	this work

MS^1 values obtained from nine diffraction patterns.

Subsequently, a slightly sub-stoichiometric lithium disilicate glass, having 32.5 ± 0.5 mol% Li_2O, was prepared and treated at the temperature of maximum nucleation rate, 454°C, for periods of 5 to 20 h. These treatments produced crystals having maximum diameters of about 0.6 μm. In some cases, a development treatment at 610°C was also used. As it is extremely difficult to prepare an absolutely stoichiometric composition (33.33333 mol% Li_2O), a sub-stoichiometric glass was chosen for this study because LS should precipitate as a stable phase in hyper-stoichiometric glass.

The heat-treated specimens were cut into 500 μm thick slices, ground and polished with CeO_2 to 10–20 μm. They were then chemically thinned with a HF 25% solution, for 1–3 min, until a hole appeared in the center, as described by Soares Jr. et al. [13,14]. Next they were coated with about 3 nm Au, used to calibrate the diffraction camera constant, and examined in a Jeol 100 kV microscope. The diffraction patterns were obtained in the selected area diffraction (SAD) mode. Indexing based on the methods

Table 2
Crystal phases in sub-stoichiometric LS_2 glasses

T (°C)	t (h)	Crystal phase	Figure
Glass 32–33% Li_2O (analyzed)			
454	5	MS^1	Fig. 2a
454	10	MS^1	–
454	20	$MS^1 + LS_2$	–
454/610	20/1 min.	LS_2	Fig. 2b
Glass 33.3% Li_2O (nominal)			
454	10	$MS^2 + LS$	–

MS^1 and MS^2 = metastable phases.

described by Beeston et al. [15] and the resulting patterns were compared with simulations performed by a home-made software.

The diffraction patterns were indexed on the basis of the lattice parameters shown in Table 1 [16]. The analysis of the diffraction spectra are shown in Table 2.

The diffraction pattern of Fig. 2a clearly shows a metastable phase (MS^1) in a glass treated for 10h at 454°C. Another phase (MS^2) having smaller lattice parameters than MS^1 (only a and b; c has not been measured yet) was also detected in the same glass. For longer treatments or at a higher temperature, the number of MS crystals decreased dramatically and LS_2 crystals appeared more frequently. Fig. 2b shows a diffraction pattern of a LS_2 crystal. A more complete account of these findings will be given in [13,14].

In summary, metastable phases may precipitate in LS_2 glasses, depending on the thermal treatment. These preliminary results confirm the findings of Deubener et al [9], although the lattice parameters do not match perfectly. Additionally, in a paper published in this same issue, James et al. describe the appearance of polymorphs of the stable phase, LS_2, in a glass having 33.9% Li_2O heat treated for 120–

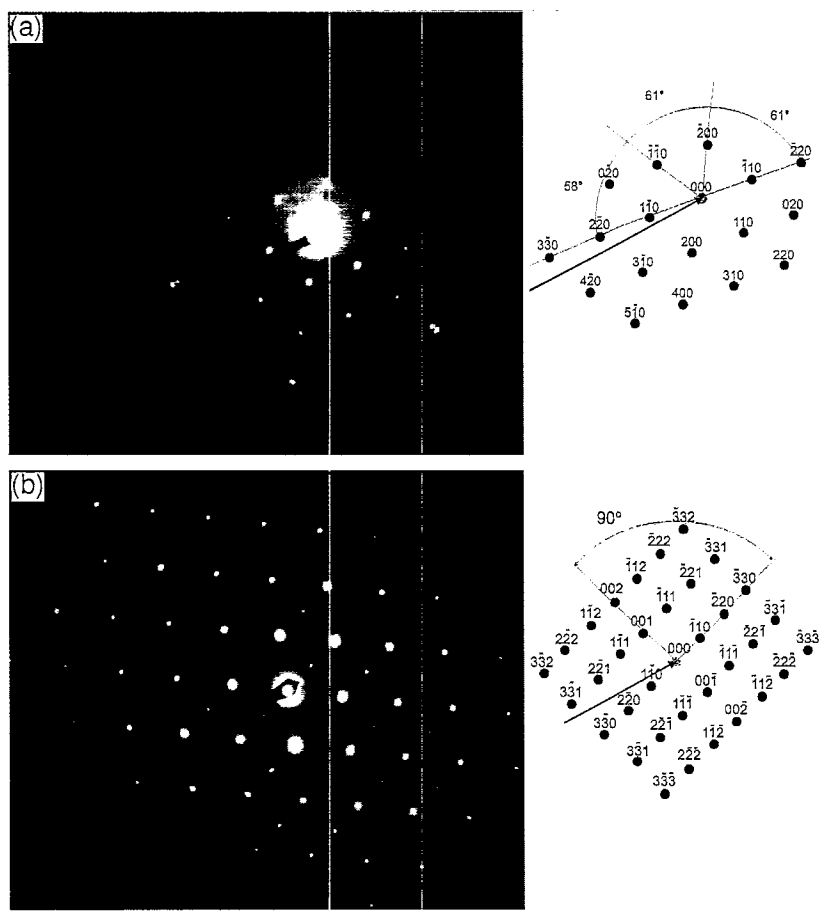

Fig. 2. (a) 33.1 mol% Li_2O glass heat treated at 454°C for 5 h. Selected area diffraction pattern of the LS phase. Electron beam direction [001]. (b) 33.1 mol% Li_2O glass heat treated at 454°C for 20 h plus a development treatment at 600°C for 1 min. Selected area diffraction pattern of the LS_2 phase. Electron beam direction [110].

550 h at 454°C. For longer treatments, only the stable LS_2 crystal was found.

3. The influence of the metastable phases on the crystallization kinetics of the stable LS_2 crystal

To check whether the metastable phases would affect the crystallization kinetics of the stable LS_2 crystal, we performed detailed nucleation, growth and overall crystallization experiments, described in the next sections.

Specimens of a LS_2 glass, having 33.2 mol% Li_2O [12], were heated at 500°C for periods of 5 to 95 h. The samples treated for short periods — 5 to 20 h — were also subjected to a 'development' treatment at 600°C for 10 min. The other specimens were treated only once (single stage). After polishing and etching, the specimens were characterized by both transmitted light (TLM) and reflected light microscopy (RLM) in a Neophot–Carl Zeiss Jena-microscope equipped with a 25 × objective for RLM and with a 100 × objective lens for TLM. About 700 crystals were counted and measured per specimen, which led to a statistical scatter of about 15%. Standard stereological procedures were employed for the determination of average number of crystals per unit volume, N_v, and largest crystal dimensions and volume fraction transformed. The single-stage data were corrected due to stereological errors [12].

3.1. Crystal nucleation behavior

The coincidence of the data points obtained by the two microscopy techniques (TLM-ST and RLM-ST) was excellent. The steady-state nucleation rates at 500°C (784–800/mm^3 h) were calculated from the slopes of N_v vs. time plots [12]. The apparent induction periods estimated from the intercept on the time axis were $t_n \sim 3.0$ and 2.4 h, for TLM-ST and RLM-ST, respectively. A composite curve, using the RLM-ST and TLM-ST data yield $I = 807/\text{mm}^3$ h and $t_n = 3.3$ h. For the double-stage method, RLM-DT, $I = 770/\text{mm}^3$ h and $t_n = 0.027$ h. Thus, the steady-state nucleation rates obtained with the three methods were very similar, while there was a pronounced difference in the non-stationary nucleation periods determined by single-stage and double-stage treatments.

3.2. Crystal growth behavior

Assuming the continuous ballistic model for crystal growth, which predicts a size dependent growth rate, Weinberg [17] demonstrated that unlike the case of transient nucleation, the induction time for crystal growth, t_g, cannot be uniquely defined and is dependent upon experimental conditions. If one attempts to determine t_g by a linear extrapolation of crystal growth data (radius vs. time plots) to the time axis, then the value of t_g which is found will depend upon the time regime where the growth data was obtained. The larger the crystal size, the larger will be the apparent value of t_g.

Despite that fact, in practice, the size dependence predicted by the ballistic model nearly ceases for crystals larger than a few nanometers. Thus, as we dealt with micron size crystals, we decided to determine t_g in an attempt to compare it with the values of the induction times, t_n, obtained from the nucleation plots [12].

The crystal growth curves for both major and minor half-axes of the ellipsoidal crystals, obtained with single-stage treatments at 500°C, with both techniques (RLM and TLM) were shown in [12]. The composite plots (using TLM + RLM data) were good straight lines and yield growth rates: $U_a = 0.00038$ mm/h, with an apparent induction period $t_g = 2.0$ h from the time intercept for the major ellipsoidal axis, and $U_b = 0.00020$ mm/h and $t_g = 0.7$ h for the minor axis measurements. Thus, within the accuracy limits of our technique, the apparent induction time, inferred from the growth plots, lie in between 0.7 and 2.0 h.

Coincidentally, therefore, the induction periods obtained from nucleation and growth experiments were quite similar, within the error limits, when they are measured using the same procedure, i.e., with a single-stage treatment. Hence, the apparent discrepancy, when the transient period is estimated from nucleation (double-stage) and growth (single-stage) experiments, merely reflects the difference in the experimental techniques.

3.3. Overall crystallization behavior

To infer the nucleation mechanism, the overall volume fractions crystallized of the stable LS_2 crystals were followed in the same specimens employed

for nucleation and growth determinations. As the LS_2 crystals are prolate ellipsoids, for the case of constant nucleation and growth rates (*homogeneous nucleation*), the general JMAK equation reduces to

$$\alpha = 1 - \exp[-Kt^4], \tag{2}$$

where $K = \pi I U_a U_b^2/3$ and U_a and U_b ($U_b \sim U_c$) are the growth rate of the major and minor half-axes of the ellipsoidal crystals, respectively [18]. For *fast heterogeneous nucleation* from a fixed number of sites N_0 per unit volume, $K = 4\pi N_0 U_a U_b^2/3$ and the time exponent should be 3 instead of 4.

Gutzow et al. [19] proposed that Eq. (2) should be corrected by the induction time t_n when non-stationary nucleation effects are significant, to give

$$\alpha = 1 - \exp\left[-K(t - t_n)^4\right]. \tag{3}$$

This equation takes into account the transient nucleation period while it assumes that the growth rate is independent of crystal size.

In a recent publication, Shneidman and Weinberg [20] have shown that Eq. (2) should also be corrected by the fact that there is always a size dependent growth rate coupled to a non steady-state nucleation period. Their final equation reads

$$\alpha = 1 - \exp\left\{-Kt^4\left[1 - (\tau/t)\ln\left[(w^*/kT) \times (t/\tau)\right]^4\right\}\right\}, \tag{4}$$

where τ is the transient time and w^* is the work of formation of a critical nucleus. From a fit to the published experimental nucleation curve (I vs. T), using a temperature dependent surface energy, I found that $w^*/kT \sim 40$ for LS_2 at 500°C. However, for that value of w^*/kT the correction predicted by Eq. (4) should be negligible [20]. hence I only use Eq. (3) in the following analysis.

Fig. 3 shows the experimental volume fraction crystallized, determined by reflected light optical microscopy (■), as well as the curves calculated by Eq. (2) for the limiting cases of homogeneous (t^4) and fast heterogeneous nucleation (t^3), for situations where the crystal growth rate is independent of time and crystal size. The experimental values of the crystal nucleation rate (I) and growth rates (U_a and U_b), independently measured by reflected light microscopy, were used in the calculations. For the heterogeneous nucleation case $N_0 = 500$ crystals/mm^3 was used to give a good fit to the first data points. Fig. 3 also shows the values of crystallinity predicted by the expression of Gutzow et al. [19] — Eq. (3) — for situations where a time dependent nucleation rate prevails.

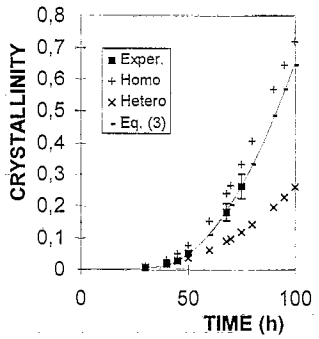

Fig. 3. Volume fraction crystallized of LS_2 glass at 500°C, determined by RLM (■), compared with values predicted by Eq. (2). +: Homogeneous nucleation with constant I and U; ———, omogeneous nucleation, Eq. (3), with $t_n = 5$ h; ×, fast heterogeneous nucleation, with $N_0 = 500$ sites/mm^3.

The previous discussions demonstrate that an apparent transient period of a few hours (2.4–3.3 h) was observed in the nucleation curve obtained with single-stage treatments. Hence, the induction time was left as the only adjustable parameter in Eq. (3). The best fit was obtained for $t_n = 5$ h. This value of induction period has the same magnitude as the induction time determined from the (single-stage) nucleation plot and merely reflects the time necessary for development of the critical nuclei to microscopic sizes at 500°C, as explained below.

The experimental time lag, t_n, determined by the x-axis intercept in N_v vs. time curves is composed of two terms:

$$t_n = b\tau + t_u, \tag{5}$$

where b ranges from $\pi^2/6$ to 0.5, depending on the mathematical solution employed, τ is the time required to establish a steady-state distribution of embryos, i.e., the nucleation incubation time and t_u is the time for growth of supercritical clusters to sizes detectable by optical microscopy. That time period (t_u) was estimated to be in the range 1.4 to 2.6 h [12] for LS_2 at 500°C. Nucleation incubation time, τ, estimated from a double-stage nucleation plot was only a few minutes [12]. Hence, the experimental

induction period t_n is mostly due to the time required for growth of the critical nuclei (a few Angstrom) to detectable (micron) sizes.

Taking into account the exponential sensitivity of Eq. (3) to U_a, U_b and I it can be concluded that the agreement between the experimental and predicted volume fraction crystallized is remarkably good up to 25% crystallinity, the limit of experimental determination in this work. Hence, crystallization of the stable LS_2 phase is well described by homogeneous nucleation.

4. Conclusions

SAXS and SAD experiments confirmed that metastable phases may precipitate concurrently with the stable LS_2 crystal in the early crystallization stages of slightly sub-stoichiometric lithium disilicate glasses. However, homogeneous nucleation is the predominant crystallization mechanism of the stable LS_2 crystal in LS_2 glass. Thus, the metastable phases do not induce heterogeneous nucleation of the stable phase, and play no significant role in overall crystallization kinetics.

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