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The nucleation mechanism of lithium disilicate glass revisited

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Abstract

Detailed nucleation, growth and overall crystallization data have been obtained for a lithium disilicate glass at 500°C, with both single-stage and double-stage heat treatments, employing reflected light and transmitted light microscopy. For single-stage treatments, the apparent ‘induction’ periods determined by these three independent kinetic measurements were quite similar (1–4 h). When double-stage treatments were used, an induction period of only a few minutes was found, which is close to the real incubation time for nucleation, reported by several authors. A calculation of the time required for growth of the critical nuclei to detectable sizes, performed with an expression which takes size dependent growth into account, resulted in a predicted time of about 1.4–2.6 h. Thus, the experimental (single-stage) induction period is mostly due to the time required for growth of the critical nuclei to sizes detectable by optical microscopy. The agreement between the experimental and predicted volume fraction crystallized was excellent for the case of homogeneous nucleation, confirming this crystallization mechanism for this glass. There was no sign of metastable phases or, alternatively, any phase that might have appeared in the early crystallization stages, had no significant influence on the overall crystallization kinetics of the equilibrium $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ crystal.

1. Introduction

Crystallization studies are important in a vast number of fields. For instance, geologists rely on ‘post-mortem’ analyzes of crystallization to understand the formation of minerals and solidified magmas. Controlled growth from seeded melts is frequently used to obtain commercially important single-crystals, such as silicon and lithium niobate. The final microstructure and properties of rapidly cooled metallic alloys strongly depend on the crystallization kinetics of the cooling path.

Turning to the glass field, the catalyzed crystal-

lization of vitreous materials can lead to a wide range of glass-ceramics having unusual microstructures and properties. From a fundamental point of view, the glassy state is only attainable when crystallization (the thermodynamically favorable path) can be avoided during synthesis. Thus the scientific and technological importance of understanding and controlling the crystallization mechanisms and kinetics of glasses is clear.

The failure of the classical nucleation theory to quantitatively describe crystal nucleation rates in glasses could, in principle, be assigned to the possible birth of metastable phases in the early crystallization stages, before the appearance of the equilibrium phase [1]. The case of lithium disilicate (LS_2) glass is particularly interesting in this respect because it is the most popular ‘model’ glass for crystallization

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studies, and several authors have proposed the appearance of metastable phases in LS_2 glasses or in neighbor compositions. For instance, in 1964, Kalinina et al. [2] observed spurious XRD peaks in substoichiometric LS_2 glasses treated for 96 h at 480°C; which were assigned to a metastable phase. Kinser and Hench [3,4], in 1971, suggested the existence of a metastable phase in similar glasses, treated for 5 h at 500°C, based on their SAXS patterns and electrical behavior. Recently, renewed interested on the subject was reawakened by the report of Deubener et al. [5]. These authors observed a difference of two orders of magnitude between the induction periods for nucleation and crystal growth at 490°C, while for other two glass families studied these periods were similar, concluding that the difference was due to the previous nucleation of a metastable phase. This point was confirmed by electron diffraction patterns of glasses treated at 454°C. Hence, Deubener et al. [5] concluded that nucleation of the stable LS_2 crystal was heterogeneous. However, Deubener [6] later mentioned that his diffraction patterns were obtained very quickly due to fast degradation of the crystals under the electron beam and, thus, the diffraction results were subject to uncertainty. Most evidence for the possible appearance of metastable phases in lithia–silica glasses is indirect. Additionally, from nucleation rate measurements in several glasses, containing between 33.3 and 40.0 mol% Li_2O , Barker et al. [7] concluded that no metastable phase appears before the stable LS_2 crystal. Thus a long standing dispute exists concerning the nucleation mechanism of LS_2 glass.

The objective of this paper is to clarify the nucleation mechanism of LS_2 glass and, in particular, to check the proposition for the early nucleation of a transient phase, as inferred from a large difference between the induction times for crystal nucleation and growth, observed in [5]. This task will be accomplished by carefully measuring the nucleation rate (I), growth rate (U), the time evolution of crystallinity and the induction times (t') for nucleation, growth and overall crystallization, with the purpose of checking whether the measured induction times for these processes are similar or not. Then, the independently determined kinetic parameters (I , U and t') will be used in the expression for the overall crystallization kinetics to test their consistency. That

theory may also allow us to decide on the nucleation mechanism, i.e., to test whether the early birth of a possible metastable phase might lead to heterogeneous nucleation of the stable crystal, as concluded in [5].

2. Theory

2.1. Nucleation, growth and overall crystallization

When a liquid is cooled below its melting point, crystal nucleation may occur homogeneously or heterogeneously, in the volume or on the sample surface. To understand and predict nucleation rates in undercooled liquids one often makes use of the classical nucleation theory (CNT), derived in the late 40 s by Turnbull and Fischer [8]. The subsequent step, crystal growth of the nuclei, can lead to a polycrystalline material. Hence, overall crystallization occurs by a combination of nucleation and growth. The kinetics of such process is usually described by a theory derived independently, in the late 30s, by Kolmogorov [9], Johnson and Mehl [10] and Avrami [11–13], best known as the Kolmogorov–Avrami or Johnson–Mehl–Avrami theory, hereafter called KJMA theory.

Avrami [11–13] has assumed that: (i) nucleation is random, i.e. the probability of forming a nucleus in unit time is the same for all infinitesimal volume elements of the assembly; (ii) nucleation occurs from a certain number of embryos (N) which are gradually exhausted. The number of embryos decreases in two ways; by growing to critical sizes (becoming critical nuclei), with rate ν per embryo, and by absorption by the growing phase; (iii) the growth rate (U) is constant, until the growing regions impinge on each other and growth ceases at the common interface, although it continues normally elsewhere.

Under these conditions, Avrami has shown that the volume fraction transformed, α , in isothermal conditions, is given by:

$$\alpha = 1 - \exp(-6gNU^3/\nu^3) \\ \times \left[\exp(-\nu t) - 1 + \nu t - (\nu t)^2/2 \right. \\ \left. + (\nu t)^3/6 - \dots \right],$$

where g is a shape factor, equal to $4\pi/3$ for spherical grains, and t is the time period.

There are two limiting forms of this equation, corresponding to very small or very large values of νt . Small values imply that the nucleation rate, $I = N\nu \exp(-\nu t)$, is constant throughout the transformation. Expanding $\exp(-\nu t)$ in Eq. (1) and dropping fifth and higher order terms gives

$$\alpha = 1 - \exp(-gIU^3t^4/4), \quad (2)$$

where $I = N\nu$. This is the special case treated by Johnson and Mehl [10] and is valid for N very large, when the number of embryos is not exhausted until the end of the transformation (homogeneous nucleation). Large values of νt , in contrast, means that all nucleation centers are exhausted at an early stage in the reaction. The limiting value of Eq. (1) is then

$$\alpha = 1 - \exp(-gNU^3t^3). \quad (3)$$

Thus, Eq. (3) applies for small N (fast heterogeneous nucleation). If the induction periods for crystallization, t' , are significant, then t should be replaced by $(t - t')$ in the above equations.

In the more general case, where I and U are time dependent, one may write

$$\alpha = 1 - \exp\left[-(4\pi/3) \int_0^t I(t^-) \left[\int_{t^-}^t U(t) dt \right]^3 dt^-\right], \quad (4)$$

where t^- is the time of birth of the new phase particles. The above treatment, while including the effects of impingement, neglects the effect of free surfaces, which are significant in thin specimens and powders. This problem was treated by Weinberg [14].

The KJMA theory can be shown to be exact within the framework of its assumptions. Hence, any violation must be a result of applying it to situations where its assumptions are violated, which may be the case in many crystallization situations. Recently, Zanotto and co-authors [15,16] carried out a series of experiments to test the applicability of the Kolmogorov–Johnson–Mehl–Avrami theory to two distinct cases of glass crystallization, homogeneous volume nucleation and surface nucleation of single-crystals. In the first case [15], the early crystallization stages of a $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ glass, were

well described by theory for the limiting case of homogeneous nucleation and interface controlled growth. For high degrees of crystallinity ($\alpha > 25\%$) both growth and overall crystallization rate decreased due to compositional changes of the glassy matrix, and the experimental kinetics could be described by theory only if diffusion controlled growth was assumed. It was concluded that if proper precautions are taken (i.e. if accurate I and U data are available) the general theory predicts well the glass-crystal transformation. In a second study [16], heterogeneous surface nucleation in a $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ (diopside) glass was followed. The evolution of the fractional area crystallized was well described by theory up to 65% crystallization, the limit of experimental evaluation. Hence, the KJMA also described well the case of rapid heterogeneous nucleation from a fixed number of sites at the glass surface.

In this study, we apply the KJMA theory to test the consistency of the experimental kinetic parameters of LS_2 glass at 500°C, with special emphasis in the induction period for crystallization. Additionally, the nucleation mechanism (homogeneous versus heterogeneous) of this glass will also be tested.

3. Experimental

The glass studied here was melted at 1350°C in a Pt crucible and contained 33.2 mol% Li_2O , 0.02 wt% ‘water’ and 0.01 wt% Na_2O , as the main impurities, the levels of Fe and Al being much lower [17]. Heat treatments were carried out in an electric furnace with a temperature control within 1°C. All specimens were heated at 500°C for periods from 5 to 95 h. Samples treated from 5 to 20 h were also subjected to a ‘development’ treatment at 600°C for 10 min, so the majority of the crystals could be seen under an optical microscope. After standard polishing and etching, the specimens were characterized by 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 an statistical scatter of around 15%, within 95% confidence limits. Standard stereological

procedures were employed for the determination of average number of crystals per unit volume N_v and largest crystal dimensions [15–17].

Depending on the heat treatment conditions, specially for single-stage treatments, many crystals (and also their two-dimensional planar cuts revealed in the RLM micrographs) might still be smaller than resolution limit of the microscope. This might lead to underestimated nucleation densities and volume fractions transformed and superestimated induction periods. Due to this problem all data were corrected by the equation derived by Zanotto and James [18] for *reflected light* microscopy,

$$N_v = N_{ve} / \left\{ 1 - (2R/\pi) \left[\ln((1 + \cos R)/R) + 1 \right] \right\}, \quad (5)$$

where N_v is the correct nucleation density (to be determined), N_{ve} is the experimental, uncorrected, nucleation density, and R (rad) is the ratio between the resolution limit of the microscope used and the largest crystal size measured in the micrographs, which should be equal to the largest crystal of the distribution in the specimen, for a given treatment.

The correction for *transmitted light* microscopy is simple given by:

$$N_v \cong N_{ve} + I_e \Delta t, \quad (6)$$

where $\Delta t = \varepsilon / (2U_a)$ is the ratio between the resolution limit of the microscope used ($\varepsilon \sim 0.3 \mu\text{m}$ for the $100\times$ objective) and U_a an estimate of the linear growth rate from half-length versus time curves. I_e is an estimate of the steady-state nucleation rate from the uncorrected N_{ve} versus time curves. In this work, the corrections for nucleation densities obtained from the TLM data were smaller than 3%, while those for the RLM data were between 6 to 14%. The systematic underestimation of the experimental volume fraction transformed was less than 1%, while the statistical scatter was about 15%.

4. Results

4.1. Crystal nucleation

Fig. 1 shows the corrected crystal nucleation density data of LS₂ glass specimens treated at 500°C

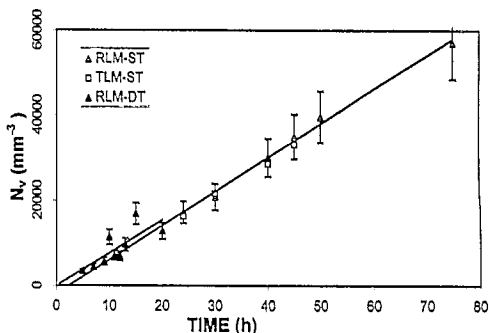


Fig. 1. Crystal nucleation curves for LS₂ glass at 500°C. The time axis intercept from the single-stage treatments (ST) data yield an apparent induction period of 2.4–3.0 h, while that from the double-stage (DT) treatment yield an induction time of only a few minutes. The single-stage points were corrected by Eqs. (5) and (6) for RLM and TLM, respectively.

($T_g \cong 450^\circ\text{C}$) for periods up to 20 h and subjected to a development treatment at 600°C for 10 min, the well known double stage treatment. The resulting microstructures were analyzed by reflected light microscopy (RLM-DT). The same figure also shows the data obtained from specimens heated for longer periods, from 24 to 75 h, with single-stage treatments, measured by both reflected (RLM-ST) and transmitted light microscopy (TLM-ST). Single-stage treatments are possible when crystal growth is sufficient to render the crystals large enough to be measured by optical microscopy, although many of them (the ones nucleated at the latest stages) might still be below the resolution limit of the microscope. Due to this problem all data presented here have been corrected by Eqs. (5) or (6).

The volume percentage crystallized of the specimen treated for 75 h was 26%, while those of the double-stage samples (before the development treatment) were less than 1%; usual for this type of treatment, because significant crystallization only proceeds during the development treatment. Thus, Fig. 1 probably shows the most complete nucleation curve ever reported for a glass at one temperature, where three different optical characterization techniques were used and a high volume fraction crystallized was reached.

It is worth mentioning that the linearity of the plot was maintained throughout the extensive range of treatment times and that the coincidence of the data

points obtained by the two techniques (TLM-ST and RLM-ST) was excellent. This detail was essential to infer the steady-state nucleation rates from the line slopes ($784\text{--}799/\text{mm}^3\text{h}$) and the induction periods from the intercept on the time axis ($t' \sim 3.0\text{--}2.4$ h, $r^2 = 0.994$), for TLM-ST and RLM-ST, respectively. For RLM-DT, $I = 770/\text{mm}^3$ h and $t' = 0.027$ h ($r^2 = 0.95$). A composite curve, using the RLM-ST and TLM-ST data gives $I = 807/\text{mm}^3$ h and $t' = 3.3$ h ($r^2 = 0.994$). If *uncorrected* RLM-ST data are used (not shown in the figure) an apparent induction period of 5 h comes out from the time axis intercept, in a clear demonstration of the essential need to correct the kinetic data from the stereological errors. It is clear that the corrected steady-state nucleation rates obtained with the three techniques coincide, while there is a pronounced difference in the induction periods determined by single-stage and double-stage treatments. This point will be discussed later.

4.2. Crystal growth behavior

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) are shown in Fig. 2. The composite plots (using TLM + RLM data) are good straight lines and yield the following growth rates: $U_a = 0.00038$ mm/h with an apparent induction period $t' = 2.0$ h ($r^2 = 0.94$) from the time

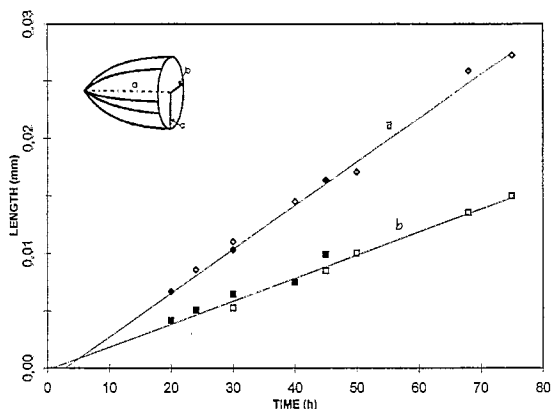


Fig. 2. Principal half-axis of the largest ellipsoidal crystals of the distribution measured by RLM-ST (\square , \diamond) and TLM-ST (\blacksquare , \blacklozenge) in a LS_2 glass treated at 500°C . The insert shows a planar cut through an ellipsoidal LS_2 crystal.

intercept for the major ellipsoidal axis, and $U_b = 0.00020$ mm/h and $t' = 0.7$ h ($r^2 = 0.96$) for the minor axis measurements. It should be stressed, however, that the accurate determination of crystal growth rates is not trivial as one might think because it involves a quest for the largest crystal of the distribution, i.e. the one which first nucleated. Thus, a large number of crystals should be measured to find the largest in each specimen. It is even more complicated when one uses RLM, because, in that case, the probability of finding one of the first born crystals, which has been cut exactly in the center by the cross section being examined, is quite small. Another difficulty is related to the fact that data points obtained for long treatment times (> 20 h) are extrapolated to zero to obtain the 'induction times', t' . Hence, there is an additional uncertainty in the experimental value of t' . From the growth plots, the induction time lies in between 0.7 and 2.0 h for the minor and major ellipsoidal axis, respectively. These different values reflect an unavoidable uncertainty, which is due to the problems discussed above, and define the accuracy limits of our data.

4.3. Analysis of induction times

It is well established that nucleation curves often display an induction period, necessary to establish a steady-state distribution of embryos. These periods vary from years, for temperatures well below T_g , to seconds, as one goes further up in temperature, as shown by Gutzow et al. [19] several years ago. The induction times for growth, however, often observed in laboratory experiments, do not have a clear physical meaning but, instead, can be related to the early appearance of metastable phases (as shown by Ramsden and James for baria-silica glasses [20]) and/or to the experimental limitations of the techniques employed to follow the crystallization behavior (see Weinberg [21]). Thus, if the times required to grow super-critical nuclei (nm range) to sizes detectable by optical microscopes (μm range) are significant, they manifest as apparent induction times in length versus time plots. We will demonstrate that this is the case for LS_2 glass treated at 500°C .

The calculation of such period, i.e. $\tau = \int dr/U(r)$, integrated from the critical radius (~ 8 Å) to a detectable size (~ 0.5 μm), can be performed through

the expression of Kelton and Greer [22], which take into account a size dependent growth rate, $U(r)$,

$$U(r) = AD \sinh(|\Delta G|(1 - r^*/r)/2kT), \quad (7)$$

where $A = 16(3v/4\pi)^{1/3}/\lambda^2$; v being the molecular volume (1.022×10^{-28}), λ the jump distance, D the effective diffusion coefficient for molecular attachment, ΔG the thermodynamic driving force and r^* the critical radius (defined by the ratio $2\sigma/|\Delta G_v|$; σ being the interfacial energy). Using the values given by Deubener et al. [5]: $AD = 7.86 \times 10^{-11}$ m/s, $\Delta G_v = 3.81 \times 10^8$ J/m³ and $\sigma = 0.154$ J/m², a numerical integration of the expression for the development time results in $\tau = 2.180$ s. However, as the calculated macroscopic growth rates (using Eq. (7) for $r \gg r^*$, $U = 2.37 \times 10^{-10}$) are 2.24–4.23 times faster than the experimental growth rate at 500°C ($U = \partial r/\partial t = 1.06\text{--}0.56 \times 10^{-10}$ m/s), the real induction times should be larger than the calculated one. Thus, we normalized the above value of τ , which yielded a growth time of 1.35–2.56 h. In the calculations with Eq. (7), the main assumptions concern the diffusion coefficient D , which was obtained in Ref. [22] by fitting the temperature dependence of transient nucleation periods in a LS₂ glass; and the surface energy, obtained from fitting the steady-state nucleation rates to the classical theory expression. Hence, if any other values of D or other parameters are used, different induction times result. However, when one normalizes by the experimental macroscopic growth rates, in the way explained above, the same value of τ results. An approximate estimate, using the experimental growth rate for the major axis of the largest crystal ($1.06\text{--}0.56 \times 10^{-10}$ m/s) gives $\tau \sim 1.3\text{--}2.5$ h, indicating that this approximation only differs by a small factor from the more rigorous evaluation using Eq. (7).

A similar trend is observed in the nucleation data. When one examines the plots obtained from single-stage treatments, the experimental induction time is 2.4–3.0 h, while that from the double treatment curve is only a few minutes. Thus, the induction periods obtained from nucleation and growth experiments are similar, within the error limits, when they are measured using the same technique (single-stage treatment). Thus, the apparent discrepancy found by Deubener et al. [5], and confirmed here, when τ is measured from nucleation (double-stage) and growth

(single-stage) experiments, merely reflects the differences in the experimental techniques and has no bearing to the birth of a metastable phase.

As the apparent, experimental ‘induction’ times are about 1–3 h, we conclude that the time required for the first crystal to grow to detectable sizes is the main component of the observed ‘induction’ periods.

4.4. Overall crystallization behavior

In order to determine the apparent induction time in a third way, independently of nucleation and growth measurements, and also to test the nucleation mechanism, the overall volume fraction crystallized of Li₂O · 2SiO₂ crystals was also followed, in the same specimens used for nucleation and growth determinations. As these crystals are prolate ellipsoids, the general Eq. (4), for the case of simultaneous homogeneous nucleation and growth, reduces to [23]

$$\alpha = 1 - \exp(-\pi IU_a U_b^2 t^4/3), \quad (8)$$

where 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, defined in Fig. 2.

Fig. 3 shows the experimental volume fraction crystallized, determined by reflected light optical microscopy, as well as the values calculated by Eq. (8), using the crystal nucleation rate (I) and growth rates (U_a , U_b), independently measured by reflected light microscopy.

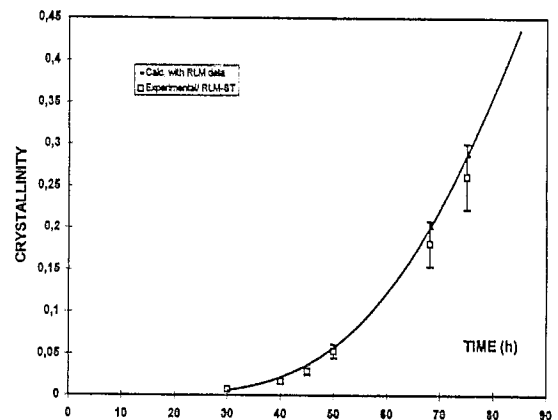


Fig. 3. Volume fraction crystallized of LS₂ glass at 500°C, determined by RLM (□), compared with predicted values using Eq. (8) with a value of $t' = 3$ h.

The discussions in Section 4.3 demonstrate that an apparent ‘induction’ period (t') of approximately 1–3 h was observed in both the nucleation and growth curves, obtained with single-stage treatments. However, as the same technique was used to measure the crystallinity, t was substituted by $(t - t')$ in the calculations of Eq. (8). The induction time, t' , was left as the only adjustable parameter, and the best fit was obtained for $t' = 4$ h. Therefore, taking into account the exponential sensitivity of Eq. (8) to U_a , U_b , I and t' , it can be concluded that the agreement between the calculated and experimental crystallinity is remarkably good up to 25% crystallinity, the limit of experimental determination of this work. As an additional test, a $\ln\{\ln[1/(1 - \alpha)]\}$ versus $\ln(t - t')$ plot yielded a straight line of slope 4.00, ($r^2 = 0.992$), as predicted by Eq. (8), if $t' = 2.5$ h was used. For smaller values of t' the slope increased, being 4.23 h for $t' = 0$. Thus, this independent test confirms that the induction period at 500°C is only a few hours, and that LS₂ glass crystallizes homogeneously.

5. Conclusions

Detailed nucleation, growth and overall crystallization data have been obtained for a lithium disilicate glass at 500°C, using both single-stage and double-stage heat treatments, employing two experimental techniques; reflected light and transmitted light microscopy. For single-stage treatments, the apparent ‘induction’ periods determined by the three independent kinetic measurements were quite similar (1–4 h). For double-stage treatments, an induction period of only a few minutes, close to the real incubation time for nucleation, reported by several authors, was found. Calculations performed to estimate the period required for growth of critical nuclei to detectable sizes, with an expression which takes a size dependent growth rate into account, resulted in a predicted time of about 1.4–2.6 h. Hence, the experimental (single-stage) induction period, is mostly due to the time required for nuclei growth to sizes detectable by optical microscopy.

Due to its exponential sensitivity, the general theory of phase transformations can describe precisely glass crystallization only if accurate values of

nucleation rates, growth rates and induction times are available. As the agreement between the experimental and predicted volume fraction crystallized was excellent for the case of homogeneous nucleation, with an induction time of 2.5–4.0 h, we conclude that this is the predominant crystallization mechanism of LS₂, and that the experimental ‘induction’ times obtained in this research are correct. Thus, no sign of metastable phases was found or, alternatively, any metastable phase that might appear in the early crystallization stages, does not lead to heterogeneous nucleation of the stable phase, and has no significant influence on the overall crystallization kinetics.

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