



ELSEVIER

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Review article

Effect of liquid phase separation on crystal nucleation in glass-formers. Case closed

Edgar Dutra Zanotto

Department of Materials Engineering - DEMA, Center for Research Technology and Education in Vitreous Materials - CeRTEV, Federal University of São Carlos, UFSCar, 13.565-905, São Carlos, SP, Brazil

ARTICLE INFO

Keywords:

Liquid phase separation
Crystal nucleation
Crystallization
Glass
Silicate

ABSTRACT

The objective of this critical review paper is to shed light on a longstanding, relevant problem in materials science: what is the possible effect of liquid phase separation (LPS) on crystal nucleation? Several decades after the first published report on this subject, the widely discussed (none? Interfacial or compositional?) role of LPS on crystal nucleation is still a matter of debate and controversy. Here, the most relevant results of a research project on the kinetic analyses of LPS and simultaneous crystallization of BaO–SiO₂ and Li₂O–SiO₂ glasses are reviewed, considering and substantially complemented by recent findings. Crystal nucleation kinetics in glasses having compositions inside and outside the miscibility gaps in both systems were determined by microscopy methods at different temperatures and complemented by small angle X-ray scattering and transmission electron microscopy analyses to probe the LPS kinetics. The effect of the liquid droplet interfaces was found to be negligible - their interfacial energy, approximately 0.004 J/m², is much smaller than that of the crystal/nucleus surface energy, 0.130–0.200 J/m² - and the number of vitreous droplets is many orders of magnitude higher than the number of crystals. The old and new results and an improved analysis demonstrate that the crystal nucleation rates in the stoichiometric glasses are higher than in their (alkali-poorer) phase separating glasses of the same system. These combined results clearly show that primary role of LPS is to **shift the composition of the glass matrix** towards that of the stoichiometric crystal phase, which leads to enhanced crystal nucleation. These findings settle an old-standing enigma in glass science.

1. Introduction

Crystallization is ubiquitous in nature and technology, and plays a fundamental role in many important processes, such as mineral, ice and snow formation, metal solidification, chemical purification processes, stability of pharmaceutical drugs, and should be avoided in glass formation or extremely controlled for glass-ceramic development and synthesis. A key step in crystallization, before crystal growth kicks in, is nucleation, however, despite intensive research effort in the past 70 years, due to the extremely small size and short time scales, the microscopic mechanisms of nucleation in glass-forming substances are still poorly understood [1–9].

On the other hand, liquid phase separation (LPS) - also called liquid-liquid phase separation, amorphous phase separation, liquid immiscibility, or liquid unmixing - is also a ubiquitous phenomenon in glass forming systems. Spontaneous LPS is unwanted because it leads to defects and impairs the glass transparency, but it has also been advantageously used in some industrial processes, for instance for the production of Vycor® and opal glasses [1]. The LPS phenomenon has

been reported to occur in oxide glasses since the early sixties when electron microscopy techniques started to be used to expose the nanostructures (vitreous droplets) of certain glasses. LPS can take place above the *liquidus* temperature, or can be metastable when it occurs below the *liquidus*. This was a very *hot* topic of glass science in the seventies and eighties, with many Ph.D. theses, articles, symposia, and two dedicated monographs [1,2] on the subject. However, the interest of the oxide glass research community in LPS has gradually declined, whereas the chalcogenide glass and metallic glass communities, e.g. Ref. [3] realized that LPS also takes place in some of their compositions and significantly affects several properties, including the glass-forming ability (GFA). Moreover, these two communities have been and are still eagerly searching for new formulations having good GFA.

It has long been known from equilibrium phase diagrams that (prior) liquid-liquid phase separation can have a marked influence on the course of crystallization in a system. Liquid unmixing may produce two compositions, one of which has a higher tendency to crystallize than the initial non-separated glass. However, it is also known that liquid phase separation is not always essential to produce internal crystal

E-mail address: dedz@ufscar.br.

<https://doi.org/10.1016/j.ceramint.2020.06.305>

Received 17 May 2020; Received in revised form 27 June 2020; Accepted 29 June 2020

0272-8842/ © 2020 Published by Elsevier Ltd.

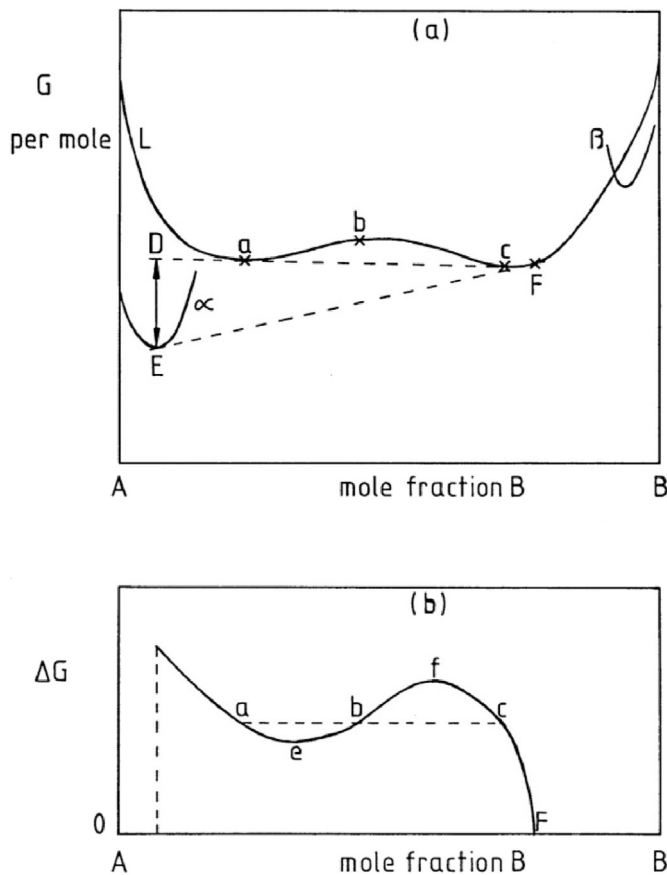


Fig. 1. (a) Schematic diagram for the thermodynamic driving force for crystal nucleation as a function of composition in a system undergoing metastable phase separation. (b) Variation of thermodynamic driving force, ΔG , with composition for a parent non-phase separated glass (solid curve) and for a phase separated glass (dotted line).

nucleation in glasses; e.g., $\text{BaO}\cdot 2\text{SiO}_2$, $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$, $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$ and other stoichiometric compositions do not show LPS and still copiously crystallize in bulk. Moreover, several glass-forming compositions in the alkali and alkaline earth- SiO_2 , alkali- B_2O_3 , and other systems show extensive liquid unmixing and still do not crystallize internally. Theoretically, liquid-liquid phase separation could influence crystal nucleation in several ways, but most of the possibilities fall into two main categories associated with either: i) the different compositions of the separating liquid phases, or with ii) the interfaces between the glassy phases. These points have been thoroughly discussed in the past by several authors, including Tashiro [4] and Hammel [5]. Extensive arguments were presented at a meeting on “The Vitreous State” in 1970, by Scholes [6], Uhlmann [7] and Zarzycki [8]. James [9] summarized the state-of-art on the subject in a comprehensive review article.

Thus, the *compositional changes* resulting from liquid phase separation may affect the nucleation kinetics (through the thermodynamic driving force, $\Delta G(T)$, or the diffusion term, $D(T)$). Fig. 1 illustrates schematically how the ΔG for crystallization may depend on whether prior metastable liquid immiscibility occurs or not. In the example shown, which represents the situation at deep supercooling below the melting point of the crystal phase (α), the driving force for crystal nucleation (DE) is increased after the occurrence of the liquid phase separation for initial parent compositions between *a* and *b*, but it is lowered after phase separation for initial compositions between *b* and *c* (Fig. 1a). In the parent, non-phase separated glass (Fig. 1b), ΔG exhibits either a maximum or minimum at the spinodal compositions (*e* and *f*). The phase-separated glass (end phase compositions *a* and *c*) has a

constant ΔG .

Liquid phase separation could also result in one of the liquid phases having an appreciably higher atomic mobility, $D(T)$, at large undercoolings than the parent liquid phase, which could also increase the homogeneous crystal nucleation rate. Moreover, in principle, the crystal nucleus/liquid interfacial energy, σ , could be lower for crystals forming in one of the liquid phases than in the parent (unmixed) supercooled liquid phase, thus having a tremendous effect on the nucleation rate of crystals.

Details of the Classical Nucleation Theory, CNT, have been discussed in several articles and books and are well-known. Here it is sufficient to recall that the steady-state nucleation rate, $I_{st}(T)$, is given by:

$$I_{st}(T) \sim C.D(T).\exp[-W^*(T)/k_B T], \quad (1)$$

where C is approximately a constant, $D(T)$ is the effective diffusion coefficient of the “structural units” controlling nucleation, k_B is Boltzmann’s constant, and $W^*(T)$ is the work of critical nucleus formation, given by:

$$W^* = 16\pi\sigma^3 / (3.\Delta G_v^2), \quad (2)$$

where $16\pi/3$ refers to spherical nuclei, and $\Delta G_v(T)$ is the thermodynamic driving force per unit volume of the crystal phase.

Mechanisms for enhancement of crystal nucleation associated with the interfaces between the amorphous phases could be of various types: i) “Direct” heterogeneous crystal nucleation at the interfaces; ii) an enrichment of some component, perhaps a nucleating agent, at the boundaries between the amorphous phases causing a locally higher ΔG or atomic mobility, $D(T)$, or even a lower interfacial energy. It has been further suggested that a sparingly soluble component might crystallize out at the interface and promote heterogeneous nucleation in the bulk of the glass [6]. (iii) Another possible mechanism, suggested by Tomozawa [10], is preferential nucleation in the diffusion zones that exist around the liquid phase droplets. This idea will be discussed further here.

This subject of LPS, including its effects on crystallization of oxide glass-formers was very “hot” in the seventies and eighties [1–17], but resurfaced in the past few years, mostly driven by the metallic and chalcogenide glass communities. In this article, I critically review and highlight relevant findings of a research project I (then a Ph.D. student) carried out in the glass technology department at Sheffield University, UK, under the supervision of the late professor Peter F. James in the early eighties. Some of the results have been previously published. However, they are scattered in different articles [11–14], some have remained “buried” in conference proceedings [15,16], whereas some relevant findings are still hibernating in this author’s thesis [17]. As a result, the overall conclusions, which are based on the whole set of papers, have been barely noticed, and also a very important open issue that will be discussed here (regarding the lithia-silica system) persists. This fact was quite clear by the numerous questions asked after my talk in the Turner Symposium in Sheffield, September 2016, which motivated me to write this critical review article. Those previous results will be complemented and better explained by new, relevant findings on lithia-silica glasses, which have not yet been related to the old results. Our aim is thus to revisit and summarize those earlier results and to combine them with newly published articles to **definitively clarify the effects of LPS on crystal nucleation**.

2. Literature review

2.1. The phase diagram of $\text{BaO}\text{--}\text{SiO}_2$

Roth and Levin [18] determined the phase diagram and discovered the polymorphic transformation of $\text{BaO}\cdot 2\text{SiO}_2$ (BS2) taking place at 1350 °C. The orthorhombic structure of the low-temperature form, l -

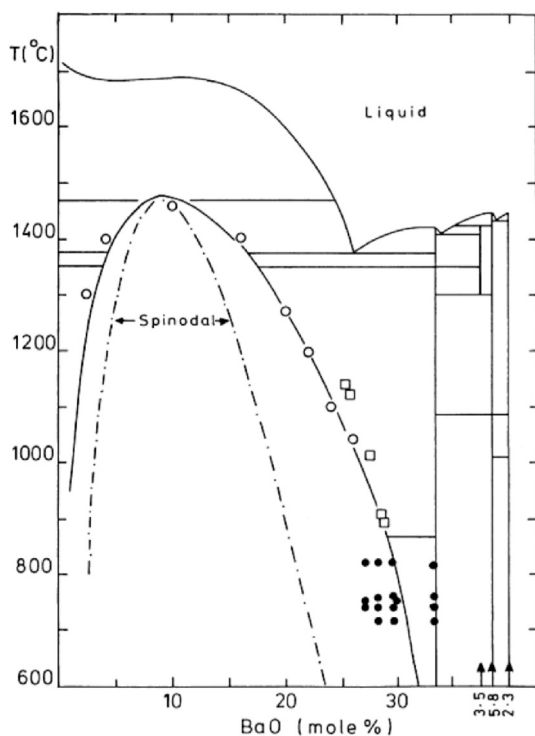


Fig. 2. Phase diagram of the BaO–SiO₂ system showing the metastable miscibility gap. The solid line represents the binodal boundary, and the dash-dotted line represents the spinodal calculated by Haller et al. [24]. The experimental points for the binodal are from: (o) Seward et al. [23]; (□) Ramsden [25]. The filled circles indicate the heat treatments used here [17].

BS2, was deduced by Douglass [19], and the high-temperature monoclinic form, *h*-BS2, was described by Katscher et al. [20]. Crystal data of all BaO–SiO₂ compounds are given by Oehlschlegal [21].

Regarding the miscibility gap, calculations by Charles [22] of thermodynamic activities indicated a critical point at 8 mol% BaO and 1600 °C. Seward et al. [23] determined experimentally the binodal curve with a critical point of 1460 °C ± 50 °C and 10 ± 1 mol% BaO. Assuming regular mixing between BaO·2SiO₂ and (SiO₂)₈ “units” the model of Haller et al. [24] can be fitted to the data of Seward et al. very successfully. Fig. 2 shows the equilibrium phase diagram with the metastable miscibility gap together with the experimental points of Ramsden [25], who used an optical microscopy technique. The spinodal region calculated by Haller et al. [24] is also depicted (see Fig. 3).

2.2. Crystallization of baria-silica glasses

MacDowell [26] showed that for glasses in the composition range BaO·2SiO₂ to 2BaO·3SiO₂, internal crystal nucleation occurs without deliberately adding nucleating agents.

Rowlands [27] measured crystal nucleation rates and showed that internal nucleation of Li₂O·2SiO₂ (LS₂) or BS₂ occurred in several compositions of the Li₂O·2SiO₂–BaO·2SiO₂ eutectic subsystem. Burnett and Douglas [28] described the growth of BaO·2SiO₂ spherulites in a 70SiO₂·20BaO·10Na₂O glass at 600 °C. Small spheres of *h*-BS2 appeared first. These nucleated needles of *l*-BS2 and the characteristic spherulite forms began to appear. After a long heating period, the spherulites transformed to laths and the remaining *h*-BS2 reverted to *l*-BS2. Freiman et al. [29] observed similar changes in microstructures from spherulites to laths in a 3BaO·5SiO₂ glass.

Oehlschlegal [21] reported a four-stage crystallization process consisting of: 1) classical nucleation, 2) spherulitic growth, 3) crystallization of *h*-BS2 and 4) 3BaO·5SiO₂ decomposes to *l*-BS2 and *l*-B5S8. For BaO·2SiO₂ glass, stage 3 represented the conversion of high to low

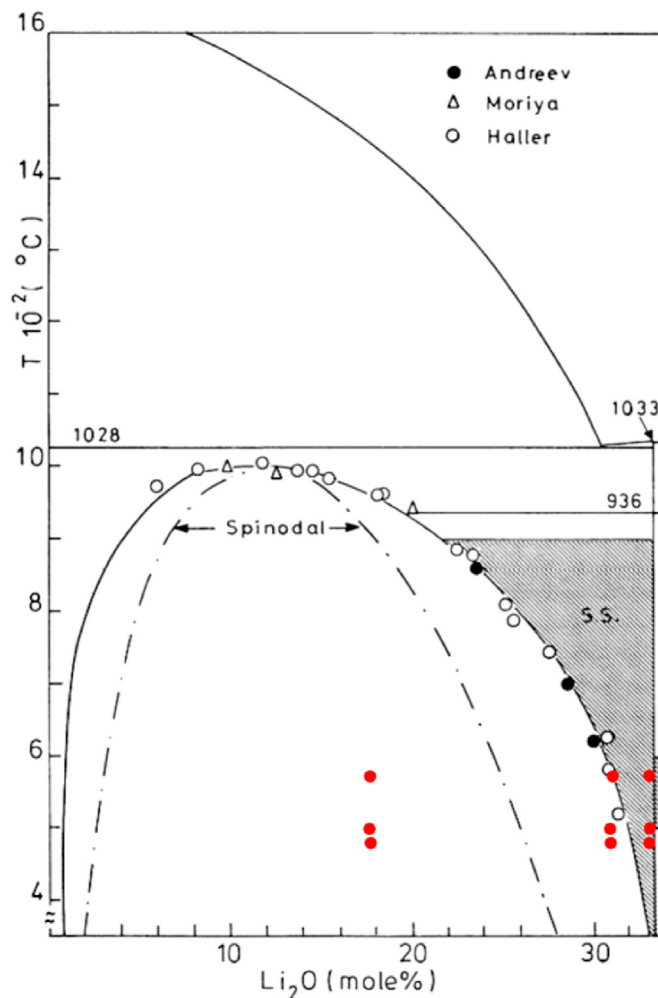


Fig. 3. Phase diagram for the Li₂O–SiO₂ system showing the metastable miscibility gap. The solid line represents the binodal, and the dash-dotted line represents the spinodal calculated by Haller et al. [24]. The experimental points for the binodal are from (●) Andreev et al. [34]; (Δ) Moriya et al. [35] and (○) Haller et al. [24]. The filled red circles indicate the heat treatments used here. The shaded area represents the range of crystalline solid solution formation [17].

BS2. Lewis and Smith [30] studied the spherulite growth in BaO–SiO₂ glasses in detail by electron microscopy and electron diffraction. They demonstrated that spherulites formed at 700 °C (close to T_g) consisted of fibrillar (~100 Å in diameter) monoclinic crystals (*h*-BS₂) in confocal arrangement with preferred crystallographic growth axes. High temperature (900 °C) spherulites were composites of radially oriented plate-shaped orthorhombic crystals (*l*-BS₂) with lateral growth of epitaxially nucleated fibrillar monoclinic crystals. At intermediate temperatures, “axialites” consisting of a single orthorhombic crystal with monoclinic fibrillar side-growth, grew in competition with the low-temperature morphology.

Ramsden [31] reached very similar conclusions in his work. He also studied the kinetics of crystal nucleation in several glasses inside and outside the miscibility gap of the system. James and Rowlands [32] determined the nucleation rates of a BaO·2SiO₂ glass from 662 to 780 °C. We will describe these results later on this article.

2.3. The phase diagram of Li₂O–SiO₂

The phase diagram of the lithia-silica system was established by Kracek [33]. The miscibility gap was determined by several authors [24,34,35], and there is good agreement between the different

determinations. Figure 2.2 shows the SiO₂-rich side of the equilibrium phase diagram and the miscibility gap. The model of Haller et al. [24] fits the existing data very well, assuming regular mixing between Li₂O·2SiO₂ and (SiO₂)₆ units. Crystallographic data for lithium disilicate have been reported by Liebau [36] who also described a polymorphic transformation at 936 °C.

2.4. Crystallization of Li₂O–SiO₂ glasses

In contrast to BaO–SiO₂ glasses, the crystal nucleation and growth of Li₂O–SiO₂ glasses have been extensively studied. This system is considered to be the “*Drosophila*” of crystallization studies because it is a relatively good glass former, it easily crystallizes at a measurable rate and is the basis of several commercial glass-ceramics. Of particular interest to the present work are some quantitative studies of crystal nucleation kinetics and attempts to correlate the liquid phase separation with crystal nucleation behavior.

The morphological aspects of the growth units were studied in detail by Tomozawa [37] and Lewis et al. [38]. They conclusively showed that the lithium disilicate (LS2) crystals consisted of faceted single crystal plates containing a high defect concentration. New branches formed on most of the crystals, probably by a twinning mechanism. The regular nature of the branching explained the morphology of crystallization after prolonged growth (clusters of single crystals). It was also shown in Ref. [39–41] that the liquid droplets did not interfere with the growing crystals, the unchanged droplets remaining embedded within the crystals.

Kinser and Hench [42] studied a 30Li₂O·70SiO₂ glass (just outside the miscibility gap) during treatment at 500 °C with electron microscopy, XRD, and dc and ac electrical measurements and concluded that metastable, crystalline lithium metasilicate (LS) precipitates first and subsequently redissolves ($t > 5$ h) before the appearance of the equilibrium LS2 crystals.

West and Glasser [43] made a comprehensive study of crystallization in this system. They also suggested that the first crystallization product of Li₂O–SiO₂ glasses is a metastable lithium disilicate solid solution (ss); its composition ranged from 28 to 38 mol% Li₂O. (Figure 2.2) The solid solution containing 28.0–33.3% Li₂O was formed at temperatures as high as 930 °C, although it decomposed rapidly at these temperatures. At lower temperatures, between 500 °C and 700 °C, the ss persisted indefinitely.

2.5. Experimental observations of the effects of amorphous phase separation on crystal nucleation

2.5.1. Multicomponent glass-forming systems

Selected studies on the relationships between liquid phase separation and crystallization (especially on nucleation) will be briefly summarized below. Some authors have suggested that the heat treatment for crystal nucleation was principally a treatment to induce phase separation, and that crystal nucleating agents, such as TiO₂, ZrO₂, and P₂O₅, were components to enhance the phase separation tendency [44].

In a review on catalyzed crystallization of glass in 1959, Stookey [45] suggested that liquid phase separation could help subsequent crystallization because homogeneous nucleation could occur in one of the separated liquid phases.

The work of Vogel and co-authors has included qualitative studies of crystallization in phase-separating glasses of the following systems: Li₂O–SiO₂, LiF–BeF₂, MgO–P₂O₅ and more complex compositions. Electron micrographs showed crystals growing in the amorphous matrix or within the droplets (Figs. 9 and 10 in Ref. [46], and Figures 182, 183, 184 and 185 in Ref. [40]). Vogel [40] stated that his results “show clearly that crystallization begins with granular formations (Li₂Si₂O₅) at the *periphery* of the larger droplet zones”. It should be stressed, however, that in Figures 110 and 111 in Ref. [40] (TEM micrographs of a 20Li₂O·80SiO₂ (mol%) glass heated for 1 h at 580 °C and 1 h at 650 °C,

respectively) the crystallization front advances into the two-phase glass by-passing the undisturbed amorphous droplets. Therefore, there is no evidence that crystal nucleation started on the interfaces of the droplets.

Ohlberg et al. [47] studied MgO–Al₂O₃–SiO₂–TiO₂, Li₂O–CaO–SiO₂–TiO₂, and Li₂O–MgO–Al₂O₃–SiO₂ glasses. They concluded that internal crystal nucleation was the result of liquid phase separation in the three cases. In the first glass, the amorphous droplets formed spontaneously on cooling and, on heating, they reached 500 Å before crystallization occurred. In the second glass, droplets having 2000 to 4000 Å in diameter also formed on cooling. During heat treatment, crystal growth in the matrix was apparently initiated at the droplets-matrix interface. In the third system, droplets as large as 60 μm were formed by heat treatment and crystal growth also appeared to start at the droplets-matrix interface.

Maurer [48,49] made light scattering studies on a SiO₂–MgO–Al₂O₃–TiO₂ glass heat treated at different temperatures and found that the scattering centers became increasingly anisotropic. This was interpreted as a crystallization of the amorphous droplets.

Kalinina et al. [50] studied the crystallization of Li₂O–SiO₂ glasses within the composition range 20.0–30.3 mol% Li₂O by DTA and XRD. Small amounts of lithium metasilicate and lithium disilicate were detected at 480–630 °C. At higher temperatures, 900–960 °C, cristobalite and tridymite appeared. They suggested that crystal nucleation started in the droplet phase, although no specific experiment to test this hypothesis was undertaken.

In a study on the physical properties of glasses in the Li₂O–Al₂O₃–SiO₂ (TiO₂, Fe₂O₃) system, Buzhinskii et al. [51] suggested that they separated into two vitreous phases with the formation of minute droplets having the composition of the crystals that subsequently appeared. Again, no direct experiment was performed to test this hypothesis.

Doherty et al. [52] studied the crystallization of Li₂O–Al₂O₃–SiO₂ glasses with and without TiO₂, and suggested that TiO₂ catalyzed internal nucleation of β-eucryptite rather than the liquid immiscibility.

In a TEM study of crystallization in Na₂O–BaO–SiO₂ glasses, Burnett and Douglas [53] suggested that “*the main effect of the liquid unmixing appears to be that of producing two compositions, one of which is more prone to crystallize*”. In this system, crystal nucleation occurred within the baria-rich phase and at a much lower nucleation density than that of the liquid separation.

In their study of Na₂O–TiO₂–SiO₂ glasses, Bayer and Hoffmann [54] showed replica micrographs of needle-shaped crystals on the borders of droplets (Fig. 6 in Refs. [54]) and concluded that in glasses with an unmixing tendency, heterogeneous nucleation takes place at the internal interfaces of the droplets.

Other systems for which it has been suggested that droplet interfaces initiate crystallization include SiO₂–Al₂O₃–CaO–MgO–TiO₂ [55], for which it was said “*It’s as if the interfaces of the separated vitreous phases act as nucleators of the crystallization of rutile from the glass phase rich in TiO₂*” (translated from French). However, conclusive evidence for the effects of phase separation was not presented.

2.5.2. Li₂O–SiO₂ glasses

McMillan and co-workers [56–58] studied glasses of the Li₂O–SiO₂–P₂O₅ system. They observed that the finest crystals were produced in glasses which contained both P₂O₅ and a phase separated microstructure. In later research, McMillan [59] studied the crystallization of a 30Li₂O·69SiO₂·1P₂O₅ glass. Specimens were nucleated at 550 °C from 0.1 to 6 h and developed at 750 °C for 1 h. Maximum nucleation efficiency was achieved with a duration of 20 min at 550 °C. There was no simple correlation between this observation and the phase separated microstructure since the number density of phase separated particles and their interfacial area continued to decrease throughout the heat treatment period. This result did not support the idea that phase separated particles (interfaces) provide nucleation sites for subsequent

crystallization. To reconcile these findings with the fact that LPS enhanced crystal nucleation rates (from earlier work), McMillan [59] proposed that after an initial period at the nucleation temperature, the number of crystal nuclei decreases because of a coarsening process. Thus, in his opinion, the occurrence of LPS in the glass could hinder the coarsening process. Therefore, the beneficial effect of prior phase separation on crystal nucleation density was seen as an indirect one, rather than the direct provision of nucleation sites.

Studying a $\text{Li}_2\text{O}-2.5\text{SiO}_2$ glass, Nakagawa and Izumitani [60] observed that the difference in the number of crystals formed in a previously phase separated specimen and in a quenched sample of the same overall composition was negligible. They also found that the maximum nucleation rate of LS2 crystals occurred at 480 °C (however, our studies on this composition indicates that the maximum is at ~455 °C), whereas that of amorphous droplets was at 450 °C. They concluded that amorphous phase separation did not influence crystal nucleation.

A very detailed study was carried out by Tomozawa [10], who compared the kinetics of liquid-liquid separation for $\text{Li}_2\text{O}-\text{SiO}_2$ glasses with crystal nucleation as a function of temperature and time. The nucleation rate of crystals, I_{st} , in a glass outside the immiscibility gap was constant with time, but for glasses that underwent phase separation simultaneously, a temporary, but marked increase in I_{st} was observed. This increase was attributed to the presence of a diffusion zone (depleted in silica), surrounding the silica-rich droplets, which might have acted as a favorable site for crystal nucleation by lowering the effective surface energy. Tomozawa pointed out that these observations could not be explained regarding the compositional shift of the matrix phase during phase separation because the (Li-rich) stoichiometric glass displays a lower nucleation rate. Moreover, straightforward heterogeneous nucleation did not provide a complete answer since the period of enhanced crystal nucleation at a given temperature did not correspond to the time for a maximum in the interfacial area of the liquid droplets. We will come back to that study in the final part of this article.

A similar study was made by Zanotto and Craievich [61] using splat cooled glasses and a rigorous technique for measuring crystal nucleation densities. Although the general conclusions were in agreement with Tomozawa's, the observed temporary increase in nucleation rates was smaller. They also showed that the crystal nucleation density (N_v) vs. time curve for glass specimens previously phase separated at 500 °C and then nucleated at 475 °C was different from that for as-quenched specimens nucleated at 475 °C. These results, therefore, did not agree with those of Nakagawa and Izumitani [60]. In that temperature, 475 °C, the crystal nucleation rates in phase-separating glasses were about 2 times higher than that in a stoichiometric LS2 glass. Therefore, the effect of LPS on crystal nucleation could not be explained regarding compositional shifts towards the stoichiometric phase (because, in that case, the stoichiometric LS2 glass would show a higher nucleation rate). Therefore, following Tomozawa's suggestion, nucleation associated with the amorphous droplet-matrix interfaces was assumed. However, this increase in crystal nucleation rates was very small if compared with the 5–6 orders of magnitude increase reported for the incorporation of 3 mol% P_2O_5 in an LS2 glass [62]. We will further discuss this work [61] in the final part of this article.

In other research, Matusita and Tashiro [62] determined the effect of a series of oxide additives on the crystal nucleation and growth of a $\text{Li}_2\text{O}-2\text{SiO}_2$ glass. They showed that the decrease in the nucleation rate caused by the additives (except P_2O_5 and V_2O_5) were due to an increase in viscosity. They also suggested that P_2O_5 and V_2O_5 influenced the nucleation kinetics by inducing liquid phase separation in this stoichiometric composition, that is, they widened the miscibility gap.

Finally, Hautojärvi et al. [63] studied $\text{Li}_2\text{O}-\text{SiO}_2$ glasses with positron lifetime, annihilation line-shape and electron microscopy. They showed that phase separation increased the number of crystals and the rate of volume crystallization.

In conclusion, the actual effect of LPS on crystal nucleation is not clear from these former studies.

2.5.3. $\text{BaO}-\text{SiO}_2$ glasses

A very extensive study was carried out by Ramsden [31] with baria-silica glasses with and without phase separation. He studied the nucleation kinetics of the barium disilicate crystal phase (BS2) for glass compositions in the range of 25–34 mol% baria. Although he could not readily compare the nucleation kinetics of the various glass compositions because his glasses had different degrees of the main impurities, i.e., Al_2O_3 (0.02–0.48 mol%) and up to 1 mol% SrO, an elegant experiment was devised. Three sets of specimens from a glass with 25.3 mol% BaO were prepared as follows: Glass A was rapidly cooled in air. Glass B was heated at 800 °C for 1 h. Glass C was heated at 900 °C for 10 min (the number and size of the SiO_2 -rich droplets were completely different in the three glasses). Then, all the glasses were nucleated at 700 °C ($T_g \cong 700$ °C for the BS2 glass) for various times and grown at 840 °C so that the crystals could be observed in an optical microscope. The effects of the different heat treatments before the crystal nucleation treatments were striking (any nucleation produced in the prior treatments was negligible in comparison to crystal nucleation at 700 °C, where the maximum in crystal nucleation rate is observed for the stoichiometric BS2 glass). Crystal nucleation was higher in glass B when compared with C (and A). This was attributed to the greater degree of phase separation initially present in B, and hence to the significant shift in matrix composition that had already occurred in this glass. Estimations of the interfacial area per unit volume of the phase separated glass using replica electron microscopy showed that this quantity changed only very slowly at 700 °C for A, B and C. However, the crystal nucleation rates changed considerably with time at 700 °C indicating that the interfacial area was not affecting crystal nucleation directly. Also, the number of droplets per unit volume in glass A was about ten times greater than in glass C, but initially A had a crystal nucleation rate less than (but similar to) C. It was concluded that the morphology of the phase separation had little or no influence on crystal nucleation and that the effects observed were due predominantly to the progressive shift in the composition of the matrix (baria-rich) phase as a result of phase separation.

One further point should be made. The apparent observation, in some cases, of heterogeneous nucleation of crystals on the droplet interfaces could imply that crystals prefer to form there. However, interfaces may migrate during heat treatment, and any relation between the interface and the crystals they nucleate might be lost. Nevertheless, the dependence of the nucleation rate on the parameters describing phase separation morphology would still be retained, and hence, in principle, it should be possible to study experimentally the importance of interfaces in nucleating crystals.

2.5.4. Recent articles on other systems

According to the Scopus database, more than 1700 articles dealing with the interrelationships between LPS and crystallization processes in inorganic, metallic, and polymer glasses have been published since 1965 at an average current rate of 65 papers/year. The words used in the Scopus search – in the article title, abstract, and keywords were “*phase separation* and (*nucleation* or *crystallization*) and *glass*”. We will restrict this article to oxide glasses. More than 100 authors have published at least 5 articles on this particular topic and have been working on it for many years. It is not the aim of this article to analyze all of those 1700 papers. We reviewed some of the pioneer reports above, and will show below that there is still ongoing activity on this relevant glass science problem.

Just to give one example of non-oxides [64], chalcogenide glasses have characteristic covalent bonds and unique combination of properties, such as broad infrared transmission window, high optical non-linearity, semi-conductivity, and photosensitivity. Inspired by the great success of oxide glass-ceramics, chalcogenide glass-ceramics (CGC) are

receiving intensive attention. A review article [64] provides a discussion of the mechanisms that underlie the resultant properties of CGC. The crystallization mechanisms of chalcogenide glasses are discussed through the comparison of molecular-scale and nanoscale phase separation assisted crystallization in oxide and oxyfluoride glasses.

Returning to oxide glasses, in a recent paper, Deng et al. [65] discovered that LPS precedes crystallization of canasite type glass-ceramics, but did not clarify its role in the crystallization process.

The study of Boulay et al. [66], focused on the interplay between prior liquid phase separation and the crystallization of fresnoite in the BaO–TiO₂–SiO₂ system. The crystallization behavior of a non-stoichiometric composition inside the miscibility gap was compared with the stoichiometric composition (*FRES*) and a non-stoichiometric composition outside the miscibility gap. Their DTA experiments showed that the two non-stoichiometric compositions exhibit predominant surface crystallization whereas the *FRES* undergoes bulk nucleation. This finding was supported by a multi-scale microstructure characterization. They concluded that the LPS did not play any significant role in the nucleation step of this system.

Regarding commercial materials, we show below selected examples for a low CTE glass-ceramic, photo-thermo-refractive glass (PTRG), which was also discovered by Donald Stookey - the glass-ceramics inventor - the famous Bioglass 45S5, and an optical glass-ceramic.

Photo-thermo-refractive (PTR) glass is an optical quality Na–Al–Zn–K–O–F–Br silicate glass doped with Ag, Ce, Sb, and Sn that undergoes photo-thermo-induced volume crystallization of nanosized NaF responsible for localized refractive index changes. PTR glass has found numerous commercial applications, but the intricate mechanism of photo-thermal crystallization is still not fully understood. In a comprehensive study, Souza et al. [67] demonstrated that additional to crystalline phase (NaF) precipitation, liquid droplets embedded in the glass matrix appear concurrently over a wide range of temperatures (Fig. 4). The droplet phase is richer in SiO₂, rendering the alkali-rich remaining glass matrix a lower glass transition temperature than the original glass. The droplet's surfaces do not catalyze NaF nucleation. Although the effects of LPS on optical properties of PTR glass are still to be explored, LPS likely contribute to unwanted scattering losses and uncontrolled refractive index change. The substantial change in the original glass composition resulting from LPS plays an important role in NaF crystallization kinetics, and therefore must be considered for an overall understanding of the crystallization mechanism underpinning the (desired) refractive index change in PTR glass.

The crystallization of the nucleation agent ZrTiO₄ in a low thermal-expansion lithium aluminosilicate glass-ceramic was monitored as a function of time by combining transmission electron microscopy with Ti–L_{2,3} X-ray absorption near-edge structure spectroscopy by Hoche et al. [68]. The formation of liquid phase droplets preceded ZrTiO₄

crystallization within the nanosized droplets of the separated liquid phase. Quantitative data on crystallized fractions revealed the self-limited growth of ZrTiO₄ nanocrystals; their growth was restricted by the outer border of the phase-separated droplets. The size of ZrTiO₄ crystallites was thus determined by the restricted volume of the phase-separation droplets they crystallize in. Hence, this study points to a compositional effect of LPS on crystallization.

Golovchak et al. [69] recently showed that, surprisingly, the famous Bioglass 45S5, discovered by Larry Hench in the early seventies, and which has found several applications in medicine and dentistry, also undergoes LPS. The type of phase separation (spinodal vs. droplet-like) has a significant effect on the activation energies of viscous flow and crystallization in this glass and should be further explored.

Another good example is given by the work of Chen et al. [70] on a bioactive material. Apatite and mica-containing K₂O–MgO–CaO–Al₂O₃–B₂O₃–SiO₂–P₂O₅–F glass-ceramics can be used to repair diseased or damaged bones and teeth. Phase separation and nucleation in these multi-phase glass-ceramics were investigated with DTA, SEM/EDAX, XRD and FTIR techniques. The resulting crystal phase relationships were discussed with regard to LPS. For the glass with a lower content of P₂O₅ + CaO, primary phase separation was reached through spinodal decomposition or by nucleation and growth. For the glass with a higher content of P₂O₅ + CaO, primary phase separation took place by spinodal decomposition. These two mechanisms resulted in different micro-morphologies. The authors suggested that LPS was favorable for nucleation of fluorophlogopite and fluorapatite micro-crystals due to: (i) the similarity of compositions and structures between the glassy phases and the corresponding crystalline phases; (ii) the large amount of liquid phase interfaces. Therefore, they could not decide for one or another mechanism.

In a creative use of LPS, Chen et al. [71] were able to precipitate lanthanide-activated cubic NaLuF₄ nanocrystals (inside one of the nanosized liquid phases) from a borosilicate glass with a specifically designed composition. The precursor glass was already phase-separated after quenching, which, according to the authors, was beneficial to controllable glass crystallization by affording desirable size, morphology and activator partition. As a result, such fabricated glass-ceramic co-doped with Yb³⁺/Er³⁺ activators exhibited intense up-conversion luminescence, which was about 10,000 times higher than that of the corresponding precursor glass, ascribed to the low-phonon-energy environment of the lanthanide ions enriched nanocrystals and the efficient Yb³⁺/Er³⁺ inter-ionic interactions. The authors anticipated that this synthesis route via LPS afforded nanostructure control and offers a great opportunity to design other highly transparent nanocomposites with a wide range of tunable optical properties.

Previous review papers on LPS on oxide glasses were published long ago, by James [72] in 1975, and by Uhlmann and Kolbeck [73] in 1976. This topic continued to be of great interest until the mid-eighties. Then it resurfaced about a decade ago, pushed by the chalcogenide and metallic glass communities. To the best of our knowledge, no review paper on LPS is yet available for chalcogenide glasses.

For the sake of completeness, phase separation phenomena in metallic glass systems were reviewed in 2013 by Kim et al. [74]. In that paper, nano-scale phase separation observed in frozen-in glass was discussed in marginal glass formers, such as Pd-, Fe, Al-base glasses, and in bulk glass formers in Cu-, Zr- and Mg-base glass systems. Thermodynamic aspects for decomposition by liquid-liquid phase separation, which include stability conditions, types of miscibility gap, calculation of bimodal and spinodal curves were introduced as a background for design of metallic glasses phase separating in the liquid state. Finally, some advantages of phase separation phenomena, such as enhanced glass forming ability (lower crystallization rates) in metallic glass systems, were highlighted.

Despite these interesting results concerning different effects of LPS on crystallization, these recent studies of complex, multi-component compositions led to a confusing situation. Some authors advocate a

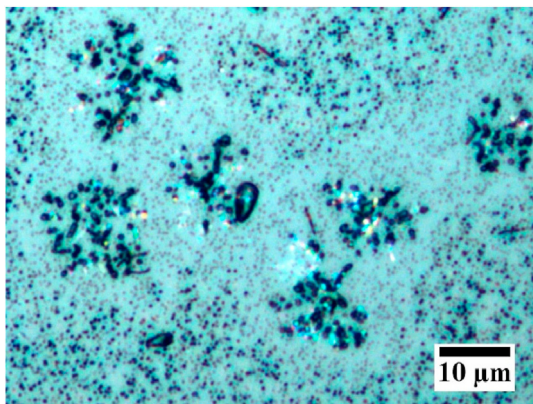


Fig. 4. Spherical droplets of silica-rich particles in a PTRG. The darker agglomerates are dendritic NaF crystals hyper-developed to reveal them at optical microscopy scale, using reflected light.

positive effect of the LPS interfaces on crystal nucleation, others defend compositional shifts, whereas some detected no significant effect at all. To conclude this brief review of the recent literature, it seems that the use of complex compositions, especially when nucleating agents are present, lead to great difficulties in interpreting the possible relationships between LPS and crystal nucleation. Therefore, the use of “simpler” systems, such as $\text{Li}_2\text{O}-\text{SiO}_2$ and $\text{BaO}-\text{SiO}_2$, likely allow more straightforward conclusions to be made.

The strategy of this article is to review in some detail systematic studies on the kinetics of liquid phase separation and crystal nucleation in $\text{BaO}-\text{SiO}_2$ glasses, with well characterized impurity contents, over a wide range of temperatures. We will also summarize some well-designed experiments on the nucleation kinetics of $\text{Li}_2\text{O}-\text{SiO}_2$ glasses with compositions inside and outside the miscibility gap and will compare those studies with a recent, relevant work, to put an end to this open-ended question. The article objective is to definitively clarify if **liquid droplet interfaces or compositional shifts caused by LPS play a role in crystal nucleation**.

3. Results and discussion of crystal nucleation and LPS in baria-silica and lithia-silica glasses

The preparation of homogenous, fast quenched glass plates and their chemical analysis were described in Ref. [17]. The thermal treatments were controlled to ± 2 °C. The designation of each glass indicates the molar percentage of BaO or Li_2O , e.g., glass 17.7 Li_2O contains 17.7 mol% Li_2O by analysis. Glasses 28.3A and 28.3B BaO mean that they have 28.3 mol% BaO, but belong to two different glass batches, made with the same chemicals, of the same lots, in different occasions. 28.3BPS refers to glass 28.3B previously phase separated at a high enough temperature before the nucleation treatment.

3.1. Crystal nucleation and LPS in $\text{BaO}-\text{SiO}_2$ glasses

3.1.1. Crystal nucleation in barium silicate glasses undergoing phase separation

After heat-treating, polishing and etching the specimens, micrographs were obtained, and the size distributions and the number of crystals per unit area were measured. The numbers of crystals per unit volume of glass were then calculated using well-known stereological equations described in Ref. [17]. Typical micrographs of baria-silicate glasses studied undergoing LPS are shown in Fig. 5a (LPS) and b

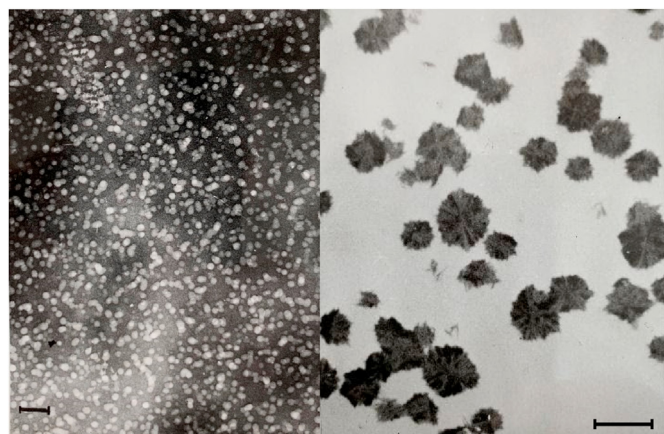


Fig. 5. A (LHS). Transmission electron micrograph of glass 28.3B 760 °C, 8.4 h, bar = 0.5 μm showing LPS (silica-rich droplets in a Ba-rich matrix). B (RHS). Optical micrograph of glass 28.3B treated for 8h at 760 °C plus 22 min at 815 °C to develop BS2 crystals. The largest crystals have approximately 15 μm in diameter (= bar size). The LPS droplets are too small to be revealed in this optical micrograph.

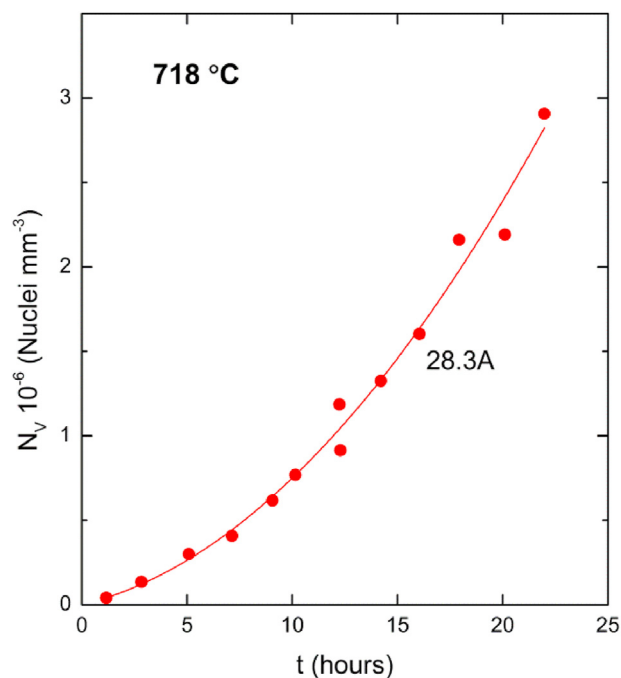


Fig. 6. Number of crystals per unit volume (N_v) versus time plot for the phase separating glass 28.3A nucleated at 718 °C. Source [17].

(crystals).

Heterogeneous nucleation of $\text{BaO} \cdot 2\text{SiO}_2$ spherulites was observed to occur on the surface of bubbles, cracks and external surfaces of the heat-treated glasses. However, the number of these heterogeneously nucleated crystals was negligible compared to the number of crystals that formed homogeneously in the interior of the glass sample. It is likely (and accepted by the glass crystallization community) that most crystals in the bulk of this particular glass nucleated homogeneously due to the very deep undercooling ($T_{\text{nuc}}/T_{\text{melt}} \sim 0.5$) necessary to observe internal nucleation. A corroborating fact is that the maximum nucleation rate, T_{max} , for BS2 glasses containing different levels of impurities is always at ca. 695–705 °C (not shown here). Therefore, the typical contaminants in this glass (Sr, Ca, Na, Al, Fe, OH ...) affect the diffusivity, but do not significantly change the nucleus/liquid surface energy, σ , and driving force, ΔG , which determine the peak position. If heterogeneous nucleation were dominant and caused by impurities, σ would change and T_{max} would be quite different for each glass batch prepared by each author, which likely contains different types and levels of impurities.

The $\text{BaO} \cdot 2\text{SiO}_2$ (BS2) spherulites in glasses 27.0, 28.3A, 28.3B, 29.0 are approximately equally shaped and spherical. The stoichiometric glasses with ~ 33.3 mol% BaO have more acicular crystals, especially when the development heat-treatment is short, i.e., for specimens nucleated at temperatures close to $T_{\text{max}} \sim 700$ °C, which had a substantial number of crystals. However, they are all spherulitic as opposed to single crystals.

Carefully designed experiments were carried out aiming at establishing possible relationships between liquid phase separation and the nucleation of crystals. For that purpose, glasses having compositions within the miscibility gap (27.0, 28A, 28B) and glasses outside the gap (33.3A) Fig. 2, close to the stoichiometric barium disilicate composition, were treated and studied at several temperatures somewhat above the transformation range. The experimental details are given in Refs. [17]. In short, small pieces of glass were nucleated at a temperature T_n , from 20 to 50 °C above the T_g of each glass, and developed at $T_d = 60\text{--}100$ °C higher than T_n . Optical micrographs were taken and manually examined by counting (N_v) and measuring (d) of all the crystals in each micrograph. A total of about 2000 micrographs were

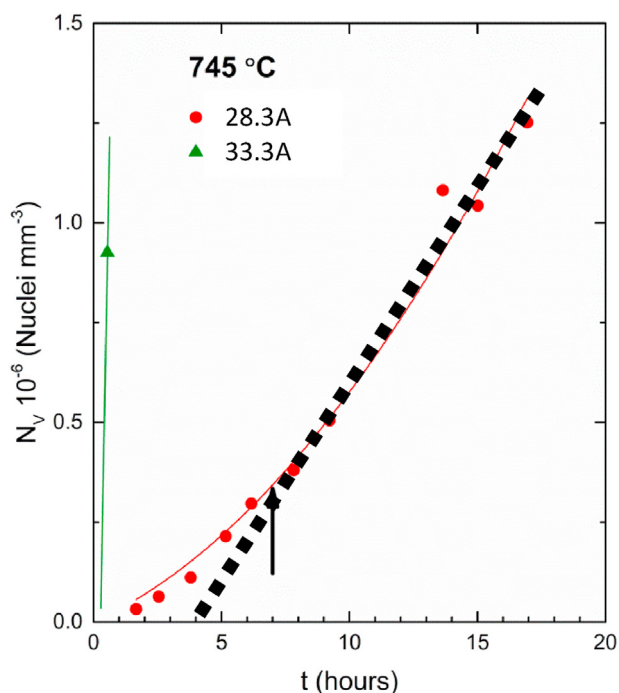


Fig. 7. Crystal nucleation (N_v versus time) plots for the phase separating glass 28.3A, and glass 33.3A (stoichiometric, outside de miscibility gap), both nucleated at 745°C. Source [17]. The black squares indicate the steady-state limit.

analyzed. The average number of crystals counted per thermal treatment was 400, which leads to a typical error of $\sqrt{400}/400 = 5\%$ in N_s (crystals per unit area). This uncertainty coupled with errors in the measurement of crystal size, d , led to combined errors of approximately 10–15% in the number of crystals per unit volume, N_v ($N_v \sim N_s / \langle d \rangle$). The error bars are not shown in the plots to render them cleaner and more easily visualized. These crystal nucleation kinetic studies were correlated with TEM (Transmission Electron Microscopy) and SAXS (Small-Angle X-ray Scattering) evaluations of the liquid-liquid immiscibility in the same glass specimens.

Fig. 6 shows crystal nucleation density (N_v) versus time curves for glasses 28.3A nucleated at 718°C ($T_g \sim 690^\circ\text{C}$). The nucleation rate, $I = dN_v/dt$, increases continuously with time up to 20 h (the limit used in these experiments). This curve could be due to transient nucleation effects, with a characteristic induction time for nucleation τ_{ind} (but at 18 °C above T_g , τ_{ind} is only a few minutes), or due to simultaneous LPS. We will discuss this matter soon in this article.

Fig. 7 shows a similar trend for glass 28.3A nucleated at 745°C. The nucleation rate increases gradually up to about 7 h and then becomes constant. The same figure shows that the nucleation rate of the stoichiometric glass 33.3A is about 20 times higher than the maximum I of glass 28.3A. In all temperatures, the nucleation rates of glasses having compositions close to the stoichiometric crystal composition (33.33 % mol Li_2O) are much higher than those of other compositions. This is a relevant fact for the explanation of the LPS effect on nucleation discussed below.

Samples of glass 28.3A were also nucleated at 760°C. Fig. 8 shows that its nucleation rate is initially lower, reaches a maximum value at about 2.5 h and levels off after 3 h approaching a constant value. The behavior is thus similar at 718 °C, 745 °C and 760 °C, it only takes longer to approach a steady-state at lower temperatures. It should be stressed that all these temperatures are well above the laboratory T_g ($\sim 695^\circ\text{C}$). Hence these curved regions of the N_v versus time plots do not refer to a classical regime of non-steady state (non-stationary) nucleation, normally observed around T_g when an equilibrium distribution of crystalline embryos is not formed in the glass matrix yet.

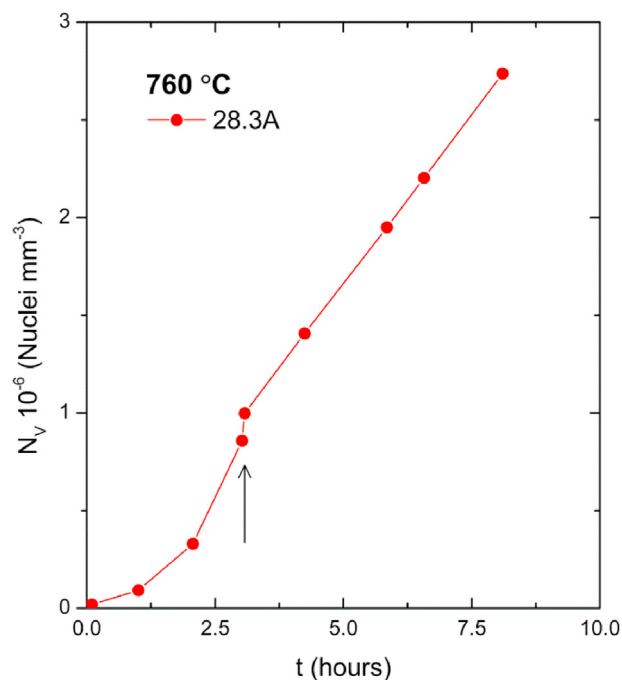


Fig. 8. Crystal nucleation (N_v versus time) plots for phase separating glass 28.3A nucleated at 760°C. An arrow shows the level-off time to approach steady-state rate. Source [17].

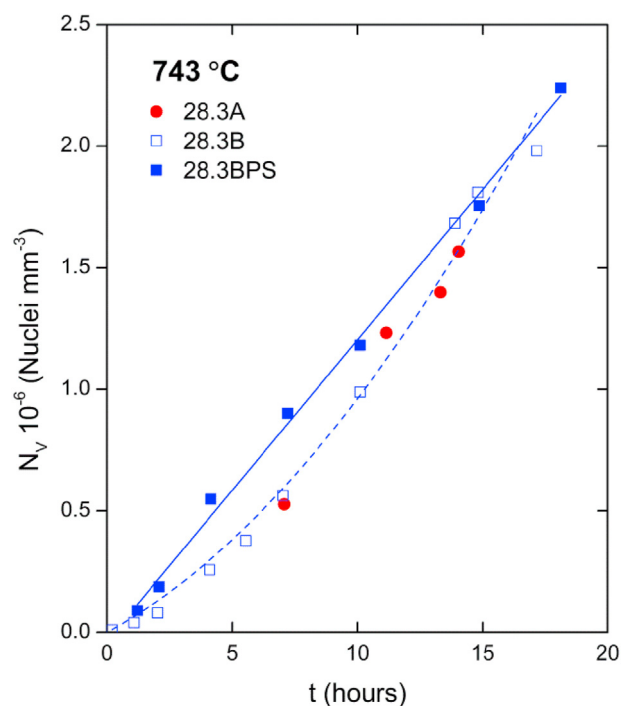


Fig. 9. Crystal nucleation curve for glass 28.3BPS (bule squares, solid straight line) that was first heat-treated at 821 °C for 22 min to cause a significant development of the liquid phase separation, then nucleated at 743 °C together with phase separating glasses 28.3 A (●) and 28.3B (□, dashed line). Source [17].

A different experiment was devised to check the possible effect of LPS on crystallization. Samples of glass 28.3B were first heat-treated at 821 °C for 22min to cause a significant development of the amorphous phase separation. The bluish appearance of the specimens and the rather large size of the silica-rich droplets (micrographs not shown) after

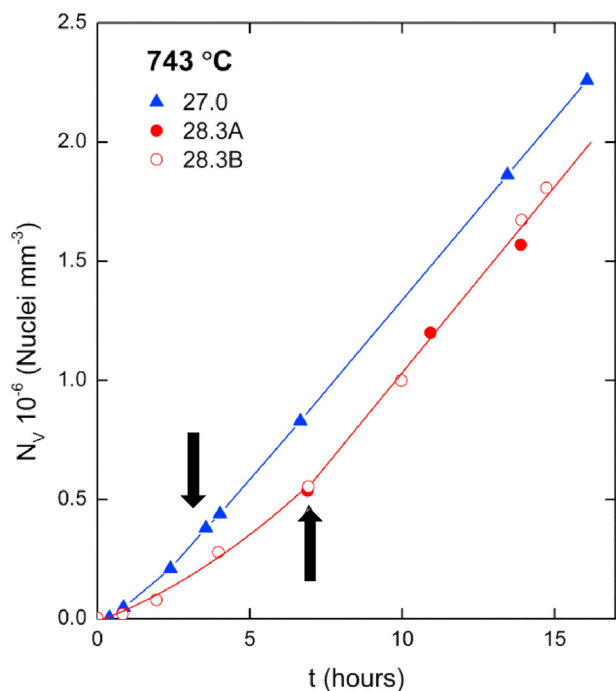


Fig. 10. Crystal nucleation plots of phase separating glasses 27.0 (triangles) 28.3A (●) and 28.3B (○) nucleated at 743 °C. The arrows indicate the start time of steady-state nucleation [17].

this treatment indicated that the LPS had reached an advanced stage. These specimens are called 28.3BPS. Then, the same specimens were subjected to the ordinary double-stage heat-treatment at 743 °C and 820 °C. A few crystals, much bigger than the average size, could be seen in the micrographs. These were formed during the first heat treatment to induce LPS and were neglected; all the other crystals were counted. Fig. 9 shows the resulting curves. The nucleation rate, I , in glass 28.3BPS is constant and higher than the initial rate of glasses 28.3A and 28.3B. These two different melts of the same chemical composition have equal nucleation rates - showing the reproducibility of the presented experiments - and increase continuously up to about 7 h when they approach a constant value, which is higher than I for glass 28.3BPS.

These results show that the crystal nucleation rates of glasses 28.3A and 28.3B, which undergo simultaneous LPS and crystallization, increase with time. The nucleation curve of glass 27.0 heated at 743 °C is shown in Fig. 10 together with the curve for glasses 28.3A and 28.3B. The nucleation rate of glass 27.0 increases up to about 2 h and reaches a steady-state regime. After these periods, the nucleation rates of the three glasses are constant and equal.

3.1.2. SAXS experiments and results with barium silicate glasses

The theoretical and experimental details of SAXS are described in Ref. [17]. For this critical review article, it suffices to know that the integrated SAXS intensity over the whole range of scattering angles, Q , is proportional to the nano structural parameters of the phase separated glasses

$$Q(t) \sim \alpha(t) \cdot [1 - \alpha(t)] \cdot \Delta\rho(t)^2, \quad (3)$$

where $\alpha(t)$ is the volume fraction of scattering particles and $\Delta\rho(t)$ is the electronic density difference between the glassy particles (silica-rich droplets) and the residual (silica-poor) glassy matrix. Both quantities increase with time of heat treatment. As for any heat treatment and composition the number of BS2 crystals is orders of magnitude smaller than the number of glassy droplets (as seen in the electron micrographs), and the chemical contrast of the crystals with the residual

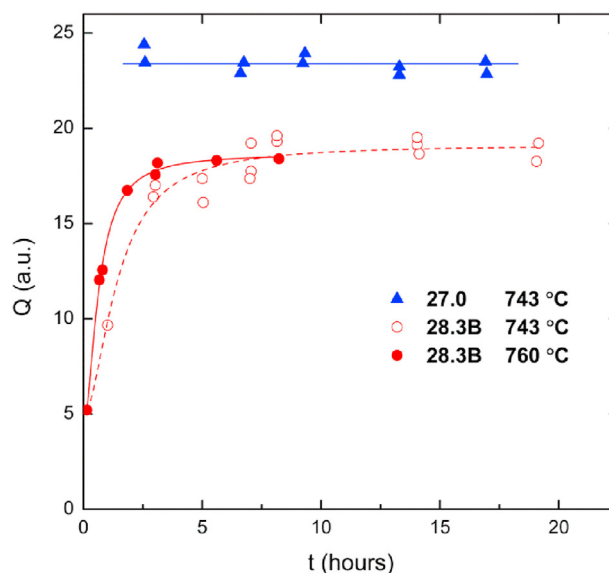


Fig. 11. SAXS integral (Q) for phase separating glasses 27.0 and 28.3B at 743 °C, and glass 28.3B at 760 °C. Source [17].

glassy matrix is also much smaller (the chemical composition of the BS2 crystals is not far from the chemical compositions of the residual glass), Q is by far dictated by the glassy droplets and, despite the fact that a certain number of critical nuclei coexist with the liquid droplets, Q is insensitive to the presence of crystals. Hence, when the process of nucleation and growth of liquid droplets finishes, the residual glass matrix reaches the binodal boundary and Q attains a constant value. This is thus a powerful method to evaluate the time necessary to reach the binodal at any temperature. After that stage, coarsening of the nanostructure starts to occur, when the largest droplets grow at the expense of the smallest and the total number of droplets decrease with time, however the compositions of both phases remain unaltered.

Fig. 11 shows the SAXS integral for samples of glasses 27.0 and 28.3B treated at 743 °C, and of glass 28.3B treated at 760 °C. These plots show that after a few hours the LPS reaches the coarsening stage in these two glasses in this range of temperatures. Most relevant for the objectives of this article is the comparison of the Q versus time plots in Fig. 11 with the nucleation rate plots of glasses 27.0 and 28.3 at 743 °C (Figs. 10) and 28.3 at 760 °C (Fig. 8). For these three situations, the times necessary for the crystal nucleation process achieve steady-state conditions coincide with the times needed for Q become constant. This is thus an obvious sign of the compositional effect of LPS on crystal nucleation because this is precisely the time needed for the composition of the glassy matrix to reach the binodal at each temperature.

3.1.3. Testing the possible effect of the droplet interfaces on crystal nucleation in baria-silica glasses

In his Ph.D. thesis, Ramsden [24] carried out a very detailed electron microscopy study of LPS in phase-separating baria-silica glasses to search for a possible correlation between the morphology (number and surface area) of liquid droplets with crystal nucleation kinetics in the same glasses and temperatures. Estimations of the interfacial area per unit volume of phase separated glasses showed that this quantity changed only very slowly at 700 °C. However, the crystal nucleation rates changed considerably with time at 700 °C indicating that the interfacial area of the droplets was not affecting crystal nucleation. Ramsden found no correlation between the surface area of the LPS droplets and crystal nucleation. Zanotto [17] extended Ramsden's study with other glass compositions and heat treatments using SAXS. Again, no correlation was found between the LPS surface area and crystal nucleation kinetics in those two glasses. Moreover, no evidence of heterogeneous crystal nucleation on liquid phase interfaces was found.

Table 1
Nucleation rates and surface energy for liquid droplets and crystals.

	Nucleation rates	Surface energy
LPS:	$I \sim 10^{20}/\text{m}^3 \cdot \text{s}$	$\sigma < 0.005 \text{ J/m}^2$
Crystal Nucleation :	$I \sim 10^{10}/\text{m}^3 \cdot \text{s}$	$\sigma \sim 0.130\text{--}0.200 \text{ J/m}^2$

A summary of the respective nucleation rates and (fitted) values of surface energies is shown in Table 1.

3.2. Lithium silicate glasses

3.2.1. Crystal nucleation in phase separated lithia-silica glasses

To generalize the findings on baria-silica glasses, we carried out similar experiments with lithia-silica glasses having compositions inside and outside the respective liquid miscibility gap. The transformation range for the studied $\text{Li}_2\text{O-SiO}_2$ glasses is situated around 450°C , and a steady-state nucleation rate is rapidly established in the stoichiometric composition for temperatures higher than about 475°C ($T_g \sim 450^\circ\text{C}$) [17]. Furthermore, the SAXS experiments of Zanotto and Craievich [61] demonstrated that the time required for the LPS to reach its final stage, in a glass with 31.0 mol% Li_2O , was about 15 h at 475°C . Therefore, 481°C was the temperature chosen for the study of crystal nucleation in the $\text{Li}_2\text{O-SiO}_2$ glasses. The liquid phase separation process should reach its final stage in a few hours at this temperature, and non-steady state nucleation effects should be negligible. Much higher temperatures would cause the nucleation rates to be too low rendering their accurate measurement more difficult, whereas much lower temperatures would mix the effects of LPS and non-stationary crystal nucleation.

Fig. 12 shows the crystal nucleation densities *versus* time for glasses 17.7, 31.0 and 33.2B at 481°C . Their positions are shown in the phase diagram. The first and most striking observation is that the crystal nucleation rates (curve slopes) in glasses 17.7 and 31.0 (inside the miscibility gap), initially increase with time and after about 4 h, they become equal. This is a clear indication of the compositional effect of

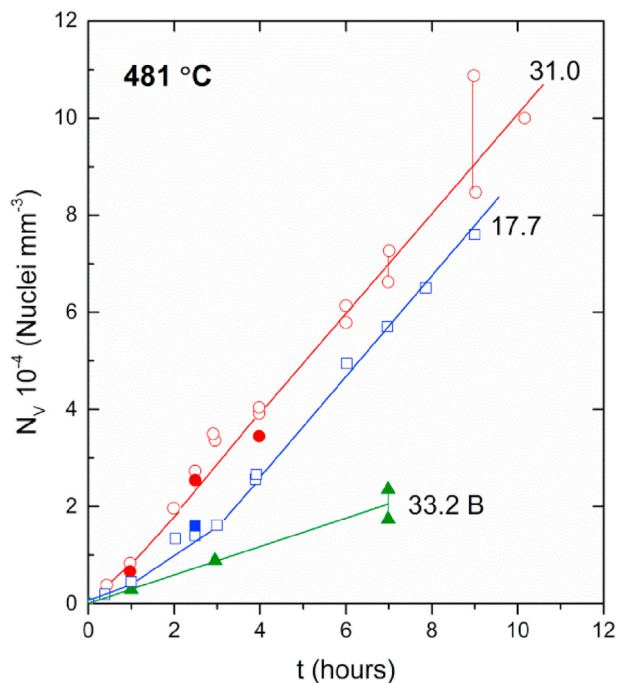


Fig. 12. Number of crystals per unit volume (N_v) *versus* time plots for $\text{Li}_2\text{O-SiO}_2$ glasses nucleated at 481°C . $T_d = 600^\circ\text{C}$ (●, ■); $T_d = 570^\circ\text{C}$ (▲, ○, □). Two data points joined by a vertical line for some treatment times refer to duplicate samples. Source [17].

LPS on nucleation, i.e., the composition of the glass matrix continuously moves towards the stoichiometric 33.33 %mol glass, eventually reaching the bimodal boundary and becoming equal. This is the same effect observed in the study with the baria-silica glasses.

However, the steady-state nucleation rates of both glasses became about 3.6 times higher than the constant rate in the (almost) stoichiometric glass 33.2B; and this is not possible to explain by compositional effects. We will return to this problem in the end of this session.

Another less visible and less important observation is that for glass 17.7, between 1 and 3 h, there are some experimental points (2.5 and 3.0 h) systematically higher than the smooth curve drawn. The same phenomenon has also been observed by Tomozawa [10] and Zanotto and Craievich [61] in the nucleation curves of $\text{Li}_2\text{O-SiO}_2$ glasses undergoing phase separation. We therefore tentatively suggested that this small additional effect in glasses 17.7 and 31.0 might be genuine, but we have had no clear explanation for it so far. In a recent personal discussion with Professor Minoru Tomozawa about the temporary increase in the nucleation rates of glasses undergoing phase separation observed in his pioneering study [10], he suggested another plausible possibility: “I will stand by my data since similar results were obtained at three different temperatures. But I would like to change my interpretation a little, given my subsequent studies of water in glasses”. It is known that the water (OH^-) solubility is lowest for silica glass and increases steadily with increasing alkali content. In a recent paper dealing with a water concentration profile during surface crystallization of SiO_2 glass, Tomozawa et al. [75] showed that water collects (on the glass side) at the crystal/glass interface since water solubility is lower in the crystal. His old results [10] show that crystal nucleation in a $\text{Li}_2\text{O-SiO}_2$ glass undergoing LPS is increased only during the early stage of phase separation. Because of the lower water solubility in the silica-rich liquid droplets compared with the lithium-rich glass matrix, water is likely expelled during the phase separation process. Then, water will be accumulated at the liquid droplet interfaces, while the growth of the phase separated phase is fast. Later on, the water concentration profile in $\text{Li}_2\text{O-SiO}_2$ glass phase will become uniform since the growth of the SiO_2 -rich droplets will be slower in the coarsening stage (proportional to $1/3$ power of time). Hence, water likely reduces the glass viscosity and increases the nucleation rate, only during the early stage of phase separation. This is Tomozawa’s new interpretation of his old data on the observed temporary increase of crystal nucleation rates in phase separating glasses.

Most experimental points in Fig. 12 were obtained after the nucleated glasses were subjected to a development treatment at 570°C . Some specimens, however, were developed at 600°C for samples 31.0 (●) and 17.7 (■) to test the possible influence of the growth (development) treatment on the N_v values. The minor differences observed for the two development temperatures are within the statistical error.

A different experiment was devised to test the effects of the advanced (coarsening) stage of LPS on crystal nucleation. Specimens of glasses 17.7 and 31.0 were first heated at 497°C for 5 h to cause the development of LPS. Samples of glass 33.2B (which do not undergo LPS) were also subjected to the same treatment for control purposes. After that, they were all nucleated at 481°C and developed at 570°C . Fig. 13 shows that, despite their widely different Li_2O contents, the crystal nucleation in glasses 17.7 and 31.0 are equal. They are approximately 2.4 times higher than the nucleation rates in glass 33.2B. In the same figure, the steady-state nucleation curves of the as-quenched glasses (dashed lines) obtained from Fig. 12 are also plotted for quenched phase separating glasses. It can be seen that the previous phase separation treatment decreases the nucleation rates. For the non-phase separating glass 33.2B, there is no change in the nucleation rates. The intercept on the N_v axis is due to prior nucleation in the initial heat treatment at 497°C .

3.2.2. Crystal nucleation in the stoichiometric lithium silicate glass 33.2B

The analyzed composition of glass 33.2B was very close to the

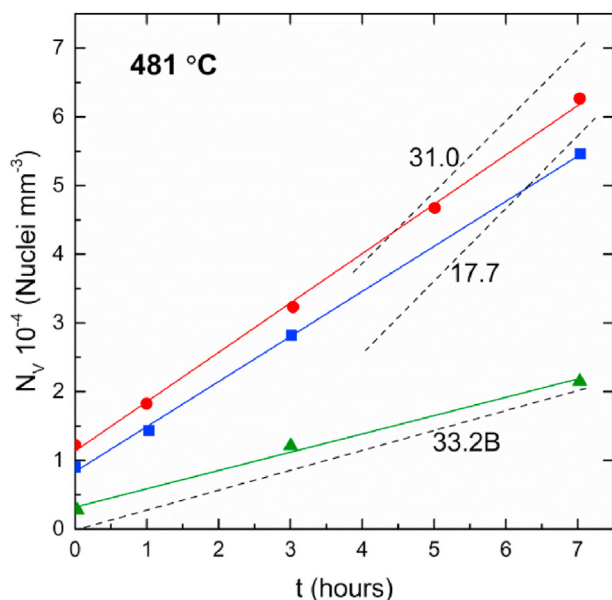


Fig. 13. Number of crystals per unit volume (N_v) versus time plots for $\text{Li}_2\text{O-SiO}_2$ glasses nucleated at $481\text{ }^\circ\text{C}$. (—) as-quenched glasses; (---) previously phase separated for 5 h at $497\text{ }^\circ\text{C}$ [17].

stoichiometric crystal $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (33.33% Li_2O) and is outside the miscibility gap. The nucleation rate at $481\text{ }^\circ\text{C}$ is compared to those of the phase-separating glasses (17.0 and 31.0) in Figs. 12–13. It should be stressed that, in this case, the results are more precise than the values obtained for the barium silicate glasses, because the nucleation rates are substantially lower for the 33.2B Li_2O glass, allowing the nucleation curves to be obtained for extended periods of time. Furthermore, the ellipsoidal shape of the crystals was very well-defined allowing the use of an accurate stereological equation for the calculation of N_v .

The overall outcome of all these experiments is that the nucleation rates of the two separating glasses become equal (despite their widely different starting compositions) and higher than that of the stoichiometric non-separating glass at this particular temperature. These similar nucleation rates of the glasses undergoing LPS must be because after phase separation is completed, the chemical compositions of the glass matrices in both glasses reach the bimodal boundary and become the same, clearly showing the compositional effect of LPS on crystal nucleation. Moreover, phase separation pushes the glass matrix composition towards that of the stoichiometric LS2 crystal, but does not reach it. Therefore, it was expected that the nucleation rates of the almost stoichiometric 33.2 glass should be higher than those of phase separated glasses 17.0 and 31.0 (as indeed shown by similar experiments with the BaO-SiO_2 glasses). However, surprisingly, they are lower. This same result was reported in the previous studies of Tomozawa [10] and Zanotto & Craievich [61] with lithia-silica glasses. Hence, this dilemma has remained for 48 years.

Fortunately, however, an explanation for this apparent impasse can now be given by carefully analyzing results published a few years ago by Sycheva [76]. She investigated the kinetics of crystal nucleation in three lithium silicate glasses containing 23.4, 26.0 and 29.1 mol% Li_2O (compositions lying inside the immiscibility region) and compared them with the nucleation rates in a stoichiometric LS2 glass (which does not undergo LPS) at several temperatures. Sycheva found that the absolute values of the steady-state crystal nucleation rates, I_{st} , in the glasses lying inside the miscibility gap are similar - which agrees with the results of this author for one temperature, $481\text{ }^\circ\text{C}$. The similarity between these two parameters, $I_{st}(T_{max})$ and T_{max} , of the separating glasses is explained by the fact that, after phase separation, the continuous glassy matrix of the 3 compositions within the immiscibility region are the same, and are displaced toward (but never reach) the

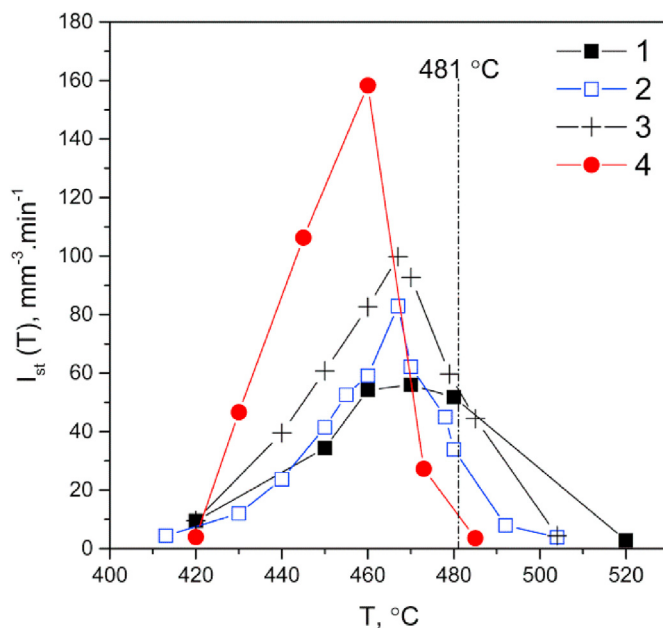


Fig. 14. Temperature dependences of the steady-state nucleation rates of lithium disilicate crystals, $I_{st}(T)$, for glasses 1 = 23.4 Li_2O , 2 = 26.0 Li_2O , 3 = 29.1 Li_2O (undergoing LPS) and 4 = 33.3 mol% Li_2O , i.e. stoichiometric lithium disilicate [76]. It should be noted that the nucleation rate curves of the phase-separating glasses are approximately equal, are shifted to the right, peak at a higher temperature, and are higher than that of the LS2 glass at $481\text{ }^\circ\text{C}$.

lithium disilicate composition. However, most importantly, she demonstrated that the temperature of maximum nucleation rate, T_{max} , for the 3 glasses undergoing LPS is higher by approximately $12\text{ }^\circ\text{C}$ as compared to the stoichiometric LS2 glass. Fig. 14 shows that, in general, the nucleation rates of the stoichiometric glass are higher than those of the phase-separating glasses (as expected), but the nucleation peak of the LS2 glass is located at a lower temperature, hence at approximately $481\text{ }^\circ\text{C}$ (where my previous studies and Tomozawa's were performed) the nucleation rate of LS2 glass is indeed lower than of the phase-separating glasses.

Therefore, almost 5 decades after the first experiments with lithia-silica glasses, these new experiments of Sycheva [76] explain the findings of Tomozawa [10], Zanotto & Craievich [61] and Zanotto [17], definitively eliminating the remaining open issue (higher nucleation rates of LPS glasses at $481\text{ }^\circ\text{C}$ than those of the LS2 glass). The crystal nucleation rates of the phase separating glasses are higher at $481\text{ }^\circ\text{C}$ because the maximum of the stoichiometric glass occurs at a lower temperature, however the I_{max} of the 33.3% glass is indeed higher than the maxima of the phase separating glasses.

This finding thus confirms the compositional effect of LPS on crystal nucleation in oxides glasses, however, there is no obvious reason why the same mechanism should not work for other glass-former families. Hence, we believe the above discussed analysis of old and new results settles an old-standing problem.

4. Summary and conclusions

We reviewed a set of suitably designed, systematic experiments using optical and electron microscopies and SAXS, carried out with baria-silica glasses inside and outside the respective liquid miscibility gap. They unmistakably demonstrate that: i) the effect of the liquid droplet interfaces is negligible because their interfacial energy ($\sim 0.004\text{ J/m}^2$) is much smaller than that of the crystal/nucleus surface energy ($0.130\text{--}0.200\text{ J/m}^2$), hence they are not privileged nucleation sites; ii) the crystal nucleation kinetics of the phase separating glasses initially increase and reach a constant value when the composition of

the liquid matrix reaches the binodal boundary; iii) LPS pushes the composition of the glassy matrix of separated glasses towards the stoichiometric composition of the crystal phase BS2 thus enhancing the crystal nucleation rates, but they never reach the values of the stoichiometric BS2 glass.

Five decades after the first experiments with lithia-silica glasses, old and new results combined definitively eliminate the remaining open issue regarding the: i) temporary increase in the nucleation rates of the phase-separating glasses, which is now reasonably ascribed to water (OH-) expelled at the silica-rich droplet interfaces and ii) the lower nucleation rates in the stoichiometric glass, LS2, in the temperature range 470–481 °C is understandable because the nucleation maxima of the phase separating glasses are shifted to higher temperatures.

Therefore, our analysis with several glasses of two silicate systems unambiguously demonstrates that the major role of LPS is to **push the composition** of the glass matrix towards that of the stoichiometric crystal phase enhancing crystal nucleation. Therefore, in our opinion, at least for oxide glasses, this case is closed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Funding from CNPq and the São Paulo Research Foundation – Fapesp grant # 2013/007793–6 is greatly appreciated. I am thankful to Prof. Minoru Tomozawa – one of the pioneers in this subject – for his valuable suggestions. The critical comments of Drs. Vladimir Fokin and Maziar Montazerian are also much appreciated. I dedicate this review article to Professors Aldo Craievich and Peter F. James⁺ who introduced me to the subjects of LPS and crystallization in glasses in the late seventies. (⁺ deceased).

References

- [1] O.V. Mazurin, E.A. Porai-Koshits, *Phase Separation in Glass*, North-Holland, Amsterdam –Tokyo, 1984.
- [2] J. Rincon, A. Duran, *Separacion de Fases en Vidrios en el Sistema Na₂O-B₂O₃-SiO₂*, Sociedad Española de Cerámica y Vidrio, Madrid, 1982.
- [3] S. Lan, Z.D. Wu, M.T. Lau, H.W. Kui, Crystallization in homogeneous and phase separated Pd₄₁.25Ni₄₁.25P₁₇.5 bulk metallic glasses, *J. Non-Cryst. Solids* 373–374 (2013) 5–12.
- [4] M. Tashiro, Nucleation and crystal growth in glasses, *Proc. VIII International Congress on Glass, Soc. Glass Technology, Sheffield, London, 1968*113.
- [5] J.J. Hammel, Phase separation in Na₂O-CaO-SiO₂ glasses, in: A.C. Zettlemoyer (Ed.), *Nucleation*, M Dekker, New York, 1969.
- [6] S. Scholes, General discussion. *Disc. Faraday Soc.* 50 (1970) 222.
- [7] D.R. Uhlmann, General discussion. *Disc. Faraday Soc.* 50 (1970) 233.
- [8] J. Zarzycki, Phase separated systems, *Discuss. Faraday Soc.* 50 (1970) 122.
- [9] P.F. James, Nucleation in glass-forming systems – a review, *Proc. symposium on nucleation and crystallization in glasses*, Washington DC, *Adv. Ceram.* 4 (1982) 1–48.
- [10] M. Tomozawa, Liquid phase separation and crystal nucleation in Li₂O-SiO₂ glasses, *Phys. Chem. Glasses* 13 (1972) 161–166.
- [11] E.D. Zanotto, P.F. James, A.F. Craievich, The effects of amorphous phase separation on crystal nucleation kinetics in BaO-SiO₂ glasses, part 3: isothermal treatments at 718–760 °C, SAXS results, *J. Mat. Science.* 21 (1986) 3050–3064.
- [12] A.F. Craievich, E.D. Zanotto, P.F. James, Kinetics of sub-liquidus phase separation in silicate and borate glasses, *Bull. Soc. Franc. Min. et Crist.* 106 (1983) 169–184.
- [13] E.D. Zanotto, Positron annihilation in phase-separated BaO-SiO₂ glasses, *J. Am. Ceram. Soc.* 66 (1983) 37–38.
- [14] E.D. Zanotto, A.F. Craievich, P.F. James, SAXS and TEM studies of phase separation in BaO-SiO₂ glasses, *J. Phys.* 43 (1982) 107–110.
- [15] E.D. Zanotto, A.H. Ramsden, A.F. Craievich, P.F. James, Influence of Amorphous Phase Separation on Crystal Nucleation and Growth in Baria Silica Glasses, *Society of Glass Technology, Symposium on Phase Transformations in Vitreous State, Extended Abstract*, (1981).
- [16] E.D. Zanotto, P.F. James, The compositional dependence of crystal nucleation in Li₂O-SiO₂ glasses, *Proceedings XIII Int. Congress on Glass, Hamburg. Glastechn. Ber.* 56 (1983) 794–799.
- [17] E.D. Zanotto, The Effects of LPS on Crystal Nucleation and Growth in Lithia-Silica and Baria-Silica Glasses, University of Sheffield, UK, 1982.
- [18] R.S. Roth, E.M. Levin, Phase equilibria in the subsystem barium disilicate dibarium trisilicate, *J. Res. Natl. Bur. Stand. (U.S.)* 62 (1959) 193–200.
- [19] R.M. Douglas, The crystal structure of sanbornite BaSi₂O₅, *Am. Mineral.* 43 (1958) 517–536.
- [20] H. Katscher, G. Rissert, F. Liebau, The crystal structure of high-temperature Ba₂[Si₄O₁₀], *Zeits. Für Krist.* 137 (1973) 146–158.
- [21] G.J. Oshllegal, Crystallization of glasses in the system BaO-2SiO₂-2BaO-3SiO₂, *J. Am. Ceram. Soc.* 58 (1975) 148–148.
- [22] R.J. Charles, Metastable immiscibility in the BaO-Li₂O-SiO₂ system, *Phys. Chem. Glasses* 8 (1967) 185–189.
- [23] T.P. Seward III, D.R. Uhlmann, D. Turnbull, Development of phase structure in glasses, with special reference to the system BaO-SiO₂, *J. Am. Ceram. Soc.* 51 (1968) 634–643.
- [24] T.P. Seward III, D.R. Uhlmann, D. Turnbull, Phase separation in the system BaO-SiO₂, *J. Am. Ceram. Soc.* 51 (1968) 278–285.
- [25] A.H. Ramsden, *Crystal Nucleation and Growth in BaO-SiO₂ Glasses*, PhD thesis University of Sheffield, UK, 1977.
- [26] J.F. MacDowell, Composition, microstructure versus heat treatment and properties given, *Proc. Br. Ceram. Soc.* 101 (1965) 229–240.
- [27] E.G. Rowlands, “Nucleation and Crystal Growth in the Li₂O-BaO-SiO₂ System” Ph, D. thesis, University of Sheffield, UK, 1976.
- [28] D.G. Burnett, R.W. Douglas, Nucleation and crystallisation in the soda-baria-silica system, *Phys. Chem. Glasses* 12 (1971) 117–124.
- [29] S.W. Freiman, G.Y. Onoda, A.G. Pincus, Controlled spherulitic crystallization in 3BaO-5SiO₂ glass, *J. Am. Ceram. Soc.* 55 (1972) 354–359.
- [30] M.H. Lewis, G. Smith, Spherulitic growth and recrystallization in barium silicate glasses, *J. Mat. Science* 11 (1976) 2015–2026.
- [31] A.H. Ramsden, P.F. James, The effects of amorphous phase separation on crystal nucleation kinetics in BaO-SiO₂ glasses - Part 1 General survey, *J. Mater. Sci.* 5 (1984) 1406–1419.
- [32] P.F. James, E.G. Rowlands, Kinetics of nucleation and growth in barium disilicate glass, *Phase Transformations*, vol. 2, The Institute of Metallurgists, London, 1979, pp. III/27–III/29.
- [33] F.C. Kracek, Phase Equilibrium relations in the system Na₂SiO₃-Li₂SiO₃-SiO₂, *J. Phys.* 6 (1939) 2863–2877.
- [34] N.S. Andreev, D.A. Goganov, E.A. Porai-Koshits, YuG. Sokolov, Chemically Heterogeneous Structure of Two-Component Sodium and Lithium Silicate Glasses vol. 3, *Catalyzed Crystallization of Glass*, 1964, pp. 47–52.
- [35] Y. Moriya, D.H. Warrington, R.W. Douglas, A study of metastable liquid-liquid immiscibility in some binary and ternary alkali silicate glasses, *Phys. Chem. Glasses* 8 (1967) 19–25.
- [36] F. Liebau, Untersuchungen an schichtsilikaten des formeltyps am(Si₂O₅)_n. Die kristallstruktur der zimmertemperaturform des Li₂Si₂O₅, *Acta Crystallogr.* 14 (1961) 389–395.
- [37] M. Tomozawa, Liquid phase separation and crystal growth in Li₂O-SiO₂ glass, *Phys. Chem. Glasses* 14 (1973) 112–113.
- [38] M.H. Lewis, J. Metcalf-Johansen, P.S. Bell, Crystallization mechanisms in glass-ceramics, *J. Am. Ceram. Soc.* 62 (1979) 278–288.
- [39] R.H. Doremus, A.M. Turkalo, Crystallisation of lithium disilicate in lithium silicate glasses, *Phys. Chem. Glasses* 13 (1972) 14–14.
- [40] W. Vogel, *Structure and Crystallization of Glasses*, Pergamon Press, Oxford, 1971.
- [41] T. Ogura, R. Hayami, M. Kadota, Kinetics and mechanism of crystallization of lithium silicate glasses, *J. Ceram. Soc. Jap.* 76 (1968) 277–284.
- [42] D.L. Kinser, L.L. Hench, Effect of a metastable precipitate on the electrical properties of a Li₂O-SiO₂ glass, *J. Mat. Science* 5 (1968) 445–448.
- [43] F.P. Glasser, Crystallisation of lithium disilicate from Li₂O-SiO₂ Glasses, *Phys. Chem. Glasses* 8 (1967) 224–237.
- [44] M. Tomozawa, *Glass: nature, structure, and properties*, Treatise on Materials Science and Technology vol. 17, Academic press, New York, 1979, pp. 71–113.
- [45] S.D. Stookey, *Catalyzed Crystallization of glass in theory and practice*, *Glastechn. Ber.* 32 (1959) 1–8.
- [46] W. Vogel, Inter-relationships between microheterogeneity, nucleation, and crystallization in glasses, *Glass Technol.* 7 (1966) 15–21.
- [47] S.M. Ohlberg, H.R. Golob, D.W. Strickler, Crystal Nucleation by Glass in Glass Separation, *The American Ceramic Society*, 1962, pp. 55–62.
- [48] R.D. Maurer, Crystal nucleation in a glass containing titania, *J. Appl. Phys.* 33 (1962) 2132–2139.
- [49] R.D. Maurer, Crystallization of a titania-nucleated glass, *J. Am. Ceram. Soc.* (1964) 5–9.
- [50] A.M. Kalina, V.N. Filipovich, N.A. Kolesova, Crystallisation products of lithium silicate glasses, *The structure of glass* 3 (1964) 53–53.
- [51] I.M. Buzhinskii, E.I. Sabaeva, A.N. Khomyakov, Variations of the physical properties during heat treatment of glasses in the Li₂O-Al₂O₃-SiO₂ system mineralised by titanium dioxide, *The structure of glass* 3 (1964) 133–146.
- [52] P.E. Doherty, P.W. Lee, R.S. Davies, Direct observation of the crystallization of Li₂O-Al₂O₃-SiO₂ glasses containing TiO₂, *J. Am. Ceram. Soc.* 50 (1967) 77–81.
- [53] D.G. Burnett, R.W. Douglas, Nucleation and crystal growth in the soda-baria-silica system, *Discuss. Faraday Soc.* 50 (1970) 200.
- [54] G. Bayer, W. Hoffman, Primary crystallisation of glasses in the system Na₂O-TiO₂-SiO₂ and its relation to immiscibility, *Glass Technol.* 7 (1966) 94–97.
- [55] L. Leger, J. Bray, *Silicate industriels. Separation de phases dans le verre* vol. 33, (1968), pp. 257–264 9.
- [56] S.V. Phillips, P.W. McMillan, Phase separation and crystallisation in Li₂O-SiO₂ and Li₂O-SiO₂-P₂O₅ glasses, *Glass Technol.* 6 (1965) 46–51.
- [57] H. Harper, P.F. James, P.W. McMillan, Crystal nucleation in lithium silicate glasses,

- Discuss. Faraday Soc. 50 (1970) 200–205.
- [58] H. Harper, P.W. McMillan, The formation of glass-ceramic microstructures, *Phys. Chem. Glasses* 13 (1972) 97–101.
- [59] P.W. McMillan, Phase-separation, crystallisation, and microstructure of glass-ceramics, *Proc. X international congress on glass*. 1 (1974) 1–12.
- [60] K. Nakagawa, T. Izumitani, Relationship between phase separation and crystallisation in Li_2O - 2.5SiO_2 glass and a lithium silicate containing a large amount of titanium oxide, *Phys. Chem. Glasses* 10 (1969) 179–184.
- [61] E.D. Zanotto, A.F. Craievich, The role of amorphous phase separation in crystal nucleation in splat cooled Li_2O - SiO_2 Glasses, *J. Mat. Science*. 16 (1981) 973–982.
- [62] K. Matusita, M. Tashiro, Effect of added oxides on the crystallisation of Li_2O - 2SiO_2 glasses, *Phys. Chem. Glasses* 14 (1973) 77–80.
- [63] P. Hautojärvi, A. Vehanen, V. Komppa, E. Pajanne, Crystallization and phase-separation of Li_2O - SiO_2 glass, *J. Non-Cryst. Solids* 29 (1978) 365–381.
- [64] C. Lin, C. Rüssel, S. Dai, Chalcogenide glass-ceramics: functional design and crystallization mechanisms, *Prog. Mater. Sci.* 93 (2018) 1–44.
- [65] Y.G. Wei Deng, C. Jin-Shu, Liquid-phase separation and crystallization of high silicon canasite-based glass ceramic, *J. Non-Cryst. Solids* 385 (2014) 47–541.
- [66] E. Boulay, C.H. Ragoen, D. Idrissi, S. Schryvers, Godet. Influence of amorphous phase separation on the crystallization behavior of glass-ceramics in the BaO - TiO_2 - SiO_2 system, *J. Non-Cryst. Solids* 384 (2014) 61–72.
- [67] G.P. Souza, V.M. Fokin, C.F. Rodrigues, A.C.M. Rodrigues, E.D. Zanotto, J. Lumeau, I. Glebova, L.B. Glebov, Liquid-Liquid phase separation in photo-thermo-refractive glass", *J. Am. Ceram. Soc.* 94 (2011) 145–150.
- [68] T. Höche, M. Mäder, S. Bhattacharyya, G.S. Henderson, T. Gemming, R. Wurth, C. Rüssel, I. Avramov, ZrTiO_4 crystallization in nanosized liquid–liquid phase-separation droplets in glass. A quantitative XANES study, *Cryst Eng Comm* 13 (2011) 2550–2556.
- [69] R.P. Golovchak, A. Thapar, D. Ingram, Jain H. Savvitskii, Influence of phase separation on the devitrification of 45S5 bioglass, *Acta Biomater.* 10 (2014) 4878–4886.
- [70] X. Chen, L.L. Hench, D. Greenspan, J. Zhong, X. Zhang, Investigation on phase separation, nucleation and crystallization in bioactive glass-ceramics containing fluorophlogopite and fluorapatite, *Ceram. Int.* 24 (1998) 401–410.
- [71] C. Daqin, Z. Yang, W. Zhongyi, H. Ping, Y. Hua, L. Hongwei, J. Zhenguo, Enhanced upconversion luminescence in phase-separation-controlled crystallization glass ceramics containing Yb/Er(Tm): NaLuF_4 nanocrystals, *J. Eur. Ceram. Soc.* 35 (2015) 2129–2137.
- [72] P.F. James, Liquid-phase separation in glass-forming systems, *J. Mater. Sci.* 10 (10) (1975) 1802–1825.
- [73] D.R. Uhlmann, A.G. Kolbeck, Phase separation and the revolution in concept of glass structure, *Phys. Chem. Glasses* 17 (5) (1976) 146–158.
- [74] D.H. Kim, W.T. Kim, E.S. Park, N. Mattern, J. Eckert, Phase separation in metallic glasses, *Prog. Mater. Sci.* 58 (8) (2013) 1103–1172.
- [75] M. Tomozawa, D.-L. Kim, V. Lou, Preparation of high purity, low water content fused silica glass, *J. Non-Cryst. Solids* 296 (2001) 102–106.
- [76] G.A. Sycheva, Nucleation and Crystal Growth in Phase Separated Glasses in the Lithium Silicate System. Chapter at Crystallization and Materials Science of Modern Artificial and Natural Crystals, (2012), <https://doi.org/10.5772/28355>.