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Glass Crystallization Research — A 36-Year Retrospective. Part I, Fundamental Studies[†]

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Over the past 36 years, our research has mainly focused on the crystallization kinetics and properties of glasses and glass-ceramics. A sampling of the most conclusive papers are reviewed here and include the following topics: the effects of liquid phase separation on crystal nucleation; tests and development of models of crystal nucleation, growth, and overall crystallization; metastable phase formation; surface crystallization; glass stability against devitrification; glass-forming ability; possible correlations between the molecular structure and the nucleation mechanism; sintering with concurrent surface crystallization; and diffusional processes that control crystallization. We conclude that despite significant advancement in the knowledge about several aspects of phase transformations in glasses that resulted from our own research and of other groups, which is not described in this review, *glass crystallization* remains an open, rich field to be explored.

Introduction

I begin with apologies because this article is based on my 2012 *G. W. Morey* award talk; therefore, I only summarized and discuss work on glass crystallization processes from our own group and collaborators and, as a result, leave aside several important papers published by other authors. In addition, due to space restrictions, no equations, figures or other details are shown in this review paper; the interested reader is cordially invited to consult the cited references for further details.

The nature and kinetics of crystallization is a vital scientific problem that governs the glass-forming ability (GFA) of molten liquids and the ultimate stability (GS) of glass against devitrification. Over the last 36 years, our research has mainly focused on fundamental studies of glass crystallization. The first step of the crystallization process — nucleation — is essentially a *nanoscale* phenomenon that faces some difficulties, not only on the theoretical side, but also in the choice and application of experimental techniques and interpretation of results. However, such studies are essential for understanding the vitreous state, as we will show in this article, and for the successful development of useful glass-ceramics, which are described in Part II.[1] Our strategy has been to strike a balance between purely fundamental research and some technological development;

we always try to maximize the study of previous articles combined with careful planning and simulations, to optimize the experimentation process. In this article, we summarize a relevant part of our scientific studies.

Effects of Liquid–Liquid Phase Separation on Crystal Nucleation

I was introduced to glass research in 1976 by the late O. J. Whittemore (Professor at Washington University, Seattle, WA) then visiting Professor at the Federal University of São Carlos) and continued in 1977 during my MSc dissertation work in Physics at the University of São Paulo under the supervision of Aldo Craievich. During this time, I also attended several lectures about glass by the late visiting American Professor Charles Greene (then retired from Alfred University, Alfred, NY).

The same line of investigation continued during my PhD studies at Sheffield University under the guidance of the late Peter James from 1979 to 1982. We continued to work on a particular problem, described below, until 1986. Due to the strong controversy that existed in the international literature at that time, we performed a detailed, systematic study aiming to establish the effects of metastable liquid–liquid phase separation (LLPS) on the kinetics of crystal nucleation and growth in glasses. We used several lithium silicate and barium silicate glasses, both with and without LLPS, and characterized the concurrent development of these two phenomena — LLPS and crystal nucleation — using optical and electron microscopy techniques as well as small angle X-ray scattering (SAXS).[2–6]

To give an example of such work,[6] we studied via optical microscopy the nucleation kinetics of barium disilicate spherulites in $BaO-SiO_2$ glasses containing 27.0–33.3 mol% BaO undergoing isothermal treatments at 718–760°C. Amorphous phase separation in these two glasses was monitored by SAXS and transmission electron microscopy (TEM). The average diameter, number, and surface area of amorphous droplets were obtained as a function of time at 743 and 760°C. In glasses that did not show amorphous phase separation, the crystal nucleation rate, I, was constant at a given temperature. In glasses undergoing liquid phase separation, I increased with time approaching a constant value, identical for phase-separated glasses with different compositions. There was a striking correlation between

the time required to reach a constant value of I and the time required to attain the equilibrium composition of the amorphous (baria-rich) matrix phase, as revealed by a constant integrated SAXS intensity. The crystal nucleation rate, I, depended primarily on the composition of the baria-rich phase. There was no apparent relationship between I and either the surface area or the number of droplets.

Our results clearly demonstrated that the role of the interfaces between the liquid phases in crystal nucleation is very small due to the small interfacial energy between the liquid phases and, hence, the compositional shift of the glassy matrix caused by LLPS is the main factor responsible for the enhancement of crystal nucleation and growth. We believe this result is now the most accepted explanation for the effects of LLPS on crystallization. At present, there is very limited activity on this subject, with the exception of some members of the metallic glass community who are still debating the reason.

On the Validity of the Classical Nucleation Theory

Next, again with Peter James, we tested the validity and applicability of the classical nucleation theory (CNT) in different ways using various glasses over several years; this study is not yet finished![7–14]

In the first part of the research study,[7] we assumed a constant value of nucleus/liquid surface energy, σ, and that the activation enthalpy for atomic jumps at the liquid/crystal nucleus interface (ΔG_d) was similar to that for viscous flow (ΔG_η), an assumption also adopted by other authors. We found a large discrepancy of 30–55 orders of magnitude between the experimental nucleation rates and the theoretical values, although the temperature dependence was well described by theory!

In a subsequent study,[8] with Michael Weinberg (another *G. W. Morey* awardee), an original, more rigorous approach was proposed and tested using transient times for nucleation instead of using the viscosity to calculate ΔG_d. Again, large discrepancies were found in the magnitude and now also in the temperature dependence of the nucleation rates for four glasses.

Then, continuing the collaboration with Michael Weinberg, the most severe assumption of CNT, *that is*, the postulate that the interfacial energy does not depend on nucleus size, $\sigma = \sigma_\infty$, was tested.[9] In this

case, the Tolman expression for $\sigma(r)$ was incorporated into CNT, but two fitting parameters were needed (Tolman's parameter, λ, and σ_∞) instead of only a fixed value of the surface energy, σ_∞, which had been used in previous tests. An impressive agreement between theory and experiment was found for this method. However, in all tests, neither σ_∞ nor $\sigma(r)$ could be determined independently and had to be fitted by forcing the temperature of the experimental and theoretical maxima to coincide.

Other related studies have been conducted with the invaluable help of graduate students, as well as Vladimir Fokin and Jürn Schmelzer. In one such work,[11] we showed that to obtain a reasonable value of σ, it was necessary to reduce the thermodynamic driving force from the classical value used for the macrophase. This result indicated that the volume properties of critical nuclei may differ from the volume properties of the macro phase.

In several studies, we discussed the assumption of CNT that the properties of the critical nuclei and macrophases are equal. However, CNT could, in principle, be modified to incorporate the nucleus size dependence of the surface energy and the driving force. Hence, after all of our findings, we propose that the main question should not focus on the validity of CNT, but it should instead consider the usefulness of CNT for describing real experiments with complex systems. In other words, do such systems satisfy the CNT model? However, for a definitive answer, the independent determination of $\sigma(r, T)$ would be necessary. Several scientists around the world are still pursuing this objective, and this field is thus open for further exploration.

Metastable Phases and Mutant Crystals in Glasses

Before an ultimate test of any nucleation theory is performed, it is essential to confirm or discard the possibility of the precipitation of metastable phases in the early stages of nucleation, because, in principle, if confirmed, the metastable phases could perhaps explain the above-described discrepancy between the predictions obtained using CNT and the experimental nucleation rates. We have carried out a few studies on this subject with several Brazilian students, especially Paulo Soares, as well as Pierre Lucas (then a graduate student) and with Michael Weinberg. In a related set of studies carried out by other Brazilian students with Vladimir

Fokin and Russian colleagues, we have shown that, even in stoichiometric glasses, a crystal phase that is enriched or depleted in some component (in relation to the expected stoichiometric crystal) may precipitate in the early stages of crystallization and that its composition changes with the evolution of the crystallization process (mutant crystals).[15–23]

In previous studies,[15,16] we considered findings about metastable phase formation in lithium disilicate glass $Li_2O \cdot 2SiO_2$ (LS_2) and its effects on the crystallization of the stable LS_2 crystal phase. The early crystallization stages of slightly substoichiometric LS_2 glasses were probed with both SAXS and selected area diffraction (SAD). Then, we carefully measured the crystal nucleation rate (I), the growth rate (U), the time evolution of crystallinity, and the apparent induction period (τ) for crystal nucleation and growth at 500°C ($T_g \sim 450$°C). Finally, the kinetic parameters I and U were used in a modified form of the Johnson-Mehl-Avrami-Kolmogorov-Yeerofev (JMAKY) equation, which also accounted for transient nucleation conditions, to test the nucleation mechanism. Depending on the heat treatment, one or more metastable phases indeed precipitated in the early crystallization stages of LS_2 glass; however, these phases did not play a significant role in the crystallization mechanism of the thermodynamically stable LS_2 phase.

In another study,[22] the relative frequency of occurrence of two phases — LS (metastable) and LS_2 (stable) — was monitored as a function of heat treatment time. Despite the poor statistics (on average, only a dozen crystals were detected in the TEM samples for each treatment time), we observed that with treatment for up to 20 h at 454°C, the relative number of LS crystals was larger than that of LS_2. The number of LS crystals decreased with increasing treatment time, but, despite the decreasing LS/LS_2 ratio, LS crystals were still present after 120 h (<0.01 crystallized volume fraction). After 312 h (3 vol.% crystallized fraction), only the stable LS_2 phase was observed (it should be stressed that the nucleation time lag at this temperature is only 1–2 h). Here, one should consider that all detected crystals had sizes of approximately 500 nm, *that is,* they were much larger than the critical nucleus size. Thus, these data all refer to the initial stage of overall crystallization, but for a relatively advanced stage of nucleation. These results showed that both phases coexisted in the early stages of crystallization in glasses with a composition similar to that of lithium disilicate.

Therefore, the following two possible situations could occur:

1. There is simultaneous homogeneous nucleation of the LS_2 and LS phases, but the LS phase disappears at some point during the heat treatment. In this case, LS is a metastable phase that does not affect the nucleation path of LS_2
2. The LS crystals nucleate first, and then the LS2 crystals nucleate heterogeneously over the LS. This mechanism could partially explain the failure of the classical nucleation theory.

Regarding the "mutant" crystals phenomenon, data were collected on the bulk crystallization kinetics of a glass with a composition very close to the stoichiometric phase $Na_2O.2CaO.3SiO_2$.[17,21,23] The effects of pre-existing crystals on the nucleation and growth behavior of secondary crystals were described for the first time. Primary crystals, grown at high temperatures, dramatically *hindered* the formation of new crystals in their vicinity at lower temperatures (the courtyard effect). The crystal growth velocity decreased with increasing crystal size. Chemical analysis by energy-dispersive X-ray spectroscopy demonstrated that the above-mentioned effects resulted mainly from compositional changes to the glass matrix near the primary crystals. Extrapolating the curve of crystal composition versus size down to size zero allowed us to estimate the critical crystal composition and conclude that the primary crystals were far from stoichiometric.

A detailed discussion on the roles of metastable phases in nucleation can be found in a review article.[24] So far, our work with these two systems has established that in the initial nucleation stages, the clusters are solid solutions (ss) with a $Li_2O.2SiO_2$ structure but are enriched in Li and are ss with an $Na_2O.2CaO.3SiO_2$ structure but enriched in Na. This fact does not contradict the conclusions of the previous studies. In summary, metastable and transitory phases indeed appear in some glasses, but apparently these phases do not explain the large discrepancies in CNT!

The Validity of the JMAKY Theory

An adequate description of the overall crystallization kinetics is of utmost importance.[25–31] In 1988, we carried out one of the first rigorous tests of the JMAKY theory of transformation kinetics, with no adjustable parameters, for homogeneous nucleation in a glass.[25] First, we measured the crystal nucleation and growth rates in a stoichiometric $1Na_2O.2CaO.3SiO_2$ glass and then calculated the expected evolution of the volume fraction crystallized using the JMAKY equation and compared it to measured values. At that time, we did not know that the crystal composition differs somewhat from that of the parent glass in the early stages. We nevertheless demonstrated that, if proper precautions are taken when determining the nucleation and growth rates, the JMAKY theory describes exceptionally well the time evolution of the overall crystallization of stoichiometric glasses.[25]

We also used the JMAKY equation to calculate the volume fraction transformed in nonisothermal situations and for small spherical glass particles (in addition to the normally assumed case of infinitely large glass samples).[27,31]

In summary, if the assumptions of the JMAKY equation are respected, it describes quite well the isothermal and nonisothermal crystallization kinetics of stoichiometric glasses.

Homogeneous Versus Heterogeneous Nucleation in Glasses

Next, from 1987 to 2003, with the invaluable insight of Eberhard Muller, Mike Weinberg and Vladimir Fokin, we were devoted to answering the following question: *Why is a thermodynamically unfavorable mechanism — homogeneous nucleation—experimentally observed in some glasses?* A series of papers[32–36] was published on this particular problem in that period.

In one of our first studies, in 1987,[32] we demonstrated that a simple rule of thumb can be used to distinguish the nucleation mechanism in stoichiometric glass-forming systems. For compositions that have small values of reduced glass transition temperatures ($T_g/T_f < 0.6$), the temperatures of the maximum nucleation rates, T_{max}, are higher than the T_g values and these systems exhibit homogeneous (internal) nucleation in laboratory time scales. Conversely, for the majority of glasses, the typical values of the reduced T_g are higher ($T_g/T_f > 0.6$), and the calculated (by CNT) values of T_{max} are significantly below T_g; only heterogeneous nucleation is observed in typical laboratory tests. To the best of our knowledge, no exception to this remarkable trend has been reported so far.

In a second study,[33] we showed that the failure to experimentally detect homogeneous nucleation in glasses for which $T_{max} < T_g$ is due to one or both of the following causes: nucleation or growth rates that are too low, or long induction times for nucleation in temperature ranges for which the predicted (by CNT) steady-state homogeneous nucleation rates are expected to be significant.

Next,[35] we showed that the mass densities of glasses that nucleate homogeneously are similar to those of their crystal phases, while those of glasses that only nucleate heterogeneously could be similar to or quite different from the densities of equivalent isochemical crystals (Table I).

Hence, structural similarity is a necessary, but not sufficient, condition for substantial homogeneous nucleation rates. It should be stressed that the density misfit is not a unique factor that determines the nucleation rates. For instance, the difference in I_{max} between $CaO.SiO_2$ and $Li_2O.SiO_2$ glasses is approximately three orders of magnitude, whereas density misfit differs only by a factor of approximately 50%.

Table I. Densities of Glass and Isochemical Crystal Phases (g/cm³)

System	Glass	Crystal	$\Delta\rho/\rho_{glass}$(%)
Homogeneous nucleation			
$BaO.2SiO_2$	3.72	3.77–3.73	1.3/0.3
$Na_2O.2CaO.3SiO_2$	2.75	2.80	1.8
$CaO.Al_2O_3.2SiO_2$	2.70	2.76	2.2
$Na_2O.SiO_2$	2.56	2.62	2.3
$2Na_2O.CaO.3SiO_2$	2.66	2.76	3.8
$Li_2O.2SiO_2$	2.35	2.45	4.3
$CaO.SiO_2$	2.90	3.09	6.6
$Li_2O.SiO_2$	2.34	2.52 (ort)	7.7
Extremely low nucleation rates or only heterogeneous nucleation			
$K_2O.2SiO_2$	2.47	2.46–2.53	0.6/2.4
$Na_2O.2SiO_2$	2.49	2.39–2.56	3.7/3.1
$PbO.SiO_2$	5.98	6.49	8.5
As_2S_3	3.17	3.46	9.1
P_2O_5	2.37	2.72	14.8
$Na_2O.Al_2O_3.6SiO_2$	2.28	2.62	14.9
GeO_2	3.65	4.23 (hex)	15.9
$CaO.MgO.2SiO_2$	2.70	3.20	18.5
B_2O_3	1.84	2.46	33.7

We then showed[36] that the maximum values of nucleation rates, I_{max}, scale with the reduced glass transition temperature, $T_{gr} = T_g/T_m$. This article provided experimental and theoretical evidence for the correlation between I_{max} and T_{gr} for 51 glass-forming liquids. In addition, it demonstrated an analogous correlation between the time lag of nucleation at T_{max} and T_{gr}.

In summary, if the density difference between a given glass and its isochemical crystalline phase is large, say >10%, it will only nucleate heterogeneously. If the densities are comparable, nucleation could be homogeneous, but this condition alone is not sufficient to ensure this nucleation mechanism (or a high and detectable nucleation rate). Based on these results, we started to think at possible structural relationships between the nucleation mechanism and at the similarity between the molecular structure of the parent glass and its crystal phase. Such studies are described below.

Molecular Structure Versus Nucleation Mechanism

We then decided to test whether the predominant nucleation mechanism (or the homogeneous nucleation rates) of a given glass composition could be correlated with the extent of structural similarity at the local and intermediate-range level between the glass and the crystal phase to which it transforms.[37–43] In 1992, we started with a simple test to check whether the local modifier cation arrangements in the glass were similar to those in their corresponding crystal phases in systems that nucleated homogeneously, whereas the modifier cation structures of the glass and crystal phases of compositions that only nucleated heterogeneously were quite distinct.[37] Following that study, we continued to search for similarities/dissimilarities at the intermediate-range order, that is, at the linkages between SiO_4 tetrahedra, which form the basic units of silicate glasses and their isochemical crystals, and the nucleation mechanism.

In another study,[38] the short-range order of several silicate glasses that nucleate homogeneously in their volume ($CaO.SiO_2$, $Na_2O.SiO_2$, $Li_2O.SiO_2$, $Li_2O.2SiO_2$, $BaO.2SiO_2$ and $CaO.Al_2O_3.2SiO_2$) as well as that of glasses that only nucleate heterogeneously on their external surfaces or in volume with the addition of nucleating agents ($PbO.SiO_2$, $Na_2O.2SiO_2$, $CaO.MgO.2SiO_2$, $K_2O.TiO_2.3SiO_2$ and $Na_2O.Al_2O_3.6SiO_2$) was analyzed and compared with the structures

of their equilibrium isochemical crystalline phases. We showed that for glasses displaying measurable homogeneous nucleation rates, both the cationic and anionic arrangements in glass and isochemical crystal are similar. For the second family of glasses, the structures of a glass and its isochemical crystal significantly differ, and only heterogeneous nucleation was observed. However, we later found several exceptions to this trend! We have been working on this particular problem with Eberhard Muller, Klaus Heide, José Schneider, Adrian Wright (another *G. W. Morey* winner), Natalia Vedisheva, the late Boris Schatmakin, Josef Zwanziger, and students having published a few articles over the last 20 years.

For instance, we tested[39] the possible existence of a relationship between the similarity of the local structure of the network-forming cation Si^{4+} (considering Q^n units and chemical shifts) in glasses and isochemical crystals, and the nucleating ability of some glasses. Four metasilicate glasses with widely different homogeneous internal nucleation rates—$Na_2Ca_2Si_3O_9$ and $Na_4CaSi_3O_9$ (very large nucleation rates), $CaSiO_3$ (intermediate) and $CaMgSi_2O_6$ (undetectably small)—were chosen. We obtained magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) data for $Na_2Ca_2Si_3O_9$ and $Na_4CaSi_3O_9$ glasses and their respective isochemical crystalline phases for the first time. Additionally, we repeated the NMR measurements of glasses and crystals that were previously studied by other authors ($CaSiO_3$ and $CaMgSi_2O_6$) to test the consistency of our experimental techniques and analytical method.[39] Different central chemical shifts of Q^2 resonances in parent glasses and their isochemical crystals were measured, thus indicating structural differences. The relative amount of Q^n groups in each glass was obtained from the deconvolution of the ^{29}Si MAS-NMR spectra. The shape of the Q^n distribution for each system was considered a measure of the similarity of the connectivities of SiO_4 tetrahedra in each glass with respect to its isochemical metasilicate crystal (which has only Q^2 groups). A correlation was found between the shape of the Q^n distribution and the nucleation tendency of these glasses, indicating that similarities between the tetrahedra connectivities in a glass and its isochemical crystal may play a role in determining the internal nucleation tendency of the metasilicate glasses studied.

Relatively little information was available to test our structural similarity hypothesis because of the lack of long-range periodicity in glass and the absence of effective analysis methods. Hence, in another work,[42] $Li_2O-2B_2O_3$ (L2B) and $Na_2O-2B_2O_3$ (N2B) glasses, which exhibit homogeneous (internal) and heterogeneous (surface) devitrification mechanisms, respectively, and their corresponding crystals were prepared and studied using multiple solid-state NMR techniques. Of those techniques, ^{11}B MAS and MQMAS (multi-quantum-magic-angle-spinning) experiments were applied to reveal short-range order information; ^7Li and ^{23}Na spin-echo decay and $^{11}B\{^6Li\}$ and $^{11}B\{^{23}Na\}$ rotational-echo double-resonance (REDOR) experiments were used to determine homonuclear and heteronuclear interactions that can reflect the intermediate-range order. We found that the local bonding environments of the L2B crystal and glass are quite similar, whereas there are significant differences in the N2B system. Moreover, the experimental results indicated that the second moment (M2) values of both homo- and heterodipolar interactions measured for the L2B glass are very close to those of its isochemical crystal. In contrast, the M2 values for N2B glass differ significantly from those of its crystal phase. These observations indicate the existence of a strong correlation between structural similarity at both the short and intermediate length scale, and nucleation mechanism.

Let us then consider two extreme cases. (i) The structure of the liquid is very close to that of its crystal form. Then, the necessary structural reorganization for crystallization is facilitated due to the reduction in the kinetic barrier for nucleation and growth, but the thermodynamic driving force will be weak. (ii) The structure of the liquid strongly differs from that of its crystal. This case corresponds to a high kinetic and low thermodynamic barrier. Because the similarity of the liquid and crystal structures affects the kinetic and thermodynamic aspects of crystallization in different ways, the final result is determined by the interplay of these factors. In any case, as the number of systems studied thus far is quite small and some exceptions to the expected structure versus nucleation relationship have been reported, this remains an open problem that deserves further attention.

Surface Crystallization

About 20 years ago, our research group started to focus on establishing the mechanisms and kinetics of

crystal nucleation and growth on free glass surfaces (by far the most common devitrification mechanism). Jointly with several graduate students, especially Nora Mora, we published several papers on this subject between 1991 and 2000.[44–51] We also significantly benefited from useful discussions carried out in the framework of the TC7—the Crystallization Committee of the ICG. Here, we should mention a fruitful collaboration work with three TC7 members: Miguel Prado, Vladimir Fokin, and Ralf Muller. Some of our papers catalyzed interest on the subject, and we believe that they were important for the development of some sintered glass-ceramics, described in Part II.[1]

Based on our results, we concluded that in most cases, surface nucleation is triggered by a certain number of impurity sites, the number of which depends on the degree of surface perfection and cleanliness. High surface nucleation rates are due to the low interfacial energy between the contaminants existing at the glass surface and the crystal nuclei. Our findings on the factors controlling the mechanisms and kinetics of surface crystallization were fundamental in moving to the next two problems: (i) glass-forming ability and (ii) viscous sintering of glass particles with concurrent surface crystallization.

Glass-Forming Ability (on cooling) Versus Glass Stability (on heating)

We have carried out a good deal of research in collaboration with *G. W. Morey* winner Donald Uhlmann on the fundamental problem of the glass-forming ability of different liquid systems.[52,53] We also developed some systematic studies that unveiled the parameters (combinations of DSC characteristic temperatures) that are best able to describe glass stability against devitrification (on heating), and its correlation with the glass-forming ability of a certain liquid (upon cooling) for oxide liquids.[54–61] These studies started with the competent work of former students and postdocs Aluísio A. Cabral, Marcio F. Nascimento, and Eduardo B. Ferreira and continued more recently in collaboration with Richard Brow (*G. W. Morey* awardee) and his group in Rolla, Missouri.

We re-evaluated, for instance, nine parameters of glass stability against crystallization determined from differential scanning calorimetry (DSC) experiments to predict the glass-forming ability of oxide liquids on cooling.[61] The GS parameters were calculated using characteristic glass transition, crystallization, and melting peaks of DSC thermograms. Using lithium borate glasses, we found that seven stability parameters gave similar trends for compositions up to 33.3 mol% lithia, where, as we expected, GS significantly decreases with lithia content. Thereafter, up to 66.7 mol% lithia, GS was approximately constant, thereby indicating that, surprisingly, the composition does not significantly affect the GFA within this wide compositional range. This result qualitatively agrees with our experience of successfully preparing glasses with compositions of up to 74 mol% lithia. The above-cited article[61] corroborates our previous studies[55,56,58] showing the adequacy of simple DSC tests to comparatively gauge the GS and GFA of glass-forming liquids.

Finally, our research work demonstrated that, for the most common cases, GFA depends on heterogeneous nucleation (that is very difficult to control), whereas GS may depend on both homo- and heteronucleation, and both GFA and GS depend on the crystal growth rate.

Sintering with Concurrent Crystallization

Using our accumulated experience on surface crystallization processes, we started to conduct a systematic study on glass sintering with concurrent surface crystallization.[62–73] This topic is a matter of keen interest because one could, in principle, produce all sorts of complex-shaped monolithic glasses and glass-ceramics by sintering powdered glasses. The key issue here is to obtain viscous flow sintering before surface crystallization takes over and imparts densification. Of special importance is one of the last papers in the series[71] that proposes and successfully tests a useful sinterability parameter. Some conclusive and practical results on this subject are summarized in a few papers coauthored by Miguel Prado, Ralf Muller, Catia Fredericci, Viviane Oliveira, Raphael Reis, in addition to our Spanish collaborators Alicia Duran and Maria Jesus Pascual, and several students.

We critically discussed the main glass sintering models—Frenkel's, Mackenzie-Shuttleworth's, Scherer's and our own *Clusters* model—and focused on the problem of sintering with concurrent crystallization in a review paper.[69] The *Clusters* model was tested for compacts of spherical soda-lime-silica (SLS) glass particles

that have a narrow size distribution and easily crystallize. Simulations for isothermal and nonisothermal sintering with simultaneous crystallization were compared with experimental data. Physical and processing parameters, such as viscosity, surface tension, crystal growth rate, number of nucleation sites, particle size distribution, and particle packing, are considered in the model. The evolution of the relative density during sintering and the pore size distribution in the final stages of sintering were reasonably predicted by the model. All results were discussed considering the assumptions made and other complicating factors, such as compositional shifts due to crystallization, temperature gradients, and degassing. Finally, we discussed the physical and processing parameters that determine whether sintering is more favorable than crystallization. We demonstrated that the *Clusters* model can describe the densification of devitrifying glass compacts for any particle size distribution.

In another study,[64] we evaluated all the previous publications and demonstrated that the *Clusters* model and related algorithm provide a powerful simulation tool for calculating or designing the isothermal or nonisothermal densification of devitrifying or stable glass compacts with any particle size distribution, thus minimizing the number of time-consuming laboratory experiments.

The recent PhD thesis[73] of our student Raphael Reis demonstrated that some fine details of the *Clusters* model must be corrected to give an even more precise description of the sinter-crystallization process in the final stages of densification. All of the required parameters (viscosity, crystal growth rates, number of active nucleation surface sites, glass-air surface energy, and particle size distribution) for simulating the sinter-crystallization processes of spherical particles can be independently measured, but one as yet unsolved problem is how to account for the odd shape of milled glass particles.

In conclusion, there are a number of open issues regarding the sinter-crystallization phenomenon that still need to be resolved.

Diffusion Processes Controlling Crystal Nucleation and Growth

More recently, our team, led by former postdocs Marcio Nascimento and Eduardo Ferreira, once more in collaboration with Vladimir Fokin, started to look in detail into the diffusion processes that control crystal nucleation, crystal growth, and viscous flow. Our research group also examined the old-standing controversy regarding the possible breakdown of the Stokes–Einstein–Eyring (SEE) equation at sufficiently low temperatures near T_g.[74–84]

In one article,[77] we analyzed extensive literature data on crystal growth rate and viscosity in the temperature range between 1.1 T_g (glass transition temperature) and the melting point of silica, T_m. We selected data for one silica glass type, the samples of which had similar impurity contents, and confirmed that the normal growth model describes quite well the experimental growth rate data in this wide undercooling range. We then calculated the effective diffusion coefficients from crystal growth rates, D_u, and from viscosity, D_η (using the SEE equation), and compared these two independent diffusivities with the directly measured self-diffusion coefficients of silicon and oxygen in the same silica glass for which viscosity was measured. Our results showed that silicon (but not oxygen) controls the diffusion dynamics involved in both crystal growth and viscous flow in undercooled silica.

Next, we evaluated[83] the kinetic coefficients of crystal growth for nine undercooled glass-forming liquids, in a wide temperature range, from slightly below the melting point down to the glass transition region T_g, thus covering a wide viscosity range: $\eta = 10^1$–10^{13} Pa.s. Viscosity was able to describe the transport part of crystal growth rates from low to moderate viscosities ($\eta < 10^6$ Pa.s), and hence, we demonstrated that the SEE equation works well in this viscosity range for all systems tested. For strong glasses, the SEE equation works well from low to high viscosities, from the melting point down to T_g! However, for at least three fragile liquids—diopside (kink at 1.1 T_g, $\eta = 1.6 \times 10^8$ Pa.s), lead metasilicate (kink at 1.1 T_g, $\eta = 4.3 \times 10^6$ Pa.s), and lithium disilicate (kink at 1.1 T_g, $\eta = 1.6 \times 10^8$ Pa.s) — there were clear signs of a breakdown in the SEE equation at these high viscosities. These results confirmed that viscosity data cannot be used to describe the transport part of the crystal growth in fragile glasses near T_g.

We also assessed[84] extensive literature data on viscous flow, crystal nucleation, and growth, in $Li_2O.2SiO_2$, over a wide temperature range, from above T_m to 0.98 T_g, where $T_g \approx 727$ K is the calorimetric glass transition temperature and $T_m = 1307$ K is the melting point. We then calculated the diffusion coefficients controlling crystal growth, D^U, and viscous flow, D^η,

and compared with the ionic diffusion coefficients of Li^{+1}, O^{2-}, and Si^{4+} obtained from experiments and molecular dynamic simulations. These values were then employed to estimate the effective volume diffusion coefficients, D_{eff}^V, resulting from their combination within a hypothetical $Li_2Si_2O_5$ "molecule". The similarity in the temperature dependencies of $1/\eta$ and D_{eff}^V corroborated the validity of the SEE equation at high temperatures around T_m. Using the equality of D_{eff}^V and D^η, we estimated the jump distance $\lambda = 2.70$ Å from the SEE equation and showed that the values of D^U have the same temperature dependence but exceed D^η by about eightfold. The difference between D^η and D^U indicates that the former represents the process of mass transport in the bulk, whereas the latter relates to the mobility of the structural units on the crystal/liquid interface. We then employed the values of $\eta(T)$ reduced by eightfold to calculate the growth rates $U(T)$. The resultant $U(T)$ curve was consistent with experimental data down to a decoupling temperature $T_d^U \approx 1.1–1.2$ T_g, when D^η started to decrease with decreasing temperature faster than D^U. A similar decoupling occurred between D^η and D^τ (estimated from nucleation time-lags) but at a lower temperature $T_d^\tau \approx T_g$. The different behaviors of $D^\tau(T)$ and $D^U(T)$ are likely caused by differences in the mechanisms of critical nuclei formation and growth. Therefore, we showed that in the deeply supercooled liquid state below T_d, mass transport for crystal nucleation and growth are not controlled by viscosity. The origin of decoupling was assigned to spatial *dynamic heterogeneity* in glass-forming melts.

Overall, our results indicated no breakdown of the SEE equation from the liquidus down to $T \sim 1.15$ T_g, but with clear signs of a decoupling of viscosity and crystallization processes at deeper undercoolings for fragile glasses. However, no decoupling has been found for strong Q^4 glasses. This breakdown or decoupling is likely due to dynamic heterogeneities in undercooled glass-forming liquids. Future studies should focus on at what happens at even deeper undercoolings, from 1.15 T_g down to approximately 0.9 T_g.

Review Papers

Summarizing the above list of original research, we have also authored some review papers. In the most extensive of these papers,[24] we evaluated the relevant results from the experiments of our group and those of other authors on the internal homogeneous crystal nucleation in silicate glasses obtained from 1965 to 2005 and their analyses in the framework of classical nucleation theory (CNT). Particular attention was devoted to studying the properties of the critical nuclei, which, to a large extent, govern nucleation kinetics. The basic regularities of both the time and temperature dependencies of nucleation rates were illustrated using experimental data. Special attention was given to serious problems that arise in the quantitative description of nucleation rates when using CNT. These problems include the dramatic discrepancy between calculated and measured nucleation rates; the high value of the crystal nuclei/melt surface energy compared with the expected value estimated via Stefan's rule; the increase in σ with increasing temperature; and the discrepancies between the values of the surface energy and the time lag for nucleation when independently estimated from nucleation and growth kinetics. As we discussed previously, analyzing the above-mentioned problems led to the following conclusion: in contrast to Gibbs' description of the heterogeneous systems underlying CNT, the bulk thermodynamic properties of the critical nuclei generally differ from those of the corresponding macrophase, thus resulting simultaneously in significant differences of the surface properties compared with the respective parameters of the planar interfaces. In particular, direct experimental evidence was presented for compositional changes of the crystal nuclei during the formation of critical nuclei and their growth from critical to macrosizes. In addition, a detailed examination of crystal nucleation and growth kinetics showed a decrease both in the thermodynamic driving force for nucleation and in the critical nuclei/liquid interfacial energy, compared with the respective properties of the macrophase.

Summary

The specific conclusions about each research topic investigated were stated at the end of each section. The research described above comprises a sequential sampling of insights and advances vital to the understanding of some relevant scientific issues related to the nature, mechanisms, and kinetics of glass crystallization. Our philosophy has been to focus on a few relevant problems for several years at the deepest possible level.

We suppose that most of the articles described were innovative and led to some advancement of the knowledge of key aspects of phase transformations in glasses. However, there is still a great scope of further study in both the scientific and technological aspects of glass crystallization!

Acknowledgments

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