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Progress and Perspective of Processing Glass Forming Melts in Low Gravity

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A review of the results from previous low-gravity experiments conducted on glass-forming melts is presented with particular emphasis on nucleation, crystallization, glass formation, and chemical homogeneity for high-temperature melts in low gravity. A review of this kind is important for 1) understanding the kinetics of glass formation (conversely, nucleation and crystallization) and the mechanism(s) of homogenization of high-temperature melts in low gravity, 2) avoiding duplication in future low-gravity experiments, and 3) properly utilizing low-gravity conditions for improving present-day glass processing techniques and, hence, the quality of glasses on Earth. It is consistently observed that glasses prepared in low gravity are more chemically homogeneous and more resistant to crystallization than those of the comparable glasses prepared on Earth, which is somewhat surprising. A hypothesis based on "shear thinning" of a melt is proposed as an explanation for these low-gravity results. A scheduled flight experiment, whose purpose is to acquire data on nucleation and crystal growth kinetics for $Li_2O.2SiO_2$ glass prepared in low gravity, is discussed.

Nomenclature

A, B, C = constants
d = diameter of the platinum capsule containing the melt, m
g = gravity level in terms of g_0
g_0 = normal gravity, $m \cdot s^{-2}$
I = nucleation rate, $m^{-3} \cdot s^{-1}$
k = Boltzmann constant, $J \cdot K^{-1}$
L = length of the platinum capsule containing the melt, m
Pr = Prandtl number
Q = cooling rate of the melt, $K \cdot s^{-1}$
Q_C = critical cooling rate for glass formation, $K \cdot s^{-1}$
R = gas constant, $J \cdot K^{-1} \cdot mol^{-1}$
Ra = Rayleigh number
T = sample or furnace temperature, K
T_m = melting or liquidus temperature, K
t = time, s
U = crystal growth rate, $m \cdot s^{-1}$
V_m = molar volume, m^3
X = volume fraction crystallized
α = thermal diffusivity, $m^2 \cdot s^{-1}$
β = coefficient of volume expansion, K^{-1}
ΔG_V = difference in free energy between unit volumes of the crystal and melt, $J \cdot m^{-3}$
ΔT = temperature difference between the flat ends of the cylindrical platinum capsule containing the melt, K
η = viscosity, $Pa \cdot s$
ρ = density, $kg \cdot m^{-3}$

Subscripts

C = critical
EE = melted on Earth and heat treated on Earth
ES = melted on Earth and heat treated in space
m = melting (or liquidus)
SE = melted in space and heat treated on Earth
SS = melted in space and heat treated in space

Introduction

THE reduction in hydrostatic pressure, sedimentation, buoyancy, or gravity-driven convective flows in a low-gravity environment have consequences for virtually all processes involving fluids, such as the solidification of melts.[1–3] Because glasses are traditionally prepared by solidifying melts, a variation in gravity level could affect the glass formation process(es) and, consequently, the properties of glasses. Furthermore, the low-gravity conditions in space offer the unique opportunity for containerless processing of high-temperature melts, thereby preparing glasses entirely free of impurities originating from the container. The elimination of container-induced impurities is expected to increase the glass-forming tendency of melts by suppressing heterogeneous nucleation/crystallization and to produce ultrapure glasses for use as benchmark standards. Glasses of ultrahigh purity have the potential to advance many modern technological applications, such as communications (optical glass fibers), high-power glass lasers, fast all-optical switches, and other photonic devices.

Recent advances in ground-based levitation techniques[4–7] have made it possible to routinely prepare glasses in a containerless fashion. However, the effect of gravity, such as the sedimentation or segregation of components of differing density, cannot be entirely suppressed in ground-based containerless melts. Also, the small amount (or size) of sample, typically from 30 to 40 mg and from 1 to 3 mm diam, obtained from such containerless processing has limited practical value. The amount of force, be it acoustic, aeroacoustic, electrostatic, or electromagnetic, required to levitate a sample on Earth (to counteract gravity) may adversely affect the characteristics and properties of the levitated melt, as well as the solidified melt. For example, the agitation or vibration caused by an acoustic or aeroacoustic force in a levitated melt enhances its crystallization tendency, thereby reducing the ability of the melt to form glass. Thus, the quiescence in a melt in the low- or microgravity environment is unique and has no clear alternative on Earth.

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The literature[8–26] contains many descriptions of glass-melting experiments in low gravity, but the results from these experiments and their implications have not been critically reviewed. A review of these results can be helpful for 1) understanding the kinetics of glass formation (conversely, nucleation and crystallization) and the mechanism(s) of homogenization of high-temperature melts in low gravity, 2) avoiding duplication in future low-gravity experiments, and 3) properly utilizing the low-gravity environment for improving current glass processing techniques and, hence, the quality of glasses prepared on Earth.

Noteworthy results consistently reported for glasses processed in low gravity are that the glass-forming tendency for a melt is enhanced (at least by a factor of from three to four), and the glasses are more chemically homogeneous and more resistant to crystallization than identical glasses prepared on Earth.[8–20] Glasses crystallized in low gravity have a microstructure composed of smaller crystals that are more uniformly distributed than equivalent samples crystallized at g_0 (Refs. 8, 10, 11, 20). Also, the low-gravity glasses are reported to have a higher mechanical strength and threshold energy for radiation damage than those of their terrestrial counterparts.[10] With only two notable exceptions[21–23] (to our knowledge), all of these results demonstrate that the quality of the glasses is improved when processed in space. These interesting results have considerable scientific and practical importance and suggest that the low-gravity environment offers the advantage for developing new glasses and glass ceramics of improved quality that are difficult to prepare on Earth. However, the reasons why glasses prepared in low gravity are more chemically homogeneous and more resistant to crystallization than comparable glasses prepared on Earth are still unknown.

Gravity-driven convection, which is the primary cause for mixing and homogenization in fluid melts at $g = g_0$, is ideally absent or highly suppressed in low gravity. Fluid flow caused by diffusion[27] and surface tension (Marangoni flow, see Ref. 28) also promotes melt mixing, but these forces are several orders of magnitude weaker than gravity-driven convection. It is logical to think that melts processed in low gravity might be less chemically homogeneous and, thus, more susceptible to crystallization. However, the observed results are just the opposite. The explanation for why a glass prepared in low gravity should be more chemically homogeneous than one prepared at g_0 remains unanswered.

The process of melt solidification is controlled by the kinetics of nucleation and crystal growth. A melt forms a glass when the thermodynamically favored steps of nucleation and subsequent crystal growth do not occur as the melt is cooled. One possible reason for the observed increase in glass-forming tendency for low-gravity melts is that the nucleation rate I and/or the crystal growth rate U (as a function of temperature) for melts in low gravity are smaller than those for identical melts at normal gravity. No attempt has been made yet to measure directly the values of I and U for melts in low gravity to verify whether they are different from the values for identical melts on Earth. One reason why these measurements have not been made is that the present equations for I and U do not contain a gravity-dependent term.

The intent of this paper is to present a comprehensive summary of the important results from previous glass melting experiments in low gravity that were conducted with or without a container and using different low-gravity facilities, such as a space shuttle, rocket, and drop shaft. The results have been analyzed to determine their implications to a scientific understanding of the dependence of gravity on physical processes for nucleation, crystal growth, and melt homogenization in undercooled, high-temperature melts.

Finally, the plans for a future flight experiment,[24] where I and U will be measured directly for a lithium disilicate ($Li_2O.2SiO_2$) glass prepared in space, are described. A hypothesis based on "shear thinning" of melts is proposed to explain why smaller values of I and U could be expected for a glass in low gravity. If these flight experiments yield the expected results (i.e., the values for I and U for a glass in space are found to be smaller than the same values for an identical glass on Earth), then the present equations for I and U will need to be modified by introducing a gravity-dependent parameter.

Previous Work

Calcia–Gallia–Silica Glass (Containerless Processing)

The first successful containerless glass-melting experiments in low gravity were conducted by Day and Ray[13,15] aboard the space shuttle in 1983 (STS-7) and 1985 (STS-61A). Spherical samples, 6–8 mm in diameter, prepared from a hot-pressed sintered compact mixture of $18.4CaO–67.8Ga_2O_3–13.8SiO_2$ (wt%) composition were melted at 1500°C and cooled to glass while levitated (for about 12 min) in a single axis acoustic levitator furnace. Of special importance was the finding that the tendency for glass formation of this calcia–gallia–silica melt in space increased by a factor of from three to four compared to that for an identical melt on Earth. This result was based on the comparison of the critical cooling rate for glass formation Q_c (defined as the slowest rate at which a melt can be cooled without crystallizing) for the identical composition measured on Earth with the cooling rate Q, which the containerless melt experienced in space (Fig. 1). The melt formed a glass in space even when cooled at a rate ($\sim 3°C/s$) which was ~ 4 times smaller than the $Q_c (\sim 12°C/s)$ measured on Earth for a melt of the same composition in contact with a container. This improvement in glass formation was attributed to containerless processing, where the heterogeneous nucleation that occurs on Earth at the melt–container interface and that prevents many melts from forming glass on Earth was ideally absent. Although this is a reasonable explanation for this particular experiment, the results from other experiments that are discussed later suggest that other gravity-dependent factor(s) may also be responsible for the improvement in glass formation for melts in space.

A second important finding from the aforementioned containerless melting experiments in space was that the space-melted calcia–gallia–silica glass was more chemically homogeneous than the control glass prepared on Earth (Fig. 2). The glass on Earth ($g = g_0$) was prepared using the same type of precursor (hot-pressed sintered compact) and the identical melting temperature and time as used in the space experiments.

Lithium Silicate Glasses (Processing in a Container)

Similar improvements in glass formation and chemical homogeneity for space melted glasses, compared to that for the same glasses melted on Earth, have been reported by several other investigators, even when the glasses in space were melted in containers. Three lithium silicate glasses with and without Pt particles as heterogeneous nucleating agents were melted and solidified in cylindrical, glassy carbon containers (diameter 7.5 mm and length 12.0 mm) in space (D-1, STS-61A) and on Earth.[11,12] Except for

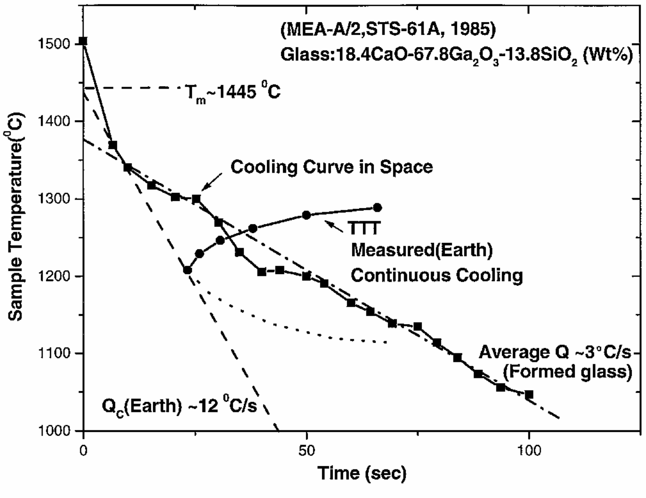

Fig. 1 Temperature–time–transformation diagram of glass on Earth and cooling rate in space for a containerless calcia–gallia–silica melt; the space melt did not crystallize (formed glass) even when cooled at a rate smaller than the critical cooling rate for glass formation R_C on Earth.

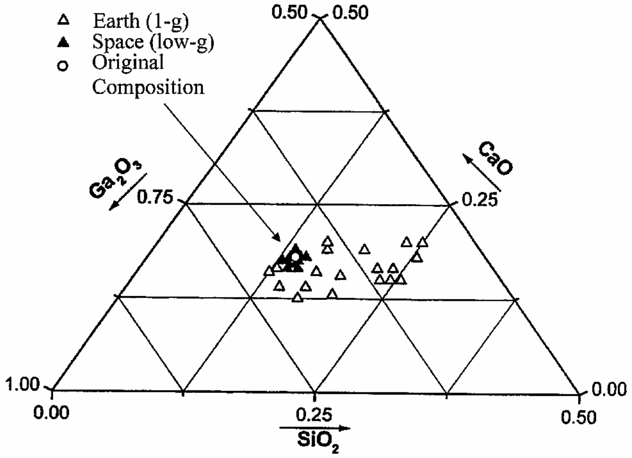

Fig. 2 Compositional analysis at different locations of a 18.4 CaO–67.8 Ga_2O_3–13.8 SiO_2 (wt%) glass prepared in space (STS-61A, MEA/A-2, 1985) and on Earth; the scatter in the data in the space glass is negligible compared to that for the glass prepared on Earth using the same melting temperature (1500°C) and time (5 min).

the zone of contact between the wall of the container and the melt (<1 mm thick), the flight sample was totally glassy, whereas the normal gravity reference glass was partially crystallized in its bulk also. These results demonstrate an improvement in glass formation for the melt processed in space.

The chemical homogeneity of these lithium silicate glasses[11,12] was determined by measuring the variation in refractive index (Shelyubskii's method) and in the silica concentration (microprobe analysis) across a cross-sectional plane parallel to the longer axis of the cylindrical glass samples. Both methods of measurements showed a significant improvement in the chemical homogeneity for the space-melted glasses. For example, the glasses melted in space had a smaller variation in the refractive index than the glasses prepared on Earth. Furthermore, the variation in silica concentration in the bulk of the space glasses, nominal composition of $24Li_2O$–$76SiO_2$ (mol%) did not exceed ±0.5 mol% over a distance of ~10 mm, except within 1 mm of the container wall. In contrast, the silica concentration varied as much as ±7.5 mol% over the entire 12-mm distance in an identical glass prepared on Earth.

When these lithia–silica glasses[11,12] were doped with 0.01 mol% Pt, microprobe analysis again showed that except within a distance of about 1 mm from the container wall, the distribution of Pt particles in the bulk of the space glass (0.01% ± 0.002%) was more homogeneous than that in the glass (0.01% ± 0.007%) prepared on Earth. Thin section microscopy of these Pt-doped glasses that had been crystallized by postflight heat treatment revealed that the crystals were more uniform and finer-grained in the samples melted in space than those that were heat-treated identically but melted on Earth. Again, the results indicate a higher homogeneity of the space glasses as compared to similar glasses prepared on Earth. Reference 12 concludes that "melting of glass under microgravity conditions is superior to normal gravity conditions, even if a crucible is used. Melting in a containerless condition in space may produce even more homogeneous glasses."

Borate and Phosphate Glasses (Processing in a Container)

Reports of a significant improvement in chemical homogeneity for space-processed borate and phosphate, in addition to silicate, glasses are also available.[10] Because the chemical homogeneity of the glasses prepared in space is reported to be improved, the properties, particularly optical, for space-processed glasses are expected to be improved as well. However, only a few reports on the properties for the space-processed glasses are available.

As mentioned, the spatial variation in the refractive index of a silicate glass processed in space was much less than that for a comparable glass processed on Earth.[11,12] In at least one experiment,[10] a phosphate laser glass (doped with Nd_2O_3) melted in space was reported to have a higher threshold energy for radiation damage than a similar glass melted on Earth, 320 Jcm^{-2} for the space glass compared to 250 Jcm^{-2} for the Earth melted glass. (The Jcm^{-2} unit for the radiation density was used by these authors[10] and is retained here.) The higher radiation resistance for this space-melted laser glass was attributed to a reduction in liquid-phase separation for space melts. For example, the diameter of chemically inhomogeneous regions (phase-separated droplets) ranged from 100 to as large as 2000 nm as measured by electron microscopy for the Earth-melted glass, whereas these regions varied from only 50–100 nm for the glass melted in space.[10]

These investigators[10] also demonstrated that the concentration limit for fluorescence quenching of Nd ions in the space-melted phosphate glass was about five times larger than that for the glass melted on Earth. The fluorescence decay time for the Nd ions decreased progressively when the concentration of Nd_2O_3 exceeded ~2 wt% in the phosphate glass processed on Earth. In the same phosphate glass processed in space, the fluorescence decay time did not decrease at Nd_2O_3 concentration below 10 wt%. These noteworthy results suggest that lasers prepared from glasses melted in space could have five times more output power per unit volume than equivalent lasers prepared from glasses melted on Earth. These investigators also remarked that the mechanical strength for the space-melted glasses was higher than that for the glasses melted on Earth, although no results were given.

Results from experiments conducted on immiscible BaO–B_2O_3 melts using a 150-m drop shaft (~10^{-5} g_0 for 4.5 s) have also led to the suggestion[26] that "phase separation was suppressed, and, consequently, the nucleation rate decreased under microgravity circumstances" as compared to the same observations made at g_0.

For a sodium metaphosphate glass, investigators have reported[22,23] results that differ somewhat from those discussed earlier. From differential thermal analysis (DTA) types of experiments conducted in space (onboard Mir), these investigators reported that a $NaPO_3$ glass containing 0.1 wt% Pd (introduced as $PdCl_3$) crystallized at a lower temperature when reheated (from room temperature) in space than when an identical glass was reheated on Earth. This result was interpreted to suggest that the crystallization tendency of the glass, rather than being suppressed as observed by many other investigators, was enhanced in low gravity. The reason for the observed enhanced crystallization tendency in space was attributed to a slower heat dissipation rate (from the sample) in low gravity due to a near absence of gravity-driven convection. The slower heat dissipation rate (in low gravity) caused the glass to overheat as compared to a similar situation on Earth. The higher sample temperature in low gravity decreased the viscosity of the glass, thereby increasing its overall tendency for crystallization. This is a unique experiment, but it does not prove or disprove that a space made glass is more resistant to crystallization because the glass used in this experiment was never melted in space, but was prepared on Earth.

Metal Fluoride and Other Chalcogenide and Tellurite Glasses

It was demonstrated[11,12] that a melt in space was essentially stagnant (quiescent) except for a little disturbance near the container wall, probably due to the effect of surface tension at the melt–container interface. The compositional inhomogeneity caused by melt disturbance was confined within a narrow region at the melt–container interface and was not transported into the bulk of the melt due to the suppression of gravity-driven convection in low gravity. Similar results were also observed in a more recent experiment[20] where a heavy metal fluoride glass (ZBLAN) containing 0.1 mol% metallic Ag was melted and cooled in sealed platinum containers in space (unmanned satellite FOTON 10, SKAT-C1A of Russian Space Mission, February–March 1995). High-resolution atomic force microscopy of the fracture surface of these glasses showed that the topography of the glass near the crucible wall was much coarser (ripples wider and larger in height) than that of the bulk glass.

Reports of a more uniform and finer-grained microstructure in low gravity are also available for chalcogenide Ge–Sb–S glasses.[8,9] These glasses were melted in quartz capsules (5-mm diam, 20 mm long) at 850°C for 5 h and cooled to ~22°C in 5 h at a level of

10^{-5}–10^{-6} g_0 on the Soyuz–Salyut 6 (MORAVA I) orbiting space station. The glass cylinder was then cut into several thin slices (1–3 mm thick) for analysis. Heating the slices of this space-melted $Ge_{25}Sb_{20}S_{55}$ glass at 400°C for 1 h showed no evidence of crystallization as detected by scanning electron microscopy, whereas samples prepared identically on Earth were heavily crystallized, forming whiskers of antimonite (Sb_2S_3) when given the same heat treatment. When heated at 420°C for 1 h, the space glass crystallized, but the extent of crystallization was much smaller. The crystals were much smaller and more uniformly distributed than in the terrestrial sample.

The preceding results, including those cited in Refs. 11, 12, and 20, demonstrate that the glasses prepared in low gravity are more resistant to crystallization than identical glasses prepared on Earth, and the low-gravity glasses, when crystallized, have a microstructure containing smaller and more uniformly distributed crystalline grains. This type of microstructure indicates that the number and size of the nuclei were much smaller, and the nuclei were more uniformly distributed in the as-quenched space glass than in a similar glass melted identically and quenched on Earth. The investigators of this work[8,9] speculated that the chalcogenide glasses in space were solidified under the condition of a larger nonequilibrium supercooling. The evolution of a finer microstructure (for the crystallized samples) is a direct consequence of the effect for larger supercooling. In other words, these results led to the suggestion that the presently known phase diagram (liquidus temperature–composition curves) for a system is only a special case for $g = g_0$ and changes with the gravity level.

More direct evidence of increasing crystallization tendency with increasing gravity level is provided by the results of experiments conducted for ZBLAN (heavy metal fluoride) glasses[17–19] aboard NASA's KC-135 and Canadian T-33 aircrafts, and in the drop shaft at the Japan Microgravity Center (JAMIC) for sodium tellurite (NT) glasses.[25] The ZBLAN glass fibers prepared on Earth did not show any evidence of crystallization when heat treated at 370 or 400°C for 20 s during the low-gravity ($g \sim 10^{-3}$ g_0) portion of the parabolic flight, whereas the fibers crystallized to a significant extent when heated under identical conditions either on Earth (g_0) or in the aircraft during its high-gravity ($g \sim 2\,g_0$) portion of the parabolic flight. Furthermore, smooth, glassy fibers were easily drawn during the low-gravity portion of the flight, when glass fibers were drawn from this ZBLAN melt in the KC-135; however, the melt at the nozzle of the fiber-drawing apparatus crystallized rapidly (no fiber could be drawn) during the 2 g_0 recovery period of the aircraft.

In the JAMIC drop shaft experiments,[25] a sodium tellurite melt, which is an excellent glass former and reluctant to crystallize at g_0, crystallized significantly within milliseconds when the capsule containing the experiment package made the transition from a low g (free fall, $g \sim 10^{-4}$ g_0) to a high g (decelerated to stop, from $g \sim 8$ to 10 g_0). This result was reproduced in about 30 drop experiments conducted at different times over a 7-year period, but attempts to reproduce the crystallized morphology observed in the drop shaft experiments were unsuccessful at g_0, even after heating the glass at its crystallization temperature (~375°C) for 24 h on Earth.

A research report[21] that concludes that a $Ge_{20}Sb_{20}S_{60}$ glass prepared in space is less chemically homogeneous than an identical glass prepared on Earth is also available. This conclusion was drawn from the comparison of density and differential scanning calorimetry (DSC) results for the glasses prepared in space (Soviet orbital laboratory, Mir) and on Earth using identical conditions for melting (1120 K for 2 h), cooling (to 998 K in 1 h), annealing (at 998 K for 3 h), and further cooling to room temperature at a rate of $10\ \mathrm{K \cdot min^{-1}}$. The melting was conducted in a sealed, evacuated quartz ampoule (6 cm long and 8 mm in internal diameter) in both cases. Compositional analysis at different portions (from the edge to the center) of the glass prepared in space showed a considerable variation, whereas the composition at different portions of the glass prepared under terrestrial conditions was nearly the same. As expected from compositional analysis, the densities, as well as the DSC results, for different portions of the space-made glass were noticeably different. However, those for different portions of the glass made on Earth were constant within experimental error. As concluded by these authors, the space-made $Ge_{20}Sb_{20}S_{60}$ glass was less chemically homogeneous than the identical glass prepared on Earth.

Current Situation

With the exception of two reports,[21–23] all of the other results[8–20,26] reported independently by several investigators on a wide variety of oxide (silicate, borate, phosphate, and tellurite) and nonoxide (chalcogenide and metallic) glasses suggest the following: 1) The glass formation tendency for a melt is enhanced. 2) Phase separation in immiscible melts is suppressed in low gravity. 3) Glasses prepared in space are more chemically homogeneous than identical glasses prepared on Earth. 4) Glasses prepared in space are more resistant to crystallization than identical glasses prepared on Earth. 5) Glasses prepared in space, but crystallized on Earth have a microstructure composed of smaller crystals that are more uniformly distributed than equivalent glasses prepared and crystallized on Earth. 6) The space melted glasses may be mechanically stronger, have a higher threshold for radiation damage, and possess improved optical properties as compared to their counterparts prepared on Earth.

Although the preceding results are very interesting and demonstrate the potential for preparing new glasses of improved quality using low gravity, the reason(s) why the space-melted glasses is/are characteristically different from Earth-melted glasses are not clearly known. The most notable of all of the differences mentioned earlier between the space- and Earth-melted glasses are the improved chemical homogeneity and higher resistance to crystallization (improved glass formation) for space-melted glasses. All other properties measured to date for the space-melted glasses, such as the refractive index uniformity, concentration limit for fluorescence quenching, or threshold energy for radiation damage, have their origin linked to chemical homogeneity and resistance to crystallization of the glass.

According to our current understanding, melts in space are expected to have less internal flow (be more quiescent) because of the absence of gravity-driven convection and, hence, have a lower rate of mass transfer than melts on Earth. Calculations for a hypothetical liquid with a viscosity of $2.3\ \mathrm{Pa \cdot s}$, confined in a cylindrical platinum container 1 cm in diameter and 2.5 cm in length, show that the rate of fluid flow or melt velocity decreases logarithmically with decreasing gravity, as shown in Fig. 3. These calculations (also calculated was the shear rate in the melt, which is discussed later) were carried out using a FIDAP fluid dynamics package (Fluent, Inc., version 8.0, 1998) and assuming the platinum cylinder containing the melt was heated in such a way that a thermal gradient of 5°C existed at its two ends. The curved wall of the cylinder was

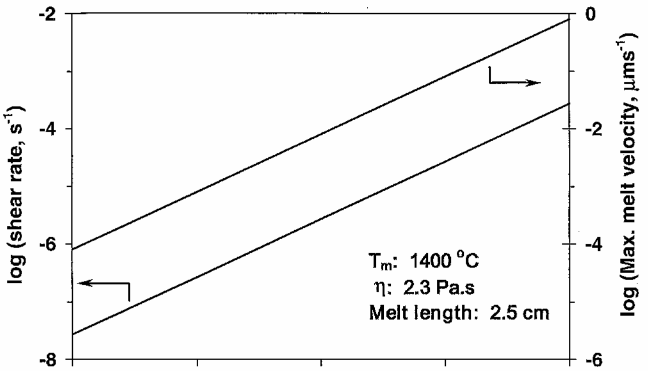

Fig. 3 Calculated shear rate and maximum melt velocity as a function of gravity for a hypothetical melt contained in a cylindrical platinum container, 2.5 cm in length and 1.0 cm in diameter, at 1400°C, assuming a temperature difference of 5°C across the 2.5-cm length of the melt; the viscosity of the melt at 1400°C is assumed to be 2.3 Pa · s.

Table 1 Fluid properties used in the calculations of melt velocity and shear rate as a function of gravity g (Fig. 3) for a melt contained in a cylinder of length L = 2.5 cm, diameter d = 1.0 cm, and a temperature difference ΔT of 5 K between the flat ends of the cylinder

Property[a]	Value
Density ρ	$2120\,\mathrm{kg \cdot m^{-3}}$
Viscosity η	$2.3\,\mathrm{Pa \cdot s}$
Thermal diffusivity α	$7.86 \times 10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$
Coefficient of volume expansion β	$7.6 \times 10^{-5}\,\mathrm{K^{-1}}$
Prandtl number Pr	1380
Rayleigh number $Ra = [g\rho\beta(\Delta T)L^3]/[\eta\alpha]$	4.371

[a] These properties are close to those for a $Li_2O.2SiO_2$ melt at 1400°C, which will be used in the proposed flight experiments.

assumed to be insulating and the gravity acting in a transverse direction to the thermal gradient. The governing equations (continuity, Navier–Stokes, and thermal conservation) and the boundary equations were solved iteratively using a segregated solver (finite element code, FIDAP), and the solutions were carried to convergence until the sum of normalized residuals was less than 10^{-5} (steady-state condition). The fluid properties used in the calculations are shown in Table 1. The equations and boundary conditions were normalized by scaling parameters, $(\alpha/d)Ra^{1/2}$ and ΔT, for velocity and temperature, respectively. The reason(s) why such a melt in space, where the rate of mixing is much slower as shown in Fig. 3, would be more chemically homogeneous than an identical melt on Earth are not obvious.

Similarly, there is no obvious explanation for the improved glass-formation tendency (decreased crystallization tendency) for melts processed in space. Glass formation is controlled by the kinetics of nucleation and crystal growth. From classical theory, the nucleation rate I and crystal growth rate U as a function of temperature T are expressed in their simplified standard forms as

$$I = (AkT/\eta)\exp\left[-B\big/(\Delta G_V)^2kT\right] \tag{1}$$

$$U = (CkT/\eta)[1 - \exp(-V_m\Delta G_V/RT)] \tag{2}$$

The volume fraction X that crystallizes from a glass on heat treatment at T for t is related to I and U approximately, as,

$$X = (\pi/3)IU^3t^4 \tag{3}$$

A reduction in either I or U separately or jointly for a melt reduces its overall tendency for crystallization X or improves its tendency for glass formation. The reported increase in glass-formation tendency for a space melt suggest that its I and U values could be smaller than those for an identical melt on Earth. However, none of the terms in Eqs. (1) and (2) depends on gravity per se, and so the reason(s) why I and U for a space melt should be different from those for a melt on Earth is/are not readily apparent.

Hypothesis

A qualitative explanation for the observed improvement in chemical homogeneity and glass formation of the space melts, compared to melts prepared on Earth, is depicted by the schematic in Fig. 4. A high rate of mass transfer due to gravity-driven convection makes the mixing or chemical homogenization of a melt faster on Earth than in space. It is possible that this higher rate of mass transfer induces larger compositional fluctuations in the melt on Earth and produces regions of varying chemical composition. Chemically inhomogeneous regions ~20 times larger in size were observed in the bulk of Earth-melted phosphate glasses as compared to such regions in identical glasses processed in space.[10] Of particular importance is the compositional change at the melt surface caused by evaporation/vaporization and dissolved impurities from the container, which are quickly convected into the bulk of the melt at g_0, thereby reducing the overall chemical homogeneity of the melt. Thus, due to a higher rate of mass transfer at g_0, the driving force for melt homogenization is simultaneously opposed (demixing) by effects that produce chemical inhomogeneities in the melt. As a result, the maximum level of chemical homogeneity attainable at g_0 is always less than the ideal (Fig. 4). The presence of these chemically inhomogeneous regions may act as potential nucleation sites (quenched-in nuclei), and makes the glass susceptible to crystallization.

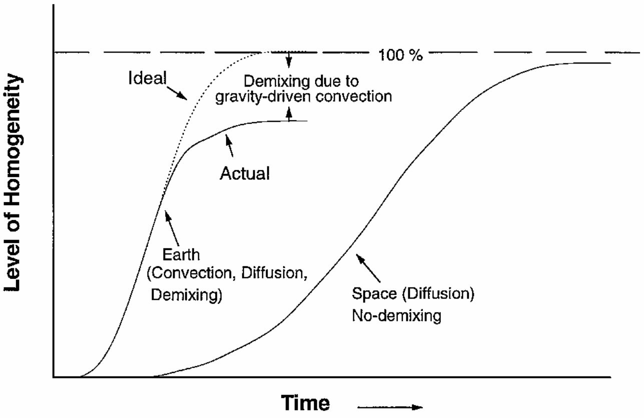

Fig. 4 Schematic of melt homogenization and final relative homogeneity for a melt on Earth and in space.

In the absence of gravity-driven convection in lowgravity, melt homogenization is expected to occur by diffusion only, which is a much slower process, that is, it may take a longer time for the melt to become homogeneous. Because of the slow rate of mass transfer in low gravity, the so-called demixing is either less likely to occur or will be completely absent in an ideally stagnant (quiescent) melt in space. As a result, the overall homogeneity of the melt in low gravity can come close to the ideal homogeneity (given sufficient time). Once homogeneous, the melt remains so for any extended period of time. This also means that the number and size of the inhomogeneous regions or quenched-in nuclei in a glass prepared in space should be smaller, making it potentially more resistant to crystallization than a comparable glass on Earth. It has been demonstrated[11,12] that the chemical inhomogeneity produced at the interface of a lithium silicate melt and carbon container in space was not transported into the bulk, but remained confined within a narrow (~1 mm) region from the melt–container interface. The remainder of the bulk glass was highly chemically homogeneous.

Another explanation for the observed higher resistance to crystallization for space-melted glasses may be that the rates for nucleation I and crystal growth U for a melt in space are smaller than those for the same melt on Earth. Although, as shown in Eqs. (1) and (2), I and U do not contain any gravity-dependent parameter, we believe that the viscosity η for a space melt at any temperature could be higher than that for the same melt on Earth because of shear thinning (a lowering of viscosity when a melt is subjected to a shear stress). Because of a smaller rate of fluid flow in low gravity, a melt is more quiescent and is expected to contain smaller shear stresses than the same melt on Earth, where the higher gravity increases convective flow. Thus, all other factors being equal, a melt in low gravity is expected to have a higher viscosity (low shear stresses) than the same melt on Earth (higher shear stresses). As shown schematically in Fig. 5, an increase in viscosity at all temperatures for a space melt should decrease its values for I and U and, hence, its overall crystallization tendency [X in Eq. (3)] as compared to a similar melt on Earth.

Shear thinning has been reported for many glass-forming melts. Documented examples of glasses showing shear thinning include a large number of commercial glasses (container, float, pyrex, and TV panel),[29] glasses in the system Rb_2O–SiO_2,[30] soda–lime–silica NBS-710 viscosity standard,[29,31] zinc–alkali–phosphate,[32–36] fluoroapatite,[37] and $Li_2O.2SiO_2$ (LS_2)[38–42] glasses. Of particular relevance will be a discussion of shear thinning for a LS_2 glass because this glass has been chosen for our proposed flight experiments in space. Under tangential flow conditions, the viscosity of the LS_2 glass has been shown to decrease,[40,41] by a factor of from

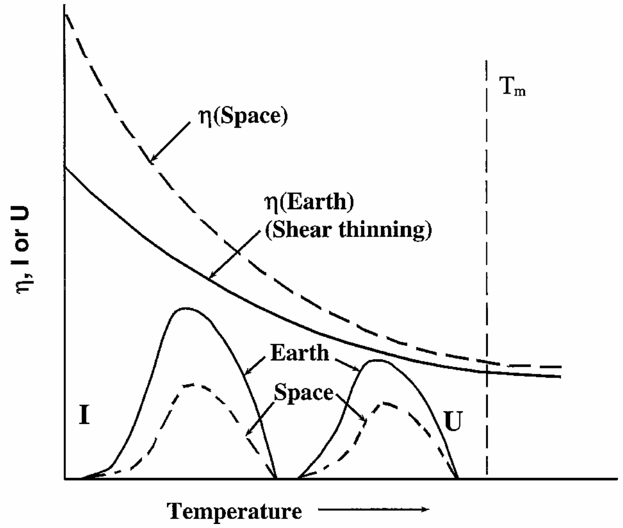

Fig. 5 Schematic of the anticipated viscosity η, nucleation rate I, and crystal growth rate U for a melt in space and for the identical melt on Earth based on shear thinning.

three to five, with increasing shear rate from its "no shear" value of 2.2×10^{10} Pa · s at 483°C, where significant nucleation occurs for this glass. A reduction in viscosity η by a factor of from three to five can increase the crystallized volume fraction X by a factor of 81–625 [Eqs. (1–3)]. In space, therefore, where the melt is expected to be essentially quiescent (negligible shear stress), the volume fraction crystallized could be reduced significantly as compared to the same melt on Earth.

Color center (CC) chronospectroscopy measurements[43] for extruded (high shear) and nonextruded LS_2 glasses, before and after X irradiation for 5 h, also show a strong response of this glass to shear thinning. Glasses were extruded at 540°C (viscosity $\sim 10^{7.5}$ Pa · s) at pressures up to 45 MPa. X-ray induced absorption spectra showed that the average distance between the recombining electron and hole CCs for the extruded glass rods was larger in the direction of extrusion than in the direction perpendicular to extrusion. This means that the glass structure is elongated or the intermolecular distance increases in the direction of extrusion or shear field. No such directional dependence on the structural length was observed in the nonextruded glasses. An ordering of structural groups in the direction of tangential shear stress can be caused by a reduction in viscosity, that is, shear thinning.

In an investigation using LS_2 glass fibers, we found that heating bent fibers at 420°C (for 1 h) shows evidence of crystallization at the bent tips (region of high bending stress, ~0.5 GPa), but no crystallization was evident in the straight fibers (no stress) when heated at the same temperature for up to 12 h. This 420°C temperature is about 150°C lower than the onset temperature (~570°C)[44–47] for crystal growth U for this glass, and so no crystallization of the straight (stress-free) fibers is expected. The crystallization at the bent, high-stress portion of the fibers clearly indicates that a bending stress (~0.5 GPa in this case) induces significant crystal growth in the LS_2 glass fibers even at such a low temperature. Crystallization of the bent (high-stress) portion of the fibers could be explained by a lowering of the viscosity (shear thinning) at the high-stressed regions, which increased I or U in Eqs. (1) and (2).

Because of gravity-driven convection at g_0, the layers of a melt are under constant flow (nonquiescent) with respect to each other. This internal flow should be negligible in a relatively quiescent melt in space, where gravity-driven convection is greatly reduced or is, ideally, absent. Therefore, it is suspected that a melt in space will contain smaller shear stresses (at least locally), and have a higher viscosity (at any temperature) than an identical melt on Earth. Calculations for an LS_2 melt contained in a cylindrical platinum container, about 2.5 cm long and 1.0 cm in diameter, also show (Fig. 3) that the shear rate in the melt decreases logarithmically with the gravity level. Thus, at a conservative gravity level of 10^{-4} g_0 in space, the shear rate in the melt is expected to be about four orders of magnitude less than that in an identical melt at g_0.

There is no evidence for how much higher the effective viscosity of the space-made glass will be compared to the viscosity for the glass made on Earth due to this four orders of magnitude smaller shear rate. However, based on available experimental data[29,31,37–42] for the dependence of effective viscosity on shear rate for various glasses, including LS_2, it is anticipated that reducing gravity to 10^{-4} g_0 for the space glass can increase its viscosity by a factor ranging from 2 to 10. This means that the overall crystallization tendency of the space melt could decrease or its glass-forming tendency could increase by factor of 16 (for a doubling in viscosity) to 10,000 (for a 10-fold increase in viscosity) [Eqs. (1–3)]. The observed results[13,15] for an increase in the glass-formation tendency for a calcia–gallia–silica melt by a factor of from at least three to four in space as compared to that for an identical melt on Earth (Fig. 1) are consistent with this hypothesis.

Planned Flight Experiment

The hypothesis of shear thinning could provide a satisfactory explanation for the difference in glass formation for melts in low and normal gravity within the framework of our fundamental understanding of the kinetics of nucleation and crystal growth in high-temperature melts in lowgravity. As discussed, there are numerous examples that qualitatively support the enhanced glass formation (suppressed crystallization) for high-temperature melts in space, but no data currently exist for the nucleation and crystal growth rates for melts prepared in space. Obtaining data for the nucleation and crystal growth rates for LS_2 glass prepared entirely in space is the primary objective of our current NASA-funded research.

As shown by our general experimental plans in Fig. 6, we intend to measure the nucleation rate I and crystal growth rate U for LS_2 glass prepared entirely in space and to compare these values with the I and U values for identical glass prepared on Earth. The LS_2 composition has been chosen primarily for the reason that it is frequently used as model glass for investigating the nucleation and crystal growth kinetics, and, thus, a large body of thermodynamic and kinetic data for nucleation and crystal growth at g_0 are available for this glass. Furthermore, shear thinning in LS_2 glass has been documented and measured at temperatures in the nucleation range that will be used to nucleate the space-melted LS_2 samples in our planned flight experiments.

The overall experimental plan in Fig. 6 includes measuring the nucleation rate I and crystal growth rate U for the LS_2 glass after melting and heat treating (for nucleation and crystal growth) at four different conditions, namely, 1) melted and heat treated in space (I_{SS} or U_{SS}); 2) melted in space, but heat treated on Earth (I_{SE} or

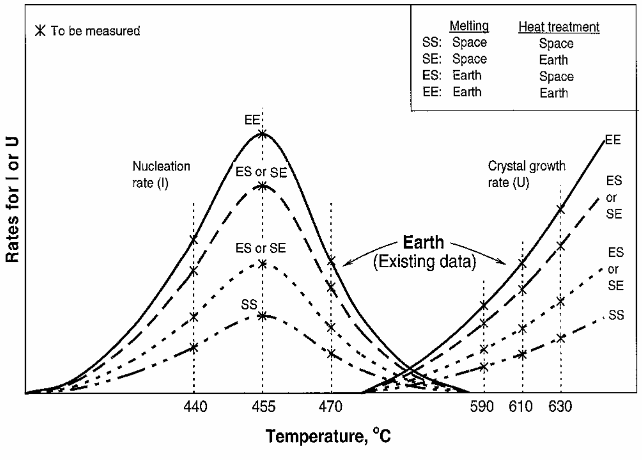

Fig. 6 Relative values for the nucleation rate I and crystal growth rate U, as expected from different melting and heat treatment experiments shown in the inset; this schematic has been designed for our planned, NASA-sponsored flight experiments to be conducted using an $Li_2O.2SiO_2$ melt.

U_{SE}); 3) melted on Earth, but heat treated in space (I_{ES} or U_{ES}); and 4) melted and heat treated on Earth (I_{EE} or U_{EE}).

Experiments for measuring I_{SS} or U_{SS} consist of remelting LS_2 glass in sealed platinum capsules, ~2.5 cm long and 1.0 cm in diameter, at 1400°C for 3 h in space and quenching the capsules at a rate fast enough (~100°C/min) for the encapsulated melt to form glass. For measuring I_{SS}, the samples will be nucleated in space at 440, 455, or 470°C for times ranging from 1 to 5 h, and given a short crystal growth heat treatment at 600°C for about 20 min. For measuring U_{SS}, the samples will be given only a single-stage heat treatment at 590, 610, or 630°C for times ranging from 10 to 40 min. The heat-treated samples will then be returned to Earth, cut into thin slices (2–3 mm), and analyzed by optical microscopy after light grinding, polishing, and etching. I_{SS} at any temperature can be determined by measuring the number of crystals as a function of nucleation heat-treatment time at that temperature, and U_{SS} can be determined by measuring the size of the crystals as a function of time at any crystal growth temperature.

Some of the capsules will be returned to Earth after the melting step. These samples will receive the same nucleation or crystal growth heat treatment as mentioned earlier to measure I_{SE} or U_{SE} on Earth. For measuring I_{ES} or U_{ES}, encapsulated glass samples prepared on Earth using the same melting and cooling procedures as will be used in space will be given only nucleation and crystal growth heat treatment in space (not remelting in space). Encapsulated glass samples melted, as well as heat treated for nucleation and crystal growth, on Earth will be used for measuring I_{EE} and U_{EE}.

A comparison of the values for I and U for the glasses prepared and heat treated under the four conditions mentioned will provide direct evidence of any dependence of I and U on gravity, as might be expected from the shear thinning hypothesis. If the space-melted glasses undergo less shear thinning, are more chemically homogeneous, and contain fewer quenched-in nuclei than identical glasses on Earth, we anticipate that I_{SS} or U_{SS} will be smaller than I_{EE} or U_{EE}, as depicted in Fig. 6.

It is not clear how the I and U values for the glasses melted in one condition, but heat treated in another condition (for example, I_{ES} and I_{SE} or U_{ES} and U_{SE}) will compare with the I and U values for the glasses melted and heat treated entirely either in space (I_{SS} or U_{SS}) or on Earth (I_{EE} or U_{EE}). However, it is expected that these values will be intermediate between I_{SS} and I_{EE} or U_{SS} and U_{EE}, as shown in Fig. 6.

Summary

The reason(s) why glasses prepared in space have been found to be more chemically homogeneous and resistant to crystallization than glasses prepared on Earth is still unknown. A fundamental understanding of the kinetics of nucleation and crystal growth for glass-forming melts in low gravity should provide an explanation for these important differences, which is the primary objective of our next flight experiments. It is believed that the nucleation rate or the crystal growth rate for the space-melted glasses could be substantially smaller than for the same glasses prepared on Earth because of differences in viscosity (shear thinning).

If our flight experiments show that I (or U) is smaller for space-melted glasses than for Earth-melted glasses, then the present theory for nucleation and crystal growth in high-temperature melts should be considered as a special case pertaining to normal gravity only. More generalized theories introducing a gravity-dependent term through the viscosity parameter [Eqs. (1) and (2)] may need to be developed. This improved knowledge for the fundamental mechanisms of glass formation, nucleation, and crystallization should improve our present-day technology for glass processing on Earth. An improved processing technology could yield glasses whose quality and properties are superior to those presently attainable and could help advance applications in communications, optical switching, and devices where glasses are used as key functional materials.

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