

FULL PAPER

Structure, properties and microgravity processing of liquids and glasses

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Containerless processing was used to access and study supercooled liquids and glasses that cannot be made using conventional melting approaches. In-situ measurements of melt atomic structure and density provided insight into how the glass forms. Experiments included making measurements in microgravity where buoyancy driven convection and sedimentation are suppressed. Here we examine the structure and properties of rare earth-aluminate composition liquids and some glasses made from them. The structures show a fundamentally different network behavior from the classical Zachariasen model. The network comprises four and about 40 % five coordinated aluminum ions that share corners or edges and often form triply bonded species with an oxygen ion. The concept of K'' is used to evaluate the glass forming behavior in terms of network connectivity and bonding. The temperature dependence of density of the liquid is reported and discussed in the context of processing molten materials in reduced gravity where bubbles can be trapped in the liquid due to lack of buoyancy. The interior structure in samples was investigated using X-ray tomography to investigate how bubbles can cluster inside a liquid drop.

Key-words : Glass, Liquid, Supercooling, Containerless processing, Atomic structure, Density

[Received March 15, 2026; Accepted March 19, 2026; Published online April 23, 2026]

1. Introduction

Much industrial value-add materials processing involves high temperature liquids. This is particularly the case for production of glass where mixtures of metal oxides are typically melted and then cooled in a way that prevents nucleation of crystals.^{1,2)} Containerless processing can enhance glass formation by avoiding both heterogeneous nucleation of crystals and chemical contamination of melts.³⁻⁵⁾ In this work, containerless processing was used to access and study supercooled liquids and glasses that cannot be made using conventional melting approaches. In addition, the use of in-situ measurements of melt properties and atomic structure were used to gain insight into how the glass forms. The research includes the use of microgravity experiments to investigate uncontained melts in conditions where buoyancy driven convection and sedimentation are suppressed.^{6,7)}

These containerless techniques expand the composition range that can be explored, enabling processing of very fragile liquids in conditions that can result in glasses with-

out the traditional network forming components. These glasses can offer fundamental insights in how the structure changes to create a non-crystalline product. It also provides samples of materials that can be used to determine properties and benchmark research directions to develop new glass materials.

2. Methods

Two containerless methods were used. Experiments in the ground-based laboratory and at synchrotron beamlines used aerodynamic levitation in combination with carbon dioxide laser beam heating.^{8,9)} This technique is useful for work with molten metal oxides ranging from borates¹⁰⁾ and carbonates¹¹⁾ to highly refractory materials such as zirconium dioxide.¹²⁾ Forces derived from gas flow through a converging-diverging nozzle can trap liquid drops from about 1 mm to several mm in diameter. Sample temperature is controlled by adjusting the laser beam heating power.

Selected compositions were investigated in microgravity using the JAXA Electrostatic Levitation Furnace (ELF).¹³⁾ The operation and methods used with the instrument is described in detail in the literature¹³⁻¹⁵⁾ and briefly summarized here. Samples develop a small charge due to loss or gain of electrons (typically loss of electrons by thermionic emission). Three orthogonal pairs of elec-

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[‡] Preface for this article: DOI <https://doi.org/10.2109/jcersj2.134.P4-1>

trodes are used to repel the sample and provide stable positioning. The sample position is monitored using an imaging system and its position is actively stabilized by controlling the voltage on the electrodes. Samples are heated using four 40 W diode lasers arranged in a tetrahedral array. As in the aerodynamic levitator, sample temperature is controlled by adjusting the laser beam heating power.

Samples levitated in the ELF are imaged by using a backlight to project a silhouette of the sample onto a video camera sensor. Analysis of video images enables calculation of the volume of the sample and hence measurement of its density.¹⁵⁾ Samples can also be excited into an oscillation mode by pulsing the voltage on the positioning electrodes at selected frequencies. This enables investigation of fluid properties such as surface tension and viscosity that can be derived from the resonance oscillation frequency and the damping of motion when the stimulation is stopped.^{13,14)}

Various glass compositions were synthesized using containerless methods. Here we will focus on rare earth aluminates as a system that exhibits some of the behavior that can occur in fragile liquids. Compositions based on ytterbium and lanthanum were of particular interest since they span a range of rare earth ion radius. The large lanthanum ion enables glass formations. Compositions based on the smaller ytterbium ion do not form glass.¹⁶⁾

2.1 Atomic structure

High-energy X-ray diffraction measurements were made at Sector 6-ID-D of the Advanced Photon Source, Argonne National Laboratory (Lemont, IL, USA). An aerodynamic levitator was used as the sample environment.⁹⁾ Samples were levitated on a stream of air and heated with a carbon dioxide laser beam until molten. Melt temperature was controlled by adjusting the incident laser beam power (measurement uncertainty of ± 30 K¹⁷⁾). X-ray diffraction measurements were collected at several different temperatures. The diffraction of 99.96 keV X-rays was measured in transmission geometry using an area detector (Varex 4343CT) arranged to provide a range of momentum transfers $0.3 < Q < 24.5 \text{ \AA}^{-1}$. Data were corrected and reduced following previously described procedures^{18–20)} resulting in the X-ray total structure factors and pair distribution functions (PDFs).²¹⁾ The PDFs were calculated with a maximum Q value of $20.5 \text{ \AA}^{-1}$ and no modification (e.g., Lorch) function was applied.

Structural models were obtained from Empirical Potential Structure Refinement (EPSR) of the X-ray structure factors measured at selected temperatures. EPSR is a reverse Monte Carlo based simulation technique, in which simple, pre-defined interatomic potentials are refined by comparing the simulated and experimental scattering to bring the former into agreement with the latter.²²⁾ The output of the EPSR model enables interpretation of the structure to provide an understanding of the coordination and bonding of cations in the sample. Details of the EPSR simulations including the initial reference potentials have been published previously – see Refs. 26) and 27).

2.2 Density

In the ELF instrument, a video image of the sample silhouette is recorded using a camera and ultraviolet backlight positioned on opposite sides of the levitation position. The camera is regularly calibrated with precision stainless steel spheres of similar diameter to the samples. For density analysis, individual frames were extracted from the video record of each sample during cooling (i.e., after the heating lasers were turned off). The perimeter of the silhouette was fitted with a sixth order Legendre polynomial, from which the spheroid sample's volume was calculated.²¹⁾ Density and thermal expansion were then calculated based on the sample volume and mass, which was measured on Earth before and after the experiments in ELF. This technique has been applied for several molten materials including lanthanoid sesquioxides²³⁾ Ga_2O_3 ,²⁴⁾ and Au.²⁵⁾ Two sets of experiments were run in ELF. The first set were run in air at a pressure of 2 bar. The second were run in high purity argon at a pressure of 2 bar.

2.3 Microstructure

X-ray microtomography measurements were performed at Sector 7-BM-B of the Advanced Photon Source, following the same setup and reconstruction procedures as described previously.¹⁷⁾ To measure internal porosity, the three-dimensional reconstructions were analyzed as sequences of individual cross-sections. In the image sequence, each frame represents a two-dimensional cross-section of the sample, with a thickness of 1 pixel. Each frame contained a bright area in the middle (the sample portion) and the surrounding background, which was darker. Macro scripts were implemented in ImageJ to run a threshold that distinguished the sample from background. Only pixels in the sample area were counted. Then, the hole filling operation was used to fill-in any internal pores, and pixels within the sample were again counted. Porosity was calculated as the ratio of filled-in pixels to the total number of sample pixels.

3. Results

3.1 Atomic structure

The atomic structure of several rare earth aluminum garnet composition melts has already been reported elsewhere.^{16,26,27)} One important finding from the structural investigation arose from a comparison of the rare earth atomic environments in aluminate melts and glasses. In binary rare earth aluminates, glass forming ability decreases as the rare earth cation size decreases,¹⁶⁾ and vitrification is not possible for rare earths smaller than thulium. This trend correlates with changes in the Al–O coordination number distributions, network linkedness and connectivity. In these systems, the atomic network comprises a mixture of Al–O polyhedra of varying coordination number linked predominantly via corner-sharing, though with up to 17 % edge-sharing in liquid above the melting point. Because the Al–O units include substantial fractions of five- and six-coordinate polyhedra (e.g., 36 and 6 % in YbAG, ytterbium aluminum garnet $\text{Yb}_3\text{Al}_5\text{O}_{12}$ composi-

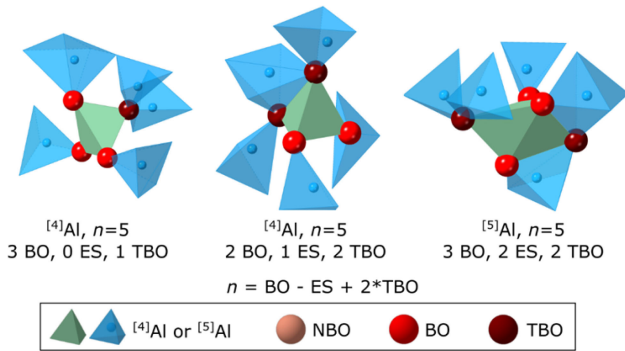


Fig. 1. Structural arrangements in molten YbAG. The connectivity metric K^n is used to quantify the number of neighboring network Al–O units to a given Al–O polyhedron. In each example, the polyhedron being analyzed is shown in opaque green, and its neighboring Al–O polyhedra are in translucent blue. For these three examples, the value of n is 5. Oxygen atoms are only shown for the central unit, for clarity. Ytterbium atoms are not shown.

tion, at 2630 K) in addition to the typical tetrahedra,²⁶⁾ the conventional Q^n connectivity analysis cannot be used to directly compare structure in different rare earth aluminate melts. The Q^n calculation assumes that the network is entirely tetrahedral with only corner-sharing and no triply bonded oxygen. In YbAG, all three of these assumptions are invalid.

In order to directly compare the connectivity of different melt structures, we have defined a new connectivity metric, K^n . Like Q^n , the value of n in K^n corresponds to the number of neighboring network units to a given unit in the network, according to:

$$n = \text{BO} - \text{ES} + 2 \times \text{TBO} \quad (1)$$

In Eq. (1), BO are the number of bridging oxygen, which link any two neighboring network units. ES are the number of edge-shares between a given network unit and its neighboring units. TBO are the number of triply-bonded oxygen, since these correspond to connections to two neighboring units. A full description of the K^n calculations and connectivity results are given in Ref. 26). A few illustrations are provided in **Fig. 1** for structural environments found in molten YbAG at 2460 K. In the first example, a [4]Al tetrahedron has three BO and one TBO. Each BO connects to one neighboring network unit, and the TBO connects to two neighboring network unit. All linkages are corner-sharing (no edge-sharing), so Eq. (1) gives $n = 3 - 0 + 2 \times 1 = 5$. If a traditional Q^n analysis was used instead, the TBO would be ignored and only 3 neighboring units would be counted, which illustrates why the assumptions of Q^n do not apply for this type of network structure.

3.2 Density and microstructure

The density of molten YbAG was measured in two separate campaigns of microgravity experiments, which each required flying samples to the International Space Station for measurements in the ELF. In the first campaign, three replicate samples of YbAG were used, which were

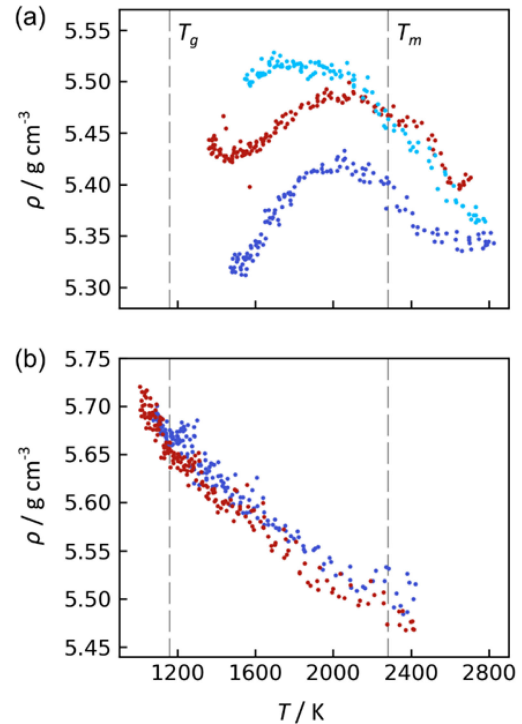


Fig. 2. Density of liquid YbAG. (a) Measurements during the first flight campaign, using three replicate samples that were later found to contain large internal bubbles. (b) Measurements of the second flight campaign, using two replicates that contained no internal bubbles. Replicates are marked in different colors.

initially polycrystalline spheroids approximately 2 mm in diameter. All three replicates were successfully levitated and melted, and their measured densities are shown in **Fig. 2(a)**. The densities were consistent within $\sim 1.5\%$ among the replicates, which is close to the typical uncertainty for ELF density measurement.¹³⁾ Intriguingly, all three replicates exhibited a density maximum ca. 2000 K, slightly below the equilibrium melting point of $T_m = 2283$ K.²⁸⁾ Anomalous density trends such as this maximum have been correlated with polyamorphic transitions in some liquids,²⁹⁾ suggesting that polyamorphism may occur in supercooled liquid YbAG. To explore this possibility, a thorough investigation was completed of the atomic structure in molten YbAG, combining X-ray diffraction, neutron diffraction with isotope substitution, and structural modeling. However, the structure measurements and simulations showed no indication of polyamorphism.

The explanation for the anomalous density trend with temperature was found using X-ray tomography to probe the internal microstructure of the YbAG samples. Because YbAG does not form a glass even in containerless conditions (for ~ 2 mm free cooled spheres), the melt quenched products were polycrystalline. As shown in **Figs. 3(a)–3(c)**, the three replicates from the first flight campaign that was run with air as the process gas contained large internal bubbles, which were likely responsible for the apparent density maximum. Each sample contained two large voids separated by a thin, 10–15 μm solid layer that presumably was a thin liquid layer held in place by surface tension

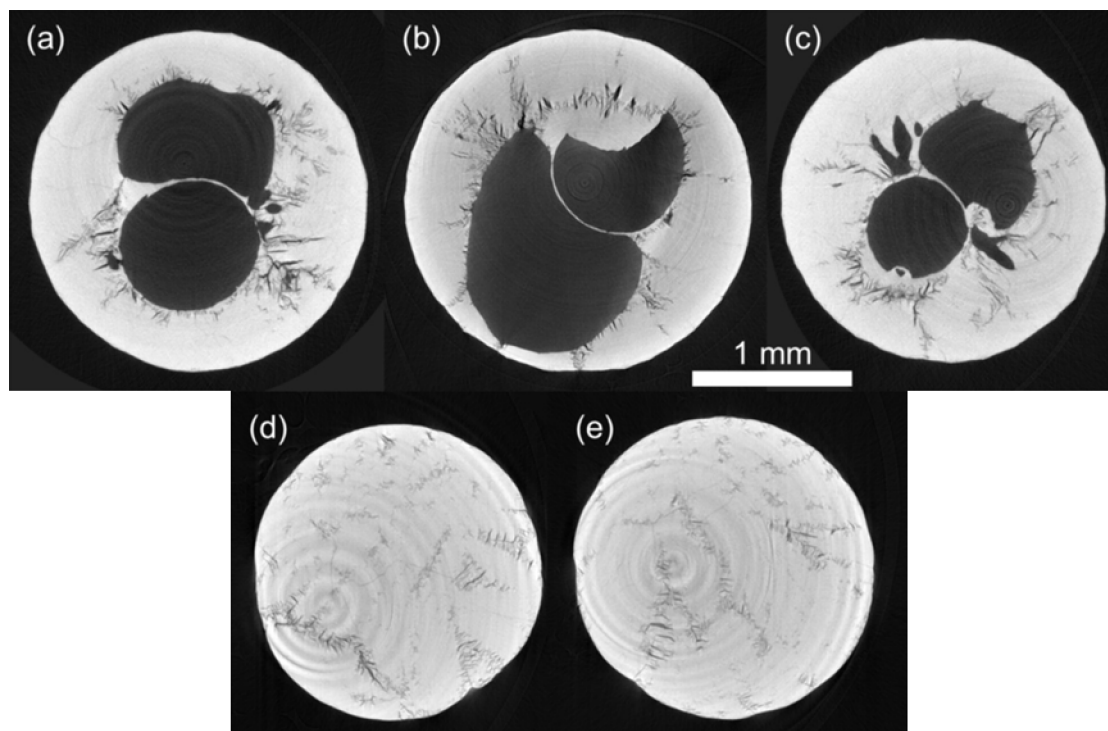


Fig. 3. Cross-sections of YbAG polycrystalline beads recovered from melt processing in microgravity. Replicates from (a–c) processed in air first and (d–e) processed in high purity argon second flight campaigns. The dark areas are voids, the light areas are oxide sample.

during the melt processing. Surprisingly, the thin features remained intact even after solidification. It is also surprising that all three samples contained similarly large voids. Other features evident in the tomography cross-sections include smaller voids and networks of cracks that likely formed during the rapid solidification.

During a second flight campaign, additional samples of YbAG samples were run in high purity argon and the density measurements were repeated. This time, the density showed a typical, monotonic thermal expansion with temperature. The densities of two replicate samples are shown in Fig. 2(b). The density of YbAG increases from 5.50 to 5.70 g cm^{-3} during cooling from 2400 to 1000 K . Both replicates spontaneously crystallized ca. 1000 K below the estimated glass transition of $T_g = 1159 \text{ K}$.

These two samples were also probed with X-ray tomography and found to contain no internal voids. Representative cross-sections are shown in Figs. 3(d) and 3(e). Similar to the first campaign, the second campaign samples contain cracks throughout the volume that likely formed due to the sudden volume change during solidification. The absence of bubbles validates the density data collected in the second campaign. Additionally, this study illustrates why ground-based characterization is essential to support microgravity experiments: the thermophysical property measurements could only be interpreted correctly by combining several ground-based probes for atomic structure and microstructure. In cases where small, roughly spherical bubbles are formed, the density can be corrected by adjusting the volume to account for the voids. However,

for the large voids like those in Figs. 3(a)–3(c), the voids likely change size during cooling due to the temperature of any entrapped gas and surface tension effects, so density correction based on tomography is not reliable in these cases.

4. Discussion

The ability to synthesize novel glasses and to access deeply supercooled liquids provides a useful way to investigate the structure and properties of unconventional glass formers.

The structure analysis for supercooled liquids shows that linkedness in the Al–O networks is mostly corner-sharing with about 40 % edge-sharing among five- and six-coordinated Al units in YbAG. If network connectivity is compared using the K^n metric, which accounts for the effects of five-coordinate Al, edge-sharing, and triply bonded oxygen, and the Q^n approach, which only considers corner-shared four-coordinate species, significant differences are apparent. Molten Yb and La based $\text{RE}_3\text{Al}_5\text{O}_{12}$ composition materials exhibit similar polyhedra linkedness in a Q^n analysis (i.e., when five-coordinate Al is excluded from network analysis). When five-coordinate aluminum is included in the analysis, the lower glass forming ability of YbAG compared to LAG correlates with larger fractions of five- and six-coordinate aluminum ions, lower connectivity among four-coordinated Al units, increased edge-sharing involving five-coordinated Al units, and a higher fraction of triply bonded oxygen.²⁶⁾ The analysis provides a tool for evaluation of glass forming tendency in fragile liquids.^{30,31)}

The K^n connectivity analysis approach is applicable across network-forming oxide materials, and its applicability will be discussed in future publications for other network-forming oxides based on silicates, aluminates, borates, and titanates. No evidence of proposed polyamorphic phase transitions was found in the atomic structure data. It is notable that the structure found in the glasses differs significantly from those of the equilibrium crystalline phases. This suggests that the energetics of glass formation will be significantly different from some of the classical glass formers such as silicates where the non-equilibrium structures are similar to the fully relaxed crystal but with free volume due to bonding of polyhedra.

The observation of multiple internal bubbles in the first campaign samples highlights an important opportunity and challenge of space-based melt processing. The delicate internal structures present in the recovered samples would not have been possible to form in a terrestrial environment because the buoyancy of the bubbles generally causes them to rise to the top of a molten sample. Bubbles the size of the observed voids typically burst when they reach the sample surface during levitation melting on Earth. The near absence of gravity eliminates such buoyancy and its associated convection in the melt, thus stabilizing the presence of bubbles. While this is potentially problematic for thermophysical property measurements, it provides a unique processing capability. For example, it could be exploited to create glass forms with intentionally patterned bubbles or domains of a second phase of different density.^{6,32} Such patterned materials may have useful applications in optical devices that exploit cavity waveguides and patterned structures with different refractive index materials to control transmission of light.³³ It is notable that the large bubbles were only present in samples processed in air and not those processed in high purity argon. All flight samples were X-rayed before launch to check for large internal voids or cracks. None of the samples measured exhibited large pores before they were processed, so the formation of the large voids is likely an effect of the oxygen-containing atmosphere in the first flight campaign.

In terms of materials processing in reduced gravity, the presence of bubbles may not always be desirable. In cases where bubbles need to be eliminated, materials may need to be processed using artificial gravity (e.g. in a centrifuge) to separate phases with different densities. These findings have practical implications for in-situ resource utilization processing that involves liquid phase processing.

5. Conclusions

Containerless liquid phase processing provides access to supercooled melts and in some cases glasses that cannot be made by conventional methods. In this work, we investigated the structure and thermophysical properties of molten rare earth aluminates that have potential applications in device materials.

The structure of non-traditional network former glasses and liquid was found to exhibit significant differences in coordination and bonding from conventional glasses.

Formation of edge shared four- and five-coordinated cations and the presence of significant amounts of three-coordinated oxygen characterized the highly disordered structures.

Experiments in microgravity revealed novel and reproducible behavior of gas bubbles in liquids. These behaviors have potential for synthesis of new and useful non-equilibrium materials in microgravity.

Acknowledgements This work was supported by the National Aeronautics and Space Administration (NASA) through grant numbers 80NSSC19K1288 and 80NSSC18K0059 and US Department of Energy grant number DE-SC0018601. This research was performed on APS beam time award (DOI: <https://doi.org/10.46936/APS-183682/60011543>) from the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science user facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

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