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Investigation of Liquid–Liquid Phase Transitions in Molten Aluminates Under Containerless Conditions

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Aluminum oxide–yttrium oxide (AY) compositions form liquids that undergo a variety of metastable behaviors including glass formation and liquid–liquid phase transitions. Containerless techniques in combination with the reduced fluid motion achieved in low gravity provide the control needed to study the kinetics of phase transitions in diffusion-limited transport conditions and to obtain accurate measurements of the viscosity of the undercooled liquid. Containerless liquid phase processing experiments have established 1) conditions for phase transitions in AY liquids, 2) that the liquid structure plays an important role in glass formation and increased liquid viscosity, and 3) requirements for microgravity experiments on AY liquids. Results of the research are discussed in the context of developing a microgravity research experiment.

Nomenclature

R_c = critical cooling rate, K/s
T_g = glass transition temperature, K
T_x = crystallization temperature, K
ΔC_p = change in heat capacity, J/g formula weight · K

Introduction

THIS research is focused on investigation of phase behavior in deeply undercooled liquids formed from aluminum oxide–yttrium oxide (AY) pseudobinary materials. These materials form extremely fragile[1] liquids, which can be cooled to form glass.[2–7] The YAG composition can be pulled into glass fibers at temperatures approximately 600 K below the melting point of the crystal.[8] The undercooled AY liquids transform to a "low-temperature" liquid phase,[3,4] which is immiscible with the host liquid. The two-phase liquid can be cooled to form a mixture of two glasses with identical chemical composition (polyamorphism).[3,4] Substitution of lanthanum for yttrium retards the phase transition and results in formation of a single-phase glass.[4]

X-ray structural studies on $Y_3Al_5O_{12}$-composition liquid[9] showed that it consists predominantly of four-coordinate Al^{3+} ions and six-coordinate Y^{3+} ions. There is a small population of six-coordinate Al^{3+} ions in the deeply undercooled liquid. The structure of the single- and two-phase glasses measured by neutron diffraction[9] showed that, like the liquid, the Al^{3+} ions are predominantly in fourfold coordination and the rare earth ions are in sixfold coordination. Structural changes associated with the liquid–liquid (L–L) transition appear to result from changes in the connectivity of the AlO_4^{5-} and YO_6^{9-} polyhedra rather than from major changes in average metal–oxygen (M–O) coordination.

In this work we are using containerless processing methods that eliminate crucible-derived heterogeneous nucleation of the undercooled liquids and avoid contamination of the corrosive liquids. Although the work is ultimately motivated by interest in developing single-phase glasses for optical applications, this study is directed toward understanding the mechanism of the L–L phase change and studying the properties of the liquid and glass materials. Experiments reported here were performed in ground-based research in which the liquid is stirred by the levitation forces. The research is leading to development of low-gravity experiments that would allow measurements on "quiescent" undercooled liquids needed to obtain accurate measurements of the L–L phase transformation kinetics.

Experimental Procedure

Containerless experiments were used to establish conditions for phase transitions in the oxide liquids and to synthesize glass materials for investigation of the structure and thermochemistry. Spheroidal samples 0.1–0.35 cm in diameter were made by fusing mixtures of high-purity metal oxide powders in a laser hearth melter. Samples were made from $Y_3Al_5O_{12}$ (YAG), $Al_2O_3 + Y_2O_3$ (AY) compositions containing 58–77 mole % Al_2O_3 in 1–2 mole % increments, $Er_3Al_5O_{12}$ (EAG) and $La_3Al_5O_{12}$ (LAG). The ionic radii of erbium and lanthanum in sixfold coordination with oxygen are 0.9 and 1.06 Å, respectively.[10] The LAG and EAG compositions were used to investigate the effects of rare earth ion radius and field strength on the liquid-phase behavior.

Polycrystalline samples were levitated in a conical nozzle aerodynamic levitator using argon or oxygen and heated with a continuous-wave CO_2 laser beam. The levitated sample was melted and superheated by 50–100 K, and the liquid was equilibrated with the process atmosphere (argon or oxygen) for approximately 1 min. The liquid was cooled either by blocking the laser beam to achieve the largest cooling rates (up to 300 K/s for small samples), or by reducing the laser power at a controlled rate so that the liquid was slowly cooled or maintained in the undercooled state. Small-diameter samples that had a relatively larger specific area were used to achieve the high cooling rates required to form glass at the limits of the range. The sample temperature was monitored with an optical pyrometer operating at a wavelength of 650 nm, the pyrometer output was acquired by computer.

The critical cooling rate for glass formation, R_C, was determined for several of the compositions by cooling the liquid at different rates and measuring the smallest cooling rate at which no detectable recalescence was observed in the pyrometer output. Samples that crystallized showed a characteristic exotherm when the heat of fusion was released (Fig. 1). Crystallization of the undercooled liquid occurred at a temperature approximately 1000 K below the melting point of crystalline YAG. The liquid could be maintained at temperatures above ~1400 K for extended periods. The cooling rate used in these experiments was approximately 120 K/s, insufficient to avoid crystallization in the conditions used. Samples that cooled without evidence of crystallization were recovered for analysis. Liquid was held in the undercooled state for periods of up to 30 min

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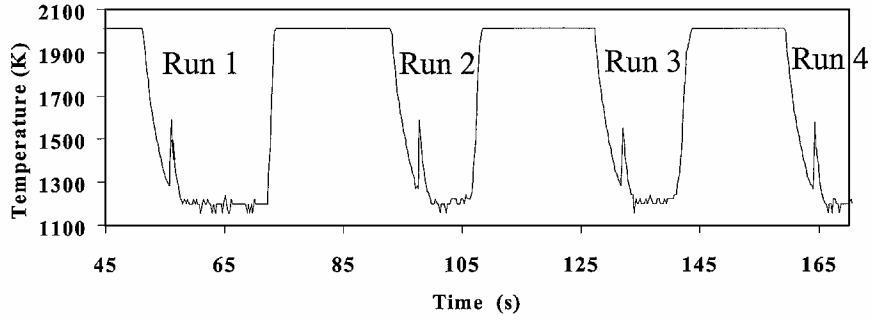

Fig. 1 Sequence of four melting and cooling cycles for YAG-composition liquid processed under containerless conditions in oxygen.

by controlling the laser heating power. After extended liquid-phase processing, glass samples were formed by blocking the laser beam. Experiments were performed in an electrostatic levitator operated at a pressure of 4 bar to determine conditions for levitation of molten oxide materials.[11,12]

Glass samples were examined at 40–100X magnification to establish whether they contained particles of a second phase. Selected glasses were examined in backscattered electron (BE) imaging with a scanning electron microscope (SEM). Chemical analysis was performed with an electron microprobe. The glass transition temperature T_g, the change in heat capacity at T_g (ΔC_p at T_g), the crystallization temperature T_x, and kinetics of selected glasses were studied using a Netszch DSC-404 differential scanning calorimeter.[13]

Results

Glass Formation and Thermal Properties of the Glasses

Figure 2 presents a schematic of the alumina-rich region of the AY phase diagram. Figure 2 shows the glass forming region explored, the temperature at which crystals formed in the undercooled liquids, and the location of the metastable $YAlO_3$–Al_2O_3 eutectic.[12] The AY liquids are remarkably stable and can be maintained at temperatures several hundred degrees below the equilibrium melting point of the solid for extended periods. The "glass forming range" indicates compositions that were made into glass by containerless cooling of liquid at rates of up to 300 K/s. The glass forming range could be further extended by increasing the cooling rate. For samples that were cooled at a rate less than the critical cooling rate for glass formation, liquid YAG crystallized at approximately 1300 K, that is, it undercooled by about 42% of the (2240 K) absolute melting temperature of YAG. The crystallization temperature of the undercooled liquid was extremely reproducible, as indicated by the cooling curves presented in Fig. 1 The crystallization temperature was not strongly dependent on composition, and so the relative undercooling was largest for the high melting compositions and correspondingly smaller closer to the eutectic compositions. Other compositions undercooled by 30–40% of their absolute melting point before spontaneous crystallization occurred.

Temperature gradients in the liquid have so far prevented holding the liquid at temperatures below ~1400 K due to crystallization of the cooler regions of the sample. Based on the results of experiments to hold undercooled liquids at temperatures below their melting point, we estimate that the top–bottom temperature gradient in 3 mm diameter samples is on the order of 100 K in a 3-mm-diam sample.

Table 1 presents the estimated critical cooling rate or upper limit on the value for glass formation, R_C, the glass transition temperature T_g, and crystallization onset temperature T_X, obtained from the containerless cooling experiments and differential scanning calorimetry (DSC) measurements on glasses. R_C was taken as the cooling rate of the liquid at 1400 K in samples that were cooled just fast enough to form glass.

The critical cooling rate for glass formation varied considerably with composition. EAG was relatively difficult to vitrify, whereas the largest LAG samples that could be levitated, approximately 3.5 mm in diameter, readily formed glass. Glass was formed from AY compositions containing 58–77 molar % aluminum oxide. Glass formation became easier with increasing aluminum oxide content from

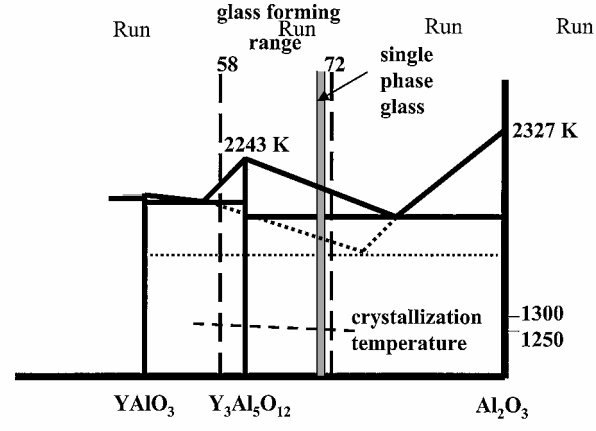

Fig. 2 Schematic of the pseudobinary Al_2O_3-Y_2O_3 phase diagram showing the composition range studied.

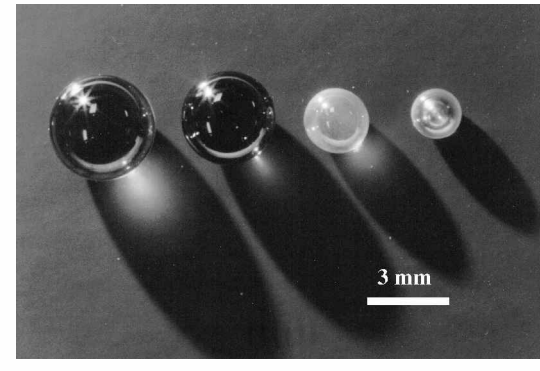

Fig. 3 Left to right: LAG-, $LaErYAl_5O_{12}$-, YAG-, and EAG-composition glasses; two glasses on left are single phase and clear, those on right are phase separated and cloudy.

62.5 (YAG) to 73 mole %. Further increase in the aluminum oxide content beyond 73% resulted in a rapid decrease in glass forming tendency. At the extremes of the AY composition range, glass formation was extremely difficult, requiring samples approximately 0.15 cm in diameter and cooling rates >300 K/s.

The extent of the phase transition was determined by examining glass samples with an optical microscope and in BE imaging in an SEM. The quantity of the spheroidal, low-temperature phase increased with critical cooling rate and for compositions containing smaller ionic radii, that is, erbium-bearing samples showed a greater degree of phase separation than yttrium-bearing samples. Glasses made from the LAG and AY compositions containing ~72 mole % Al_2O_3 were single phase. Figure 3 is a photograph of single- and two-phase glasses. Figure 4 presents a backscattered SEM image of a two-phase glass. Electron microprobe analyses showed that the chemical composition of the two phases was virtually identical. Table 2 shows results obtained from analysis of 10 representative points in the "matrix" and "spheroid" phases of a two-phase glass.[4]

Table 1 Critical cooling rate R_C, glass transition temperature T_g, and crystallization onset temperature T_x for RE-Al glasses

Composition	R_c, K/s at 1400 K	T_g, K	T_x, K
LAG	<70	1117	1218[a]
YAG	70	1147	1196
EAG	100	1141	1193
AY, 58-77 Al_2O_3	70–300	1140–1160	1190–1215[a]

[a] Onset temperature for first of two thermal events that occurred during the crystallization for several compositions; values accurate to ±5 K (see also Ref. 11).

Table 2 Wavelength dispersive analysis of two-phase YAG-composition glass[a]

Area of sample	O (At%)	Standard deviation	Al (At%)	Standard deviation	Y (At%)	Standard deviation
Matrix phase	58.91	0.12	26.34	0.08	14.75	0.09
Spheroid phase	58.65	0.10	26.50	0.06	14.85	0.05

[a] Image of the glass microstructure in Fig. 4.

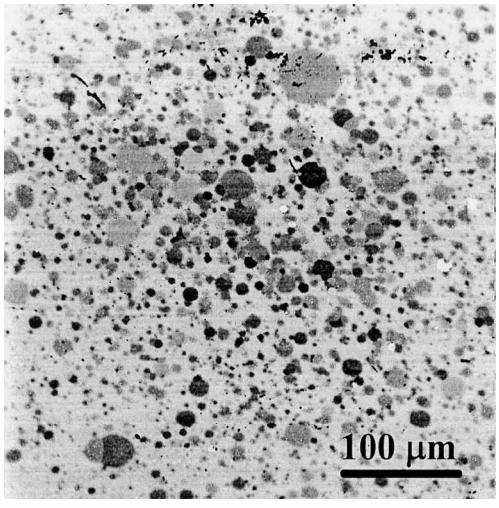

Fig. 4 BE image of a two-phase YAG-composition glass.

The values of ΔC_p at T_g determined by DSC were 72–80 J/g formula weight · K for the samples that contained no crystallites. Smaller values were obtained for samples close to the glass forming limits where crystallites were sometimes present in the glass. The glasses crystallized at a temperature close to T_g, and there was virtually no supercooled liquid region accessible in most of the compositions.

Discussion

Rare earth–aluminum oxide materials can be undercooled by a large fraction of the melting point of the corresponding crystalline phases. Even so, the liquids are very reluctant glass formers requiring cooling rates of up to 300 K/s under containerless conditions to avoid crystallization. The large values of the enthalpy of vitrification[13] and ΔC_p at T_g (about twice the typical value for a silicate glass) are consistent with the extremely fragile behavior of the aluminate liquids.[13] Crystallization is kinetically constrained in part because the garnets have a large, complex unit cell which contains both four- and six-coordinate aluminum ions.[14] It seems that the undercooled liquid can exploit glass formation, metastable crystallization, and L–L phase transitions as mechanisms to lower its energy without actually forming the thermodynamically stable crystalline phase.

The crystallization temperature of the undercooled liquid is remarkably constant over the range of materials studied. In contrast to the binary liquids, the terminal phases alumina and yttria exhibit only mild undercooling.[15] The values of T_g increased from 1146 to 1156 K with increasing alumina content in the AY materials, which indicated a weak composition dependence, consistent with the behavior of yttrium aluminosilicate glasses.[16] The T_g values for EAG and YAG were similar and lower for LAG (Table 1). The crystallization onset temperatures increased slightly with increasing alumina content. There was no evidence of departure from the trend at the glass forming limits where traces of crystals might be expected to enhance crystallization, further confirming the resistance to crystallization of the AY materials.

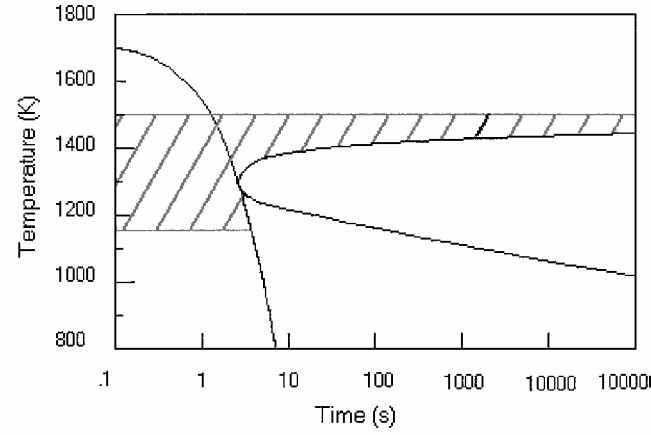

Fig. 5 Estimated TTT diagram for YAG-composition material: shaded region indicates range where L–L transition can be accessed and points on lower part of curve obtained from DTA measurements.

The L–L phase transition temperatures were estimated from the microstructure of samples held in the undercooled state for extended periods and then quenched to form glass. These experiments showed trends but were not fully conclusive due to temperature gradients in the liquid leading to crystallization as the lower temperature limit was approached. The results were interpreted in the context of Aasland and McMillan's[3] assessment of the nucleation temperatures for the low-temperature liquid phase, and using results of differential thermal analysis (DTA) studies of the crystallization kinetics in heat treated glasses.[17] Figure 5 presents the estimated time–temperature–transformation (TTT) diagram for the YAG composition. The lower part of the diagram is based on DTA measurements of the crystallization kinetics of glass samples.[15] The upper part of the diagram was obtained from temperature measurements in slow cooling experiments that led to crystallization and from experiments on the undercooled liquid. The shaded area marks the region in which the polyamorphic phase transition can be accessed, its upper limit is from Aasland and McMillan,[3] and the lower limit is the glass transition temperature.

The propensity for the phase transition is strongly dependent on the average ionic radius of the rare earth ion. Formation of glasses containing Er^{3+} and Lu^{3+}, which are both smaller ions than Y^{3+}, requires increased cooling rates and yields a highly phase separated glass material. Substitution of the larger La^{3+} ion for Y^{3+} suppresses the phase transition and decreases the critical cooling rate for glass formation. Substitution of lanthanum leads to single-phase glass either by making the second liquid unstable relative to the first, or by reducing the phase transition or nucleation temperature for the second liquid below the glass transition temperature.

Transmission electron microscopy of bulk two-phase glasses revealed nanocrystals in some samples.[17] The presence of a trace of crystallinity in the two-phase glasses was also observed in the nuclear magnetic resonance (NMR) measurements. The structural rearrangements which accompany the L–L transition result in a liquid that crystallizes more easily than does the high-temperature host. Although the L–L transition forms a metastable liquid that is presumably more stable than its host, the homogeneous nucleation temperature of the new liquid may actually be higher than that of the host liquid for some compositions. Thus, formation of the new liquid may be associated with the onset of crystallization. The slow kinetics of crystallization of the complex YAG structure[18] limits the degree of crystallization before the glass transition arrests the process. Successful implementation of the experiments to study the L–L transition kinetics will, therefore, require precise control of sample temperature and a uniform sample temperature.

Requirements for the Microgravity Experiment

The microgravity experiment that is being developed will investigate the kinetics of the L–L phase transition in undercooled oxide liquids and determine the viscosity of the liquid as a function of temperature. To study the kinetics of the reactions in an L–L system, it is important to decouple diffusion and convection transport. In low gravity, it is potentially possible to access "quiescent" liquid samples under containerless conditions required to undercool the liquids. In addition, the two liquid phases have different densities and sedimentation of the denser phase occurs on Earth unless the melt is well stirred. Recent advances in the application of electrostatic levitation to oxide liquids[11,12] mean that the viscosity of undercooled liquids may be measured in using the ground-based techniques. Accurate measurements of melt viscosity, which is sensitive to subtle variation melt composition, will require the use of large samples as can be achieved in low gravity experiments.[19]

Conclusions

1) Under containerless conditions, glasses can be formed from many rare earth aluminate liquids. When the liquid is cooled at a rate less than the critical cooling rate for glass formation, nucleation of crystals occurs at a temperature equal to approximately 60% of the absolute melting point of the corresponding crystalline phases.

2) The undercooled liquid exhibits a congruent L–L phase transition and can be cooled to form a two-phase glass material. Substitution of a large rare earth ion such as La for Y suppresses the phase transition, reduces the critical cooling rate, and enhances glass formation.

3) Containerless techniques coupled with the control of fluid motion possible in reduced gravity offer the potential to investigate the kinetics of the L–L transition and to enable accurate measurements of liquid viscosity.

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