

High-energy X-ray Studies of Rare Earth Aluminate Glasses

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Introduction

Polyamorphic transitions (liquid-liquid transitions) are first-order transitions between different structured amorphous phases with identical compositions. They are directly analogous to polymorphic transitions in crystalline phases. Polyamorphic transitions have been reported in several systems, most notably in H₂O [1-3]. Y₂O₃-Al₂O₃ aluminate liquids close to Y₃Al₅O₁₂ (YAG) composition also have been reported to show a polyamorphic (liquid-liquid) transition from a stable high-density liquid to a lower-density liquid when supercooled [4-6]; this direct observation of the liquid-liquid transition is notable because it occurs at 1 atm and also because Y-A liquids are generally considered complex and would be more likely to undergo “conventional” phase separation.

Two-state liquid models are frequently used to interpret the onset of polyamorphism. In these types of models, the liquid-liquid transition is viewed as a critical-like phenomenon that is driven by thermodynamic (enthalpy, entropy, and volume) differences between arbitrary liquid species. These thermodynamic differences imply structural differences between the different amorphous phases, which, in the simplest case, are assumed to have short-range structures similar to those of low- and high-pressure crystalline polymorphs [7].

Neutron diffraction data for three aluminate glass samples [8] have been collected to elaborate on the structural changes that accompany the liquid-liquid transition. These data include yttrium and lanthanum aluminate samples; lanthanum aluminate liquids, although they have high configurational entropy, are not polyamorphic. X-ray diffraction experiments have been used to obtain structural data for similar values for the scattering vector of 30-40 Å⁻¹. These data yield pair-correlations with comparable real-space resolution to the neutron data, and they can be used to complement the neutron data set by providing the distance information between 3 and 5 Å, the range characteristic of mid-range structure.

Methods and Materials

Three glass samples were studied, a single-phase yttrium aluminate (AY25), a partly transformed two-phase yttrium aluminate (AY20) with both high- and low-density amorphous phases present, and a single-phase lanthanum aluminate (La25). Glasses were prepared from

calcined sol-gel precursors in a Xe-arc image furnace by using a rapid drop quench method. The glasses, which range in composition from 20 mol % Y₂O₃ to 25 mol % Y₂O₃-75% Al₂O₃ and 25% La₂O₃-75% Al₂O₃, are produced in a compositional range that intercepts a metastable eutectic projected from YAlO₃ and α-Al₂O₃.

High-energy x-ray measurements were performed at the Basic Energy Sciences Synchrotron Radiation Center Collaborative Access Team (BESSRC-CAT) beamline 11-ID-C at the APS, with an incident beam energy of 114.92 keV. The glass samples were placed in a 4-mm-wide aluminum frame with thin Mylar windows. The sample was arranged so that the 1×1-mm x-ray beam was only incident on the glass fragments. X-ray data were collected for a range of Q from 0.4 to 35 Å⁻¹, giving a maximum real space resolution of 0.18 Å.

Results

The single-phase AY25 glass has a pair correlation function from the x-ray diffraction data that can be compared directly to the $T(r)$ from the neutron data (Fig. 1). The peaks between 3 and 5 Å reflect Al-Al, Y-Al, and Y-Y distances. The prominent peak at 3.6 Å in the $T(r)$ results from the Y-Y correlation and has contributions from both edge- and corner-shared polyhedra that have Y-Y distances of 3.26 and 4.66 Å, respectively.

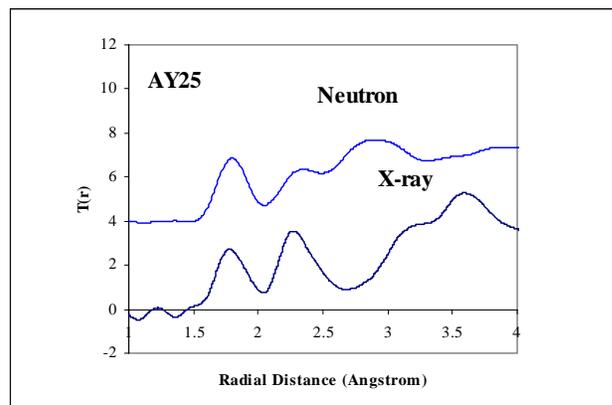


FIG. 1. Total pair correlation function $T(r)$ for x-ray and neutron diffraction data for single-phase AY25 (25% Y₂O₃) aluminate glass.

In the La25 sample, there are some noticeable differences in the total pair correlation functions $T(r)$ (Fig. 2). The La-O distance, which can be compared with that obtained from the neutron diffraction data, is 2.53 Å, which reflects differences in ionic radius. There are further changes in the magnitude of the two peaks between 3 and 4 Å. The data suggest an equal proportion of edge- and corner-shared LaO_6 and AlO_4 units. In the AY20 sample, the combined neutron and x-ray data show marked differences in the metal-metal correlations when compared with the AY25 sample (Fig. 3). Most obvious is the sharp peak at 5 Å, which is broader in the

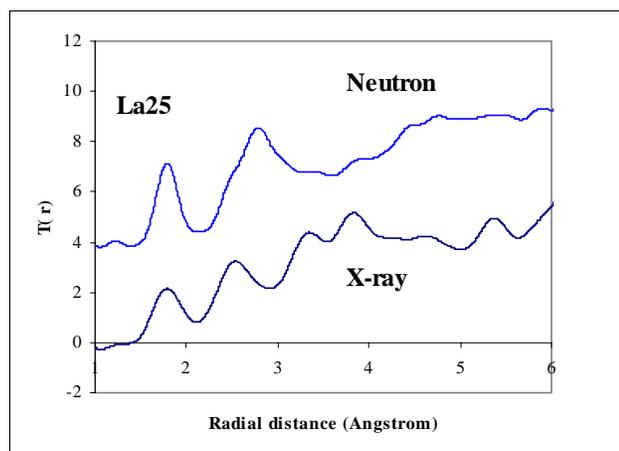


FIG. 2: Total pair correlation function $T(r)$ for x-ray and neutron diffraction data for single-phase La25 (25% La_2O_3) aluminate glass

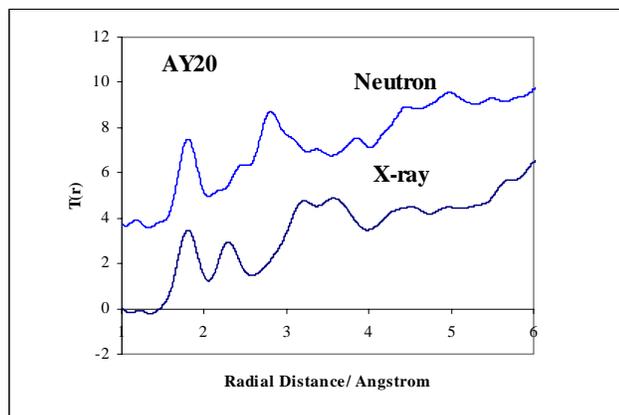


FIG. 3: Total pair correlation function $T(r)$ for x-ray and neutron diffraction data for partly transformed AY20 (20% Y_2O_3) aluminate glass.

AY25 sample and indicates an increase in mid-range ordering (longer-range structure) in the two-phase sample. This is also consistent with a reduction in configurational entropy at the liquid-liquid transition.

Discussion

The x-ray diffraction data on three glass samples suggest that the main structural differences between the different amorphous yttrium aluminate phases are in the relative proportions of corner- and edge-shared AlO_4 and YO_6 polyhedra. Differences in the Y-Al and Al-Al correlations determined from reverse Monte Carlo simulations suggest that approximately 70% of the AlO_4 and YO_6 polyhedra are corner-shared in the single-phase glass that is quenched from the stable, high-density liquid. In addition, YO_6 polyhedra are 70% edge-shared with other YO_6 polyhedra. In contrast, for the equivalent La composition, the relative proportions of the edge- and corner-shared units are different. The number of edge-shared LaO_6 units is apparently reduced, and there are more edge-shared AlO_4 and YO_6 units. This suggests that the lanthanum aluminate is more ordered than yttrium aluminate liquids of equivalent composition. It is this order (cooperativity) that prevents polyamorphism in the lanthanum liquid [4-6, 8]. For the two-phase, partly transformed sample, there are changes in the magnitude of the Y-Al and Y-Y peaks, in part because of a difference in composition. This suggests changes in the relative proportions of the polyhedral units: specifically, the number of corner-shared AlO_4 and YO_6 polyhedra is increased in the AY20 (two-phase) composition, while the proportion of YO_6 units edge-shared with other YO_6 polyhedra is decreased.

Acknowledgments

Samples were prepared and characterized in the Goldwater Materials Science Laboratories of the Center for Solid State Science at Arizona State University, with support from National Science Foundation Grant No. NSF-DMR-9802956 to P. F. McMillan. Neutron scattering experiments were carried out at the IPNS at ANL, operated under the auspices of the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under Contract No. W-31-109-ENG-38. We are grateful to J. Urquidí and J. Siewenie, who, with C. Benmore, helped analyze the x-ray data. X-ray diffraction measurements were performed at the APS. Use of the APS was supported by the DOE BES under Contract No. W-31-109-Eng-38. P. F. McMillan is a Wolfson-Royal Society Research Merit Award holder.

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