Investigating the mechanism for the liquid-liquid transition in the system Y_2O_3-Al_2O_3 by X-ray diffraction and small angle X-ray scattering.

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Introduction

The structures of liquids and glasses can change significantly as a function of pressure and temperature. Under certain conditions supercooled liquids can change structure over a narrow interval in temperature, a phenomenon referred to as polyamorphism [1]. Polyamorphism exhibits the characteristics of a first-order transition. One family of liquids that has been shown to undergo a transition between high-density, high entropy stable liquid stable at high temperatures and a low-density, low entropy liquid are those in the system Y_2O_3-Al_2O_3[2]. This transition (HDL-LDL) occurs when the stable high-density liquid (HDL) is supercooled. Identifying the structural changes responsible for this unusual phenomenon is experimentally challenging because the transition occurs in the supercooled liquid regime which is difficult probe experimentally. In this contribution we report the results of two X-ray studies which have probed *in situ* the structure of Y_2O_3-Al_2O_3 liquids using containerless techniques. A combined wide angle and small angle X-ray study performed at the Synchrotron Radiation Source, Daresbury UK and a high energy X-ray diffraction study recently competed at the Advanced Photon Source, Argonne National Laboratory.

Methods and Materials

The Y_2O_3-Al_2O_3 samples were levitated by Ar gas and heated by continuous wave CO_2 laser. This technique allows X-ray study of liquid drops without a sample container and is a technique particularly well-suited to stuctural studies of refractory and deeply undercooled liquids[3]. The drop resides in a conical nozzle and a gas film between the dropand the nozzle itself prevents contact with the nozzle and avoids heterogeneous nucleation. This means that the liquid droplets can be super-cooled several hundred K below the stable melting temperature. This technique enables the temperature regime of the HDL-LDL transition to be probed for Y_2O_3-Al_2O_3 liquids. In these experiments two slightly different containerless nozzeles were used. Small and wide angle X-ray scattering data was collected simultaneously using multi wire micro-gap gas detectors. The incident energies used for the X-rays was 16 keV. The high energy X-ray diffracion data was obtained at 11 ID-C (APS) with incident X-ray energies of 115 keV. The scattered X-rays in this case were detected using a MAR-345 area detector.

Results

Small Angle data for supercooled yttrium-aluminate liquid with 20% Y_2O_3 (AY20) was collected at a constant attenuation value from a temperature of 2400 K to 1573 K. In contrast to other refractory liquids such as Al_2O_3, there is a maximum in the SAXS signal at temperatures of between 1848 and 1873 K (Fig. 1). This temperature is slightly higher than that reported for liquid-liquid transition. When the liquid is cooled below this regime, the SAXS signal decreases although segregations of the second liquid phase (LDL) are visible on the the droplet. Glasses of this composition typically yield the high- and low-desnity amorphous forms.

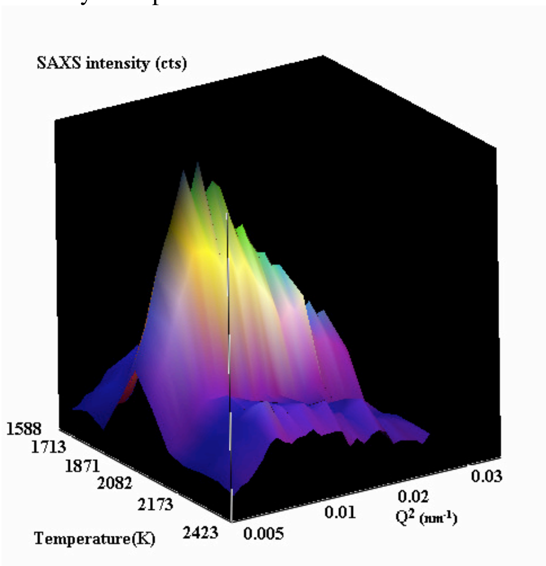

Fig 1. The results of SAXS experiments on leviated, super-cooled 20% Y_2O_3-80% Al_2O_3 liquid.

Wide angle X-ray scattering (diffraction) data were collected for the levitated liquid simultaneously with the SAXS data. The incident X-ray energies of 16keV are reltively low and the range of scattering vector is accordingly limited. Nevertheless it is possible to establish changes in the total structure factor, particularly the first peak in the diffraction pattern. The nature of these structural changes can be compared with compositional changes in structure that were carried out between YAG and Al_2O_3 end members using high energy X-rays (Fig 2).

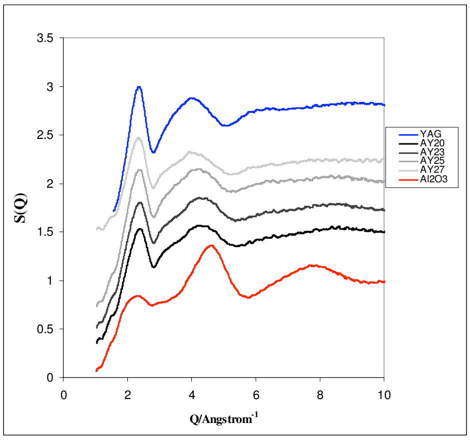

Fig 2. High energy X-ray diffraction data obtained for Y_2O_3-Al_2O_3 liquids.

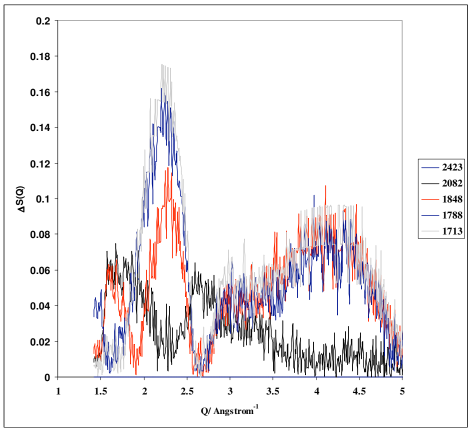

Fig 3. Differences in S(Q) obtained for levitated 20% Y_2O_3 liquid

Discussion

The change between high- and low- density liquids in Y_2O_3-Al_2O_3 and other polyamorphic liquids is believed to be a critical transition[4]. One characteristic feature of critical systems is the increase in density fluctuations as the critical temperature is approached. The slope of the natural log of intensity versus Q^2 (Fig. 1) shows that the there is an increase in the so-called Guinier radius in the super-cooled liquid. These are small fluctuations in the correlation length of the transient aggregate formed in the hig desnity liquid consistent with the small changes in the direct correlation function. We interpret this as scatter from density fluctuations at the polyamorphic transition between high- and low-desnity liquids ((HDL-LDL). The SAXS signal is decreased once the LDL phase begins to nucleate.

Wide angle X-ray scattering (diffraction) data were collected for these levitated liquid simultaneously with the SAXS data. The incident X-ray energies of 16keV are reltively low and the range of scattering vector is accordingly limited. These data can be compared with the high energy X-ray diffraction data recetnly obtained and trends identified. The S(Q) data for the Y_2O_3-Al_2O_3 liquids shows two peaks, one at 2.2 $Å^{-1}$ and one at 4.13 $Å^{-1}$. These peaks are also seen in the high energy X-ray diffraction data of AY20 glass and also in levitated Y_2O_3-Al_2O_3 liquids (Fig. 2)[5]. Reverse Monte Carlo (RMC) fits to diffraction data obtained from Y_2O_3-Al_2O_3 glasses [6] show that this peak has contributions from the Al-Al, Y-Y and Y-Al partial structure factors. The Al-O partial S(Q) contributes to the peak at 4.4$Å^{-1}$ in the S(Q) for both the AY20 and Al_2O_3 liquids. Changes in the AY20 structure factor are as a function of temperature can be evaluated by determining the ratio of the S(Q) at several temperatures over a range of 700 degrees, (Fig 3).

There are discontinuous changes in the S(Q) with temperature. There is a jump in the ΔS(Q) between 1973 and 1848 K, the same region in the supercooled liquid where there is a maximum in the SAXS signal. These differences are seen as an increase in the magnitude of the peak at 2.2. $Å^{-1}$and the growth of a shoulder to the 4.4 $Å^{-1}$ peak, in the ΔS(Q) this is seen as the growth of a feature at 3.5 to 4 $Å^{-1}$ (Fig. 3). This suggests that the transiton observed in Y_2O3-Al_2O_3 liquids is a rearrangement of Y-O and Al-O polyhedra..

References

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