Structural properties of $Y_2O_3 - Al_2O_3$ liquids and glasses: an overview

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Liquids in the system $Y_2O_3 - Al_2O_3$ have been the subject of considerable study because of the reported occurrence of a first-order density and entropy-driven liquid-liquid phase transition (*LLPT*) in the supercooled liquid state. The observations have become controversial because of the presence of crystalline material that can be formed simultaneously and that can mask the nucleation and growth of the lower density liquid. The previous work is summarised here along with arguments for and against the different viewpoints. Also two studies been undertaken to investigate the *LLPT* in this refractory system with emphasis on determining the structure of unequivocally amorphous materials. These include the *in situ* high energy X-ray diffraction (HEXRD) of supercooled $Y_2O_3 - Al_2O_3$ liquids and the low frequency vibrational dynamics of recovered glasses. Many-body molecular dynamics simulations are also used to interpret the results of both studies. The HEXRD measurements, combined with aerodynamic levitation and rapid data acquisition techniques, show that for the 20 mole % Y_2O_3 (i.e. *AlY20*) liquid there is a shift in the position of the first peak in the diffraction pattern over a narrow temperature range (2100-1800K) prior to crystallization. Microbeam Raman spectroscopy measurements made on *AlY20* glasses clearly show contrasting spectra in the low frequency part of the spectrum for low- (*LDA*) and high-density (*HDA*) glassy regions. The molecular dynamics simulations identify contrasting coordination environments around oxygen anions for the high- (*HDL*) and low-density (*LDL*) liquids.

I. INTRODUCTION.

The system $Y_2O_3 - Al_2O_3$ has emerged as a model *polyamorphic system* that is believed to show consistent with the onset of a first order liquid-liquid phase transition (*LLPT*). From 1994 onwards¹ there have been reports of the nucleation and growth of a low density amorphous form (*LDA*) as $Y_2O_3 - Al_2O_3$ liquids are supercooled. The observations by Aasland and McMillan in 1994¹ first

suggested the nucleation and growth of a second liquid phase within supercooled $Y_2O_3 - Al_2O_3$ liquids. The two liquids were quenched to metastably coexisting glasses that were proposed to differ in their density and entropy properties, but had identical chemical compositions. The result was confirmed by Wilding *et al.*²⁻⁵ who confirmed the contrast in thermodynamic properties along with the constancy of chemical composition. The postulated density-, entropy-driven *LLPT* was suggested to drive a large change in rheology of the supercooled liquid⁶. Recent studies using small-angle X-ray scattering (SAXS) combined with levitation techniques have identified critical features associated with the onset of the *LLPT*⁷. In addition, polarizable ion molecular dynamics (PIMD) simulations showed the emergence of unexpected large and randomly occurring fluctuations in the system density that could be interpreted as sampling the *LLPT* above the thermodynamic critical point⁸. However there have also been concerns that the polyamorphic effect does not exist at all, but is instead associated with formation of nanocrystalline material during quenching^{9,10}. In studies of supercooled $Y_2O_3 - Al_2O_3$ liquids Barnes *et al.*¹¹ did not obtain comparable results to those of Greaves *et al.*, although the experiments were apparently conducted in an analogous fashion. However, the various and often diverging observations and interpretations can be rationalized once it is understood that the *LLPT* event takes place in a deeply supercooled liquid regime, where it must occur in competition with stable and metastable crystallization events. It becomes necessary to consider the timescale of the different events occurring, when analyzing the results of quench experiments that can and must give rise to varying fractions of *HDA* vs *LDA* glass, along with included crystalline material. Finally, although the *LLPT* is driven by T- and P-dependent parameters of entropy and density contrast between the two liquid phases, the overall effect is highly composition dependent within the $Y_2O_3 - Al_2O_3$ system, mirroring the effects of Y:Al ratio on the crystal-liquid phase relations. In the discussion below we review some of these considerations, before presenting new data on the high energy, high angle X-ray scattering of levitated $Y_2O_3 - Al_2O_3$ liquids in the supercooled regime, combined with microbeam Raman data on coexisting *LDA* and *HDA* glasses produced by quenching melts at the *AlY20* composition, and analysis by PIMD simulations of the cation and anion coordination states in the high- and low-density liquids and vibrational dynamics of the glassy states.

II. METHODS

A. Sample preparation

The starting materials for the two sets of experiments were prepared by two different methods. For the liquids studied by high energy X-ray diffraction, ceramic precursors were made by mixing stoichiometric amounts of Y_2O_3 (Sigma Aldrich 99.99%) and Al_2O_3 (Sigma Aldrich 99.99%) powders. These were pressed into pellets and sintered to form a hard ceramic which was fused into spheres on a copper hearth prior to levitation. The compositions were verified using electron microprobe analysis following the X-ray experiments¹².

The $Y_2O_3 - Al_2O_3$ glass studied by Raman spectroscopy was produced by a different synthesis route, using a drop quench technique, developed at Arizona State University. This technique uses a Xe lamp imaging furnace(XIF) to heat the tip of a ceramic rod suspended in the focus of an Au-plated parabolic mirror. A homogeneous feed rod is required and for these samples, ceramic precursors were produced by a citric acid-acrylamide sol-gel route¹³. The Al_2O_3 and Y_2O_3 components were obtained from aluminum nitrate (Sigma Aldrich, $\geq 98\%$) and yttrium nitrate (Sigma Aldrich 99.8 %) respectively. These were dissolved into the aqueous citric acid solution prior to formation of the acrylamide gel. The initial gel is calcined at 800°C and the resulting fine powders examined by X-ray diffraction. The X-ray amorphous or nanocrystalline (YAG_{ss}) powder was then cold-pressed and sintered to form feed rods. The tip of the feed rod was heated to temperatures above the melting point, accessing the same temperature regime as in the aerodynamic levitation experiments ($\approx 2500K$). Fully molten pendant droplets are formed at the tip and allowed to fall by gravity to pass through a Pt wire grid (to increase their surface area) and quenched in water

(or another high heat capacity liquid). Although this technique is less controllable than alternatives such as aerodynamic levitation, the quench rates seem to be faster and different types of completely glassy with homogeneous or *HDA* – *LDA* coexistence textures or glass-ceramic mixtures containing nanocrystalline materials can be obtained.

The *LDA* polyamorphs can be readily identified by reflected light optical microscopy (figure 1). Such images clearly show the separation between the *HDA* and *LDA* amorphous forms, identified by different resistance to mechanical damage during polishing and by their contrast in reflected light. Confocal Raman spectroscopy was used to distinguish fully glassy *LDA* segregations and *LDA* segregations that contain a nanocrystalline component. In the example shown in figure 1 the division between the high- and low-density amorphous forms is clearly shown, this is for a sample of *AlY20* composition. The *LDA* glass forms a relatively large segregation, approximately $150\mu\text{m}$ wide. Small crystallites are present at the *HDA* – *LDA* interface and indicate that the interface between the two glassy forms can act as nucleation sites for the nanocrystalline phases. The low frequency Raman spectra used to investigate the glassy nature of the two amorphous forms were collected away from this interface region.

Electron microprobe analysis (EMPA) and back scattered electron (BSE) imaging for the glassy sample is shown in figure 1 is shown in figure 2. The interface between these two glasses is clearly marked by small crystallites, although the two glasses themselves are free from crystalline contaminants (as verified by Raman spectroscopy). Notable in this sample is the lack of contrast in BSE image (difference in mean electron density), which is identical in both *HDA* and *LDA* glasses. This sample has 20 mole % Y_2O_3 (*AlY20*) composition, the composition where the *LLPT* is most likely to be encountered¹². Traverses across the interface confirm that both the *HDA* and *LDA* glasses have identical composition. At the interface itself, the Y_2O_3 and Al_2O_3 contents vary as would be expected if garnet (*YAG*), perovskite (*YAP*) and alumina were to crystallise, although the crystallites cannot be resolved sufficiently well for quantitative EMPA. The *Al*, *Y* and *O* totals were low for these samples; further analysis revealed the presence of an ≈ 4.5 mol % (2 wt %) SiO_2 component incorporated (to equal concentration) in both the *LDA* and *HDA* samples. This is most likely to have originated in the silica glass containers used for sintering the feed rods. Addition of silica to improve glass-forming ability is known for this system, however the presence of up to 4 mol % of SiO_2 in this sample and the clear identification of the two identical composition glasses indicates that the *LLPT* persists in the ternary Y_2O_3 – Al_2O_3 – SiO_2 system at the 20 mole % Y_2O_3 composition.

B. High energy X-ray diffraction

High energy X-ray diffraction experiments have been combined with aerodynamic levitation to study stable and metastable Y_2O_3 – Al_2O_3 liquids. These have been reported elsewhere^{12,14}. Aerodynamic levitation is a containerless technique that is particularly effective in the study of refractory liquids. This sample environment can be fully integrated into X-ray beam lines enabling *in situ* diffraction measurements without the need for furnace or container corrections. For this study high energy X-ray diffraction measurements were made on liquids of five different compositions at 11 – *ID* – *C* (APS) using X-rays with incident energies of 115keV . Recently developed rapid acquisition techniques synchronized with quenching enables the full diffraction patterns to be collected (in 200ms)¹⁴ as the liquid is supercooled. The 2D diffraction pattern was collected on an amorphous silicon detector and the 1D diffraction patterns are obtained by integrating over all pixels using the Fit2D package¹⁵. The total X-ray diffraction is obtained using PDFgetX2 software¹⁶. Form factors and Compton scattering are obtained from tabulated values¹⁷.

C. Vibrational spectroscopy

Samples for Raman spectroscopy were mounted on glass slides using low fluorescence Loctite[®] epoxy and polished to reveal the interfaces between LDA and HDA regions that were identified and studied subsequently using electron microprobe analysis and BSE imaging. Initial identification of purely glassy samples was carried out using a Renishaw Raman microscope at University College London (UCL) using 514nm excitation. These Raman spectra were used to identify sharp features that correspond to the presence of nanocrystalline YAP or YAG phases in excess of 10 – 30nm in dimension. Low frequency Raman data were then collected using a XY Dilor triple spectrograph at Lyon. This permitted measurement of the Raman spectra to 20 – 30cm⁻¹. The exciting source was a frequency doubled 532 nm line of a Nd³⁺ YAG crystal source with 200mW power and a pre-monochromator to eliminate the elastic line. Both Raman studies use a confocal optical arrangement which provide a lateral spatial resolution of 2μm and a depth resolution of $\simeq 2 - 3\mu m$.

D. Polarizable Ion Molecular Dynamics

The methods of polarizable ion molecular dynamics applied to the Y₂O₃ – Al₂O₃ have also been discussed by Wilson *et al.* in earlier publications^{8,18}. Polarizable ion molecular dynamics is a mixed-potential approach that uses ion-ion interactions modeled pair-potentials augmented by many body ion polarization effects. The potential model is constructed by reference to that previously used to model pure Al₂O₃^{8,19}. Ion-ion interactions are modeled using pair-potentials augmented with a description of the many-body dipolar ion polarization effects^{20,21}.

To investigate the liquids studied by high energy X-ray diffraction a range of compositions, containing 10%, to 37.5% Y are considered. Two system sizes were used, containing 640 and 3240 ions. Simulations are performed in the constant pressure/temperature (NpT) ensemble throughout and temperature is controlled using Nosé-Hoover thermostats²². Constant pressure is maintained by applying isotropic barostats²³ with a barostat parameter of 10000au (as defined in refs.²³ and¹⁸). The initial configurations were generated by reference to pure Al₂O₃ simulations with the required number of Al³⁺ ions being transmuted into Y³⁺ in a random sequence. Initial pre-production runs of 250000 steps were performed using a time-step of 25au (total run-time of $\simeq 150ps$) at 3200K in order to produce proper equilibrium starting configurations. Constant pressure simulations were then performed while the systems were gradually cooling the system close to the estimated melting points (of the order of 2100-2200K).

III. RESULTS

A. High energy X-ray diffraction

X-ray diffraction patterns collected for five Y₂O₃ – Al₂O₃ liquids studied and the were reported in Wilding *et al.* 2013¹². As the liquids are quenched to access the metastable liquid regime, four composition liquids crystallize, while one (30 mole % Y₂O₃) forms a glass. The diffraction data for the stable liquids are similar and have few distinguishing features and on quenching show changes are in the first peak in the diffraction pattern, at $\sim 2\text{\AA}^{-1}$. With one exception the changes in structure on cooling are subtle and there is nothing to distinguish these supercooled patterns from a liquid that is either vitrified or crystallizes. However for the the 20 mole % Y₂O₃ composition (AlY20) the position and intensity of the first peak changes prior to crystallization.

The shift in position of the first peak with temperature for the AlY20 liquid is shown in figure 3¹². This can be compared with the change in position of the first peak for the glass-forming AlY30 composition over the same temperature range. The changes in peak position show two distinct

trends for the *AlY30* and *AlY20* liquids. The position of the first peak in *AlY30* changes from 2.16 to 2.20 Å⁻¹ as the liquid is quenched from 2398K to 800K. The *AlY20* liquid shows a shift from 2.17 to 2.20 Å⁻¹ in a narrower temperature interval of 200K.

The *AlY20* composition is the controversial composition explored by Greaves *et al.*⁷ and later by Barnes *et al.*²⁴. In the high energy X-ray study¹² the *AlY20* liquid crystallizes, shown by Bragg peaks in the 1D diffraction data and single crystal peaks in the 2D pattern, however it is prior to crystallization that changes in liquid structure occur. Two dimensional patterns collected at 2270 K and 1754 K are unequivocally liquid in character and the integrated difference pattern emphasizes the changes in both position and intensity of the first peak.

The change in *AlY20* occurs entirely within the supercooled liquid region and there is no evidence for the formation of crystals in the data shown in figure 3¹². While these changes occur at the same composition studied by Barnes *et al.* and Greaves *et al.* it is possible that different quench regimes are sampled in these studies. The crystallization temperatures for the liquids studied as part of this work are higher than those reported by Skinner *et al.*²⁵ and Barnes *et al.*²⁴ and direct comparison even within limited compositional ranges is challenging.

B. Vibrational spectroscopy of glassy samples (*AlY20* composition)

Samples free from macroscopic crystalline segregation and with *HDA* and *LDA* present were examined by Raman spectroscopy and samples with nanophase crystals eliminated from further study. A sample with unequivocally amorphous forms of *HDA* and *LDA* is shown in figure 1. Confocal Raman spectra was used to investigate the two amorphous forms, high spatial resolution allowing spectra to be collected away from this interface region (figures 1 and 2). Crystalline regions that give rise to a Raman signal can be estimated from recent studies of nanocrystal formation in glasses (e.g. Alekseeva *et al.*²⁶) and we estimate these to be $\simeq 4 - 5nm$, the fraction of crystals that could be detected by XRD for example is much greater ($\simeq 3$ volume %) and given the greater sensitivity of Raman spectroscopy we conclude that in the absence of nanocrystalline peaks the samples are amorphous.

The low frequency Raman spectra for the *HDA* and *LDA* glasses are shown in figure 4. The reduced Raman spectrum I^{red} is related to the observed Stokes Raman spectrum according to:

$$I^{red} = I^{Stokes} \nu \exp(\hbar\nu/kT)(\nu^* - \nu)^{-4}$$

and the Raman active part of the VDOS is related to I^{red} according to $I^{red} = D(\nu)g(\nu)$. Here ν and ν^* are the (absolute) Raman shift and the incident laser frequency respectively (both in Hz), $\hbar$ is Planck's constant divided by 2π , k is Boltzmann's constant, and $T = 300K$. The vibrational density of states (VDOS) is $g(\nu)$ and $D(\nu)$ is a frequency and polarization dependent coupling parameter. This latter term has been determined experimentally for *a - Si* and between 100 and 550 cm^{-1} . Below 100 cm^{-1} and above 550 cm^{-1} , $D(\nu)$ was extrapolated from the measured values as being proportional to ν^2 and ν , respectively²⁷.

In figure 4 the low frequency Raman spectrum for the *HDA* spectrum can be compared with reported by Nasikas *et al.*²⁸ for $Y_2O_3 - Al_2O_3$ glasses that ranging from 24 to 41 mole % Y_2O_3 . Nasikas *et al.* identify three broad bands at frequencies of approximately 780, 560 and 450 cm^{-1} in $Y_2O_3 - Al_2O_3$ glasses, consistent with distorted polyhedral structures expected in a vitreous sample. There is also a prominent *boson peak* at 100 cm^{-1} . The *AlY20* glass samples have no feature at 450 cm^{-1} , consistent with the compositional trends identified by Nasikas *et al.*. This part of the spectrum is dominated by vibrations in the YO_x polyhedra (Nasikas *et al.*²⁸, Replin *et al.*, Lu *et al.*), the decreased intensity of this broad band is therefore expected for this low Y_2O_3 content sample (*AlY20*).

Nasikas *et al.*²⁸ have assigned the bands at 780 cm^{-1} Q^2 -like species. These are analogous to the Q^n species in modified network glasses such as silicates. As these latter networks become progressively depolymerized the number of non-bridging oxygens increases, with n the number of non-bridging

oxygens^{29–31}. The Q^2 band in these spectra have frequencies close to those of YAG crystals³² (Q^2 formed from AlO_4 units with two non-bridging oxygens and calcium aluminate glasses³³). The band at 650cm^{-1} is assigned to Al-O-Al bending modes in connected AlO_x polyhedra²⁸. Nasikas *et al.*²⁸ have shown that as there is an increase in Y_2O_3 content the extent of Al-O-Al bonding decreases and the connectivity of YO_x polyhedra increases. Y-O-Y and Y-O-Al bridges will dominate the high Y_2O_3 glasses, while Al-O-Al and Y-O-Al is expected to dominate in the lower Y_2O_3 compositions. The *HDA* glass (20 mol % Y_2O_3 compares well with that shown by Nasikas *et al.* for their most Y_2O_3 -poor glass and is essentially a featureless spectrum.

Nasikas *et al.*²⁸ have studied spectra collected from the inclusions at high Y_2O_3 content. Those provided are similar to the Raman spectra of YAG. The spectra for the inclusions in the Nasikas *et al.* study are not however consistent with them being the *LDA* glass. The *LDA* segregation identified here has a different spectrum to that shown by Nasikas *et al.*²⁸. The *LDA* segregation of the *AlY20* glass is also distinguished from the spectrum from crystalline material. While the presence of crystals in high Y_2O_3 content samples is consistent with the observation of Nagashio *et al.* who argue *LDA* inclusions are nanophase garnet. The thermodynamic², HEXRD¹² and PIMD⁸ evidence all suggests that the *LLPT* will *not* be encountered in the more Y_2O_3 rich parts of the phase diagram including the regions close to YAG studied by Nasikas *et al.*²⁸ and Nagashio *et al.*⁹.

There are quantitative differences between the *HDA* and *LDA* spectra for the *AlY20* composition (Figure 4) most notably the presence of the broad feature centered at 475cm^{-1} . Similarly there is the difference in intensity of spectrum in the 675cm^{-1} region. Crudely this can be interpreted as an increased degree of structural ordering in the *LDA* glass, consistent with a decrease in configurational entropy and a change in $YO_x - AlO_x$ connectivity, an increase in $Y - O - Al$ linkages at the expense of $Al - O - Al$. At lower frequency the differences between the two spectra are more pronounced. The *LDA* and *HDA* glasses show a prominent broad peak at 100cm^{-1} which is within the range of the so-called *boson peak*. Although, as noted above, there is SiO_2 present in the *HDA* and *LDA* glasses the compositions of both are identical. A preferential partitioning of SiO_2 into one or the other of the amorphous forms could account for some difference in spectra but this is clearly not the case. The two glasses thus clearly fulfill the conditions for a *polyamorphic* sample, i.e. they are identical in chemical composition and crystal-free.

C. Polarizable Ion Molecular Dynamics

The results of the PIMD simulations^{8,12} have been reported elsewhere and are summarized here. The Q -space analysis indicates that there are significant structural differences in the three sub-densities (oxygen, yttrium and aluminum) as a function of composition and the partial contributions indicate a change from an Al-centered network to a network of Y-centered coordination polyhedra as the Y_2O_3 content increases. Further interpretation of the structure have been made in real space by considering the changes in the local structure around oxide anions as a function of composition¹² (figure 5). For relatively high Y content these results show more configurations of the form Al_2Y_2 (meaning one oxygen anion has two Al^{3+} and two Y^{3+} neighbors) and AlY_3 (three Y^{3+} neighbors and one Al^{3+}) than expected for a purely random distribution, while there are fewer Al_4 and Al_3Y configurations. For low yttrium compositions there are more Al_3Y and Al_2Y_2 but there are fewer Al_4 configurations than expected from a random distribution. At intermediate Y compositions, *AlY17* – *AlY20*, there are more Al_3Y and Al_2Y_2 and fewer Al_4 configurations than expected for a purely random distribution.

In our previous PIMD studies of $Y_2O_3 - Al_2O_3$ liquids⁸, as the temperature was decreased towards the predicted *LLPT* regime, we observed the occurrence of large and temporally random fluctuations in the system volume. The results indicated the system was spontaneously sampling two different sub-regions of the ionic configuration space, that differed in their molar volume by approximately 4%. The result could be best interpreted in terms of the PIMD model system sampling high- and low-density liquid (*HDL*, *LDL*) liquid configurations as the temperature approached the *LLPT*. The actual first-order *LLPT* could not be realized in these simulations because of the very long

run times and spatial scales that would be necessary for nucleation and growth to occur. However, the observation of spontaneous density fluctuations of the same magnitude as the contrast between *LDA* and *HDA* polyamorphs studied experimentally^{12,34} provides strong support for the suggested *LLPT*. The fluctuations in the system volume are largest in the *AlY*17 and *AlY*20 compositions, intermediate between those configurations which favour Al_2Y_2 coordination polyhedra (about four coordinate oxide anions) and those which favour Al_3Y polyhedra¹².

IV. DISCUSSION

Thermodynamic analysis and the PIMD simulations both suggest that at ambient pressure the composition where the *LLPT* is most likely to be intercepted is at 20 mole % Y_2O_3 . At higher Y_2O_3 contents crystallization will occur before the *LLPT* is encountered¹², at lower Y_2O_3 contents the *LLPT* will occur at higher pressures. The HEXRD liquids where there are changes in the supercooled liquid structure have 20 mole % Y_2O_3 . The glass samples used for Raman spectroscopy also have this composition. The presence of SiO_2 in the drop-quenched sample shows that the apparent *LLPT* is not masked by this additional component. The thermodynamic arguments for the *LLPT* in these and other liquids is based on a regular solution model^{35–37}, this is the simplest thermodynamic explanation for the *LLPT* and as far as we are aware, no model other than the regular solution model has been proposed. It is consistent that the *LLPT* would have a manifestation in a ternary system, although this may be restricted to low silica content, it offers an opportunity for future study.

The PIMD simulations show fluctuations in volume at *AlY*17 to *AlY*20, the composition where the *LLPT* would most likely be encountered. This compositional region is shown to be a region of transition between two different types of liquids, one that favors a AlY_3 configuration (surrounding a four-coordinate oxygen anion) and one that favors Al_3Y configurations, fluctuations in density are interpreted as oscillations between these low *LD*- and high *HD*-density configurations. The high energy X-ray diffraction data shows structural changes in the supercooled liquid regime for one composition only, that of *AlY*20. These changes are seen in the position and intensity of the first peak in the diffraction pattern (figure 3) prior to crystallization. The total structure factors for the two configurations at the volume extremes are compared with the high- and low-temperature structures for the supercooled *AlY*20 composition liquids and compare favorably (figure 6). Analysis of the partial structural contributions of the liquids at these volume extremes are consistent with the sampling of two different yttrium sub structures.

If we accept that the volume fluctuations observed in the PIMD simulations correspond to sampling the *HDL* and *LDL* configurations just above the *LLPT*, we can then use calculated vibrational dynamics for the two sub-populations (i.e., considering the configurations obtained at the low- and high-density extrema of the simulation runs) to interpret the experimental spectra of the *LDA* and *HDA* glassy regions. The liquid state simulations obviously give rise to a fraction of the VDOS intensity due to "imaginary modes", that correspond to translational relaxation components associated with the ion displacements, rather than true vibrational contributions. We have "removed" these by re-distributing the partial contributions from the ionic displacements proportionally among the VDOS, to provide an estimate of the glassy vibrational spectrum (Figure 7). We also indicate the partial VDOS contributions for Al-Al, Y-Y and O-O sub-densities. The *HDL* VDOS shows increased intensity at $\omega \approx 600\text{cm}^{-1}$ and a corresponding reduction at $\omega \approx 200\text{cm}^{-1}$. These suggest changes in the oxygen sub-lattice and are consistent with changes in Al-O-Y connectivity. The VDOS calculated from the low frequency compares with that calculated from the PIMD simulation (Figure 7). The glassy peaks are sharper but show differences in the $\approx 300 - 400\text{cm}^{-1}$ and $\approx 600 - 800\text{cm}^{-1}$ frequency ranges that are consistent with two different connectivities of YO_x and AlO_x polyhedra and suggest that the two glasses are representatives of the *HDL* and *LDL* liquids.

The presence of a boson feature in the low frequency Raman spectrum provides further evidence that both *HDA* and *LDA* samples (figures 1 and 2) studied here are glassy rather than crystalline. The boson feature typically corresponds to a maximum observed in the low frequency (e.g., $20 - 100\text{cm}^{-1}$)

region of the vibrational spectra of glassy samples, after removal of various frequency- and T-dependent effects on Raman or neutron scattering intensities^{38–41}. It corresponds to an excess build-up in the VDOS of glassy samples compared with corresponding crystalline materials, that can be linked to nanoscale heterogeneities in the mechanical properties of the amorphous solid. It can also appear for certain mesoscopically ordered materials such as large-pore zeolites and colloidal crystals⁴², but no such phases are expected to appear in the Y₂O₃-Al₂O₃ system studied here. The presence of the boson feature for both LDA and HDA polyamorphs is thus indicative of their fully glassy state. In addition, the differences in the shape and position of the boson peak is further consistent with two different glassy structures with associated differences in the low temperature heat capacity of the two amorphous forms^{39,40,43,44} (7,8). A comparison of the reduced vibrational density of states obtained from the low frequency vibrational spectra and the PIMD simulations shows a shift to lower frequency of the boson peak for the *LDA* form. This suggests different local structure of the *LD* form and reduction of the contribution to the low temperature heat capacity (Figure 8).

V. SUMMARY

The results of two recent sets of experiments on Y₂O₃-Al₂O₃ liquids and glasses are presented. Both aim to explore the reported liquid-liquid phase transition (*LLPT*) in this liquid. High energy X-ray diffraction experiments have been used to study the structure of supercooled Y₂O₃-Al₂O₃ liquids while low frequency Raman spectroscopy was used to determine the difference in the *HDA* and *LDA* glasses produced from this *polyamorphic* transition. These two sets of data were compared with the results of polarizable ion molecular dynamics simulations obtained across the same compositional range.

The high energy X-ray diffraction data show a change in structure in liquids of 20% Y₂O₃ (*AlY20*) composition, the composition where a liquid-liquid transition is reported. The changes in structure are observed in the un-corrected diffraction pattern and are seen as a shift in both position and intensity of the first peak in the diffraction pattern which occurs across a narrow temperature interval. These differences in structure suggest a change in the connectivity of *AlO_x* and *YO_x* polyhedra which occurs unambiguously within the liquid.

Polarizable ion molecular dynamic simulations on these liquids indicate that there are different favored coordination environments around oxygen anions depending on composition. At relatively high yttrium content liquids Al₂Y₂ and AlY₃ are favored while Al₄ and Al₃Y are favored in at lower yttrium content liquids. The compositions *AlY17* and *AlY20*, where the diffraction data shows the greatest changes in structure are intermediate between these two liquid types. Furthermore these two compositions show the abnormal volume fluctuations, interpreted as the fluctuations between the two liquid configurations with different densities (i.e. *HD* and *LD*). The differences in structure at these volume *extrema* match the difference in the diffraction pattern of high and low-temperature *AlY20* liquids.

In a *AlY20* sample in which two crystal-free and unambiguously glassy *HDA* and *LDA* forms are identified, there are quantitative differences in Raman spectra. This is most obvious in for the broad feature centered at 475cm⁻¹ and the difference in intensity of spectrum in the 675cm⁻¹ region. This can be interpreted as an increased degree of structural ordering in the *LDA* glass, consistent with a decrease in configurational entropy and a change in *YO_x* – *AlO_x* connectivity, an increase in Y-O-Al linkages at the expense of Al-O-Al. The simulation results can also be used to interpret the vibrational spectra. By assuming the extreme fluctuations in volume represent the oscillation between the low- and high-density configurations and the vibrational density of states and boson peak can all be calculated for *HD* and *LD* forms. The simulations and low frequency Raman data are consistent, although the peaks from the simulation are broader, there is intensity in the 600cm⁻¹ range in the *HD* liquid and in the glass and in the *LD* liquid and glass more intensity in the 400cm⁻¹ region. In both the simulation and the experiment the boson peak for the *HD* form occurs below that of the *LD* form.

The diffraction, Raman and simulation data all suggest a change in structure that is consistent with the sampling of the two different configurations and we conclude that the *HDL* – *LDL* transition in $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ liquids is restricted to compositions where high and low density basins in the underlying energy landscape can be sampled. These compositions, *AlY17* and *AlY20*, are where the diffraction data shows the greatest changes in structure are intermediate between these two liquid types and furthermore show the abnormal volume fluctuations. These high and low density states reflect different coordination polyhedra around the oxygen anions. The lower density configuration is favored on cooling and is responsible for the nucleation and growth of a separable, low density liquid in deeply supercooled *AlY20* liquids. Raman spectra from *HDA* and *LDS* glasses produced in this way are consistent with these changes in Al-O-Y connectivity.

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FIG. 1: Reflected light image of the *LDA/HDA* texture of the *AlY20* composition. The *HDA* and *LDA* regions are marked. The polarized reflected light image of the same *LDA/HDA* sample shows that the interface between the two glassy forms is marked by crystallites and suggests that the interface is a nucleation site for crystalline phases. Raman spectra have been collected away from this interface.

FIG. 2: Back scattered electron image of composite sample shown in figure 1a there is no obvious distinction in the mean atomic number even though both forms yield distinct amorphous spectra. The crystallites at the interface are clearly seen

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FIG. 3: Change in peak position as a function of temperature for AlY_{30} and AlY_{20} liquids. The position of the first peak in the diffraction pattern is plotted as a function of temperature. The different symbols represent different quenching experiments. The vertical lines highlight the melting and glass transition temperatures (T_m and T_g respectively). The peak position for AlY_{30} shows a simple linear trend with temperature, shifting from $2.16 \text{ \AA}^{-1}$ to $2.20 \text{ \AA}^{-1}$ when quenched. The AlY_{20} liquid shows a similar shift in position but in a narrow temperature range between 2000 and 1750 K (b).

FIG. 4: Low frequency Raman spectra of *HDA* (a) and *LDA* (b) regions in the samples shown in figures 1 and 2 collected using the XY Dilor triple spectrograph (Lyon), the *HDA* spectrum compares with the spectra obtain by Nasikas *et al*²⁸ on glasses of low Y_2O_3 content.

FIG. 5: The difference in local coordination environment about the four-coordinate oxide anions as a function of Al/Y composition with respect to a compositionally-averaged random distribution. The local coordination polyhedra is defined as $\text{OAl}_{4-k}\text{Y}_k$. Key: magenta - AlY10, cyan - AlY15, yellow - AlY17, blue - AlY20, green - AlY25, red - AlY30, black - YAG.

FIG. 6: The difference in X-ray scattering function (a) for the *AlY*20 liquid as a function of temperature prior to crystallization compared to the difference in X-ray scattering function of the glass-forming *AlY*30 liquids over the sample temperature range. Panel (b) shows the difference in total X-ray scattering function with temperature, $\Delta F^{(X)}(Q) = F^{(X)}(Q, T_1) - F^{(X)}(Q, T_2)$ for simulation (black line, $T_1 = 3000K$, $T_2 = 2500K$) compared with the experiment (red line, $T_1 = 2770K$, $T_2 = 1754K$).

FIG. 7: Vibrational density of states calculated from the low frequency Raman spectra (a). Differences between the two amorphous forms are clearly shown, notably in the region of $\approx 400\text{cm}^{-1}$ and $\approx 600\text{cm}^{-1}$. Panel (b) shows the vibrational density of states calculated from configurations extracted from PIM simulations on the *AlY20* composition. the spectra shown are obtained by quenching out imaginary frequency modes. In both figures the full and dashed lines are for the LDL (LDA) and HDL (HDA) forms respectively. The black lines show the full VDOS whilst the red, green and blue lines show the respective O, Al and Y partial contributions to the VDOS.

FIG. 8: Raman spectra shown as $g(\omega)/\omega^2$ obtained from (a) experiment and (b) PIM simulations. In both cases clear Boson peaks are observed with a greater intensity in the LDA form.