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# Thermodynamic and structural aspects of the polyamorphic transition in yttrium and other rare-earth aluminate liquids

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## Abstract

A first-order transition between two liquids has been reported in yttrium–aluminate liquids close to  $Y_3Al_5O_{12}$  (YAG) composition. This transition is seen as the nucleation and growth of a low-density phase in a matrix of a higher density liquid when  $Y_2O_3$ – $Al_2O_3$  liquids are cooled below the liquidus. Both liquids are quenched to glass before the transition is complete. Analysis of the resulting composite samples shows that the two glasses are identical in composition although the two glasses differ in density by 4%. There are also mechanical differences between the two glasses; the low-density glass is more resistant to polishing, while the high-density glass becomes highly scratched.

Following the initial observation, recent research has focused on establishing the thermodynamic and structural features of  $Y_2O_3$ – $Al_2O_3$  liquids which lead to liquid–liquid transitions. In addition, studies of other rare-earth aluminate compositions have been used to determine what, if anything makes the yttrium-bearing liquids exceptional. Differential scanning calorimetry (DSC) has been used to establish the onset of glass transition and, when combined with the heat capacity of crystalline phases, the jump in heat capacity at the point of glass transition. The DSC data enable the liquid fragility to be established and show the high-density liquid to be characterized by a non-Arrhenian viscosity–temperature relation. DSC studies of La–aluminates also show fragile liquid behavior, although liquid–liquid transitions have not been reported for these compositions. A combination of DSC and solution calorimetry has been used to evaluate the energetic differences between the two liquid phases of yttrium–aluminates and these data can also be used to estimate the changes in entropy. The entropy differences between the two phases also indicate differences in liquid rheology with the high- to low-temperature liquid transition also being a transition from a fragile to strong liquid.

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The structural differences between the two liquid polymorphs of  $Y_2O_3-Al_2O_3$  are difficult to discern. The stable crystalline phase is garnet-structured YAG but this is difficult to nucleate and a metastable assemblage of  $\alpha-Al_2O_3$  and  $YAlO_3$  perovskite tend to crystallize. This has led to the suggestion that the high temperature liquid is dominated by octahedral aluminum, which is consistent with a higher density. Neutron diffraction studies of Y- and La-aluminate glasses show that the liquid structure is very different from that of the crystalline phases, the aluminate liquids are dominated by a tetrahedral aluminate framework and there is little change in the mean Al–O coordination number either at the liquid–liquid transition or when La(III) is substituted for Y(III). The main differences in structure are seen in the ordering of the rare earth coordination polyhedra and network topology, the La- and the low-density Y-aluminate glasses showing increased rare-earth oxygen distances and more mid-range order. Nuclear magnetic resonance studies also show little change in Al(III) coordination although there are differences in the degree of disorder. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Polyamorphic transitions are structural transitions between high-density (HDA) and low-density (LDA) amorphous phases. These transitions can be understood in terms of crystalline polymorphism, but while polymorphic transitions in crystalline phases are accomplished by abrupt rearrangement of structural units, the lack of the periodicity that characterizes the amorphous state means that different structural configurations as temperature and pressure change and the response of a liquid to increase in, for example, pressure is expected to be continuous. Studies of amorphous phases under pressure suggest that the structure can, however, change over a narrow pressure range and in some cases these structural changes are discontinuous. Several systems with these types of first-order amorphous–amorphous transitions have been reported [1–3], one of the most notable being  $H_2O$  [1,4,5]. A liquid–liquid transition has also been observed in super-cooled  $Y_2O_3-Al_2O_3$  liquids, close to  $Y_3Al_5O_{12}$  (YAG) composition [6–8] (Fig. 1). The direct observation of a polymorphic transition between high-density (HDA) and low-density (LDA) amorphous phases, without discernible differences in composition, in super-cooled YAG-like liquids is notable because the transition occurs at one atmosphere in super-cooled liquids which are considered to be complex, that is, other structural configurations, such as conventional phase-separation would be anticipated.

Two-state models [9–14] are frequently used as a tool to describe the onset of liquid–liquid (HDA–LDA) transitions. These models reflect the application to regular solution thermodynamics to one component systems with either maxima or negative  $dT/dP$  slopes to the melting curve originally developed to describe the overturn of melting curves [15–17]. Since negative melting curves indicate an increase in liquid density relative to the crystalline phase, it was suggested that the liquid comprised two liquid species of different density with the proportion of the two species dependent

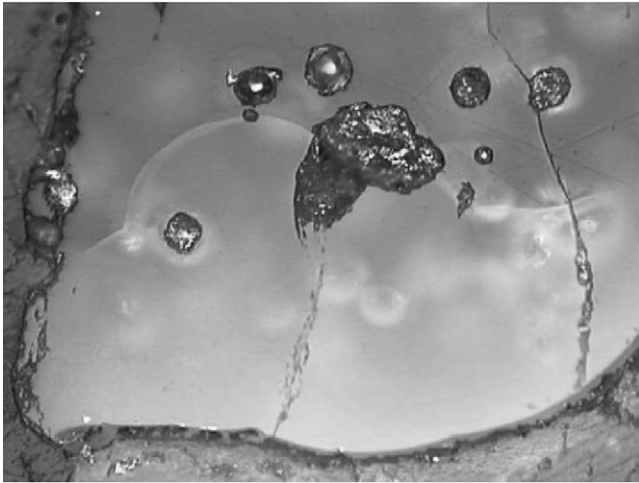


Fig. 1. Plane polarized light image of two-phase  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$  glass. This sample represents the partly complete transition from a high-density liquid, stable at high pressure to a lower density phase. The two glasses have identical composition.

on pressure and temperature [9,10]. The two species are considered as thermodynamic components and the mixing to the two components is described by a regular solution interaction parameter  $W$ . One feature of this mixing parameter is the appearance of a critical point, below which there can be a first-order transition between two liquids of different density. The two-state model is based on the presence of two liquid species which can be modeled on local configurations present in the crystalline phases of comparable density. While this may be applicable for simple elemental liquids, liquid–liquid transitions have been either reported or suggested for a variety of liquids ranging from metallic to complex organics and a more general form of the two state models has been developed, based on the changes in the degree of excitation in a liquid lattice [12–14]; bonds are broken and reformed as density is increased. In this more general model the specific structure of the liquid species is not required and, more importantly, the number of broken bonds (degree of excitation) can be used to obtain the configurational entropy and hence viscosity of the different liquid phases. An important feature of the bond-excitation model is that it demonstrates that liquid–liquid transitions are driven by a reduction in entropy and are accompanied by a change from fragile liquid to strong liquid behavior [12,13]. The parameter  $W$ , the non-deal interaction parameter becomes a measure of the contribution to the overall free energy resulting from the cooperativity of bonding [12,13].

The occurrence of an amorphous–amorphous transition in super-cooled Y–A liquids suggests that this type of liquid behavior is more general than at first realized. In this study, we explore the thermodynamic and structural parameters that result in this transition in  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$  liquids. Differential scanning calorimetry measurements (DSC) are used to establish the onset of the glass transition and also the change in heat

capacity at the point of glass transition. Solution calorimetry using molten lead borate is used to measure the enthalpy of solution of the different glasses and in combination with the DSC data is used to establish the differences in enthalpy and entropy. Nuclear magnetic resonance (n.m.r.) measurements have been made on glasses in order to establish changes in the speciation of Al(III), using the 3Q-MAS technique to determine differences in the abundance of four- five- and six-coordinate Al(III) and further insight into the glass structure is obtained through the use of combined neutron and X-ray diffraction.

## 2. Calorimetry measurements

The results of DSC measurements on both  $Y_2O_3$ – $Al_2O_3$  glasses show the onset of glass transition at 1120–1150 K (Fig. 2). This transition is seen in both single-phase glasses, quenched from the HDA liquid, and composite (HDA+LDA) samples. The glass transition between 1120 and 1150 K is attributed to that of the high-density amorphous (HDA) phase and has the characteristic features of a fragile liquid. At the glass transition there is a large increase in heat capacity ( $\Delta C_p$ ) and the glass transition itself is narrow, both features characteristic of a fragile liquid [18,19]. In  $Y_2O_3$ – $Al_2O_3$  DSC traces there are two exothermic peaks (Fig. 2), one of which results from the partial crystallization of the relaxed super-cooled liquid, the other is interpreted as a transition from the high-density super-cooled liquid to the more stable, low density (LDA). This interpretation is supported by two observations: first, the integrated area under the exothermic peaks is substantially less than the heat of vitrification of YAG [20] and second, examination by X-ray diffraction shows few crystals present in the heat-treated samples. A similar transition was reported in the super-cooled liquid regime of high-density amorphous ice [5] but is only

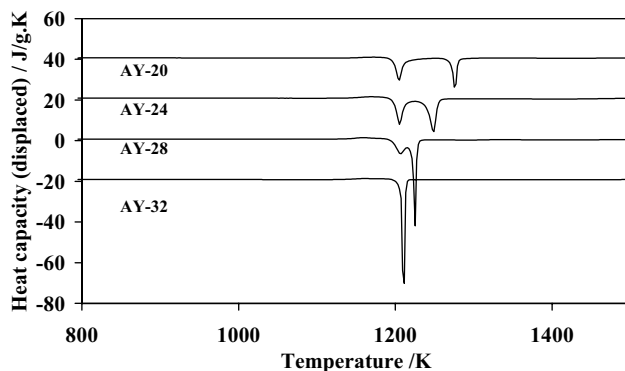


Fig. 2. Differential scanning calorimetry results for  $Y_2O_3$ – $Al_2O_3$  glass samples heated from room temperature to 1500 K. The exothermic peak at 1200 K represents crystallization from the super-cooled high-density phase, while the higher temperature exothermic peak is interpreted as a transition from the super-cooled high-density phase to a more stable low-density glass. This peak merges with the peak at 1200 K as the  $Y_2O_3$  content of the glass is increased.

possible in super-cooled  $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$  liquids because slow kinetics inhibit crystallization of YAG.

Calorimetry measurements on single-phase (HDA) yttrium–aluminate glass yield a heat of drop solution of  $196.0 \pm 3.4$  kJ/mol. This value can be combined with the heat of drop solution for crystalline YAG ( $422.6 \pm 14$  kJ/mol) and the enthalpy of vitrification, calculated. This value,  $280 \pm 11$  kJ/mol at 298 K, is directly comparable to the value  $276.5 \pm 5.4$  kJ/mol obtained from a previous study [20]. When a single-phase high-density glass is heated to the transition from the super-cooled high-density phase to the more stable low-density glass, the heat of drop solution is increased to  $355.4 \pm 21.1$  kJ/mol. While the heat of drop solution for two-phase glass samples is  $256.0 \pm 9.2$  kJ/mol, this value has contributions from both the low- and high-density amorphous phases. These heats of the solution can be used to estimate the difference in enthalpy between the two phases and based on these data the  $\Delta H$  for the transition from high- to low-density amorphous yttrium–aluminates is 182 kJ/mol at 298 K. The large value of  $\Delta C_p$  seen in the DSC traces indicates a strong temperature dependence of  $\Delta H$ . The adjusted value for  $\Delta H$  based on the anticipated change with temperature is  $-35$  kJ/mol, consistent with that estimated from the DSC traces (Fig. 2).

These values of  $\Delta H$  and an estimated  $\Delta S$  of  $3R$  J/mol K (where  $R$  is the gas constant) can be used to establish the changes in rheology on transition from the high-density to low-density liquids. The configurational entropy of the higher density liquid can be calculated from the DSC and adiabatic heat capacity data [21]. The Adam–Gibbs model [22] is used to calculate the viscosity curve which agrees well with a viscosity curve estimated from a Volger–Tamman–Fulcher fit to the glass transition data and existing viscosity data [23]. A reduction of configurational entropy based on the differences in  $\Delta S$  between the two amorphous phases yields a stronger liquid, consistent with the bond-excitation model. The values of the non-ideal interaction parameter ( $W$ ), defining the critical temperature for the liquid–liquid transition are 28–30 kJ/mol [24].

### 3. $^{27}\text{Al}$ nuclear magnetic resonance spectroscopy

Triple quantum  $^{27}\text{Al}$  MAS spectroscopy data have been collected for single-phase, heat-treated and two-phase  $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$  glasses (Fig. 3). The spectra show the presence of three structural units ( $\text{AlO}_4$ ,  $\text{AlO}_5$  and  $\text{AlO}_6$ ) which are present in all spectra; these units form three broad peaks, typical of amorphous materials [25,26]. For the single-phase (HDA)  $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$  glass the  $\text{AlO}_4$ ,  $\text{AlO}_5$  and  $\text{AlO}_6$  peaks are broad and indicates distortion of the Al–O bonds in the aluminate framework consistent with high configurational entropy for the high-density liquid. For the same composition sample, heated to the transition between the super-cooled high-density phase and the low-density glass (Fig. 2) there are changes in the width of the three amorphous peaks, but no discernible change in relative abundance of the main structural units. On transition the peaks for all three structural units become narrower; this suggests that there are changes in the degree of distortion of the aluminate polyhedra, again consistent with a reduction in configurational entropy. The composite (HDA + LDA) glass sample also shows no

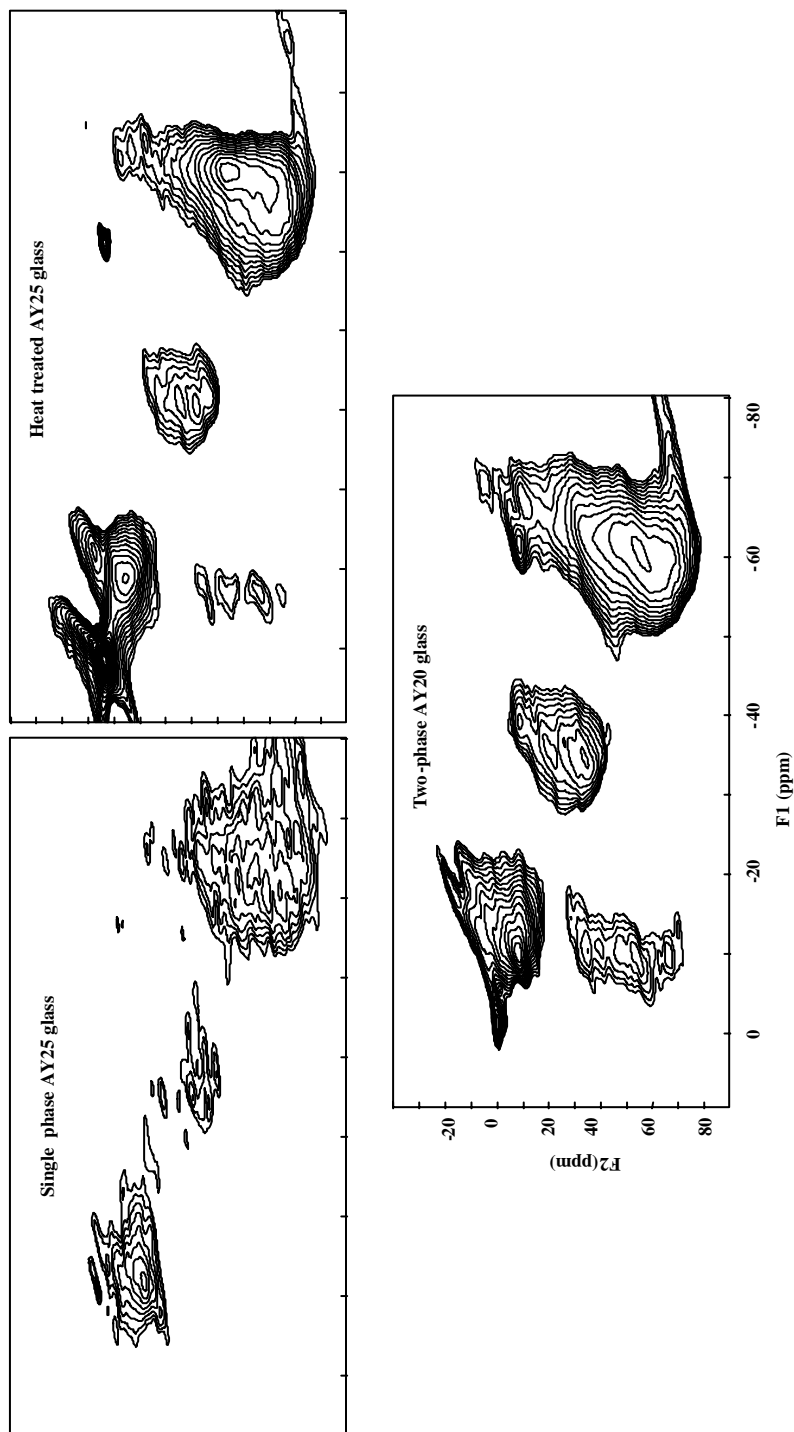


Fig. 3. Two-dimensional  $^{27}\text{Al}$  3Q nmr data for single-phase AY25 aluminate glass, single-phase AY25 heated to the transition between the super-cooled high-temperature liquid and the low-density glass and for two-phase AY20 glass. The tetrahedral ( $\text{AlO}_4$ ) site is centered at  $-40$  ppm relative to  $\text{AlCl}_3$  in the isotropic dimension (f1) and 50 ppm in the MAS (f2). The less abundant octahedral species is represented by a well-resolved peak at  $-10$  ppm in the isotropic dimension and 10 ppm in the MAS dimension, while the  $\text{AlO}_5$  unit occurs at  $-25$  ppm in f1 and 30 ppm in f2.

detectable difference in the relative abundance of the three aluminate units, although the peaks are again narrower. These data suggest that the liquid–liquid transition in  $Y_2O_3$ – $Al_2O_3$  liquids does not involve a change in Al–O coordination number but does involve a decrease in the degree of distortion in the Al–O units and an increase in mid-range order.

#### 4. Neutron diffraction

Neutron scattering were collected for a single-phase (HDA) glass (AY25: 25% $Y_2O_3$ –75% $Al_2O_3$ ) and a two-phase (HDA + LDA) sample (AY20: 20% $Y_2O_3$ –80% $Al_2O_3$ ). The neutron diffraction data for the single-phase AY25 glass yield a total pair correlation function  $T(r)$  similar to that derived from X-ray diffraction studies of the levitated, stable liquid [27] (Fig. 4). Three Gaussian peaks, centered at distances of 1.79, 2.3 and 2.88 Å, correspond to the Al–O, Y–O and O–O correlations, respectively [25]. The Al–O coordination obtained from these data is 4.16, and the Y–O coordination number is 6.64 [28]. The neutron diffraction data for the two-phase sample yield a mean Al–O coordination number of 4.38 and indicate little or no change in Al(III) coordination on transition. There are, however changes in the Y–O correlation with the peak at 2.3 Å

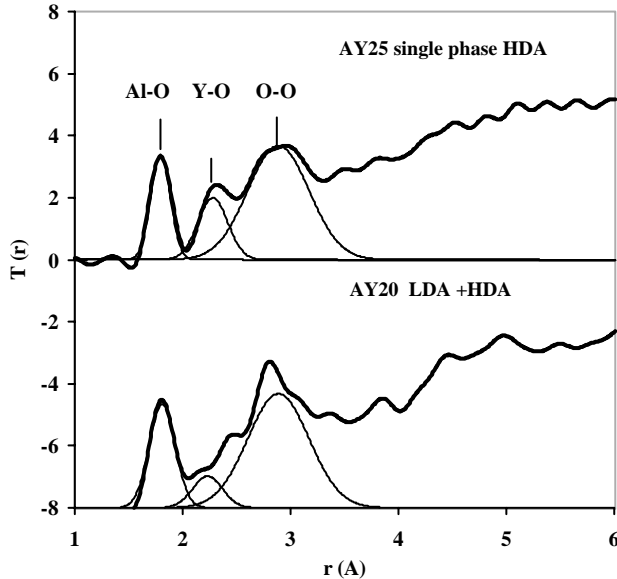


Fig. 4. Total pair-correlation functions for single-phase AY25 (HDA) and two-phase (HDA–LDA) glass (AY20). Three Gaussian peaks correlating with the Al–O, Y–O and O–O correlation can be used to deconvolute the neutron  $T(r)$  data. The Al–O coordination number is unchanged on transition from HDA to LDA although there is an increase in the Y–O distance and in mid-range order, shown by peaks at radial distances greater than 3 Å.

reduced in magnitude and an apparent additional Y–O correlation, superimposed on the O–O peak. The neutron data indicate that the local structure of the high-density  $Y_2O_3$ –aluminate liquid is dominated by a tetrahedral aluminate framework and not, as previously suggested, by octahedral Al(III). These data indicate that the polyamorphic transition between high- and low-density  $Y_2O_3$ – $Al_2O_3$  liquids cannot reflect a transition between local structures similar to the  $Y_2O_3$ – $Al_2O_3$  crystalline ( $Y_3Al_5O_{12}$  and  $YAlO_3$ ) phases.

## 5. X-ray diffraction

X-ray diffraction measurements on the AY25 and AY20 glasses used in the neutron study yield complementary real-space distance information. Increased scattering intensity in the X-ray data enable the metal–metal correlations, masked by the oxygen signal in the neutron data, to be discerned. Correlations between 3 and 5 Å reflect the different configurations of the  $AlO_4$  and  $YO_6$  coordination polyhedra. For the AY25 glass (Fig. 5), the prominent peak at 3.6 Å in the  $T(r)$  results from the Y–Y correlation and includes contributions from both edge- and corner-shared  $YO_6$  units with Y–Y distances of 3.26 and 4.66 Å, respectively. The Y–Al and Al–Al correlations change as

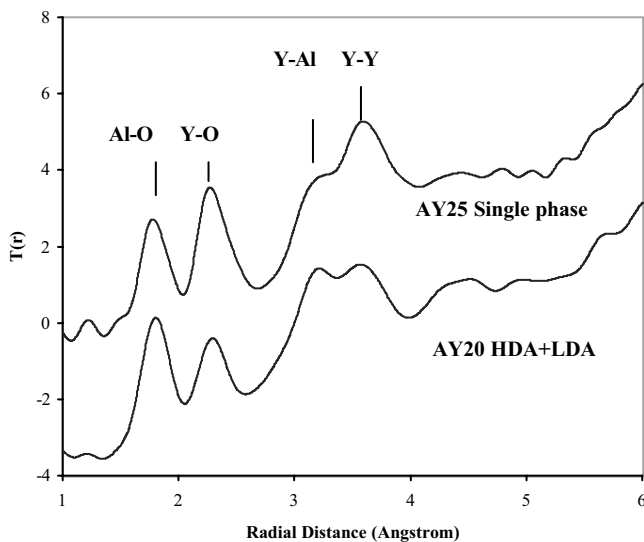


Fig. 5. Total pair correlation function for AY25 and AY20 glasses from X-ray data. In these data there is a prominent peak at 3.7 Å in the Y–Y correlation attributed to corner-shared  $AlO_4$  and  $YO_6$  polyhedra. Total pair correlation function for two-phase AY20 glass. The X-ray and neutron diffraction data for the same glass sample show some differences in Al–O and Y–O correlations. This may be due to the smaller sample used for the X-ray experiment. The X-ray data of the peaks between 3 and 4 Å suggest a dramatic reduction in the number of corner-shared  $AlO_4$  and  $YO_6$  and edge-shared  $YO_6$  polyhedra as the liquid–liquid transition is approached.



the number of corner-shared and edge-shared  $\text{AlO}_4$  and  $\text{YO}_6$  units is changed. The approximate concentration of  $\text{YO}_6$  units edge-shared with other  $\text{YO}_6$  polyhedra is 70% for the glass quenched from the high-density liquid (AY25) and 60% of the  $\text{AlO}_4$  units are corner-shared with  $\text{YO}_6$ .

In the  $T(r)$  for the two-phase sample there are changes in the magnitude of the Al–Al, Al–Y and Y–Y peaks. In part this is due to changes in composition, but these changes also represent a change in the arrangement of the  $\text{YO}_6$  and  $\text{AlO}_4$  polyhedra. The most obvious difference between the two pair correlation functions is the decrease in the magnitude of the peak at 3.67 Å and an increase in the peak at 3.26 Å. These changes correspond to changes in the Y–Y and Y–Al distances and changes in the abundance of corner- and edge-shared  $\text{YO}_6$  and  $\text{YO}_6$  and  $\text{YO}_6$  and  $\text{AlO}_4$  polyhedra. There is a decrease in the number of edge-shared  $\text{YO}_6$ , to 60% and Reverse Monte Carlo models also indicate that the  $\text{YO}_6$  unit is less distorted in the LDA phase. The number of edge- and face-shared  $\text{AlO}_6$  and  $\text{YO}_6$  units is increased in the LDA phase (to  $\sim 70\%$ ) at the expense of corner-shared units. The structural mechanism for the HDA–LDA transition in  $\text{Y}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$  liquids on this basis is an increase in the dominance of the aluminate network in the lower density, LDA phase with an increase in the number of edge- and face-shared  $\text{YO}_6$  and  $\text{AlO}_4$  units at the expense of the distorted edge-shared  $\text{YO}_6$  units which dominate the HDA phase. This is consistent with a reduction in configuration entropy by first-order transition (Fig. 6) to a more ordered configuration associated with an increase in longer range-structure and more ordered oxygen correlations.

## 6. Conclusions

- Calorimetric studies of yttrium–aluminate glasses confirm the liquid–liquid transition to be a transition from a fragile to strong liquid.
- Neutron and X-ray diffraction data show that the liquid–liquid transition is a result of changes in the metal–metal coordination.
- Two-dimensional nmr spectra show a reduction in the distortion of the Al–O bond on transition which also correlates the reduction in configurational entropy and change in rheology.
- Bond-breaking associated with the change from corner- to edge-shared  $\text{AlO}_4$  and  $\text{YO}_6$  units results differences in thermodynamic properties between the two amorphous phases.
- The differences in structure are consistent with a reduction in configurational entropy on transition and a stronger, low-density liquid.

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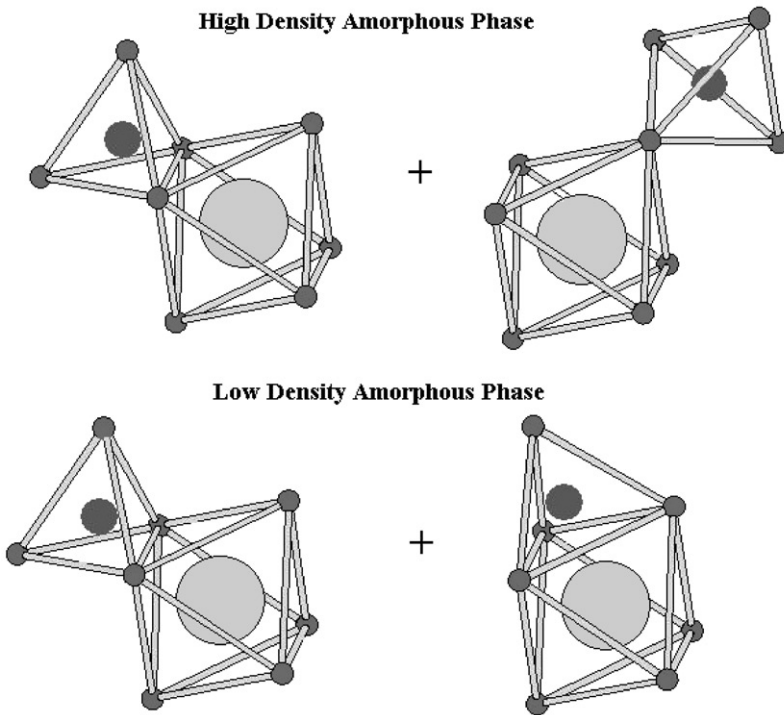


Fig. 6. Proposed structural changes in polyamorphic yttrium–aluminate liquids. The high-density amorphous phase is a mixture of face- and corner-shared  $\text{AlO}_4$  and  $\text{YO}_6$ . On transition there is a reduction in the number of corner-shared polyhedra and the amorphous phase comprises a mixture of face- and edge-shared  $\text{AlO}_4$  and  $\text{YO}_6$ . The HDA phase is dominated by distorted  $\text{YO}_6$  polyhedra edge-shared with other  $\text{YO}_6$  units, these become corner-shared in the LDA phase.

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