

Experimental Report: HD- 231

Proposal Title Solidification behaviour and polyamorphism of levitated liquid yttrium aluminates

In this experiment we undertook a careful study of the structure of liquid $(Y_2O_3)_x-(Al_2O_3)_{1-x}$ in both the liquid and supercooled liquid states and by time resolved measurements as the liquid was quenched to form a glass or to crystallise. The motivation of the experiment was to look for and to identify if possible the liquid-liquid (LL) transition that is believed to occur in this material. The experiment exploited a Conical Nozzle Levitation system with laser heating that could be synchronised with X-ray data acquisition to obtain time resolved diffraction patterns with a resolution of 30ms. We carried out a series and exhaustive range of compositions between $0.2 < x < 0.375$ with the aim of identifying any such structural changes. Subsequent to this experiment in June a paper was published in Science [1] which claimed to observe such behaviour at the composition $x=0.2$ (AY20). We will therefore concentrate this report on this composition, comparable data and conclusions have been obtained at the other compositions. Figure 1 shows the corrected and normalised structure factor of AY20 in the steady liquid (2000°C) and steady supercooled states at temperatures of 1800,1600,1400 and 1300°C.

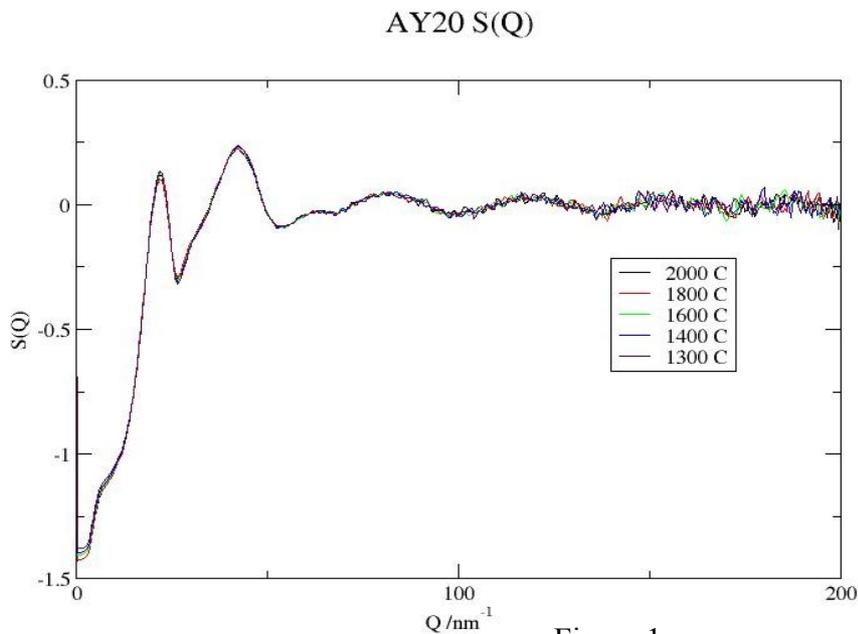


Figure 1.

It is notable that there is very little change in the structure of the liquid over the whole of this 700°C temperature range. This is in direct contrast to reference [1] where it is claimed an LL transition, notable by a step change in the position of the position of the first peak in $S(Q)$ at $\sim 21.5 \text{ nm}^{-1}$, occurs at 1515 °C. Figure 2 shows a plot of the position of the position of the first peak as function of temperature from our static measurements and from the 30ms slices as the sample was rapidly quenched. The purple diamonds indicate the position of this peak obtained from the five diffraction patterns shown in figure 1. The red diamonds are the corresponding changes reported in [1]. The small dots (black, red, green, blue, dark purple) show the evolution of the peak as the sample rapidly cools from 2000, 1800, 1600, 1400 and 1300 °C respectively. The sudden upturn at the time step ~ 60 on the graph is the point, T_{recal} , at which the sample recalesces and crystallises and has been used as the reference point in this graph. In practise there was a variation of the recalescence temperature of about 50°C with a tendency for a reduction in T_{recal} as the starting temperature was lowered. Between time step 60 and 90 (corresponding to $\sim 1 \text{ s}$ duration) the diffraction pattern showed a mixture of a crystalline powder pattern and the liquid structure with a distinct bimodal peak. This mixed pattern corresponds to the characteristically slow rise in temperature at T_{recal} for

samples of this composition (shown in figure 3). The final peak at $\sim 24 \text{ nm}^{-1}$ corresponds to a single strong peak in the crystalline powder diffraction pattern. The inset shows the corresponding $S(Q)$'s and the final crystallization from the liquid.

Position of the first peak in $S(Q)$

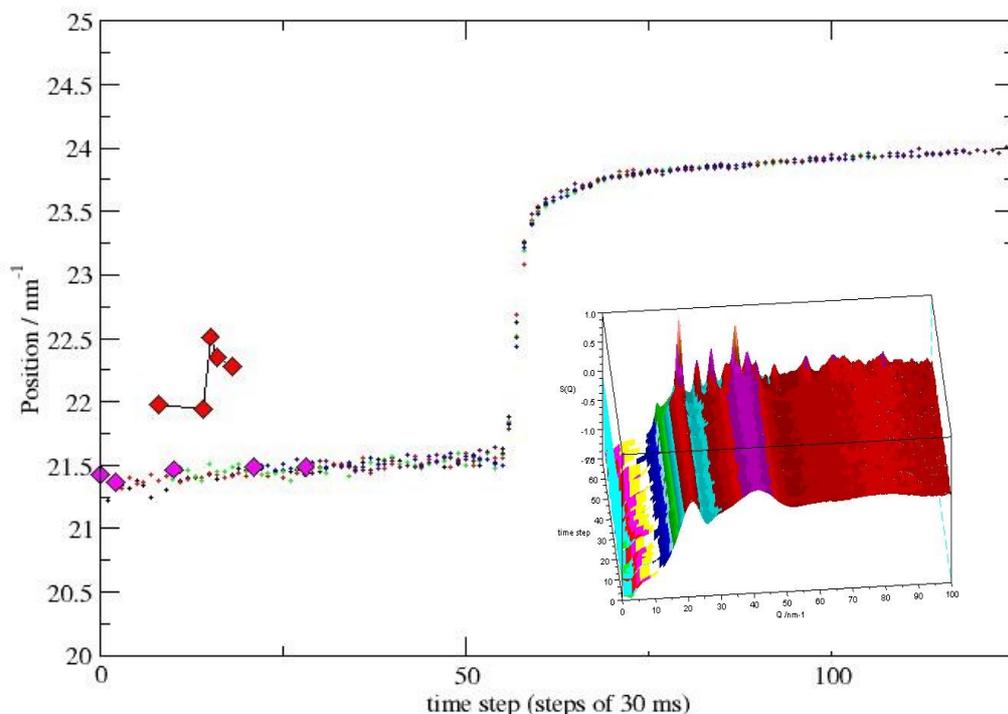


Figure 2.

Figure 3 shows the pyrometry from the sample as it was supercooled from the temperatures shown above. The results are fully consistent with an extensive set of similar pyrometric measurements we have made in our laboratory in Bristol and show now evidence at all of an thermodynamic event taking place before the recalescence. The extended recalescence as indicated by the bar takes place over a period of about one second and is fully consistent with the observation of the slow crystallization in the diffraction patterns.

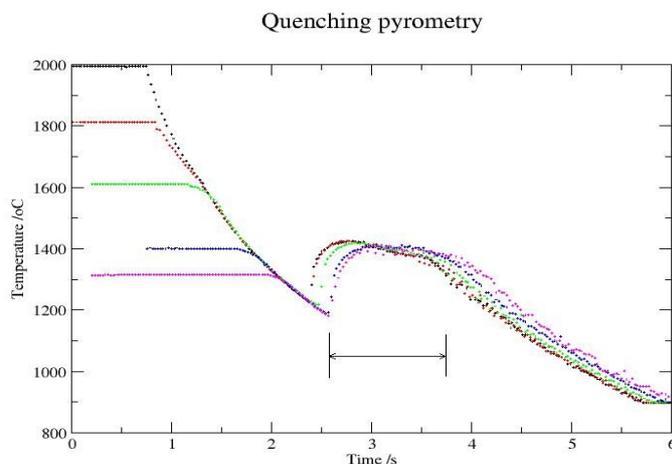


Figure 3.

Figure 4 shows the evolution of the corresponding $G(r)$'s again showing the final crystallization. No evidence, within error, was found for any shift in the peaks in $G(r)$ *before crystallization*, especially with regards to the peak at ~ 34 nm where the changes in the Y-Y structure as proposed in reference [1] should take place.

In conclusion and in contrast to recently published work we have *not* observed any evidence of a liquid-liquid transition in $(Y_2O_3)_x-(Al_2O_3)_{1-x}$ at any composition in both quasi-static measurements or in time resolved measurements with a time resolution of 30 ms. These results are consistent with the work we have already published on the structure and crystallization in this system.

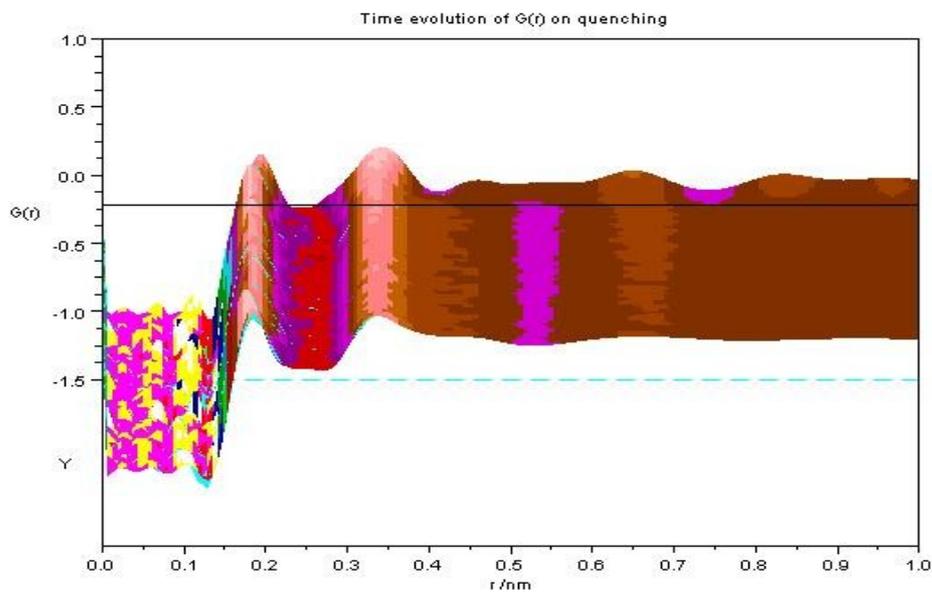


Figure 4

References.

- [1] Greaves, G.N. et. al. (2008) *Science*, **322**,566
- [2] Skinner, L.B. et. al. (2008) *J. Phys. Cond. Matt.* **20**, 205013