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Comment on “Liquid-Liquid Phase Transition in Supercooled Ytria-Alumina”

We welcome efforts made by Barnes *et al.* to study liquid-liquid transitions (LLT) in supercooled $Y_2O_3-x-Al_2O_3(100-x)$ or AY_x melts reported in a recent Letter [1]. The first order LLT in AY_{20} , which we have identified *in situ* under equilibrium conditions [2,3] has a well-defined temperature T_{LL} at ambient pressure and a critical point at negative pressure. The LLT is also composition dependent, rising as x falls [3,4]. We identified this at 1788 K from (i) a peak in the small angle x-ray scattering (SAXS) intensity, (ii) a discontinuity in the structure factor $S(Q)$, and (iii) a “polyamorphic rotor” caused by periodic LLTs [Fig. 1(a)]—the flipping time and associated temperature spikes yielding the LLT density and entropy discontinuities in agreement with *ex situ* experiments [4]. Barnes *et al.* used similar experiments but could not reproduce (i) or (ii) in AY_{20} at 1788 K and attributed (iii) to 60 K instabilities sometimes encountered during sample conditioning [1]. We consider their null results for AY_{20} are due to (A) large neutron beam sizes in small angle neutron scattering (SANS), and (B) doubts in AY_x composition. Moreover, comparison with our work [2] is obscured in [1] by reliance on apparent temperatures uncorrected for emissivity [5] and by inconsistent molar normalization leading to flaws in modelling LLTs from our data [3].

(A) In their SANS measurements [1] the mm radius droplet was overspilled by a 2 mm radius 4.5 \AA beam. Because of the spherical liquid surface this results in total external reflection and cross fire contamination up to at least $2 \times 0.013 = 0.026 \text{ \AA}^{-1}$. Sub mm focused SAXS has none of these disadvantages [2] which is why it is sensitive to the rise and fall in scatter that occurs below 0.03 \AA^{-1} [2] at the LLT (Fig. 1). Importantly, polyamorphic rotor action was recorded by L. Hennet during the SANS experiments with periodic 150 K spikes centered at 1940 K [Fig. 1(b)]. Polyamorphic rotors have large repetitive spikes thermally distinct from the oscillations illustrated in [1] which sometimes occur when molten drops contain inclusions.

(B) The sample preparation method of fusing 85 mg drops from weight-matched beads of separate oxides [6] is unreliable without validation of recovered samples. We fused mm radius drops by weighing material from 5 g powdered batches following repeated sintering and re-grinding. Composition checks post experiment confirm $x < \text{mol } 1\%$ accuracy. $S(Q)$'s of AY_x melts at 2300 K are composition sensitive (Fig. 1). Measurements at 11-ID-C (APS) [2] and at ID11 (ESRF) [7] are in good agreement, with the positions of the first and second peaks Q_1 and Q_2 , and size of the principal peak $S(Q_1)$ all scaling almost linearly with x , except for values fitted from the peak maxima at 2300 K from [1] Fig. 1. Rather than AY_{20} , these triangulate with the composition $AY_{14} \pm 1$. We already investigated AY_{15} until crystallization intervened at 1927 K [2] close to the rotor temperature shown in

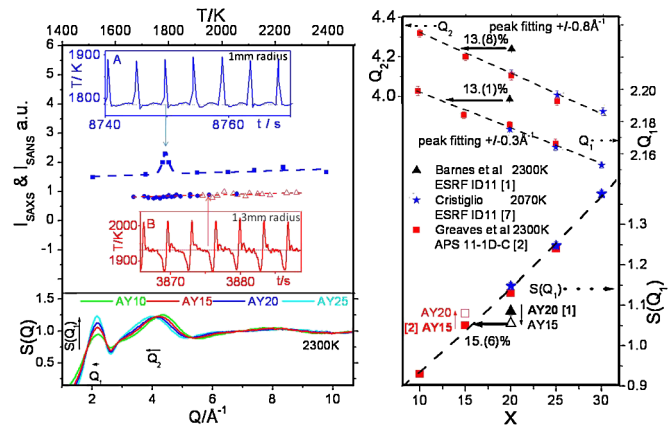


FIG. 1 (color online). Left. Upper: SAXS for AY_{20} \blacksquare and AY_{15} \blacktriangle from [2] scaled to SANS for AY_{20} \bullet from [1], together with LLT rotor motion (A and B). Lower: $S(Q)$ for AY_x liquids from [2] corrected for detector scattering angle thickness, with compositional changes marked. Right: trends in Q_2 , Q_1 and $S(Q_1)$ with x . 2σ errors for Q_1 and Q_2 from peak-fitting and for $S(Q_1)$ from [1] within symbol size. Arrows between closed and open symbols \updownarrow show shifts in $S(Q_1)$ for alternative compositions $x = 15 \leftrightarrow 20$. Horizontal arrows show $x = 14\% \pm 1\%$ as the likely composition for the Letter [1] rather than AY_{20} .

Fig. 1(b). If 1940 K marks the LLT for AY_{15} then, with our observation of 1788 K for AY_{20} [2], these results further demonstrate that for AY_x liquids T_{LL} rises as x falls [3,4], and provide scope for future collaboration.

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