Thermal disorder and melting in supercooled alumina

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Introduction

At high temperatures the mean square displacement or Debye-Waller Factor (DWF) of the average atom, mass $\overline{m}$, from the average lattice site is given by $\overline{\mu^2} = 9T\hbar^2 / k_B \overline{m}\Theta_D^2$, where Θ_D is the Debye temperature [1]. At the melting point, T_M, for close packed crystals like alumina $\sqrt{\mu^2}$ is approximately 10% of the mean interatomic separation $\overline{r}$ - Lindemann's Melting Law [1]. In ionic and covalent solids thermal displacements are ~ 40% correlated and the relative DWF for interatomic distances, r_{ij}, $\mu_{ij}^2 \approx 1.2\mu^2$ [2]. $\overline{\mu_{ij}^2}$ is measured in EXAFS [2] and is also contained in the Debye expression for diffuse scattering

$$QS(Q) = \sum_i \sum_{j \neq i} N_{ij} f_i(Q) f_j(Q) \frac{\sin Qr_{ij}}{r_{ij}} \exp -(\frac{Q^2 \overline{u_{ij}^2}}{2})$$

where N_{ij} is the coordination number for ij correlations and $f_i(Q)$ and $f_j(Q)$ are the scattering factors. Ratioing

$$\frac{S(Q)_{ref}}{S(Q)_T} = \frac{N_{ij}(ref)}{N_{ij}(T)} \frac{r_{ij}(T)}{r_{ij}(ref)} \exp -(\frac{Q^2}{2}[\overline{u_{ij}^2}(ref) - \overline{u_{ij}^2}(T)])$$

in which case the relative DWF, $[\overline{u_{ij}^2}(ref) - \overline{u_{ij}^2}(T)]$, can be obtained from the slope of $\ln(S(Q)_{ref} / S(Q)_T \; versus \; Q^2$ if the structure factor, $S(Q)$, is dominated by nearest neighbour correlations. This is approximately true for liquid alumina [3]. A similar approach has been used to obtain $\overline{\mu_{ij}^2}$ for SiO_2 phases by ratioing the elastic and static structure factors [4] and earlier, in EXAFS analysis, where the relative DWF was obtained by ratioing unknown spectra against model compounds [5]. Accordingly, if $S(Q)_{ref}$ is taken at a fixed temperature, T_{ref}, $\mu_{ij}^2(T_{ref})$ can evaluated from the Debye model [1], and values for $\overline{\mu_{ij}^2(T)}$ obtained in the supercooled state from $S(Q)_T$ data as T approaches T_M.

Methods and Materials

In situ XRD experiments on alumina were performed at Station 6.2 at the SRS using an aerodynamic levitation furnace [6] and a RAPID 2 WAXS detector, from the above T_M to the recalescent point, T_R, where recrystallisation occurs in the supercooled state.

Results

Experimental $S(Q)$s for supercooled alumina are plotted as $\ln(S(Q,T_R) / S(Q,T) \; versus \; Q^2$ in Fig.1 between T_R and T_M. The similarity of the intercepts, indicates little change in local order between melting at T_M (2423K) and recalescence at T_R (1723K) i.e. $N_{Al-O}(T_R) r_{Al-O}(T) \approx N_{Al-O}(T) r_{Al-O}(T_R)$. However, the slopes decrease with increasing temperature, following the increase in thermal disorder. DWFs calibrated at T_R are plotted in Fig. 2.

Discussion

From the Debye model $\overline{\mu^2}$ for α-Al_2O_3 falls from 0.046Å^2 at T_M to 0.035 at T_R. Taking the density of liquid alumina [3] and the measured speed of sound [7] at T_M, $\overline{\mu^2}$ decreases from 0.101Å^2 at T_M to 0.088Å^2 at T_R. The Debye temperatures Θ_D for crystal and liquid are 1040K and 701K respectively, reflecting the change in local structure on melting from $N_{Al\text{-}O}$ = 6 and $N_{O\text{-}Al}$ = 4 to $N_{Al\text{-}O}$ = 4.1 and $N_{O\text{-}Al}$ = 2.8 on melting [3]. Interestingly $\sqrt{\overline{\mu^2}} / \overline{r} \sim 0.10$ for α-Al_2O_3 at T_M and also for liquid Al_2O_3 at T_R, both reminiscent of Lindemann's Law [1]. From $\overline{\mu^2}$ =0.088Å^2 at T_R $\overline{\mu}_{Al-O}^2$ equals 0.11Å^2 which is used to calibrate the relative DWFs obtained from Fig. 1. Thermal disorder in crystalline and supercooled Al_2O_3 between T_M and T_R are compared in Fig. 2. Measured $\overline{\mu}_{Al-O}^2$ values fall below the Debye model, pointing to increasing anharmonicity as T_M is approached.

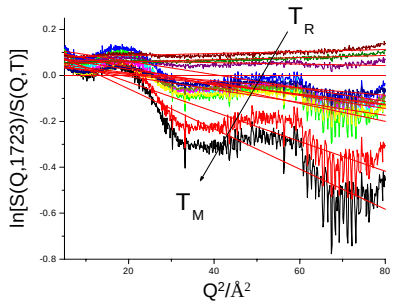

Fig 1. In situ XRD S(Q)s for supercooled alumina ratioed against S(Q) at 1723K.

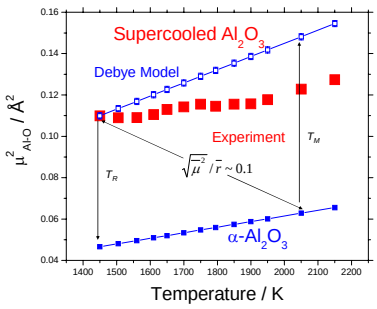

Fig 2. Measured relative DWF versus T for supercooled alumina and α-Al_2O_3 compared to Debye mode valuesl.

References

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