

The Different Structural Roles of Na, Ca and Al in Silicate Melts

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The multiple structural roles which Al^{3+} in tetrahedral co-ordination assumes in silicate melts as a function of the number, charge and radius of the charge balancing cations as well as the Al/Si ratio leads to a complex variation in the physical and thermodynamic properties of the melt, as well as in the flow mechanism of the melt.

Literature data shows that there is a change in viscosity trend in aluminosilicate melts as a function of composition when there are no longer enough charge balancing cations available for the Al^{3+} in tetrahedral co-ordination. This has been observed for Li^+ -, Na^+ - and Ca^{2+} -bearing melts. No change in viscosity trend as a function of Mg/Al is seen for Mg^{2+} -bearing aluminosilicate melts; suggesting that the structural role of Al^{3+} in these melts is further modified by the size of the small Mg^{2+} cation.

Here we show that the configurational heat capacity (C_p^{conf}) of aluminosilicate melts also shows changes in trend as a function of the cation/ Al^{3+} ; with a minimum in C_p^{conf} occurring in melts in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ series at $\text{Na}=\text{Al}(\text{atoms})$, and a maximum in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ series at $\text{Ca}=2\text{Al}(\text{atoms})$ (the mol% SiO_2 is held constant in these melts). There is however, a minimum in C_p^{conf} in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ series at the condition $\text{Ca}=\text{Al}(\text{atoms})$, suggesting that a further modification of the melt structure occurs when there are no longer enough Ca^{2+} such that each Al^{3+} can have its own charge-balancing cation, and the Al^{3+} must begin to share the calciums. Investigation of the metaluminous $\text{CaO}-\text{Al}_2\text{O}_3 - \text{CaO}-\text{SiO}_2$ system ($\text{CaO} > \text{Al}_2\text{O}_3$) supports this conclusion as there is a maximum in both C_p^{conf} and viscosity at the $\text{Ca}=\text{Al}(\text{atoms})$ condition.

C_p^{conf} is a measure of the energy required for the melt structure to rearrange to be in equilibrium with temperature. There is, however, no clear correlation between the magnitude of the viscosity or T_g^{12} (temperature at which viscosity is 10^{12} Pa s) and the C_p^{conf} data for the different series of compositions. There does however appear to be a good correlation between fragility and the magnitude of C_p^{conf} ; as expected from the Adam-Gibbs description of viscosity as a function of configurational entropy.

A further complexity associated with the structural role of Al^{3+} in silicate melts occurs in melts with a high Al/Si. Frequency-dependent forced oscillation measurements of the shear modulus indicate that the relaxation of the melt structure occurs faster than predicted from the Maxwell equation; with the departure from the calculated relaxation time increasing as the Al/Si increases. This suggests that the flow mechanism of the melt becomes increasingly influenced by the short lived Al-O bond lifetimes rather than being only a function of the longer Si-O lifetimes.

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