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The viscosity of Na_2O-CaO-Al_2O_3-SiO_2 melts

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Abstract: The viscosity of melts in the Na_2O-CaO-Al_2O_3-SiO_2 system follows the same trend as a function of composition as that observed in the Na_2O-Al_2O_3-SiO_2 system; in that there is a local maximum in viscosity at the condition Na_2O+CaO ~ Al_2O_3. This is despite the difference in charge of Na^+ and Ca^{2+}, the similarity in their radius, and XANES data together with MD calculations from the literature that Ca^{2+} has an affinity to form NBOs with Si^{4+} tetrahedra, thus possibly leaving Na^+ to act as a charge-balancer for Al^{3+} in tetrahedral co-ordination. The overall description of melt structure and the general flow mechanism appear to be the same for Na_2O-Al_2O_3-SiO_2 and CaO-Al_2O_3-SiO_2 melts as there are no anomalous changes in viscosity (or glass density) which could be associated with a strong preference for Ca^{2+} to form NBOs; or geometrical difficulties accompanying the need for 2 Al^{3+} tetrahedra to be charge-balanced by the same Ca^{2+} in the Al^{3+}-rich composition melts.

Key-words: melt structure, CaO, Na_2O, viscosity, peraluminous.

1. Introduction

The structure of peralkaline sodium-aluminosilicate melts is well established (*e.g.* Mysen, 1987; Stebbins, 1995); with Al^{3+} in tetrahedral co-ordination being charge-balanced by Na^+; and the remaining Na^+ acting as network modifiers. This structure must change as the number of charge-balancing Na^+ becomes less than the number of Al^{3+}. Lacy (1963) discussed a range of possible structures, and showed that the most energetically and geometrically probable structure is a charge-balanced unit consisting of a tri-cluster in which one O^{2+} is the apex of 2 Si^{4+} and one Al^{3+} tetrahedra. Alternatively, the Al^{3+} could exist in network-modifying octahedral sites (Mysen *et al.*, 1981). Such structural units would result in a decrease in viscosity. Taylor & Rindone (1970), Hunold & Brückner (1980) and Toplis *et al.* (1997a,b) observed a local maximum in viscosity at $Na^{atom} \sim Al^{atom}$ in Na_2O-Al_2O_3-SiO_2 melts. The data of Webb *et al.* (2004) showed that for $\gamma^1 = Na_2O/(Na_2O+Al_2O_3) < 0.5$, the viscosity of peraluminous melts with a constant SiO_2 content is essentially constant and independent of the Al_2O_3 content. These viscosity data support the conclusion of Toplis *et al.* (1997a,b) that Al^{3+} continues to exist in peraluminous melts in tetrahedral co-ordination in a fully polymerised melt. A small amount of higher co-ordinated Al^{3+} has been observed in NMR determinations of the structure of Na_2O-Al_2O_3-SiO_2 glasses. There is, however, not enough higher co-ordinated Al^{3+} to account for all of the Al^{3+} which has no charge-balancing Na^+ (*e.g.* Stebbins & Farnan, 1992; Poe *et al.*, 1994; Toplis *et al.*, 2000). Tri-clusters have not been observed by NMR, and modelling has shown that the peak for a tri-cluster would lie under a much larger peak for Si-O-Si bonds (Kubicki & Toplis, 2002).

The mechanism by which silicate melts flow determines their viscosity and the energy required for viscous flow to occur. While the basic flow mechanism is the exchange of Si-O bonds, variations in melt structure with composition introduce pre- and post-Si-O bond exchange structures that have varying bond energies, timescales and probabilities. In a simple Na_2O-SiO_2 melt, the flow process involves; breaking a Na-O bond; creating a 5-coordinated silicon (Si^V) using the free O-bond; destroying the Si^V co-ordination to produce a new free O-bond; creating a new Na-O bond (Stebbins, 1995).

If the melt composition is changed by adding more SiO_2, proportionally fewer Na atoms exist, the probability of creating a free O-bond by breaking a Na-O connection becomes less, and free O-bonds created by breaking an Si-O bond become more important in the pre-Si^V part of the flow mechanism (Toplis, 2001). This slows the process of flow. The replacement of some of the Na_2O by Al_2O_3 reduces the number of Na-O bonds available for the flow-model described above and increases the polymerisation of the melt. This change in structure also slows the process of flow. Webb *et al.* (2004) observed that the activation energy required for viscous flow in peralkaline Na_2O-Al_2O_3-SiO_2 melts of constant SiO_2 content remains essentially constant, independent of Na^{atom}/Al^{atom}. With increasing substitution of Al^{3+} for Na^+, there is a point at which all of the Na^+ is used to charge-balance the Al^{3+} in tetrahedral co-ordination and no NBOs (non-bridging oxygens) exist.

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[1] $\gamma = (Na_2O+CaO)/(Na_2O+CaO+Al_2O_3)$ in mole fraction; see Gwinn & Hess (1989); Toplis *et al.* (1997a,b).

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