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Pressure dependence of self-diffusion in the $NaAlO_2$-SiO_2 system: Compositional effects and mechanisms

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ABSTRACT

Molecular Dynamics (MD) simulations were used to study the relationship between structure and transport properties in five liquids ($NaAlO_2$, $Na_2Al_2SiO_6$, $NaAlSiO_4$, $NaAlSi_2O_6$, and $NaAlSi_3O_8$) in the system $NaAlO_2$-$NaAlSi_3O_8$ at temperatures ranging from 4000 to 6000 K and pressures from 0 to 55 GPa. Seventy simulations were carried out in the microcanonical ensemble using a simple pair-wise additive potential with Coulombic interaction and Born-Mayer repulsion. Detailed study of the coordination of O and network forming cations provides a master set of coordination environment or speciation curves. These master curves were applicable to all compositions and temperatures and were most explicit when compression (V_r/V; where V_r is the molar volume at a reference pressure) was used as the independent variable. The universality implied that coordination environments for network atoms O, Al, and Si depend weakly upon Si/Al, T/O, or Na/T atomic ratios for the compositions studied. Self-diffusion coefficients, computed from analysis of mean-square displacements, were used to evaluate the activation enthalpy ($H_a = E_a + PV_a$) for self-diffusion for each species. The activation energy (E_a) for Na was independent of composition, whereas E_a for O, Si, and Al increased as Si/Al increased. Activation volume (V_a) at pressure < 15 GPa was positive for Na and negative for O, Si, and Al and decreased with increasing Si/Al for all species. An extension of the Adam-Gibbs-DiMarzio configurational entropy theory taking explicit account of $^{[2]}O$ and $^{[3]}O$ mixing explained both the variation of the pressure-derivative of the shear viscosity as a function of composition and the disappearance of ''anomalous'' viscosity behavior at $P > \sim 25$ GPa for all compositions in the system $NaAlO_2$-$NaAlSi_3O_8$.