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First-principles study of self-diffusion and viscous flow in diopside ($CaMgSi_2O_6$) liquid

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ABSTRACT

We have carried out equilibrium molecular dynamics simulations of $CaMgSi_2O_6$ (diopside) liquid as a function of pressure (up to 150 GPa) and temperature (2200 to 6000 K) using density functional theory. Self-diffusion of Mg/Ca atoms decouples most from that of framework (Si/O) atoms at 2200 K and zero pressure, and all diffusivities become increasingly similar as temperature and pressure increase. The predicted temperature variations of all transport coefficients at zero pressure closely follow the Arrhenian law with activation energies of 107 to 161 kJ/mol. However, their pressure variations show significant deviations from the Arrhenius behavior. Along the 3000 K isotherm, the Si and O self-diffusivities show non-monotonic variations up to 20 GPa and then rapidly decrease upon further compression. The melt viscosity also shows a weak anomaly in the low-pressure regime before it starts to increase rapidly with pressure. Our results agree favorably with experimental observations of low-pressure non-uniform variations of Si and O self-diffusivities and viscosity. The predicted complex dynamical behavior requires pressure-volume dependent activation volumes and can be associated with structural changes occurring on compression.

Keywords: Diopside liquid, diffusion, viscosity, first-principles simulations, high pressure