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Disorder among network-modifier cations in silicate glasses: New constraints from triple-quantum ^{17}O NMR

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Abstract

The state of ordering among network-modifier cations in molten silicates has a potentially large effect on their overall configurational entropy, on free energies of mixing, and on viscosity and diffusivity. Most models of thermodynamic and transport properties assume random mixing, but there is relatively little direct microstructural information to constrain the real extent of this disorder. Two-dimensional ^{17}O NMR can produce spectra that are free of quadrupolar broadening and thus in which peak widths for non-bridging oxygen sites directly reflect the extent of disorder in the local structural environment. In this report, we describe new data from triple-quantum magic-angle-spinning (3QMAS) NMR for a series of barium and calcium silicate glasses. Results are best explained by completely random mixing of Ba and Ca, confirming conventional modeling assumptions. Other recent data show, however, that significant ordering may be present (at least at the temperature of the glass transition) for modifier cations with greater differences in size or charge, and among network-forming cations.