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Cation dynamics and premelting in lithium metasilicate (Li_2SiO_3) and sodium metasilicate (Na_2SiO_3): A high-temperature NMR study

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ABSTRACT

Premelting effects are common in silicates and have been mostly observed as significant heat capacity anomalies beginning 100 to 200 °C below congruent melting points. To assess the role of cation dynamics in this phenomenon, we collected nuclear magnetic resonance (NMR) spectra and relaxation time data to within 20 to 50 °C of the melting points of sodium metasilicate (Na_2SiO_3), which displays a large premelting effect, and isostructural lithium metasilicate (Li_2SiO_3), which displays little premelting. From ^{7}Li NMR, Li^+ site hopping is clearly observed in Li_2SiO_3 by a partial averaging of the ^{7}Li quadrupolar peak shape, requiring exchange among a few, ordered orientations of LiO_4 tetrahedra. From ^{23}Na NMR, Na^+ site hopping in Na_2SiO_3 appears to involve a more liquid-like behavior, implying exchange among many sites with different orientations in a disordered fashion. For this phase, ^{29}Si spectra indicate that in an oxidizing environment, no liquid phase is present at 20 °C below the melting point, well within the calorimetric premelting regime. However, partial averaging of the low-temperature, biaxial chemical shift powder pattern (typical of Si sites in chain silicates) occurs, suggesting some kind of extensive, librational motion of SiO_4 tetrahedra that is possibly linked to rapid Na^+ diffusion near the melting point. In contrast to the simple Li^+ diffusion in Li_2SiO_3, this process may require considerable non-vibrational energy and may thus be related to the heat capacity anomaly just prior to melting.