

## **Cation dynamics and premelting in lithium metasilicate ( $\text{Li}_2\text{SiO}_3$ ) and sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ): 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 ( $\text{Na}_2\text{SiO}_3$ ), which displays a large premelting effect, and isostructural lithium metasilicate ( $\text{Li}_2\text{SiO}_3$ ), which displays little premelting. From <sup>7</sup>Li NMR, Li<sup>+</sup> site hopping is clearly observed in  $\text{Li}_2\text{SiO}_3$  by a partial averaging of the <sup>7</sup>Li quadrupolar peak shape, requiring exchange among a few, ordered orientations of  $\text{LiO}_4$  tetrahedra. From <sup>23</sup>Na NMR, Na<sup>+</sup> site hopping in  $\text{Na}_2\text{SiO}_3$  appears to involve a more liquid-like behavior, implying exchange among many sites with different orientations in a disordered fashion. For this phase, <sup>29</sup>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  $\text{SiO}_4$  tetrahedra that is possibly linked to rapid Na<sup>+</sup> diffusion near the melting point. In contrast to the simple Li<sup>+</sup> diffusion in  $\text{Li}_2\text{SiO}_3$ , this process may require considerable non-vibrational energy and may thus be related to the heat capacity anomaly just prior to melting.