

Melting, crystallization, and the glass transition: Toward a unified description for silicate phase transitions

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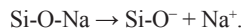
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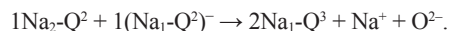
ABSTRACT

The melting mechanism of Na₂SiO₃, a crystal with pyroxene structure, includes three distinct reactions. All are driven by heating with each reaction commencing at a different temperature. The first two reactions proceed within the crystal at temperatures well below the melting point and are expressed by distinctive crystallographic, calorimetric, and Raman spectroscopic changes to the crystal. With the reactions identified and explained for Na₂SiO₃(c) and the melting mechanism elucidated, the Na₂SiO₃ system becomes the “Rosetta Stone” by which to decipher the melting mechanisms of all pyroxenes and other silicate minerals.

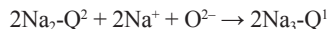
The first reaction produces itinerant Na⁺ within the crystal. Itinerancy results from dissociation of some NBO-Na bonds due to heating, with dissociation commencing at ~770 K. The reaction proceeds according to:



The Si-O⁻ moiety remains attached to its SiO₃ chain and it is charged because one of its NBO atoms has no associated Na ion. The second reaction is characterized by the appearance of a Q³ band in Raman spectra of the crystal at temperatures >770 K. It is produced via a polymerization reaction involving the Si-O⁻ species, a product of the first reaction, and a Q² species of an adjacent SiO₃ chain according to:



Na atoms are included with each Q species to preserve mass balances and (Na₁-Q²)⁻ is equivalent to the Si-O⁻ species. The produced Q³ species form cross-chain linkages that affect the crystallographic properties of the crystal. They are responsible for the cessation of thermal expansion of the Na₂SiO₃ unit cell in the **a-b** axial plane at *T* > 770 K, and the near-constancy of *a* and *b* unit-cell parameters between ~770 and ~1300 K. The presence of Q³ species in Raman spectra and the inhibited expansion in the **a-b** axial plane provide exceedingly strong evidence for this reaction. The third reaction commences at ~1200 K where Q¹ Raman band first appears. It can be produced *only* through depolymerization of Q² chains according to:



where Na⁺ and O²⁻ are itinerant species produced by the second reaction. With conversion of Q² to Q¹ species, SiO₃ chains are ruptured, long-range order is lost, and melt is produced at 1362 K.

The last two reactions proceed by nucleophilic substitution where Si centers are attacked to form fivefold-coordinated activated complexes. Si-O⁻ acts as nucleophile in the second reaction (producing Q³ species), and O²⁻ acts as nucleophile in the third reaction (producing Q¹). Taken in reverse, these mechanisms describe the formation of nuclei in crystallizing melts and in addition provide insight into the elusive changes that occur at the glass transition. Elucidation of the melting mechanism could thus provide a unified framework within which melting, crystallization, and the glass transition can be understood.

Keywords: Premelting of minerals, melting of minerals, melting mechanism, crystallization, ²⁹Si NMR and Raman spectra of glasses and melts