

Defect contributions to the heat capacities and stabilities of some chain, ring, and sheet silicates, with implications for mantle minerals

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ABSTRACT

At temperatures less than ~1500 K, previously published C_p data demonstrate that the heat capacities of orthoenstatite, proto-enstatite, diopside, and pseudowollastonite include primarily Debye type vibrational and anharmonic contributions, whereas the alkali chain, sheet, and ring silicates, Na_2SiO_3 , Li_2SiO_3 , K_2SiO_3 , and $\text{Na}_2\text{Si}_2\text{O}_5$ include a third contribution. The third contribution to C_p arises from defect formation due to the mobility Na, K, Li, and O^{2-} . The contribution becomes apparent at temperatures above 700–800 K for Na and K silicates, and above 900–1000 K for Li metasilicate. With strong thermal agitation, alkali-non-bridging oxygen (NBO) bonds are ruptured with the cations exiting their structural sites to occupy interstitial sites, thereby producing intrinsic Frenkel defects, which contribute to the C_p of the alkali silicates. The magnitudes of the C_p defect contributions correlate inversely with cation-oxygen bond strengths, as measured by bond dissociation energies. K-O and Na-O bond strengths are weak (239 and 257 kJ/mol) and defect contributions are large for these alkali chain, ring, and sheet silicates. The greater bond strength of Li-O (341 kJ/mol) correlates with a weaker defect contribution to the C_p of Li_2SiO_3 . Mg-O and Ca-O bonds are stronger still (394 and 464 kJ/mol) and no C_p defect contributions are observed for the pyroxenes and pseudowollastonite up to ~1500 K.

Above ~800 K a polymerization reaction occurs in Na_2SiO_3 , which produces some Q^3 species and free oxygen (O^{2-} or oxide ion). The polymerization reaction annihilates an oxygen structural site so that the O^{2-} produced must reside on non-structural sites thus producing intrinsic anionic defects. The same reactions likely occur in $\text{Na}_2\text{Si}_2\text{O}_5$ and K_2SiO_3 . Raman spectra of Na_2SiO_3 indicate >10% of Na^+ and ~1.7% of O^{2-} on interstitial sites at 1348 K.

Ca- and Mg-bearing mantle minerals subjected to temperature greater than ~1500 K experience the destabilizing effects of disordering (Frenkel defect formation). The minerals may respond either by changing their composition or by changing phase. An abundance of Ca and Na defects in pyroxenes, for example, likely promotes production of new components (e.g., $\text{CaAl}_2\text{SiO}_6$, $\text{NaAlSi}_2\text{O}_6$) in pyroxenes. By their production, Ca and Na defect concentrations are reduced thereby stabilizing the phases. Mg-O bond dissociation and production of intrinsic Mg^{2+} and O^{2-} point defects within olivine likely destabilize it and promote the phase transition to wadsleyite at the base of the upper mantle.

Keywords: Heat capacity of silicate minerals, Frenkel defects in silicates, cation disorder, silicate mineral stability, stability of mantle minerals