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 Cₚ 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, Na₂SiO₃, Li₂SiO₃, K₂SiO₃, and Na₂Si₂O₅ include a third contribution. The third contribution to Cᵥ arises from defect formation due to the mobility Na, K, Li, and O²⁻. 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 Cᵥ of the alkali silicates. The magnitudes of the Cᵥ 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 Cᵥ of Li₂SiO₃. Mg-O and Ca-O bonds are stronger still (394 and 464 kJ/mol) and no Cᵥ defect contributions are observed for the pyroxenes and pseudowollastonite up to ~1500 K.

Above ~800 K a polymerization reaction occurs in Na₂SiO₃, which produces some Q³ species and free oxygen (O²⁻ or oxide ion). The polymerization reaction annihilates an oxygen structural site so that the O²⁻ produced must reside on non-structural sites thus producing intrinsic anionic defects. The same reactions likely occur in Na₂Si₂O₅ and K₂SiO₃. Raman spectra of Na₂SiO₃ indicate >10% of Na⁺ and ~1.7% of O²⁻ 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., CaAl₂SiO₆, NaAlSi₂O₆) in pyroxenes. By their production, Ca and Na defect concentrations are reduced thereby stabilizing the phases. Mg-O bond dissociation and production of intrinsic Mg²⁺ and O²⁻ 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

INTRODUCTION

Richet et al. (1996) compared the temperature dependence of the heat capacities (Cᵥ) of the isostructural chain silicates Li₂SiO₃(c) and Na₂SiO₃(c), and noted that Cᵥ of Na₂SiO₃(c) was consistently greater than that of Li₂SiO₃(c), regardless of temperature. The differing values below ~600 K may be due to different Debye temperatures (θ) of the phases because θ affects mostly the low-temperature Cᵥ values of a phase. At higher temperatures, θ values have minimal effect on heat capacity at constant volume (Cᵥ), or on Cₛ in that Cᵥ approaches the universal value of 3nR regardless of θ values. Richet et al. (1996) explored these differences at both low and high temperatures using sophisticated Cᵥ models (e.g., Kieffer 1982, 1980), which included anharmonic effects, and they summarized the situation by stating that the excess Cᵥ of Na₂SiO₃ remained unexplained. We address this conundrum by evaluating previously published contributions to Cᵥ of eight chain, ring, and sheet silicates, orthoenstatite (MgSiO₃), proto-enstatite (MgSiO₃), diopside (MgCaSi₂O₆), pseudowollastonite (CaSiO₃), Na₂SiO₅, Na₂Si₂O₅, K₂SiO₃, and Li₂SiO₃. All crystals contain Q³ species (silicate chains or rings) except Na₂Si₂O₅, which is a sheet silicate consisting of Q¹ species (where Q represents a Si tetrahedron and the superscript indicates the number of bridging oxygen atoms bonded to the central Si atom of the tetrahedron).

Cations of some crystals, heated to high temperature, may become mobile through rupture of oxygen-cation bonds (e.g., Nesbitt et al. 2017; George et al. 1998) thereby contributing to disorder by forming intrinsic defects (e.g., Frenkel defects). There is overwhelming evidence for high temperature alkali and alkaline earth cation disorder in chain and ring silicates.