

Compressibility and thermal expansion of hydrous ringwoodite with 2.5(3) wt% H₂O

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ABSTRACT

Ringwoodite (γ -Mg₂SiO₄) is the stable polymorph of olivine in the transition zone between 525–660 km depth, and can incorporate weight percent amounts of H₂O as hydroxyl, with charge compensated mainly by Mg vacancies (Mg²⁺ = 2H⁺), but also possibly as (Si⁴⁺ = 4H⁺ and Mg²⁺ + 2H⁺ = Si⁴⁺). We synthesized pure Mg ringwoodite containing 2.5(3) wt% H₂O, measured by secondary ion mass spectrometry (SIMS), and determined its compressibility at 300 K by single-crystal and powder X-ray diffraction (XRD), as well as its thermal expansion behavior between 140 and 740 K at room pressure. A third-order Birch-Murnaghan equation of state (BM3 EOS) fits values of the isothermal bulk modulus $K_{T0} = 159(7)$ GPa and $(dK_T/dP)_{P=0} = K' = 6.7(7)$ for single-crystal XRD; $K_{T0} = 161(4)$ GPa and $K' = 5.4(6)$ for powder XRD, with $K_{T0} = 160(2)$ GPa and $K' = 6.2(3)$ for the combined data sets. At room pressure, hydrous ringwoodite breaks down by an irreversible unit-cell expansion above 586 K, which may be related to dehydration and changes in the disorder mechanisms. Single-crystal intensity data were collected at various temperatures up to 736 K, and show that the cell volume $V(\text{cell})$ has a mean thermal expansion coefficient α_{V0} of $40(4) \times 10^{-6}/\text{K}$ (143–736 K), and $29(2) \times 10^{-6}/\text{K}$ (143–586 K before irreversible expansion). $V(\text{Mg})$ have α_0 values of $41(3) \times 10^{-6}/\text{K}$ (143–736 K), and $V(\text{Si})$ has α_0 values of $20(3) \times 10^{-6}/\text{K}$ (143–586 K) and $132(4) \times 10^{-6}/\text{K}$ (586–736 K). Based on the experimental data and previous work from ²⁹Si NMR, we propose that during the irreversible expansion, a small amount of H⁺ cations in Mg sites transfer to Si sites without changing the cubic spinel structure of ringwoodite, and the substituted Si⁴⁺ cations move to the normally vacant octahedral site at (½, ½, 0). Including new SIMS data on this and several Mg-ringwoodite samples from previous studies, we summarize volume-hydration data and show that the Mg²⁺ = 2H⁺ dominates up to about 2 wt% H₂O, where a discontinuity in the volume vs. H₂O content trend suggests that other hydration mechanisms become important at very high H₂O contents.

Keywords: Compressibility, hydrous ringwoodite, irreversible thermal expansion