

High-temperature structural behaviors of anhydrous wadsleyite and forsterite

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ABSTRACT

The thermal expansion of anhydrous Mg_2SiO_4 wadsleyite and forsterite was comprehensively studied over the temperature ranges 297–1163 and 297–1313 K, respectively, employing X-ray powder diffraction. Experiments were carried out with two separately synthesized samples of wadsleyite (numbered z626 and z627), for which room temperature unit-cell volumes differed by 0.05%, although the determined thermal expansions were identical within error. The high-temperature thermal expansions of wadsleyite and forsterite were parameterized on the basis of the first-order Grüneisen approximation using a Debye function for the internal energy. Values for hypothetical volume at $T = 0$ K, Debye temperature and Grüneisen parameter are 536.86(14) Å³, 980(55) K, 1.28(2) and 537.00(13) Å³, 887(50) K, 1.26(1) for z626 and z627, respectively, with the bulk modulus fixed to a literature determination of 161 GPa. For forsterite, the respective values are 288.80(2) Å³, 771(9) K, and 1.269(2) with a constrained bulk modulus of 125 GPa. These quantities are in good agreement with literature values obtained independently from sound velocity and heat capacity measurements, giving strong support to the applicability of Grüneisen theory in describing the thermal expansion of wadsleyite and forsterite. In addition, high-temperature structural variations were determined for wadsleyite from Rietveld analysis of the X-ray diffraction data. The pronounced anisotropy in thermal expansion of wadsleyite with a more expandable *c*-axis, similar to the compressional anisotropy, arises from specific features of the crystal structure consisting of the pseudolayers of MgO_6 octahedra parallel to the *a*-*b* plane with cross-linking Si_2O_7 dimers along the *c*-axis. Although anisotropic compression and expansion originate from the same structural features, the details of structural changes with pressure differ from those caused by temperature. The longest Mg-O bonds, which are roughly parallel to the *c*-axis in all three octahedral sites of wadsleyite, dominate the compression, but these bonds do not exhibit the largest expansivities.

Keywords: Forsterite, wadsleyite, thermal expansion, Mg_2SiO_4 polymorphs, powder diffraction