High-temperature structural behaviors of anhydrous wadsleyite and forsterite

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Abstract

The thermal expansion of anhydrous Mg$_2$SiO$_4$ 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) Å$^3$, 980(55) K, and 1.28(2) and 537.00(13) Å$^3$, 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) Å$^3$, 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 octahedra parallel to the a-b plane with cross-linking Si$_2$O$_5$ 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$_2$SiO$_4$ polymorphs, powder diffraction

Introduction

The Mg$_2$SiO$_4$ polymorphs, forsterite and wadsleyite, are major mineral components within the Earth’s upper mantle and transition zone. The olivine-wadsleyite transition of (Mg,Fe)$_2$SiO$_4$ is considered to cause a seismically detectable discontinuity in elastic properties at approximately 410 km depth (e.g., Ringwood 1975). Precise information on the physical properties and stability fields of wadsleyite and olivine at high temperatures and pressures is of primary importance to geophysics. To calculate stability fields and seismic wave velocities of mantle minerals, thermodynamic parameters are often refined from high-pressure experimental phase relations and equation of state data. This permits phase boundaries and seismic wave velocities to be determined at conditions beyond the range of experimental measurements and allows multiple studies to be compared and uncertainties in pressure and temperature to be addressed. Such calculations are far more constrained if parameters such as thermal expansivity and bulk modulus can be accurately determined independently. Thermal expansion measurements provide particularly useful constraints on elastic properties due to very low-experimental uncertainties. However, there is significant divergence between results of previous thermal expansion studies performed on Mg$_2$SiO$_4$ polymorphs and a strong divergence in some equations used to parameterize these measurements when extrapolated beyond the measured range.

The thermal expansivity of forsterite has been previously measured up to its melting point of approximately 2150 K by Bouhifd et al. (1996) employing energy-dispersive powder X-ray diffraction. Moreover, Bouhifd et al. (1996) made a comprehensive comparison with results of previous high-temperature diffraction investigations of Skinner (1962), Takeuchi et al. (1984), Vokurka and Rieder (1987), Kajiyoshi (1986), and dilatometry studies of Suzuki et al. (1984), Matsui and Manghnani (1985), and White et al. (1985). Good agreement was observed with the data of Kajiyoshi (1986) and with values optimized by Gillet et al. (1991) and Fei and Saxena (1986) from various high-temperature data. The recent work of Ye et al. (2009) reports expansivity data for anhydrous forsterite up to 889 K obtained using single-crystal X-ray diffraction. Both Bouhifd et al. (1996) and Ye et al. (2009) describe the thermal dependency of the volumetric thermal expansion using linear functions.