

Thermal expansivities of stishovite and akimotoite by high-pressure Raman and high-temperature X-ray diffraction methods

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High-pressure high-temperature experiments suggest that SiO₂ stishovite and MgSiO₃ akimotoite are constituents of subducted oceanic plate and continental crust. Because they are unstable at 1 atm and at high temperatures, it is difficult to directly measure their thermal expansivities. Therefore, they have been poorly constrained. In this study, we have determined thermal expansivities of SiO₂ stishovite and MgSiO₃ akimotoite by theoretical calculation based on high-pressure Raman spectroscopic data and high-temperature X-ray diffraction measurements.

High-pressure Raman spectroscopy was performed in a pressure range from 1 atm to 10 GPa using a diamond anvil cell and a micro-Raman spectrometer. SiO₂ stishovite and MgSiO₃ akimotoite samples were synthesized at high pressure and high temperature. The thermal Gruneisen parameters were obtained from weighted average of the mode-Gruneisen parameters which were determined from pressure shifts of Raman peaks. Thermal expansivities were calculated from the Gruneisen equation. The heat capacities at constant volume (C_V) were calculated using lattice vibrational model. High-temperature X-ray diffraction measurements of MgSiO₃ akimotoite were performed in a temperature range of 293.8 - 773 K. The thermal expansivity was determined from the temperature dependence of the unit cell volume.

Obtained thermal expansivities were expressed using the polynomial of temperature: $\alpha = a + bT + cT^{-1} + dT^{-2}$. The coefficients for SiO₂ stishovite and MgSiO₃ akimotoite were determined to be $a = 1.85E-5$, $b = 3.25E-9$, $c = -2.41E-3$, $d = -1.11E-1$, and $a = 2.53E-5$, $b = 7.62E-9$, $c = -8.63E-4$, $d = -5.51E-1$, respectively.

The thermal expansivity of SiO₂ stishovite in this study is smaller than that obtained from high-pressure high-temperature in situ XRD measurements by Nishihara et al. (2005), and agrees with that obtained from optimization of thermodynamic data assessment by Mao et al. (2001). The heat capacity at constant pressure (C_P) calculated using the thermal expansivity by Nishihara et al. (2005) is 5 % larger than that measured by thermal relaxation method by Akaogi et al. (2011). On the other hand, C_P calculated using the thermal expansivity of this study shows good agreement with Akaogi et al. (2011). Therefore, our thermal expansivity of stishovite is internally consistent with the measured heat capacity data.

Our thermal expansivity of MgSiO₃ akimotoite derived by the theoretical method is closer to those determined by high-temperature XRD measurements in this study and Ashida et al. (1988) rather than that of Wang et al. (2004) obtained from high-pressure high-temperature in situ XRD measurements. This result suggests that the thermal expansivity of MgSiO₃ akimotoite is larger than previously reported values.

Keywords: akimotoite, stishovite, thermal expansivities, high-pressure Raman spectroscopy, high-temperature X-ray diffraction measurements