

## **Experimental and thermodynamic investigations on the stability of $\text{Mg}_{14}\text{Si}_5\text{O}_{24}$ anhydrous phase B with relevance to $\text{Mg}_2\text{SiO}_4$ forsterite, wadsleyite, and ringwoodite**

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### **ABSTRACT**

High-pressure high-temperature phase relation experiments in  $\text{Mg}_{14}\text{Si}_5\text{O}_{24}$  were performed using a 6–8 multi-anvil high-pressure apparatus in the pressure range of 12–22 GPa and temperature range of 1673–2173 K. We first found that  $\text{Mg}_{14}\text{Si}_5\text{O}_{24}$  anhydrous phase B (Anh-B) dissociates to  $\text{Mg}_2\text{SiO}_4$  wadsleyite (Wd) and MgO periclase (Per) at about 18 GPa and 1873 K. From the results of the high-pressure experiments, the phase boundaries of  $5 \text{ Mg}_2\text{SiO}_4$  forsterite (Fo) + 4 Per = Anh-B and Anh-B = 5 Wd + 4 Per were determined. In addition, the isobaric heat capacity ( $C_p$ ) of Anh-B was measured by differential scanning calorimetry in the temperature range of 300–770 K and the thermal relaxation method using a Physical Property Measurement System (PPMS) in the range of 2–303 K. From the measured low-temperature  $C_p$ , the standard entropy ( $S_{298.15}^\circ$ ) of Anh-B was determined to be 544.4(2) J/(mol·K). We also performed high-temperature X-ray diffraction measurements in the range 303–773 K to determine the thermal expansivity ( $\alpha$ ) of Anh-B. The obtained  $C_p$  and  $\alpha$  were theoretically extrapolated to higher temperature region using a lattice vibrational model calculation partly based on Raman spectroscopic data. Thermodynamic calculations by adopting the thermochemical and thermoelastic data for Anh-B obtained in this study and the estimated formation enthalpy for Anh-B of –13 208 kJ/mol gave phase equilibrium boundaries for  $5 \text{ Fo} + 4 \text{ Per} = \text{Anh-B}$  and  $\text{Anh-B} = 5 \text{ Wd} + 4 \text{ Per}$  that were consistent with those determined by the present high-pressure high-temperature experiments. The results clarified that, in the  $\text{Mg}_{14}\text{Si}_5\text{O}_{24}$  system, Anh-B is stable between 12 and 18 GPa at the expected temperatures of the Earth's mantle.

**Keywords:** Anhydrous phase B, phase boundary, heat capacity, entropy, thermal expansivity, Raman spectrum, wadsleyite, ringwoodite