Determination of low-temperature heat capacity and standard entropy of $Mg_{14}Si_5O_{24}$ anhydrous phase B

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It is expected that $Mg_{14}Si_5O_{24}$ anhydrous phase B (Anh-B) forms in the Earth's mantle by the reaction $5Mg_2SiO_4$ forsterite (Fo) + $4MgO = Mg_{14}Si_5O_{24}$ Anh-B when SiO_2 component in olivine and pyroxenes dissolves selectively into fluid and the residue is rich in MgO component. Entropy of Anh-B, which is needed to examine its thermodynamical stability, has not been determined experimentally yet. In this study, low-temperature heat capacity (Cp) was measured using PPMS equipment and standard entropy at 298 K was determined from the obtained heat capacity. The measured low-temperature Cp was also applied to modeling of a vibrational density of state used for Kieffer model calculation of the high-temperature Cp.
High-pressure synthesis of Anh-B was performed using a Kawai-type multi-anvil high-pressure apparatus. The starting material of the mixture of Fo and MgO (5:4 in mole ratio) was kept at 15 GPa and 2073-2273 K for 3 hours. After quenching, the sample was decompressed to ambient pressure. Micro-focused X-ray diffractometry and SEM-EDS analysis confirmed that the recovered samples were the single phase of Anh-B. Low-temperature Cp was measured in the temperature range of 2-307 K and with the step of about 2 K using PPMS (Quantum Design) by the thermal relaxation method. The bottom of the cylindrical samples was polished into very flat for better thermal contact with a heating stage. The total weight of the samples used for the PPMS measurement was 10.988 mg.
Low-temperature Cp was measured with the accuracy of about 0.3% at each measurement temperature. The Cp around 300 K obtained in this study is the same as that determined by our DSC measurement. This indicates the validity of the present measurement. By integrating Cp/T from 0 to 298 K using the obtained Cp, the standard entropy at 298 K was determined to be 554.17(1) J/mol.K. This value is smaller than 561.2 J/mol.K obtained by ab initio calculation of Ottonello et al. (2010) and is in good agreement with 547.3 J/mol.K estimated from entropies of the constituent oxides by Ganguly and Frost (2006). In addition, by the Kieffer model calculation using a vibrational density of state model which reproduces the low-temperature Cp measured in this study, the high-temperature Cp was extrapolated above 800 K at which Cp cannot be measured due to the collapse of the crystal structure by heating at 1atm. The Cp was obtained to be $Cp(T)=6.624\times10^{2}+2.123\times10^{4}T^{-0.5}-4.827\times10^{6}T^{-2}+2.221\times10^{9}T^{-3}-1.061\times10^{-1}T-3.643\times10^{5}T^{-1}$ in the range from 300 to 2000 K.

Keywords: anhydrous phase B, heat capacity, entropy, thermodynamical stability, lattice vibrational model calculation

