

Redetermination of enthalpy and reassessment of thermodynamic data set for SiO₂ stishovite

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SiO₂ stishovite (St) is a high pressure polymorph of SiO₂ and believed to be one of major constituent minerals of the subducted slab. Thermodynamic parameters of SiO₂ St used for thermodynamic examination of the stability field of SiO₂ St or a phase assemblage containing it have not yet been constrained well. In particular, standard enthalpy of formation largely affects a position of a calculated phase boundary. Since previous enthalpy measurement of SiO₂ St by Akaogi et al. (1995) was performed using the differential drop-solution calorimetry, measured enthalpy included heat effect from not only SiO₂ St sample but also silica capillary tubes as a container and Pt chips as a weight. In this study, heat effect of only SiO₂ St was measured by the drop-solution calorimetry. Furthermore, to give an internally-consistent thermodynamic data set, high temperature heat capacity of SiO₂ St was reassessed based on an equation of state (EoS).

SiO₂ St samples for the drop-solution calorimetry were synthesized by heating reagent grade SiO₂ quartz (Qz) at 15 GPa and 1673 K using a Kawai-type high-pressure apparatus at Gakushuin University. It was confirmed that synthesized samples were single phase of SiO₂ St by micro-focused X-ray diffraction method. The drop-solution calorimetry was performed using a Calvet-type high-temperature calorimeter (SETARAM, HT-1000). A sintered SiO₂ St sample with weight of 3-6 mg was dropped directly into lead borate solvent (2PbO·B₂O₃) placed in the calorimeter at 978 K. Drop-solution enthalpy (ΔH_{d-s}), which is the summation of heat content from room temperature to 978 K and solution enthalpy at 978 K was measured. To hasten the solution of the samples, the solvent was stirred by bubbles of Ar gas.

In the reassessment of isobaric heat capacity (Cp) of SiO₂ St, isochoric heat capacity (Cv) was calculated using the Kieffer model with adjusting a VDoS model to reproduce low-temperature Cp data measured by Akaogi et al. (2011) and Yong et al. (2012). The anharmonic effect was calculated using isothermal bulk modulus, its temperature derivative and thermal expansivity derived from the EoS of Wang et al. (2012). From the average of six data, ΔH_{d-s} (SiO₂ St) was determined to be 3.8 ± 0.4 kJ/mol. This value is slightly larger than 3.0 ± 0.9 kJ/mol measured by Akaogi et al. (1995), though within the experimental errors. The difference between ΔH_{d-s} (SiO₂ Qz) [40.1 ± 0.4 kJ/mol, Akaogi et al. (1995)] and the present ΔH_{d-s} (SiO₂ St) gives the phase transition enthalpy from Qz to St of 36.2 ± 0.5 kJ/mol which provides the standard enthalpy of formation from elements of -874.5 ± 0.5 kJ/mol. The calculated Cp of SiO₂ St agrees well with high-temperature Cp data measured by Akaogi et al. (1995). However, our Cp extrapolated to higher temperature region than 700 K shows slightly larger value (5% at 2000 K) than that by Cp equation of Akaogi et al. (2011). Thermodynamically calculated coesite-stishovite phase equilibrium boundary using the reassessed thermodynamic data set for SiO₂ St is consistent with the experimentally determined phase boundaries by Zhang et al. (1996) and Ono et al. (2017a). When the new thermodynamic data set for SiO₂ St is applied to thermodynamic calculation of the Mg₂SiO₄ ringwoodite (Rw) + SiO₂ St = 2MgSiO₃ akimotoite boundary, the phase transition pressure at 1000 K is obtained to be 18 GPa and it is about 3 GPa lower than experimentally determined boundaries (e.g., Ono et al., 2017b), implying that the meta-stable region of Rw + St assembly is relatively extensive.

Keywords: SiO₂ stishovite, thermodynamics, enthalpy, heat capacity, equation of state, phase equilibrium boundary