Calorimetric study of perovskite solid solutions in the CaSiO3-CaGeO3 system

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In this study, drop-solution calorimetry of perovskite solid solutions in the CaSiO3-CaGeO3 system at 973 K with 2PbO.B2O3 solvent was made to obtain the formation enthalpy for CaSiO3 perovskite. The drop-solution enthalpy for CaSiO3 perovskite was estimated to be 0.2+/-4.4 kJ/mol from a linear extrapolation of the drop-solution enthalpy data for CaSiO3-CaGeO3 perovskite solid solutions. Combining with thermochemical data for CaSiO3 wollastonite, the formation enthalpy for CaSiO3 perovskite from CaO (lime) + SiO2 (quartz) was obtained as 14.8+/-4.4 kJ/mol.

It is accepted that CaSiO3 perovskite is an important mineral constituent in the Earth's lower mantle. CaSiO3 perovskite is stable only at high-pressure and is not quenchable to ambient pressure. Therefore, it is impossible to make a calorimetric measurement of CaSiO3 perovskite directly. Calcium germanate, CaGeO3 assumes the perovskite structure at high-pressure as well as CaSiO3. Fortunately, the CaGeO3 perovskite can be quenched to ambient condition. In this study, drop-solution calorimetry of perovskite solid solutions in the CaSiO3-CaGeO3 system was made to obtain the formation enthalpy for CaSiO3 perovskite.

Perovskite solid solutions were synthesized using a multi-anvil high-pressure apparatus at Gakushuin University. Starting materials were wollastonite solid solutions in the CaSiO3-CaGeO3 system. Four perovskite samples which have compositions of CaGeO3, Ca(Si0.1Ge0.9)O3, Ca(Si0.2GeO0.8)O3, Ca(Si0.3Ge0.7)O3 were prepared. XRD and EPMA results showed that the synthesized samples contained only the perovskite phase and were homogeneous. Drop-solution calorimetry of the perovskite samples was performed by using "Ultrasensitive calorimeter", which has six time higher sensitivity than that of a regular Calvet type calorimeter. Powdered sample was pressed into pellet (2-3 mg for each drop) and was dropped from room temperature into molten 2PbO.B2O3 solvent at 973 K.

The drop-solution enthalpies for perovskite solid solutions were obtained as 62.70+/-1.98 kJ/mol, 57.56+/-1.02 kJ/mol, 50.17+/-0.91 kJ/mol and 44.20+/-1.12 kJ/mol for CaGeO3, Ca(Si0.1Ge0.9)O3, Ca(Si0.2GeO0.8)O3 and Ca(Si0.3Ge0.7)O3, respectively . The result shows that the drop-solution enthalpy decreases linearly with increasing CaSiO3 component. The drop-solution enthalpy for CaSiO3 perovskite can be estimated to be 0.2+/-4.4 kJ/mol from linearly extrapolating obtained drop-solution enthalpies of perovskite solid solutions by assuming ideal solid solution. Combining with thermochemical data for CaSiO3 wollastonite, the formation enthalpy for CaSiO3 perovskite from CaO (lime) + SiO2 (quartz) was estimated as 14.8+/-4.4 kJ/mol.

The obtained formation enthalpy for CaSiO3 perovskite was applied to thermodynamic calculation of high-pressure phase equilibrium boundary between CaSiO3 perovskite and Ca2SiO4 + CaSi2O5 phases. Calculations were made for two reference points by high-pressure experiments. By considering those calculated phase boundaries, the phase equilibrium boundary might be between 11.5 and 12.5 GPa around 1500 K.