Calorimetry of high pressure phases of CaSiO3 and CaSi2O5-CaTiSiO5 systems and high pressure phase relations of CaSiO3

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Low-pressure polymorphs of CaSiO3 are rock forming minerals in the Earth' crust, and it is accepted that high-pressure CaSiO3 perovskite is one of constituents of the lower mantle. Phase relations of CaSiO3 have been studied by high-pressure experiment, but have not yet been fully studied by thermodynamics approaches. With increasing pressure, CaSiO3 transforms as pseudowollastonite (pwo) - wollastonite (wo) - walstromite (wal) - CaSi2O5 titanite (tit) + Ca2SiO4 larnite (lar) - CaSiO3 perovskite (pv), where ( ) denote abbreviations of the phases. In this study, these polymorphs were synthesized and enthalpies of the phases were measured. Then high- pressure phase equilibrium relations of CaSiO3 ware calculated.

Among the polymorphs in CaO-SiO2 system, CaSi2O5 (tit), Ca2SiO4 (lar), CaSiO3 (pv) cannot be quenched at 1 atm. Drop solution enthalpy of CaSiO3 (pv) was estimated from those of perovskite solid solutions of CaSiO3 - CaGeO3 system by Kojitani et al. (2001). In this study, CaSiO3 (pwo), (wo), (wal) and titanite solid solutions of CaSi2O5 - CaTiSiO5 systems were synthesized and the drop solution enthalpy of them were measured. Drop solution enthalpy of CaSi2O5 (tit) were estimated from those of titanite solid solutions of CaSi2O5 - CaTiSiO5 system by extrapolation.

CaSiO3(pwo) was synthesized from an equimolar mixture of CaCO3 and SiO2 H2O11wt% by palletizing and heating at 1350 C for 30 h. CaSiO3 (wo) was synthesized by heating at 950 C for 73 hours. CaSiO3 (wal) was synthesized from CaSiO3 (pwo) by keeping at 5 GPa, 1200 C for 2 hours. Titanite solid solutions of CaSi2O5 - CaTiSiO5 system were synthesized from glasses of the same compositions by keeping at 11 GPa, 1300 C for 4 hours. CaTiSiO5 (tit) was synthesized from the glass by keeping at 1100 - 1050 C for 124 hours. It was confirmed that the synthetic samples were single phase materials by using a powder X ray diffractometer.

The drop solution calorimetry was performed by using a Calvet type calorimeter kept at 978 K with 2PbO B2O3 solvent at Gakushuin University. Ti-contained samples are generally not easily dissolved in the solvent. Therefore Ar bubbling method was tried to quickly dissolve the samples in the solvent.

Transition enthalpies were estimated from the drop solution enthalpies, and phase boundaries were calculated. CaSiO3 (pv) by Kojitani et al. (1994) was used in the calculation. Comparing the calculated results in this study with results of high-pressure experiments by Huang and Wyllie (1975) and Gasparik et al. (1994), it is suggested that the results in study agree with those by Huang and Wyllie (1975), but are not in harmony with Gasparik et al. (1994). It is suggested that stability field of CaSiO3 (pv) is placed at higher pressure than that of Gasparik et al. (1994).