Calorimetry of Al containing MgSiO3 perovskite with oxygen vacancy

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It is thought that MgSiO3 perovskite is main host phase for Al component in the Earth's lower mantle. Recently, in our high-pressure experiments along the MgSiO3-MgAlO2.5 join, it was found that the synthesis of Al containing MgSiO3 perovskite with oxygen vacancy is possible. That means a substitution reaction (1) 2Si = 2Al + Vo (oxygen vacancy) is needed to consider the Al substitution in MgSiO3 perovskite as well as the Tschermakitic substitution reaction (2) Mg + Si = 2Al. To discuss the stability of such an Al containing MgSiO3 perovskite with oxygen vacancy thermodynamically, its thermochemical data is desired. In this study, drop-solution calorimetry of the perovskite was made and then a formation enthalpy of it was determined.

Samples for a calorimetric measurement were synthesized at 26 GPa and 1873 K by using 6-8 multi anvil type high-pressure apparatus at State University of New York at Stony Brook. The mixture of MgO, Al2O3 and SiO2 with the bulk composition of MgSi0.9Al0.1O2.95 was used as a starting material. It was confirmed that synthetic samples were a single phase of perovskite by using a micro focus X-ray diffractometer and EPMA. The drop-solution calorimetry was performed by using the Ultrasensitive calorimeter with 2PbO.B2O3 solvent (973 K) at University of California at Davis. A sample of 1-1.5 mg was dropped into the calorimeter at one run, where the samples were poly crystalline without crushing to prevent their amorphization. Calibration of the calorimeter was done by transposed temperature drop calorimetry of alpha-Al2O3 (1 mg). Drop-solution calorimetry of MgSiO3 orthoenstatite was also performed just before the perovskite sample runs to confirm the suitability of used calibration factors.

The drop-solution enthalpy for MgSiO3 orthoenstatite was obtained as 108.2+/-0.7 kJ/mol (8 data). It shows good agreement with 110.52+/-2.74 kJ/mol by Ito et al. (1990). The observed drop-solution enthalpies for MgSi0.9Al0.1O2.95 perovskite were –9.33, 5.96 and 14.52 kJ/mol. Only one sample indicated an exthothermic enthalpy of –9.33 kJ/mol. It is presumed that considerably shorter heating duration of 15 minutes during a high-pressure synthesis than 4 to 5 hours for other two samples caused the exthothermic enthalpy. Therefore, from the average by excluding the exthothermic data, drop-solution enthalpy of the perovskite was obtained as 10.24+/-4.28 kJ/mol. By using drop-solution enthalpy data for MgO, Al2O3 and SiO2 (alpha-quartz) from previous works, the formation enthalpy from oxides for the perovskite at 298 K is determined to be 66.82+/-4.32 kJ/mol. A drop-solution enthalpy for Mg0.95Si0.95Al0.1O3 perovskite with the substitution reaction (2), which has the same Al content as the perovskite described above, has been obtained as 16.44+/-0.92 kJ/mol by Akaogi and Ito (1999), namely a formation enthalpy of 60.76+/-1.07 kJ/mol. The larger formation enthalpy for MgSi0.9Al0.1O2.95 perovskite than that for Mg0.95Si0.95Al0.1O3 perovskite indicates that the former is less stable than the latter at the ambient condition.