

Formation enthalpies and thermodynamic stability of high-pressure ABO₃ phases with perovskite structure

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Perovskite has a dense structure suitable to high-pressure conditions, as recognized from the fact that MgSiO₃-rich perovskite is the most abundant mineral in the lower mantle. Many ABO₃ compounds with various structures other than perovskite transform to perovskite structure at high pressures. We have measured enthalpies of formation of various ABO₃ perovskites using calorimetric techniques. In this study, we have measured enthalpies of formation for SrGeO₃ and CaGeO₃ perovskites. Using the data with other published data, we have examined relationship between enthalpies of formation and ionic radii of A²⁺ and B⁴⁺ cations. We have also examined high-pressure phase transitions in SrSiO₃ and found a new high-pressure phase with perovskite structure.

Using multianvil apparatus, SrGeO₃ phase II and perovskite and CaGeO₃ garnet and perovskite were synthesized at 3-15 GPa and 1000 C. Enthalpies of drop-solution of the above samples into lead borate solvent were measured using a Calvet-type microcalorimeter operated at 705 C. Using the calorimetric data, enthalpies of formation of the perovskites from mixed oxides (AO + BO₂) were obtained. Phase relations in SrSiO₃ were also examined using multianvil apparatus and diamond anvil cell up to about 25 GPa and 1500 C.

The measured enthalpies indicated that enthalpies of transitions of SrGeO₃ pseudowollastonite-II and II-perovskite were 2.3 and 49.4 kJ/mol, respectively, and those of CaGeO₃ wollastonite-garnet and garnet-perovskite were 3.6 and 39.6 kJ/mol, respectively. The enthalpies of formation of SrGeO₃ and CaGeO₃ perovskites from SrO (or CaO) + GeO₂ rutile were 39.3 and 17.8 kJ/mol, respectively. Combining the above data with published data on A²⁺B⁴⁺O₃ perovskites (A=Mg, Fe, Mn, Cd, Ca, Sr, Ba; B=Si, Ge, Ti, Zr) stable at atmospheric and high pressures, we have found a relationship between enthalpies of formation of the A²⁺B⁴⁺O₃ perovskites and ionic radii of A²⁺ and B⁴⁺. The enthalpies of formation of perovskites change systematically with changes of ionic radii of A²⁺ and B⁴⁺ from the lowest enthalpy (BaTiO₃) to the highest (MgSiO₃). The enthalpies of formation increase with decrease of tolerance factor ((R_A+R_O)/2(R_B+R_O)) of perovskite structure in different way for each B⁴⁺ cation. Above about 20 GPa at 1200-1500 C, SrSiO₃ crystallized to a high-pressure phase which was converted to an amorphous phase upon decompression. In situ X-ray observation indicated that this phase has a perovskite structure at high pressure. The stability of SrSiO₃ perovskite is compatible with the general trend of enthalpies of formation of perovskites described above.