Formation of the perovskite solid solution in the system of CaSiO$_3$-MnSiO$_3$ at high pressure and high temperature

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Introduction

According to the earth modeling PREM, the lower mantle continues from 660 km down to the core–mantle boundary, located at approximately 2900 km depth. It is making up 82% of the volume and 65% of the mass of the earth. High pressure and high temperature experiments indicate that the most probable mineral phases in lower mantle conditions were mainly: (Mg,Fe)SiO$_3$–perovskite (Mg-Pv, ~70vol%), (Mg,Fe)O-magnesiowüstite (Mw, ~20vol%), CaSiO$_3$-perovskite (Ca-Pv, ~5%). CaSiO$_3$ is believed to be the third important major phase in the lower mantle, for further understanding of the deep earth, it is necessary to pay more attention on Ca-Pv. An important note about CaSiO$_3$-perovskite is stable in the pressure range of the Earth’s mantle. While (Mg,Fe)SiO$_3$-perovskite transfers to mineral of post-perovskite structure, the structure of CaSiO$_3$-perovskite will keep just only some change from the lattice parameter. Another interesting point should be note on the Ca-Pv, is the low solubility of Ca in (Mg,Fe)SiO$_3$-perovskite, Fe in CaSiO$_3$-perovskite. Recently, our team has found that MnSiO$_3$ has the perovskite structure [1], and it seems stable under the lower mantle temperature pressure conditions. Except those chemically pure minerals, solid solutions seem to be more common in the lower mantle as (Mg,Fe)SiO$_3$-perovskite. To obtain a more realistic picture of the lower mantle, therefore, it is necessary to consider the minerals as solid solutions, existing in nature. From the foregoing knowledge, both of CaSiO$_3$ and MnSiO$_3$ have perovskite structure at lower mantle condition; it is interesting to study the phase relation of the two perovskite.

Experimental

In CaSiO$_3$-MnSiO$_3$ binary system, gels with 10%, 25%, 50%, 75% of CaSiO$_3$ contents were synthesized by conventional sol-gel method. Then we heated them at 1023 K for 3 hours under the controlled oxygen fugacity in order to keep Mn$^{2+}$. We finally made starting materials with desired chemical compositions.

High pressure conditions were generated using diamond anvil cells (DAC) with 200 or 300 µm culets diamond anvils. Sample was sandwiched between NaCl pellets and loaded into the DAC. NaCl works not only as a pressure transmitting materials but also as a thermal insulator. Small amount of gold powder was added to the sample as internal pressure marker. The diameter of a sample chamber in a pre-indentend Re gasket is 80-100 µm. Samples in a DAC are heated from both sides with an YLF or YAG laser. The synthesis conditions were at pressures of 35-50 GPa and at temperatures of 1500-1800K, keeping the heating duration in between 40-120 min. Monochromatic synchrotron X-ray diffraction experiments were performed at AR-NE1A of Photon Factory KEK. X-ray diffraction patterns were measured by an angle dispersive method using an imaging plate (IP). Two dimensional IP data were integrated along Debye-Scherrer rings and converted to one dimensional data by the software IPAnalyzer [2]. Chemical analysis was conducted for recovered samples by FE-SEM with the EDS detector in Hokkaido University.

Results and Discussion

The symmetry of the perovskite is cubic when the MnSiO$_3$ content in the solid solution varies from 0% to 50%, and the perovskite has the orthorhombic structure when the MnSiO$_3$ content varies from 75% to 100%. The author’s present experiments on the CaSiO$_3$-MnSiO$_3$ system give out an exciting result, which shows that this system almost bears complete solid solubility in the entire composition range with the perovskite structure. Because of the large cationic size of Ca$^{2+}$, and the quite stringent cubic perovskite structure of CaSiO$_3$, (Mg,Fe)SiO$_3$ cannot be the ideal candidate for substitution by Ca$^{2+}$. But for MnSiO$_3$ side, this orthorhombic perovskite just very little modified from the cubic may cause the possibility to form the solid solution with CaSiO$_3$ cubic perovskite.

References


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