

Determination of Transition Boundary between Garnet and Perovskite in CaGeO₃

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It is known that some ABO₃ compounds are excellent analogues of MgSiO₃ or CaSiO₃, which are major constituents of the Earth's mantle. Calcium germanate (CaGeO₃) exhibits a sequence of phase transitions from a pyroxenoid to a tetragonal garnet phase, and subsequently to an orthorhombic perovskite phase. The phase boundaries in CaGeO₃ have been also used as a pressure calibration point at high temperatures in high-pressure experiments, such as for SiO₂ and Mg₂SiO₄. Therefore, the precise phase boundary of CaGeO₃ needs to be determined. The transition pressure of CaGeO₃ has been investigated in static high-pressure experiments using quench [1] and in situ methods [2]. According to previous high-pressure experiments, the transition pressure is ~6 GP and this boundary had a negative slope. In contrast, Ross et al. [1] also estimated the value of dP/dT slope of this transition using calorimetry data, and calculated the slope to be 2-3 times more negative than the value determined from high-pressure experiments. Therefore, we reinvestigated the dP/dT slope of garnet-perovskite transition in CaGeO₃ using the high-pressure experiments.

In this study, the use of a multi-anvil high-pressure system combined with a synchrotron radiation source made it possible to acquire precise data from samples under high-pressure and high-temperature conditions [3]. The starting material was CaGeO₃ wollastonite, synthesized at 1473 K for 5 hours from a starting mixture composed of finely powdered CaCO₃ and GeO₂. In our experiments, pressure was applied to the sample by generating an anvil load from the desired oil pressure in the press. The sample was then slowly heated to avoid the temperature overshoot until it reached the desired temperature for a given oil pressure. After reaching the required pressure and temperature, we performed in situ measurements using the synchrotron X-rays. The duration of heating was 0.5-2.0 hours. At the end of the experimental runs, the sample was quenched by cutting off the electrical power. This heating procedure was the same as that used in typical quench experiments.

We performed approximately 30 experimental runs, and the boundary determined in this study is in general agreement with that reported in previous high-pressure experiments [1,2]. However, the value of our dP/dT slope was 2-3 times more negative than that in previous experiments [3]. The calculated value of the dP/dT slope using calorimetry data [1] is consistent with our value of dP/dT [3]. It is likely that the discrepancy between previous and our high-pressure experiments is due to the kinetics of the structural phase transition. In previous in situ experiments [2], the P-T condition was changed several times during each run while observing the transition from the garnet to the perovskite structure. It is known that a metastable overshoot (pressure and/or temperature) is required to provide a sufficiently large energy driving force to overcome a nucleation and/or growth barrier for the transition in previous experiments [2]. To avoid any influence of the kinetic effect, we used the same heating cycle as that used in conventional quench experiments.

References

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