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Structural Phase Transition in $CaGeO_3$

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1 Introduction

The phase transformation and physical properties of the garnet and the perovskite structures at high P-T conditions have attracted attention to understand the dynamics of the Earth's interior because major compositions ($MgSiO_3$ or $CaSiO_3$) have these structures in the Earth's mantle. It is known that some ABO_3 compounds are excellent analogues of $MgSiO_3$ or CaSiO3. Calcium germinate ($CaGeO_3$) 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 $CaGeO_3$ have been also used as a pressure calibration point at high temperatures in high-pressure experiments, such as for SiO_2 and Mg_2SiO_4. Therefore, the precise phase boundary of $CaGeO_3$ needs to be determined.

2 Experiment

The starting material was $CaGeO_3$ wollastonite, synthesized from a starting mixture composed of finely powdered $CaCO_3$ and GeO_2. High-pressure X-ray diffraction experiments were performed using a multi-anvil high-pressure apparatus. The cubic anvil assembly was compressed using a "Max III" high-pressure apparatus, and was combined with a synchrotron radiation source located at the KEK in Japan. The diffracted X-rays were detected using a germanium solid-state detector at an angle of $2\theta = 6.0°$. A cylindrical graphite heater was inserted into the octahedral pressure medium and enclosed within a ZrO_2 sleeve for thermal insulation [1]. The powdered sample and platinum, which was used as pressure calibrant, were loaded directly into the graphite heater, which also served as a sample capsule. The pressure was determined from the unit cell volume of platinum using the equation of state for platinum. After reaching the required temperature, we performed in situ measurements using the synchrotron X-rays. The duration of heating was 0.5-2.0 hours. Determination of the stable phase in each experimental run was carried out by observing the X-ray diffraction pattern of the sample. To check the identification of each phase in the in situ experiments, the recovered samples were also examined using micro Raman spectroscopy.

3 Results and Discussion

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. However, the value of our dP/dT slope was 2-3 times more negative than that in previous experiments. The calculated value of the dP/dT slope using calorimetry data in previous study is consistent with our value of dP/dT [1]. It is likely that the discrepancy between previous and our high-pressure experiments dues to the kinetics of the structural phase transition. In previous in situ experiments, 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 (ΔP or ΔT) is required to provide a sufficiently large energy driving force to overcome a nucleation and/or growth barrier for the transition. To avoid any influence of the kinetic effect, we used the same heating cycle as that used in conventional quench experiments.

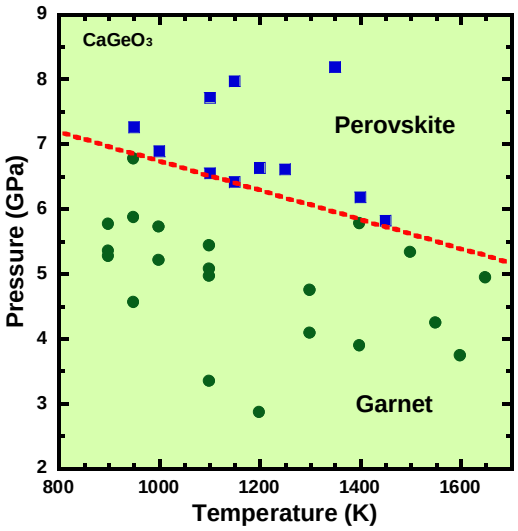

Fig. 1: Experimental results and phase boundary of the garnet-perovskite transition in $CaGeO_3$. The solid circles and squares denote the conditions where the garnet and perovskite phases were stable, respectively. The dashed line shows the inferred phase boundary between the garnet and perovskite phases.

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References

[1] S. Ono *et al.*, (2011) Phys. Chem. Minerals **38** (2011) 735-740.

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