Preliminary reports on in-situ X-ray observation of “post-perovskite” in CaRuO₃

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Abstract. Phase transformation from perovskite to “post-perovskite” and reserve transition in CaRuO₃ was observed by in situ X-ray diffraction at pressure of 20-22 GPa and temperature of 1173-1523 K. These pressure and temperature conditions are 1-2 GPa lower than previous results by quenched method. The axial compressibility is estimated to be \( a/a_0 > b/b_0 > c/c_0 \). This result is inconsistent with previous result on CaIrO₃.

1. Introduction

Since the discovery of post-perovskite in MgSiO₃ (CaIrO₃-type) [1], many workers have been having great interests in the phase transformation from perovskite to post-perovskite phase because this transformation affects significantly the interpretation of the structure and the dynamics in the deep lower mantle [2]. However, the stability of MgSiO₃ post-perovskite locates at very high pressure more than 120 GPa and MgSiO₃ post-perovskite is an unquenchable phase to ambient conditions. These facts indicate that the difficulty to investigate the nature of this transformation and properties of post-perovskite phase such as elasticity, plasticity and thermodynamics.

Researches on analogue materials are useful to investigate the crystal chemistry, elasticity and rheology if analogue materials can be synthesized at lower pressure and stable at ambient conditions. Germanates often work well as analogue of silicate [3], however, germanate post-perovskites are unquenchable phase and can be synthesized more than ~60 GPa [4, 5]. On the other hand, Kojitani et al. [6] reported that perovskite transforms into post-perovskite in CaRuO₃ at relatively lower pressure of 22-24 GPa and 1273-1473 K and determined the phase boundary between perovskite and post-perovskite based on the high pressure quenching experiments. In the present study, we conducted in situ X-ray observation at high pressures and temperatures to observe in situ phase transformation from perovskite to high pressure phase “post-perovskite” on CaRuO₃. As a result, we accurately determine the phase boundary between perovskite and the high pressure phase and the compressibility of the high pressure phase.

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2. Experimental methods

We used a multianvil high-pressure apparatus (Kawai-type cell) composed of eight cubic second-stage anvils of tungsten carbide (WC) with an edge length of 26 mm and 2.0 mm truncation edge length. Using the facilities at SPring-8 in Japan, the cubic anvil assembly was compressed by the high-pressure apparatus combined with a synchrotron radiation source. A 1500-ton multianvil press (SPEED 1500) installed on beamline BL04B1 was used to compress the Kawai-type cell. This apparatus is equipped with an energy-dispersive X-ray diffraction system with a Ge solid state detector and a CCD camera for radiographic imaging of the sample. An incident X-ray beam collimated to dimensions of 50 μm horizontally × 200 μm vertically was directed at the sample through the gaps between the second stage anvils. Diffracted X-rays were collimated to 50 μm horizontally using a collimator and 100 μm horizontally × 2000 μm vertically using a receiving slit. A multi-channel analyzer was connected to the SSD which was used to acquire photons in the range 20-150 keV and was calibrated with characteristic fluorescence X-ray lines from reference metals. The precision of the energy measurements was approximately ± 30 eV per channel. The detector was located at 20° with respect to the incident beam direction. The 20 angle was accurately calibrated using known diffraction peaks from standard materials such as MgO. The uncertainty of the diffraction angle was typically ± 0.002° in each experiment.

To prepare the starting material, CaRuO₃ perovskite was synthesized from a reagent mixture of CaCO₃ and RuO₂ at 873 K for 5 hours and 1273 K for 24 hours in atmosphere. By using X-ray diffractometer, all peaks were assigned as perovskite. Pyrophyllite and ZrO₂ were used as the gasket and the pressure medium, respectively, for high pressure experiments. LaCrO₃ heater was used with X-ray window of graphite as shown in Fig. 1. The sample with diameter of 0.7 mm was enclosed in a semi-sintered MgO capsule. Temperature was monitored by a W97%Re3%-W75%Re25% thermocouple with a diameter of 0.1 mm and the hot junction was located just below the sample capsule (Fig. 1). Fluctuations of temperature were less than ±10 °C throughout the run and the pressure effect on the EMF of the thermocouple was ignored in the temperature measurement. Pressure was determined using the equation of state of MgO [7] which was sandwiched by two sample disks. Uncertainties in the pressure determination were mostly within ±0.1GPa. Determination of the phase present under each condition was carried out by in situ observation of the X-ray diffraction patterns from the sample.

3. Experimental results and discussion

In the experiment, we initially compressed the sample at room temperature to the target pressure of ~22 GPa (530 ton of press load) referred from previous study [6], then we heated to 973 K. After cooling, we compressed to 600 ton press load because the first heating caused a pressure drop to 19.0 GPa. At 21.2 GPa and 1073 K, we observed only perovskite peaks (Fig. 2A), whereas new peaks appeared when we increased pressure and temperature to 20.4 GPa and 1173 K (710 ton of press load) (Fig. 2B). The phase change from perovskite to new phase was not completed within 10 min. After the appearance of new peaks, we increased again pressure and temperature to 21.7 GPa and 1523 K (950 ton of press load) and we observed the relative growth of perovskite peaks (Fig. 2C, D).

In general, the phase transition was sluggish for an aggregate annealed at high temperature and/or grains transformed at high temperature because these samples are almost free from defects in crystal and grain boundaries where the phase transition starts. In this study, we increased temperature very rapidly (~50°C/sec) to generate stress on the sample by anisotropic thermal expansion and...
hence enhanced the transformation kinetics [8]. In some cases, the small amount of surviving metastable phase that was observed by X-ray as relict peaks played a role as “seed crystal(s)” for the next transition. To determine the stable phase under certain conditions by observation of X-ray diffraction, we adopted the criteria of the relative peak growth of perovskite or new phase with time at constant pressure and temperature although it is difficult to obtain the powder pattern for the sample when the grain size is large. The phase boundary between perovskite and the new phase in CaRuO$_3$ was located between 20.4 GPa and 1173 K and 21.7 GPa and 1523 K, showing that the boundary location in this preliminary results is 1-2 GPa lower than the pressure reported in previous result by quenching method [6] (Fig. 3).

As shown in Fig. 2, we assigned new peaks to post-perovskite (CaIrO$_3$-type) and (lattice constants are determined to be $a$-axis=2.9992(3), $b$-axis=9.4776(17) and $c$-axis=7.1869(9) at 21.2 GPa and 1323 K, corresponding to $a/a_0=0.9628$, $b/b_0=0.9645$ and $c/c_0=0.9850$ (lattice constants at ambient condition are referred from Kojitani et al. [6]). These lattice constants suggest that the compressibility of $c$-axis is much lower than those of $a$ and $b$-axis. The present results on axial compressibilities show the inconsistency with those for CaIrO$_3$ post-perovskite, $c/c_0>a/a_0>b/b_0$ [9]. Moreover, it is expected that the relation of $a/a_0>c/c_0>b/b_0$ is considered from the crystal structure of post-perovskite (CaIrO$_3$-type). Additional experiments under pressures ranging from 0 GPa to high pressure are necessary to investigate the inconsistency in axial compressibility. Furthermore, another series of experiments are needed to determine the phase boundary precisely to address the systematic of phase transformation from perovskite to post-perovskite.

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