In situ X-ray diffraction study of the phase boundary between diaspore and $\delta$-AlOOH

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To determine the phase boundary between diaspore ($\alpha$-AlOOH) and $\delta$-AlOOH, in situ X-ray diffraction experiments were carried out using a multi-anvil high-pressure apparatus and synchrotron X-ray. The stability of each phase was determined by observing the change in powder X-ray diffraction patterns. The equilibrium phase boundary is described by the formula $P$ (GPa) = 12.2 ($\pm$4.9) + 0.0027 ($\pm$0.0044) × $T$ (K). The boundary determined in this study is located at a lower pressure than that estimated by previous quenching experimental studies.

Keywords: Aluminum oxyhydroxide, Diaspore, $\delta$-AlOOH, Phase boundary, High pressure

INTRODUCTION

Water (hydrogen) is transported by subducting slabs to the Earth’s interior. Consequently, the stability of hydrous minerals in sediment and MORB has been investigated under high pressures and high temperatures. Ono (1998) investigated phase relationships in hydrated sediment from 6 to 15 GPa and showed that the stable hydrous phase at 15 GPa was phase egg (AlSiO$_3$OH). Previously, we conducted an in situ X-ray diffraction study using synchrotron X-ray and revealed that phase egg is stable at least up to 31 GPa and decomposes into $\delta$-AlOOH and stishovite at higher pressure (Abe et al., 2018). Ono (1998) also showed that lawsonite is stable in hydrous MORB up to 9 GPa. The stability of lawsonite was investigated by Pawley (1994), and diaspore was identified as a breakdown product at 14 GPa and 1013 K. Schmidt (1995) carried out high-pressure experiments on the CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O (CASH) system and reported that diaspore was stable up to 15.0 GPa and 1123 K.

Diaspore ($\alpha$-AlOOH) is an important hydrous mineral and is found in bauxite and emery deposits (Deer et al., 2013). Suzuki et al. (2000) synthesized a new high-pressure form of AlOOH and named it $\delta$-AlOOH. The structure of $\delta$-AlOOH consists of a chain of AlO$_6$ octahedra connecting edges and running along the c axis. Recently, Sano–Furukawa et al. (2018) carried out neutron diffraction experiments on $\delta$-AlOOH under high pressure and observed the formation of the symmetric hydrogen bond above 18 GPa. High pressure experiments have revealed that $\delta$-AlOOH is stable up to the conditions of the core–mantle boundary of the Earth (e.g., Sano et al., 2008). Our recent study showed that the solid solution of $\delta$-(Al,Fe)OOH is an important water storage in the lower mantle and causes seismic anomalies (Ohira et al., 2021). However, the low-pressure limit, that is, the phase boundary between diaspore and $\delta$-AlOOH has not been clearly determined. Schmidt (1995) reported that diaspore was stable up to 15.0 GPa and 1123 K in the CASH system. Sano et al. (2004) carried out in situ X-ray diffraction study on AlOOH under high pressures and high temperatures. They observed the formation of $\delta$-AlOOH at the conditions higher than 20.9 GPa and 1273 K. However, the stability of $\delta$-AlOOH at pressures lower than 20.9 GPa is not clearly understood. Ohtani et al. (2001) reported that diaspore was synthesized from gibbsite at 17.1 GPa and 1273 K. They used a mixture of gibbsite and corundum with AlOOH composition. The mixture was heated to 1373 K at 17.0 GPa. The recovered sample was $\delta$-AlOOH. They concluded that $\delta$-AlOOH is stable at pressures higher than 17 GPa. In contrast, Fukuyama et al. (2017) reported that $\delta$-AlOOH + stishovite was stable at 16 GPa and 1073 K in high-pressure experiments on phase egg (AlSiO$_3$OH) using a large volume press.

In this study, I conducted in situ X-ray diffraction study at high pressures and temperatures to determine the phase boundary between diaspore and $\delta$-AlOOH.
EXPERIMENTAL METHODS

The starting material was a mixture of diaspore, δ-AlOOH, and NaCl (Merck Suprapur®) at a volume ratio of 1:1:2. δ-AlOOH was synthesized at 18 GPa and 1000 K for 30 min from natural diaspore, which was used in my previous study (Suzuki, 2009). Pressure was determined using an equation of state of NaCl (Brown, 1999). Experiments were carried out using a Kawai-type multi-anvil apparatus driven by a MAX-III uniaxial press (Fig. 1), which is installed in the AR-NE7A station at KEK (High Energy Accelerator Research Organization) in Japan. Tungsten carbide cubes (Tungaloy F-grade) with 22 mm edges were used as the second stage anvils. The size of the truncated corners of the second stage anvil was 3 mm. High-pressure cell assembly was the same as that described previously (Suzuki, 2018). Semi-sintered zirconium oxide was used as the pressure-transmitting medium. A cylindrical heater was manufactured using the BN Composite EC (Denka, Co. Ltd.), which consists mainly of boron nitride and titanium boride. The mixture of diaspore, δ-AlOOH, and NaCl was directly loaded into the heater, of which inner diameter was 1.6 mm. The sample temperature was monitored using a W97Re3-W75Re25...
thermocouple. No correction was made for the effect of pressure on the thermocouple EMF. The white X-ray beam from the bending magnet of the PF-AR storage ring was collimated to dimensions of 0.1 mm × 0.2 mm and directed to the sample through an X-ray window made from a mixture of amorphous boron and epoxy resin in a pressure–transmitting medium and pyrophylite gaskets. X-ray diffraction data were collected close to the thermocouple junction (<50 µm) using a pure-Ge solid-state detector using the energy-dispersive method with a fixed Bragg angle of 2θ = 6°. Based on the cell parameter of NaCl collected by changing the beam positions and an equation of state, the temperature gradient around the thermocouple junction was estimated to be approximately 10 K/0.1 mm assuming that the pressure is homogenized at high temperature.

RESULTS AND DISCUSSION

The experimental conditions and results are summarized in Table 1. The sample was first compressed at room temperature. Next, the sample was heated, and the time-resolved X-ray diffraction patterns were collected. When the phase transition was observed, the sample was rapidly cooled to 400 or 700 K, and the press load was changed. Therefore, the stable phase at each experimental condition was determined to be δ-AlOOH. Figure 3 shows the P–T conditions, where the phase transitions from diaspore to δ-AlOOH and from δ-AlOOH to diaspore were observed. Time-resolved X-ray diffraction measurement confirmed the stable phase at each experimental condition. No change was observed around the phase boundary (Fig. 3). On the basis of these experimental results, the phase boundary can be described by the following linear formula:

\[ P \,(\text{GPa}) = 12.2 \, (\pm 4.9) + 0.0027 \,(\pm 0.0044) \times T \,(\text{K}). \]

Phase transition from diaspore structure to the InOOH-type structure has been observed in various oxyhydroxides of the trivalent cations (e.g., Chenavas et al., 1973). The phase boundaries of these two phases in ScOOH (Ito et al., 2021) and FeOOH (Voigt and Will, 1981) are located at approximately 4 and 5 GPa at 300 K, respectively. This study showed that the phase boundary between diaspore and δ-AlOOH is located at around 15 GPa. The ionic radii of six-coordinated Sc3+, Fe3+, and Al3+ under ambient conditions are 0.745, 0.645, and 0.535 Å, respectively (Shannon, 1976). The pressure conditions

| Pressure (GPa) | Lattice parameter (Å) | Temperature (K) | Observed transition | Stable phase |
|---------------|-----------------------|----------------|---------------------|--------------|
| 13.62±0.04    | 5.1757±0.0009         | 980            | δ to Dsp            | Dsp          |
| 13.66±0.02    | 5.1722±0.0005         | 940            | δ to Dsp            | Dsp          |
| 13.67±0.01    | 5.1691±0.0003         | 900            | δ to Dsp            | Dsp          |
| 14.49±0.04    | 5.1625±0.0008         | 1100           | δ to Dsp            | Dsp          |
| 14.50±0.01    | 5.1577±0.0002         | 1020           | δ to Dsp            | Dsp          |
| 14.70±0.11    | 5.1603±0.0024         | 1140           | δ to Dsp            | Dsp          |
| 15.14±0.04    | 5.1529±0.0008         | 1180           | δ to Dsp            | Dsp          |
| 15.60±0.05    | 5.1248±0.0010         | 860            | Dsp to δ            | δ            |
| 15.70±0.07    | 5.1249±0.0014         | 900            | Dsp to δ            | δ            |
| 15.78±0.01    | 5.1254±0.0002         | 940            | Dsp to δ            | δ            |
| 15.79±0.09    | 5.1361±0.0019         | 1140           | Dsp to δ            | δ            |
| 15.82±0.10    | 5.1401±0.0022         | 1220           | Dsp to δ            | δ            |
| 16.03±0.02    | 5.1289±0.0005         | 1100           | Dsp to δ            | δ            |
| 16.08±0.12    | 5.1338±0.0026         | 1210           | Dsp to δ            | δ            |
| 16.25±0.26    | 5.1263±0.0053         | 1140           | Dsp to δ            | δ            |
| 16.35±0.09    | 5.1158±0.0019         | 980            | Dsp to δ            | δ            |
| 16.36±0.07    | 5.1199±0.0014         | 1060           | Dsp to δ            | δ            |
| 16.44±0.08    | 5.1161±0.0017         | 1020           | Dsp to δ            | δ            |
| 16.73±0.24    | 5.1036±0.0048         | 900            | Dsp to δ            | δ            |
| 16.79±0.16    | 5.1176±0.0034         | 1180           | Dsp to δ            | δ            |
| 17.67±0.07    | 5.0840±0.0013         | 860            | Dsp to δ            | δ            |
| 18.06±0.04    | 5.0780±0.0007         | 900            | Dsp to δ            | δ            |

Dsp, diaspore; δ, δ-AlOOH.

Figure 2. Change in the X-ray diffraction patterns indicating the phase transition at 860 K. The elapsed time of each profile at the end of exposure was 600, 1200, and 1800 s. D, diaspore; δ, δ-AlOOH.
of the phase boundaries are inversely correlated with ionic radii.

Schmidt (1995) reported that diaspore was stable up to 15.0 GPa and 1123 K in the CASH system. The result obtained in this study is consistent with those of Schmidt (1995). Ohtani et al. (2001) investigated the stability of δ-AlOOH at 17.1 GPa and 1273 K. They also performed experiments using a mixture of Al(OH)3 and Al2O3 with the composition of AlOOH and synthesized δ-AlOOH at 17.0 GPa and 1373 K. They concluded that δ-AlOOH is stable at pressures higher than 17.0 GPa. Recently, Yoshino et al. (2019) conducted phase equilibrium experiments and estimated the phase boundary. The phase boundaries obtained by Ohtani et al. (2001) and Yoshino et al. (2019) are indicated in Figure 3 as O01 and Y19, respectively. These boundaries are located at a higher pressure than that determined in this study. It can be estimated that this discrepancy is due to the uncertainty of the pressure calibration in the quenching experiments.

In this study the phase boundary between diaspore (α-AlOOH) and δ-AlOOH was investigated using in situ X-ray diffraction experiments. The result is consistent with the transition pressure predicted by theoretical calculations (e.g., Cedillo et al., 2016). Further studies of the thermodynamic properties and experiments under higher temperature conditions are required to constrain the boundary more precisely.

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