

Equation of state of the hydrous phase δ -AlOOH at room temperature up to 22.5 GPa

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[1] The equation of state of δ -AlOOH has been determined at room temperature up to 22.5 GPa by angle-dispersive x-ray diffraction using synchrotron radiation. The isothermal bulk modulus K_{0T} was found to be $252 (\pm 3)$ GPa, assuming that its pressure derivative K'_{0T} is 4, by fitting a third order Birch-Murnaghan equation of state. δ -AlOOH is thus the least compressible hydrous phase known with compressibility comparable to that of corundum and stishovite, confirming that this phase can be stable at the lower mantle conditions. **INDEX TERMS:** 3919 Mineral Physics: Equations of state; 3924 Mineral Physics: High-pressure behavior; 5430 Planetology: Solid Surface Planets: Interiors (8147); 8147 Evolution of the Earth: Planetary interiors (5430, 5724)

1. Introduction

[2] Hydrous phases have recently attracted great attention since they are responsible for water transport into the deep mantle [e.g., Schmidt and Poli, 1998; Ono, 1998]. An important candidate for the water reservoir in the crustal components of the slabs descending into the transition zone depths is phase Egg, AlSiO_3OH [Ono, 1999; Schmidt *et al.*, 1998]. Recent in situ x-ray diffraction studies at high pressure and high temperature have revealed that phase Egg decomposes into δ -AlOOH and stishovite, $\text{AlSiO}_3\text{OH} = \text{AlOOH} + \text{SiO}_2$ at 23 GPa and 1000°C [Suzuki *et al.*, 2001]. Therefore, the water stored in phase Egg up to the bottom of the transition zone can be transported further by δ -AlOOH into the deeper lower mantle.

[3] The zero-pressure calculated density of δ -AlOOH is 3.533 g/cm^3 , which is 15% greater than that of diaspore, α -AlOOH, a low-pressure polymorph of AlOOH. The δ -AlOOH has been synthesized by Suzuki *et al.* [2000] and its crystal structure has been solved. It was found to be orthorhombic, with space group $P2_1nm$, and shows some structural similarities with the CaCl_2 -type stishovite, $Pnnm$, in their oxygen packing arrangement. In this paper we report the room-temperature equation of state of δ -AlOOH up to 22.5 GPa and compares it to that of stishovite and other minerals.

2. Experimental Procedure

[4] We used a Kawai anvil (MA8 type multianvil) device [e.g., Kawai *et al.*, 1973] driven by the 3000-ton uniaxial press with the cubic guide block at Tohoku University [Ohtani *et al.*, 1998] for synthesis of δ -AlOOH. We have used the reagent grade $\text{Al}(\text{OH})_3$ as the starting material. The sample was synthesized by heating the reagent at 25.5 GPa and 1005°C for 3.4 hours. The run product was identified to be a pure δ -AlOOH by x-ray powder diffraction and micro-Raman spectroscopy.

[5] δ -AlOOH was loaded in a Mao-Bell type diamond-anvil cell [Piermarini and Block, 1975] with helium as a pressure-trans-

mitting medium to ensure highly hydrostatic conditions. Rhenium was used as a gasket material. Pressure was applied up to 30 GPa. X-ray diffraction data were collected on decompression at the beamline BL13-A at Photon Factory [Yagi *et al.*, 2001], using a 2-D image-plate area detector. The wavelength was set up at 0.4265 Å. Pressure was measured with the ruby-fluorescence technique with accuracy of ± 0.02 GPa. The volume of the sample was determined by measuring the positions of the strongest peaks (0 1 1), (2 1 0), (0 3 0), (0 1 2) and (4 1 0) in the diffraction patterns. The unit cell was refined by the software UnitCell from Holland and Redfern [1985].

3. Results and Discussion

[6] The pressure-volume equation of state of δ -AlOOH is shown in Figure 1 along with other minerals. A least-square fit using a third order Birch-Murnaghan equation of state produces a bulk modulus $K_{0T} = 252 (\pm 3)$ GPa when the pressure derivative K'_{0T} is fixed at 4. A least-square fitting with two variable parameters gives $K_{0T} = 228 (\pm 3)$ GPa with $K'_{0T} = 7 (\pm 1)$. This value is comparable to that of corundum Al_2O_3 with $K_{0T} = 253 (\pm 1)$ GPa with $K'_{0T} = 5 (\pm 0.4)$ [Richet *et al.*, 1988] and stishovite SiO_2 with $K_{0T} = 291 (\pm 1)$ GPa with $K'_{0T} = 4.79 (\pm 0.05)$ [Andraut *et al.*, 1998].

[7] The bulk modulus of δ -AlOOH differs from other hydroxides, such as brucite $\text{Mg}(\text{OH})_2$ with $K_{0T} = 39.6 (\pm 0.1)$ GPa and $K'_{0T} = 6.7 (\pm 0.7)$ [Xia *et al.*, 1998] and $\text{Ca}(\text{OH})_2$ with $K_{0T} = 37.8$

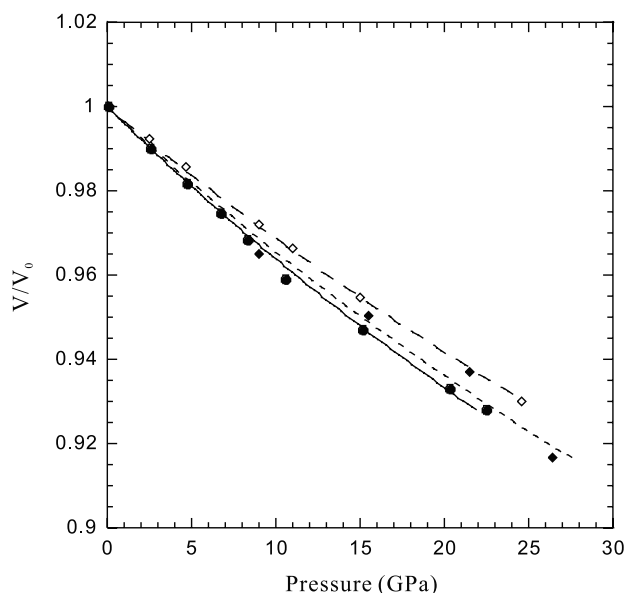


Figure 1. The pressure-volume equation of state of various minerals. The filled circles (●) represents the data for the δ -AlOOH (this work), the open diamonds (◇) with the dotted line stishovite [Andraut *et al.*, 1998] and the diamonds (◆) with the dotted line corundum [Richet *et al.*, 1988].

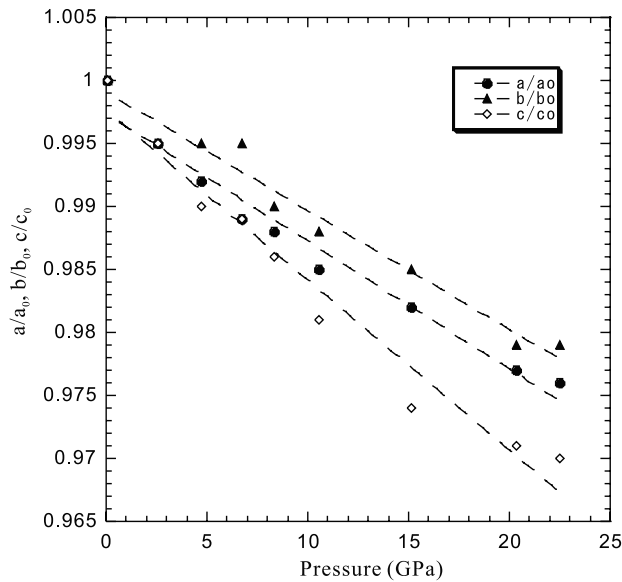


Figure 2. The equation of state of δ -AlOOH, showing that this phase is more compressible along the c-axis.

(± 1.8) GPa and $K'_{OT} = 5.2$ (± 0.7) [Meade and Jeanloz, 1990]. Those hydroxides have a crystal structure made from layers of oxygen (perpendicular with the O-H bonds) where compression occurs. However in aluminium hydroxide, as diaspore, the mechanism of compression takes place by the shortening of the Al-O bonds, as in corundum, leading to comparable compressibilities [Xu *et al.*, 1994]. The Al-O bond lengths in δ -AlOOH (1.87 Å and 2 Å) are comparable to those of diaspore (1.85 Å and 1.98 Å). Since δ -AlOOH does not have a layered structure made from oxygen as most hydroxides, it is likely that the compression mechanism in the δ -AlOOH is similar to that of diaspore.

[8] We have also examined the changes in the unit cell dimensions with pressure and found that the compressibility of δ -AlOOH is anisotropic. As illustrated in Figure 2, the δ -AlOOH is the most compressible along the c-direction. The c/a ratio remains nearly constant over the whole pressure range studied (from 0.601(5) to 0.597(6) at 22.5 GPa), probably confirming quasi-hydrostatic conditions during decompression. A summary of the decompression data is given in Table 1.

[9] The compressibility of δ -AlOOH is very different compared to the elastic properties of stishovite. Both minerals have similar structures [Ohtani *et al.*, 2001] as they are both made of SiO_6 -type octahedrons orientated in the same directions when viewed from the c-axis. The arrangement corresponds to the distorted rutile structure in δ -AlOOH, a very dense phase, where the oxygen sublattice is close to the hexagonal close-packing (hcp) configuration. However in stishovite the c-axis is less compressible than the a-axis at least up to 45 GPa [Andraut *et al.*, 1998; Liu *et al.*,

Table 1. Room-Temperature Decompression Data for δ -AlOOH

Pressure	a	b	c	V
22.51	4.600(2)	4.127(3)	2.741(1)	52.03(5)
20.34	4.607(6)	4.138(3)	2.755(1)	52.53(7)
15.16	4.632(3)	4.165(3)	2.763(8)	53.3(1)
10.56	4.646(1)	4.179(1)	2.781(1)	54.01(1)
8.35	4.658(1)	4.186(3)	2.796(1)	54.52(4)
6.73	4.665(7)	4.20(1)	2.804(7)	55.1(1)
4.76	4.679(3)	4.206(2)	2.809(2)	55.28(6)
2.58	4.69(1)	4.208(6)	2.822(4)	55.7(1)
0	4.715(8)	4.228(3)	2.836(2)	56.54(9)

Table 2. The Bulk Modulus of the Various Hydrous Phases Expected to Exist in the Transition Zone and Lower Mantle

Phase	K_{OT} (GPa)	K'_{OT}	References
Hydrous ringwoodite ^a	148 ± 1	5	Yusa <i>et al.</i> [2000]
Hydrous ringwoodite ^b	155 ± 2	4.3	Yusa and Inoue [1997]
Phase A	145	4	Pawley <i>et al.</i> [1996]
Superhydrous B	142.6 ± 0.8	5.8 ± 0.2	Crichton <i>et al.</i> [1999]
Phase E	112	—	Bass <i>et al.</i> [1991]
Phase G	200 ± 7	4	Frost and Fei [1998]
Diaspore	167.5 ± 2	4	Mao <i>et al.</i> [1994]
δ -AlOOH	252 ± 3	4	present work
	228 ± 7	7 ± 1	present work

^a The amount of water contained in hydrous ringwoodite was 2.8 ± 0.2 wt %.

^b the water content of hydrous wadsleyite was 2.5 ± 0.3 wt %.

1999]. The reason for this could be that, in stishovite, the O-O distance is the largest in the a-b plane (perpendicular to the c-axis) with a value of 3.020 Å, which corresponds to the octahedral interstice, compared to that of the edge-shared octahedron of 2.29 Å and the non-edge shared O-O distance of 2.668 Å along the c-axis [Andraut *et al.*, 1998]. In addition, the deviation from the ideal hcp structure is larger along the a-axis, making this direction more compressible. In δ -AlOOH, the situation is opposite. Compressibility is favored along the c-axis as the oxygen arrangement along that direction is the furthest from the ideal hcp packing. The O-O distance along the c-axis is much larger (2.834(2) Å) than that of the vacant octahedra, found in the a-b plane (2.408(5) Å). Therefore it is not surprising that the compressibility of δ -AlOOH is higher along the c-axis. Table 2 compares the bulk modulus of the various hydrous phases expected to exist in the transition zone and lower mantle.

[10] Phase Egg, AlSiO_3OH , is an important candidate for water storage in the crustal component of slabs descending into the transition zone and the uppermost part of the lower mantle. Formation of phase Egg by reaction AlOOH (diaspore) + SiO_2 (stishovite) \rightarrow AlSiO_3OH (phase Egg) is reported by Schmidt *et al.* [1998] at around 15 GPa and 1000°C. However, Suzuki *et al.* [2001] showed a decomposition reaction of phase Egg into δ -AlOOH and stishovite at 23 GPa and 1000°C, strongly suggesting that δ -AlOOH is a probable candidate for water storage in the slabs descending into the lower mantle, although it can not be stable along the normal mantle geotherm. No water release is expected by the decomposition reaction of phase Egg.

[11] In addition, Ohtani *et al.* [2001] shows that δ -AlOOH is also observed in the CMAS pyrolite- H_2O system coexisting with garnet. Its chemical composition implies a significant amount of octahedrally coordinated silicon and magnesium ions and small amounts of calcium ions as a solid solution.

[12] The present work reveals that δ -AlOOH is the least compressible hydrous phase yet reported, although it contains a large amount of water to 15%. This phase is expected to exist in the mantle and its bulk modulus is comparable to the lower mantle minerals such as Mg-perovskite, Ca-perovskite, stishovite and corundum. Therefore, δ -AlOOH is expected to be stable in the slabs descending into the deep lower mantle. Further work is now needed to confirm the stability limit of this phase at high pressure and high temperature.

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