LETTER

X-ray diffraction study of high pressure transition in InOOH

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We performed high-pressure and high-temperature X-ray diffraction experiments on InOOH using laser heated diamond anvil cells. After heating at 1300 K, pyrite-type InOOH was formed at 14 GPa and it was stable up to at least 30 GPa. Pyrite-type InOOH partially transformed back to distorted rutile-type InOOH after recovery. The lattice constant and unit-cell volume of pyrite-type InOOH were determined to be $a_0 = 5.3151(8)$ Å and $V_0 = 150.15(7)$ Å³ at ambient conditions, respectively. The density difference between pyrite-type and distorted rutile-type InOOH was 5% at ambient condition.

Keywords: InOOH, Pyrite-type structure, High pressure

INTRODUCTION

Rutile-type structure is commonly found in AX₂-type compounds and its high-pressure behavior has long been attracted. The general pathway of transition of AX₂-type compounds with increasing pressure is as follows; rutile → distorted rutile (CaCl₂) → α-PbO₂ → pyrite (FeS₂) (e.g., Léger et al., 1998). Coordination number increases from 6 to 6 + 2 during these transitions. For example, SiO₂, which is one of the important components of the earth's crust, undergoes transitions from stishovite to distorted rutile-type and then to α-PbO₂ structure at 50 GPa (Kingma et al., 1995) and at 120 GPa (Murakami et al., 2003), respectively. Pyrite-type SiO₂ becomes stable at 268 GPa (Kuwayama et al., 2005).

Oxyhydroxide [M³⁺O(OH)] such as α-FeOOH (goethite) and α-AlOOH (diaspore) found to takes diaspore-type structure at ambient conditions, which is explained as a double-chained rutile-type framework. These compounds transforms into distorted rutile-type structure at high pressure. The distorted rutile-type structure of FeOOH is formed at 8 MPa and 773 K in hydrothermal

study (Chenavas et al., 1973). α-AlOOH transforms to distorted rutile-type phase, which is named as δ-AlOOH, above 18 GPa (Suzuki et al., 2000; Ohtani et al., 2001). This phase remains stable in the condition of the lower mantle, and no transition to higher-pressure phase was found even at 134 GPa (Sano et al., 2008). Therefore it is not clear whether or not the oxyhydroxide follows common pathway of AX₂-type compound. Theoretical studies predicted that in δ-AlOOH a symmetric hydrogen bond is formed at ~ 28–50 GPa (e.g., Tsuchiya et al., 2002). The formation of symmetric hydrogen bond is expected to affect the physical properties such as compression behavior. Neutron diffraction study confirmed the existence of strong hydrogen bond in δ-AlOOH (Vanpeteghem et al., 2007).

This work intends to explore the high-pressure polymorphs of distorted rutile-type oxyhydroxide having strong hydrogen bond in its structure. InOOH was selected because it is expected to have lower transition pressure than that of AlOOH due to the effect of chemical pressure. Distorted rutile-type InOOH was first synthesized by hydrothermal method at 973–1073 K and 2.5–5 GPa by Christensen (1971). The neutron diffraction study has clarified that the distorted rutile-type InOOH is isostruc-

Figure 1. X-ray diffraction patterns obtained before heating (a), and after heating (b), (c) at high pressure. Abbreviations are as follows: D, distorted rutile-type InOOH; Pt, platinum; P, pyrite-type InOOH; *, unreacted starting material; +, unknown cubic phase.

tural with δ -AlOOH having strong hydrogen bonds (Lehmann et al., 1970). The hydrogen bond geometry consists of the O–O distance of 2.54 Å and the O–H distance of 1.08 Å.

EXPERIMENTAL

Two starting materials were used, reagent grade of $\text{In}(\text{OH})_3$ and distorted rutile-type InOOH. $\text{In}(\text{OH})_3$ takes ReO_3 -type structure at ambient conditions which is described as an A-site deficient hydroxy-perovskite structure (Mullica et al., 1979). The distorted rutile-type InOOH was synthesized using cubic-anvil type high pressure apparatus at ISSP. $\text{In}(\text{OH})_3$ was loaded into a gold capsule and placed into a cylindrical graphite heater with a insulator of boron nitride sleeve. It was kept at 4 GPa and 873 K for 1 h. Recovered sample was analyzed by micro focused X-ray diffractometer with a rotating Cr anode operated at 40 kV and 200 mA. It was confirmed to have distorted rutile-type structure with lattice constants of $a = 5.267$ (3), $b = 4.5698$ (3), $c = 3.282$ (2) Å. Both starting materials were grounded in the agate mortar and mixed with platinum black, which serves as a laser absorber and pressure standard, and loaded into a hole of a rhenium gasket of diamond anvil cells.

Figure 2. X-ray diffraction pattern of (a) recovered sample obtained at ambient conditions and the calculated peak positions and intensities of (b) distorted rutile-type InOOH, (c) pyrite-type InOOH (Space group $P2_13$, Tsuchiya et al., 2007), and (d) hexagonal In_2O_3 (PDF no. 01-073-1809). Abbreviations are the same as Figure 1.

Angle dispersive X-ray diffraction experiment using Imaging Plate (IP) was conducted at BL13A beamline of KEK, Photon Factory in Tsukuba, Japan. Monochromatic X-ray of approximately 29 keV was collimated into 30–50 μm in a diameter. Pressure was calculated from the unit cell volume of platinum using equation of state of Holmes et al. (1989) within the margin of error less than 2 GPa. The sample was heated by a multimode Nd:YAG laser or fiber laser for 10–20 min. The laser spot was slowly scanned during heating to heat the entire sample. Temperature was measured by the spectroradiometric method and its fluctuation was 100–200 K. After the sample was quenched to room temperature, X-ray diffraction patterns were corrected at high pressure to determine the synthesized phase with an exposure time of 10–15 min. The one-dimensional profile was obtained by integrating the two-dimensional diffraction image.

RESULT AND DISCUSSION

In the run using InOOH as a starting material, sample was compressed to 16 GPa and then heated at 1300 K. Distorted rutile-type InOOH was observed before the heating although peaks were broadened considerably because of the nonhydrostaticity (Fig. 1a). After heating, the diffraction peaks of distorted rutile-type InOOH almost disap-

Table 1. Observed and calculated d -value of pyrite-type InOOH and platinum at 30 GPa

$d_{\text{obs.}}$	I/I_0	Pyrite			Platinum		
		$d_{\text{calc.}}$	$d_{\text{obs.}} - d_{\text{calc.}}$	hkl	$d_{\text{calc.}}$	$d_{\text{obs.}} - d_{\text{calc.}}$	hkl
3.2859*	>1						
2.9277	100	2.9264	0.0013	111			
2.6710*	3						
2.5355	61	2.5343	0.0012	200			
2.2674	5	2.2668	0.0006	210			
2.2266**	14						
2.2006	27				2.2003	0.0003	111
2.0705	3	2.0693	0.0012	211			
1.9304**	5						
1.9070	12				1.9056	0.0004	200
1.7930	52	1.7921	0.0009	220			
1.5287	62	1.5283	0.0004	311			
1.4649	23	1.4632	0.0006	222			
1.3632**	3						
1.3476	6				1.3474	0.0002	220
1.2673	3	1.2672	0.0001	400			
1.1627	15	1.1628	-0.0001	331			
1.1491	7				1.1491	0.0000	311
1.1333	19	1.3334	0.0001	420 +002			
1.1127**	1						
1.1000	2				1.1002	-0.0002	222
1.0343	11	1.0346	-0.0002	422			

$d_{\text{obs.}}$, observed d -value; I/I_0 , observed intensity that is normalized by the most intense peak; $d_{\text{calc.}}$, calculated d -value; *, unreacted starting material; **, unknown cubic phase.

peared and many new sharp peaks appeared. The remained small peaks would be scattered from the unheated sample near the diamond anvils (Fig. 1b). The new peaks were well explained by pyrite-type phase that was theoretically predicted (Tsuchiya et al., 2008). Most of the peaks are explained by fcc structure. However, the existence of 210 and 211 reflections suggests that oxygen sublattice is not fcc structured as fluorite is, but is explained by pyrite-type structure. It is indexed as a cubic lattice with $a = 5.185(2) \text{ \AA}$ and a unit cell volume was determined to be $139.4(1) \text{ \AA}^3$ at 14 GPa. Pyrite-type InOOH remained stable at 30 GPa after heating at 1700 K. The lattice constant and unit cell volume at 30 GPa were $a = 5.0687(6) \text{ \AA}$ and $V = 130.22(4) \text{ \AA}^3$, respectively.

After the sample was recovered to ambient condition, the intensity of diffraction peaks from the distorted rutile-type InOOH increased and those from the pyrite-type InOOH became relatively weak, suggesting that the

pyrite-type phase partially retransformed back to distorted rutile-type InOOH (Fig. 2). The lattice constant and unit cell volume of pyrite-type InOOH at ambient conditions was determined to be $a_0 = 5.3151(8) \text{ \AA}$ and $V_0 = 150.15(7) \text{ \AA}^3$. The densities of distorted rutile-type and pyrite-type InOOH were 6.22 g/cm^3 and 6.54 g/cm^3 , respectively; therefore the density increase is about 5%. Some of pyrite-type high-pressure polymorphs of AX_2 -type components such as MgF_2 and SnO_2 transforms into α - PbO_2 -type phase during decompression (Haines and Léger, 1997, Haines et al., 2001). These compounds have intermediate α - PbO_2 -type phase between rutile-type and pyrite-type structures. However, no evidence of such transformation was observed in InOOH. Small amount of hexagonal corundum-type In_2O_3 phase was observed. Probably it was formed by the dehydration of InOOH at high temperature region during heating. We note that some unidentified peaks were also observed after heating at high pressure and in the recovered sample (Figs. 1b, 1c and Fig. 2). All of them were observed next to the peaks of platinum at lower 2-theta angle side and could be indexed by a cubic lattice, suggesting the possibility that a partial reaction of platinum with starting material has occurred. Although the nature of the reaction remains unclear, it would not affect the pressure determination using the platinum equation of state, since the lattice constant of the recovered platinum at ambient condition ($a = 3.9433(4) \text{ \AA}$) was not significantly different from that of pure platinum.

Formation of pyrite-type InOOH was also confirmed in the run using $\text{In}(\text{OH})_3$ as a starting material. $\text{In}(\text{OH})_3$ underwent amorphization during compression and only platinum was found in the diffraction pattern before heating. Pyrite-type InOOH and H_2O -Ice were formed at 22 GPa after heating at 1500 K.

Present experimental study is in agreement with the theoretical study, which has predicted that pyrite-type InOOH becomes stable above 15 GPa (Tsuchiya et al., 2008). They also suggested that the hydrogen locates at the midpoint between two oxygen atoms forming symmetric hydrogen bond in pyrite-type InOOH above 30 GPa. The space group of pyrite-type InOOH differs between asymmetric and symmetric hydrogen bond models, which is assumed to be $P2_13$ and $Pa\bar{3}$, respectively. However, it was difficult to distinguish these two structural models by the present study because of a subtle difference of X-ray diffraction patterns of $P2_13$ and $Pa\bar{3}$ models. Further study such as Raman spectroscopic or neutron diffraction study is needed to examine whether the hydrogen bond in pyrite-type InOOH is asymmetric or symmetric.

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