LETTER

First principles prediction of new high-pressure phase of InOOH

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We have predicted a new high-pressure phase of InOOH by first principles density functional calculations, which stabilizes at ~ 15 GPa under the static 0 K condition. The structure obtained at 15 GPa has a pyrite-type InO_2 framework with the interstitial asymmetric hydrogen bonds, which is assigned to the space group $P2_13$ (No. 198). The cell parameters and internal atomic coordinates optimized at 15 GPa are $a = 5.265$ Å, $\text{In}_x = 0.005$, $\text{O1}_x = 0.367$, $\text{O2}_x = 0.633$, and $\text{H}_x = 0.487$. Relative enthalpies also indicate that the dehydration of this phase into $\text{In}_2\text{O}_3 + \text{H}_2\text{O}$ is unlikely to occur at least up to 50 GPa under the static condition. To our knowledge, this is the first report on the high-pressure isochemical phase transition of oxyhydroxide compounds to the pyrite-type structure. The new phase of InOOH has been identified in an experiment, as reported in detail in a separate paper. We have also found that the low-pressure-type asymmetric hydrogen bond in the new pyrite-type phase changes to the symmetric hydrogen bond over 30 GPa. The present results suggest that a similar phase relation is expected in other group IIIB oxyhydroxides such as AlOOH and GaOOH.

Keywords: InOOH, First principles, High pressure, Hydrogen bond

INTRODUCTION

δ -AlOOH is a high-pressure phase of AlOOH (diaspore) that has recently been found at ~ 21 GPa and 1000 °C (Suzuki et al., 2000). The δ -AlOOH phase has the CaCl_2 -type structure (Fig. 1a) and is found to be stable under the P and T conditions inferred for cold slabs subducting into the deep mantle (Ohtani et al., 2001). Due to the high stability of this phase under high pressure, it is proposed to be a possible carrier and reservoir of water in the deep Earth (Sano et al., 2004). Therefore, its high-pressure structural behaviors have attracted considerable geophysical interest. In particular, it is interesting to determine whether this phase remains stable, decomposes into an anhydrous phase and H_2O , or transforms into a higher-pressure hydrous phase at the Earth's lower mantle pressures.

We have recently reported pressure-induced hydrogen bond symmetrizations in δ -AlOOH and phase D

($\text{MgSi}_2\text{O}_6\text{H}_2$) occurring above ~ 30 and ~ 40 GPa, respectively (Tsuchiya et al., 2002, 2005). Since among the known hydrous minerals, only these two phases are reported to be stable at lower mantle pressures (Ohtani et al., 2001; Sano et al., 2004), it is presumable that the hydrogen bond symmetrization stabilizes hydrous minerals under high pressure. However, the stability limit and further high-pressure structural evolution of these phases have not been well understood.

Considering the above-mentioned facts, we first focus on the high-pressure behavior of InOOH since In^{3+} is homologous to Al^{3+} and InOOH can be expected to behave as a low-pressure analog of AlOOH. InOOH has the CaCl_2 -type structure, even under ambient conditions; this structure is isostructural to δ -AlOOH. Therefore, a high-pressure phase of InOOH, if found, would suggest a new high-pressure phase transition of δ -AlOOH. The studies of analog materials are meaningful and helpful, particularly for high-pressure experiments. Since the transition pressures expected in InOOH are less than those expected in AlOOH, the study will increase the feasibility of the

Figure 1. Crystal structures of (a) CaCl₂ and (b) pyrite-type InOOH. Large, medium, and small spheres denote In, O, and H atoms, respectively.

experimental corroboration of the transitions (Sano et al., 2008).

The CaCl₂-type structure has been reported in several M^{3+} OOH oxyhydroxide compounds (M = Al, Sc, V, Cr, Mn, Fe, Ni, Rh, and In) (Chenavas et al., 1973; Baneyeva and Bendeliani, 1973; Suzuki et al., 2000). However, to the best of our knowledge, there is no report on the high-pressure structure transition of these CaCl₂-type oxyhydroxides. In this study, we explore the new phase relation of InOOH using the first principles density functional techniques by testing the energy balance of several structure models which are potentially possible to exist as post-CaCl₂ oxyhydroxide.

CALCULATION METHODS AND STRUCTURE MODELS

Our computations are based on the density functional theory with the generalized gradient approximation (GGA) to the exchange-correlation functional (Perdew et al., 1996). The GGA is critical for the accurate simulation of the weak hydrogen bond (Hamann, 1997). Pseudopotentials (Troullier and Martins, 1991; Rappe et al., 1990) are applied to describe the ionic core potentials of O ($2s^2$ and $2p^4$), H ($1s^1$), and In ($4d^{10}$, $5s^2$, and $5p^1$). The electronic wave functions are expanded by plane waves with an energy cutoff of 80 Ry (1 Ry = 13.6058 eV). We calculate the following four structures of InOOH: orthorhombic diaspore structure, CaCl₂ structure, α -PbO₂ structure, and cubic pyrite structure. In addition, anhydrous In₂O₃ and H₂O are computed to investigate the possible high-pressure dehydration reaction. In the pressure range considered in this study ($P < 50$ GPa), In₂O₃ and H₂O are reported to crystallize into orthorhombic Rh₂O₃(II) and tetragonal ice VIII structures, respectively (Yusa et al., 2007; Song et al. 2003). The irreducible parts of the Brillouin zones of the diaspore, CaCl₂, α -PbO₂, pyrite-type InOOH, Rh₂O₃(II)-type In₂O₃ and ice VIII structures are sampled on $1 \times 4 \times 2$, $2 \times 2 \times 4$, $4 \times 2 \times 2$, $4 \times 4 \times 4$, $4 \times 4 \times 4$ and $4 \times 4 \times 4$ Monkhorst-Pack meshes (Monkhorst and Pack, 1976), respectively. The effects of larger energy cutoffs and k -point samplings on the calculated properties are found to be insignificant. All structural parameters are fully relaxed to static (0 K) configurations using the damped variable cell shape molecular dynamics method (Wentzcovitch, 1991) implemented with the PWscf code (<http://www.pwscf.org>) until residual forces become less than 1.0×10^{-5} Ry/au.

The major part of this study involves the construction of high-pressure model structures of post-CaCl₂-type InOOH. We have constructed these structures crystallographically as follows. The CaCl₂-type structure can be adapted to the high-pressure form of group IVB dioxides, AO₂ (A = Si, Ge, Sn, and Pb). This suggests that the high-pressure phase relation in InOOH might also follow the high-pressure phase sequence of group IVB dioxides. In the case of SiO₂, the CaCl₂ phase has been reported to transform into α -PbO₂ structure at ~ 100 GPa and further into the pyrite phase above 200 GPa (e.g., Tsuchiya et al., 2004b; Kuwayama et al., 2005). Therefore, we construct the post-CaCl₂ model structures that have the α -PbO₂ and pyrite-type InO₆ octahedral frameworks with hydrogen atoms in their interstitial spaces. In addition to the InOOH polymorphs, we test the possible stability of the dehydration of InOOH into Rh₂O₃(II)-type In₂O₃ and ice VIII, as mentioned earlier.

Figure 2. Relative enthalpies of InOOH polymorphs with respect to CaCl_2 -type phase. Dashed lines indicate the low-pressure metastable symmetric hydrogen bond states of CaCl_2 and pyrite-type structures.

Figure 4. Calculated and experimental (Sano et al. 2008) X-ray ($\lambda = 0.4266 \text{ \AA}$) diffraction patterns of pyrite type InOOH obtained at 30 GPa.

RESULTS AND DISCUSSION

All the structural parameters of the initial model structures are first fully relaxed at pressures from 0 to 50 GPa under the static 0 K condition. Figure 2 shows the calculated static enthalpies of the model structures relative to the CaCl_2 -type structure as a function of pressure. Diaspore type structure is found to be more stable than CaCl_2 -type structure at 0–3 GPa, although the experiments report that CaCl_2 -type structure is stable under ambient conditions (Christensen et al., 1964). This discrepancy is

Figure 3. Equations of state of the pyrite (circles) and CaCl_2 -type (triangles) phases. Solid and dashed lines indicate the symmetric and asymmetric hydrogen bond states, respectively.

due to the general tendency of the GGA to overestimate (typically by 5–10 GPa) the stability range of low-pressure structures (e.g., Tsuchiya et al., 2004a). With increasing pressure, an enthalpy crossover appears at ~ 15 GPa, where the pyrite structure becomes more stable than CaCl_2 -type structure. To our knowledge, this is the first report on the high-pressure isochemical phase transition of oxyhydroxide compounds to the pyrite-type structure. Although $\alpha\text{-PbO}_2$ is reported to be the post- CaCl_2 phase in group VIB dioxides, the enthalpy of $\alpha\text{-PbO}_2$ structure is significantly higher than that of pyrite structure in InOOH. This indicates that there is no stability field for $\alpha\text{-PbO}_2$ in InOOH. The higher lattice energy of $\alpha\text{-PbO}_2$ -type InOOH is probably because of the very small hydrogen-hydrogen distances ($\sim 2.78 \text{ \AA}$), which are estimated by the hydrogen positions in this structure. Moreover, the calculated enthalpy of $\text{Rh}_2\text{O}_3(\text{II})$ -type $\text{In}_2\text{O}_3 + \text{ice VIII}$ is considerably higher than that of pyrite-type InOOH, even at 50 GPa. This means that the dehydration reaction is thermodynamically unfavorable at least under static 0 K condition.

Figure 3 shows the equations of state of the CaCl_2 and pyrite-type phases. The zero-pressure bulk moduli (pressure derivatives) for the CaCl_2 and pyrite type phases are determined to be 109.5 GPa (6.47) and 128.2 GPa (5.82), respectively, by the least-square fitting of the P – V relation to the Vinet equation (Vinet et al., 1989). A volume reduction of $\sim 3.9\%$ is expected for the transition from the CaCl_2 to pyrite at 15 GPa (Fig. 3). Pyrite-type InOOH has been successfully identified by complementary high-pressure experiments (Fig. 4). The results will be

Table 1. Crystal structures of the CaCl_2 and pyrite-type InOOH

	CaCl_2		Pyrite		
P (GPa)	0	30	0	15	30
S.G.	$P2_1nm$	$Pnmm$	$P2_13$	$P2_13$	$Pa\bar{3}$
a (Å)	5.381	5.136	5.423	5.265	5.156
b	4.649	4.367	-	-	-
c	3.349	3.176	-	-	-
In(x,y,z)	(0, 0.227, 0)	(0, 0, 0)	(0.010, 0.010, 0.010)	(0.005, 0.005, 0.005)	(0, 0, 0)
O(x,y,z)	(0.366, 0.482, 0)	(0.365, 0.219, 0)	(0.365, 0.365, 0.365)	(0.367, 0.367, 0.367)	(0.367, 0.367, 0.367)
O(x,y,z)	(0.636, 0.025, 0)	-	(0.633, 0.633, 0.633)	(0.633, 0.633, 0.633)	-
H(x,y,z)	(0.480, 0.302, 0)	(0.5, 0, 0)	(0.477, 0.477, 0.477)	(0.487, 0.487, 0.487)	(0.5, 0.5, 0.5)
H-bond	Asymmetric	Symmetric	Asymmetric	Asymmetric	Symmetric

Figure 5. Relationships between $\text{O}\dots\text{O}'$ and $\text{O}-\text{H}$ distances of CaCl_2 (triangles) and pyrite-type (circles) structures. Pressure interval between adjacent dots and triangles is 5 GPa, and longest and shortest $\text{O}\dots\text{O}'$ lengths corresponds to lowest and highest pressures of 0 and 50 GPa, respectively. Dashed line represents the distance corresponding to $\text{O}-\text{H} = 1/2(\text{O}\dots\text{O}')$.

reported in detail separately (Sano et al., 2008). The most stable hydrogen positions in these structures are determined by the structure optimization with the calculation of the total energies of trial structures in which hydrogen atoms are placed at several vacant sites between two oxygen atoms in the interstitials of the InO_6 octahedra. Then, we have found the most stable hydrogen positions with the lowest energy in the CaCl_2 and pyrite structures. They have the asymmetric hydrogen bonds at 0 GPa, which cause a slight distortion of InO_6 octahedron. Therefore, the structures are less symmetric than the ideal CaCl_2 and pyrite structures. The CaCl_2 and pyrite structures at 0 GPa can be assigned to the space groups $P2_1nm$ (No. 31) and

$P2_13$ (No. 198), respectively (Table 1).

In our previous study, the pressure-induced hydrogen bond symmetrization in $\delta\text{-AlOOH}$ was reported to occur at ~ 30 GPa (Tsuchiya et al., 2002), which was achieved by the continuous displacement of hydrogen atoms from the asymmetric off-centered position between two neighboring oxygen atoms (O and O' in Fig. 1) to the symmetric centered position. We have carefully determined the hydrogen positions of InOOH polymorphs and found that the symmetric hydrogen bonds are formed in the CaCl_2 and pyrite-type structures at 25 and 30 GPa, respectively. In relation to these changes in the hydrogen bonds, the crystallographic symmetries of the CaCl_2 and pyrite phases increase to the space groups $Pnmm$ and $Pa\bar{3}$, respectively (Table 1).

Figure 5 shows the relationships between the distance between two neighboring oxygen atoms ($\text{O}\dots\text{O}'$) and the bond length of oxygen and hydrogen atoms ($\text{O}-\text{H}$) in the CaCl_2 and pyrite structures (Fig. 1). In both the structures, the $\text{O}-\text{H}$ lengths first increase under compression and approach half the value of the $\text{O}\dots\text{O}'$ distances. This indicates the strengthening of the hydrogen bond and the weakening of the $\text{O}-\text{H}$ bond. Then, the symmetrizations are achieved at an $\text{O}\dots\text{O}'$ distance of ~ 2.37 Å in both the CaCl_2 and pyrite structures. After the hydrogen bond symmetrization, the $\text{O}-\text{H}$ lengths begin to decrease along the $\text{O}-\text{H} = 1/2(\text{O}\dots\text{O}')$ line. It should be noted that the relationship between the $\text{O}-\text{H}$ lengths and $\text{O}\dots\text{O}'$ distances appears to be independent of the structure type. In the present study, we neglect both the quantum and thermal vibration effects of the light hydrogen atoms. These effects are expected to decrease the pressures of the hydrogen bond symmetrization (Benoit et al., 1999).

CONCLUSIONS

We have reported new high-pressure phase relations in indium oxyhydroxide (InOOH) predicted by first princi-

ples calculations. Pyrite-type InOOH is found to stabilize above ~ 15 GPa instead of the CaCl_2 -type phase. No dehydration reaction is observed at least up to 50 GPa under athermal condition; the $\alpha\text{-PbO}_2$ -type phase also is observed to be unstable. Calculations indicate that the CaCl_2 and pyrite-type structures have the symmetric hydrogen bonds over 25 and 30 GPa, respectively. Similar transitions from the CaCl_2 to pyrite-type phase are expected in other group IIIB oxyhydroxides such as AlOOH and GaOOH, although their transition pressure would be higher than that of InOOH.

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