LETTER

Sound velocity measurements of ε-FeOOH up to 24 GPa

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The sound velocity and density of ε-FeOOH have been simultaneously measured up to 24 GPa at room temperature using an ultrasonic pulse-echo-overlap method and a Kawai-type multi-anvil apparatus at BL04B1 in SPring-8. In the experimental pressure range, the velocity of both the P- and S-waves of ε-FeOOH was ~ 15% lower than that of an isostructural phase δ-AlOOH. The pressure dependence of the determined adiabatic bulk modulus (K_s) increased in the higher pressure range beyond 17 GPa, whereas that of the axial ratios a/c and b/c did not transition from negative to positive. A similar change of pressure dependence of K_s was observed in δ-AlOOH, which is followed by a transition of proton distribution state to disordered, but the axial ratios of ε-FeOOH indicate that the transition would not occur up to 24 GPa.

Keywords: Iron oxide hydroxide, Hydrous phase, High pressure, Sound velocity, Hydrogen bond symmetrization

INTRODUCTION

Iron oxide hydroxide, FeOOH, is abundantly present on the Earth’s surface as goethite (α-FeOOH). Its high-pressure polymorph ε-FeOOH is stable over a wide range of pressures and temperatures (e.g., Gleason et al., 2008; Otte et al., 2009; Nishi et al., 2017) and is therefore considered to be a crucial hydrous phase in the upper to lower mantle. ε-FeOOH is potentially a water carrier in subducted basaltic crusts up to the mantle transition zone, as determined based on high-pressure experiments of the phase relations in the system FeOOH-TiO_2 (Nishihara and Matsukage, 2016). The transition from the α- to ε-phase has been predicted to occur at 5–7 GPa based on a first principle calculation (Otte et al., 2009), but the results of experiments to determine the pressure-temperature phase boundary (e.g., Gleason et al., 2008; Wiethoff et al., 2017) still present inconsistencies.

ε-FeOOH is isostructural with InOOH, which has an orthorhombic structure with the space group P2_1/mn under ambient conditions (Chenavas et al., 1973; Pernet et al., 1975). The structure is a distorted derivative of rutile and consists of columns of edge-sharing FeO_6 octahedra along the c axis. Columns occupied by hydrogen atoms separate the FeO_6 columns and the hydrogen atoms form O–H–O hydrogen bonds that lie in the a-b plane (Botolina et al., 2008).

Many oxyhydroxides of trivalent cations have isostructural phases with ε-FeOOH. Among these distorted rutile-type M^3+OOH phases, δ-AlOOH is the most important hydrous mineral in the mantle and its features (e.g., structure, stability field) have been well-investigated (e.g., Suzuki et al., 2000; Komatsu et al., 2006; Sano et al., 2008). δ-AlOOH is predicted to exhibit pressure induced symmetrization of hydrogen bond at ~ 30 GPa by first principle calculations (e.g., Tsuchiya et al., 2002). Hydrogen bond symmetrization is well-known to occur in high-pressure ice, and is a process in which the proton potential that leans to one side at ambient pressure breaks up into a symmetric double-well potential and subsequently merges into a single minimum at the center along compression (e.g., Holzapfel, 1972). In the state with a double-well potential, proton have half occupancy in each well and the state is referred as ‘disordered state’ hereafter. In δ-AlOOH, first principle calculations revealed that the symmetrization would accompany increases of the compressibility of the a and b axes, in addition to the bulk modulus (Tsuchiya et al., 2002; Tsuchiya and Tsuchiya, 2009). These increases were ex-
experimentally observed at a lower pressure of ~ 10 GPa and 6-15 GPa, respectively (e.g., Sano-Furukawa et al., 2009; Mashino et al., 2016). Recently, hydrogen bond symmetrization of δ-AlOOH was directly observed in neutron diffraction studies (Sano-Furukawa et al., 2018). The results indicated that the compressibility of the $a$ and $b$ axes changed at 9.0 GPa, corresponding to the transition to the disordered state, and that symmetrization is completed at 18.1 GPa.

$\epsilon$-FeOOH was predicted to exhibit hydrogen bond symmetrization at a pressure below 43 GPa based on a first principle calculation and the change in the compressibility of the $a$ and $b$ axes at ~ 45 GPa were experimentally confirmed (Gleason et al., 2013). Moreover, in the same report, a high–spin to low–spin transition in iron was predicted at 64.8 GPa based on calculations and were experimentally confirmed to occur between 40 and 60 GPa via X-ray emission spectroscopy. The sound velocity of $\epsilon$-FeOOH is also anticipated to exhibit abnormal changes (e.g., having a higher rate of increase) accompanied by hydrogen bond symmetrization because of the structural similarity to δ-AlOOH. A density functional theory calculation study of $\epsilon$-FeOOH was performed to investigate the sound velocity (Thompson et al., 2017). However, in the report, hydrogen bond, iron, and temperature were defined to be symmetric, the low–spin state, and 0 K, respectively. In this study, we measured sound velocities and lattice parameters of high–spin $\epsilon$-FeOOH under ambient-temperature and high–pressure conditions, using an in–situ ultrasonic technique and X–ray diffraction method to elucidate the relationship between elasticity and structural changes.

**EXPERIMENTAL METHODS**

The sample used was polycrystalline $\epsilon$-FeOOH, which was synthesized in advance from a powder of reagent grade 99% α-FeOOH (Kojundo Chemical Laboratory) at the pressure–temperature condition of 8 GPa and 480 °C for 1 h using the 3000–ton Kawai-type multi–anvil apparatus installed at Tohoku University. The synthesized material was identified as a single $\epsilon$-phase based on a powder X-ray diffraction method using a diffractometer (D8 ADVANCE, Bruker) installed at Tohoku University. High–pressure ultrasonic measurements were performed at the BL04B1 beamline of the SPring–8 facility in Japan. The 1500-ton Kawai-type multi–anvil apparatus (SPEED–1500) was used for high–pressure generation. Tungsten carbide cubes with a 26-mm edge length and a 5.0-mm truncated edge length were used as second stage anvils and a Co–doped MgO octahedron with a 10.0-mm edge length was used as the pressure medium. A φ1.5–mm hole was bored perpendicularly through the center of a facet of the pressure medium and the sample which was sandwiched between an alumina mirror polished buffer rod and an alumina mirror polished backing plate was placed into the hole. Platinum foils with a thickness of 5 µm were placed on both surfaces of the sample to make the boundaries clear in X–ray radiography images.

The travel times of the P– and S–waves through the sample were determined using a pulse–echo overlap technique. The detailed experimental setup was presented in Higo et al. (2008, 2009, 2018). Both the P– and S–wave ultrasonic signals were simultaneously produced and received by the 10°–rotated Y–cut LiNbO$_3$ transducer with a thickness of 0.05 mm and a diameter of 2.8 mm that was pasted on the truncated outside corner of one of the second stage anvils. An electrical sine wave (three cycles) was produced by a waveform generator and inputted into the transducer via an amplifier, a duplexer, and a 50 Ω attenuator. Then, a series of reflected P– and S–wave signals propagated back to the duplexer and were measured using a digital oscilloscope. The frequencies used for analysis were 47 and 40 MHz for the P– and S–waves, respectively.

Synchrotron white X–ray was used for X–ray radiography and diffraction experiments. X–ray radiographic images were obtained by the transmitted X–rays that illuminated a fluorescent YAG crystal that was captured using a CCD camera. The capture data was used to determine the sample length at high pressure. Energy–dispersive X–ray diffraction (XRD) measurements were conducted at the fixed diffraction angle of 2θ = 6°. The size of the incident and receiving slits were 0.2 × 0.1 mm and 2.0 × 2.0 mm, respectively. The obtained XRD patterns of the sample yielded the lengths of the unit–cell axes and the unit–cell volumes of the sample. The unit–cell volumes were used to estimate the experimental pressures in combination with the equation of state for $\epsilon$-FeOOH (Suzuki, 2016).

**RESULTS AND DISCUSSION**

Ultrasonic measurements of $\epsilon$-FeOOH were performed in the pressure range of 4.8–24 GPa at room temperature. The sample was confirmed to be $\epsilon$-FeOOH under experimental conditions based on XRD. The experimental conditions and results are summarized in Table 1. The pressure dependence of the P– and S–wave velocities ($V_P$ and $V_S$) are displayed in Figure 1. The $V_S$ at 4.8 and 5.9 GPa were not obtained because the contact between the sample and alumina was insufficient to obtain reflections of the S–wave. For comparison, velocities of δ-AlOOH ob-
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Table 1. Lattice constants and sound velocity of $\varepsilon$-FeOOH as a function of pressure

| $P$ (GPa) | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ ($Å^3$) | $V_p$ (km/s) | $V_s$ (km/s) |
|-----------|---------|---------|---------|-------------|-------------|-------------|
| 0.0001    | 4.955(2) | 4.457(1) | 3.0039(8) | 66.34(9) | - | - |
| 4.8(4)    | 4.902(2) | 4.408(2) | 2.970(1) | 64.2(1) | 7.65(7) | - |
| 5.9(4)    | 4.893(2) | 4.395(2) | 2.965(1) | 63.8(1) | 7.83(7) | - |
| 9.8(5)    | 4.865(2) | 4.355(2) | 2.9438(9) | 62.4(1) | 8.26(7) | 4.89(4) |
| 12.8(8)   | 4.859(3) | 4.318(3) | 2.930(2) | 61.5(2) | 8.43(8) | 5.06(5) |
| 15.2(9)   | 4.840(3) | 4.300(3) | 2.920(2) | 60.8(2) | 8.62(8) | 5.23(5) |
| 17(1)     | 4.822(3) | 4.290(3) | 2.910(2) | 60.2(2) | 8.72(8) | 5.37(5) |
| 20(1)     | 4.813(3) | 4.267(3) | 2.901(2) | 59.6(2) | 8.87(8) | 5.49(5) |
| 21(1)     | 4.806(2) | 4.255(2) | 2.896(1) | 59.2(1) | 9.07(8) | 5.55(5) |
| 24(1)     | 4.792(3) | 4.243(2) | 2.888(1) | 58.7(1) | 9.25(9) | 5.62(5) |

The adiabatic bulk modulus ($K_S$) and share modulus ($G$) were calculated using the following equations:

$$K_S = \rho V_p^2 - \frac{4}{3} \rho V_s^2$$  \hspace{1cm} (1)$$

and

$$G = \rho V_s^2$$  \hspace{1cm} (2),$$

where $\rho$ is the density. The calculated moduli are shown in Figure 2 as a function of pressure. The pressure dependence of $K_S$ increased in the higher pressure range beyond 17 GPa, and that of $V_p$ also increased slightly at the same time. First-principle calculations of $\delta$-AlOOH showed that similar changes of $K$ and $V_p$ occur in the pressure range 25–35 GPa, and that hydrogen bond symmetrization is completed at ~ 30 GPa (Tsuchiya et al., 2002; Tsuchiya and Tsuchiya, 2009). Besides combining the direct observation of the transition to the disordered

Figure 1. $V_p$ and $V_s$ of polycrystalline $\varepsilon$-FeOOH as a function of pressure. The vertical error bars of the measurements are smaller than the symbol size. The velocities of $\delta$-AlOOH obtained by Brillouin spectroscopy (Mashino et al., 2016) are plotted.

Figure 2. Calculated $K_S$ and $G$ of $\varepsilon$-FeOOH as a function of pressure.
state using the neutron diffraction method by Sano–Furukawa et al. (2018) and the determination of sound wave velocities based on Brillouin spectroscopy by Mashino et al. (2016), it is assumed that the increasing rates of \(V_p\) and \(K_S\) become larger than usual preceding the transition to the disordered state. The elastic behavior of \(\varepsilon\)-FeOOH will be like that of \(\delta\)-AlOOH because of the structural similarity between \(\varepsilon\)-FeOOH and \(\delta\)-AlOOH. As such, we estimated that the observed elastic changes are the same preceding changes as those of \(\delta\)-AlOOH and that the transition to the disordered state occurs at a higher pressure than 17 GPa.

In addition, \(V_p\) and \(V_s\) were fitted up to 17 GPa to the following third-order Eulerian finite-strain equations as a function of density to obtain the adiabatic elastic moduli and their pressure derivatives, which are shown in Table 2:

\[
\rho V_p^2 = (1 - 2\varepsilon)^{5/2}(L_1 + L_2\varepsilon)
\]

and

\[
\rho V_s^2 = (1 - 2\varepsilon)^{5/2}(M_1 + M_2\varepsilon)
\]

where \(\varepsilon\) is strain given by

\[
\varepsilon = \frac{1}{2} \left[ 1 - (\rho/\rho_0)^{2/3} \right]
\]

\(\rho\) is the density, \(\rho_0\) is the zero-pressure density. The fitting coefficients \(L_1, L_2, M_1,\) and \(M_2\) were used to obtain the adiabatic bulk modulus and share modulus (\(K_{S0}, G_0\)) and their isothermal pressure derivatives (\(\partial K_S/\partial P, \partial G/\partial P\)) based on the following equations:

\[
G_0 = M_1
\]

\[
K_{S0} = L_1 - \frac{4}{3} G_0
\]

\[
\frac{\partial G}{\partial P} = \frac{1}{3} \left( 5M_1 - M_2 \right)/K_{S0}
\]

\[
\frac{\partial K_S}{\partial P} = \frac{5L_1 - L_2}{3K_{S0}} - \frac{4}{3} \frac{\partial G}{\partial P}
\]

where \(\rho_0\) is the zero-pressure density, \(\rho\) is the density, \(\varepsilon\) is strain, \(L_1, L_2, M_1,\) and \(M_2\) are the fitting coefficients, \(K_{S0}\) and \(G_0\) are the adiabatic bulk modulus and shear modulus, respectively.

Figure 3. Pressure dependence of the normalized unit-cell parameters of \(\varepsilon\)-FeOOH.

\[
\frac{\partial \ln V}{\partial \ln m_{\text{CS}}} \approx -\frac{1}{2}
\]

Based on Birch’s law (Birch, 1961), silicates and oxides with the same crystal structures have a velocity-density relation with a slope given by:

\[
\frac{\partial \ln V}{\partial \ln m_{\text{CS}}} = -\frac{1}{2}
\]

where \(m_{\text{CS}}\) is the mean atomic weight, \(V\) is the sound velocity, and CS stands for constant structure (e.g., Chung, 1972). The bulk sound velocity, \(V_b\), of \(\varepsilon\)-FeOOH at ambient conditions calculated using the obtained coefficients is 5.5 km/s, and \(V_b\) of \(\delta\)-AlOOH is 6.7 km/s (Mashino et al., 2016). Then, the slope \(\Delta \ln V_b/\Delta \ln m\) is calculated to be \(-0.50\), which is consistent with that of silicates and oxides.

The pressure dependence of the relative lattice constants of \(\varepsilon\)-FeOOH is shown in Figure 3. In addition to the compressibility of other distorted rutile type M\(^{3+}\)OOH (e.g., Ga, In, and CrOOH in Sano–Furukawa et al., 2012; MnOOH in Suzuki, 2013), the compressibility of \(\varepsilon\)-FeOOH displays an anisotropic behavior; the \(b\) axis is more compressible than the \(a\) and \(c\) axes. This combination of the directions of compressibility is consistent with the XRD studies of \(\varepsilon\)-FeOOH (Gleason et al., 2013; Suzuki, 2016), \(\delta\)-AlOOH (Sano–Furukawa et al., 2009; Suzuki, 2009), GaOOH and InOOH (Sano–Furukawa et al., 2012).

**Table 2.** Adiabatic elastic moduli and their pressure derivatives in the pressure range 4.8–17 GPa.

| \(K_{S0}\) (GPa) | \(\partial K_S/\partial P\) | \(G_0\) (GPa) | \(\partial G/\partial P\) |
|-------------------|------------------------|--------------|------------------|
| 133(7)            | 4(2)                   | 71(2)        | 4.6(5)           |

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\(\varepsilon\)-FeOOH is a magnetic oxide with a high Curie temperature. It is known to exhibit magnetic and electronic properties that are dependent on pressure and temperature. The high Curie temperature makes it an interesting material for magnetic refrigeration and high-temperature electronic applications. The magnetic properties of \(\varepsilon\)-FeOOH can be studied using techniques such as magnetic susceptibility measurements and neutron diffraction. These techniques can provide insights into the magnetic interactions and exchange energies in the material.

The electronic properties of \(\varepsilon\)-FeOOH can be studied using techniques such as ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS). These techniques can provide information about the electronic structure of the material and the electronic states at the Fermi level.

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In conclusion, the high Curie temperature and magnetic properties of \(\varepsilon\)-FeOOH make it a promising material for applications in magnetic refrigeration and high-temperature electronics. Further studies are needed to understand the magnetic and electronic properties of this material under various conditions, such as pressure and temperature. This will help in the development of new magnetic materials with enhanced properties.
To further examine the change of compression behavior, the variations in $a/c$ and $b/c$ are plotted in Figure 4. The ratios are similar to the values obtained by Suzuki (2010, 2016) at each pressure except for $b/c$ ratios at high pressure (5–10 GPa). The difference may have been caused by the deviatoric stress in the experimental cell under high pressure. The neutron diffraction experiment of $\delta$-AlOOH by Sano–Furukawa et al. (2018) revealed that the stiffening of the $a$ and $b$ axes, namely the switching of the pressure dependence of $a/c$ and $b/c$ from negative to positive, would be indicative of the transition to the disordered state. Other distorted rutile-type $M^3$OOH ($M$: Ga, In, and Cr) were confirmed to have similar changes in their $a/c$ and $b/c$ or only $b/c$ (Sano–Furukawa et al., 2012), and it is plausible that the transitions induce switching of the pressure dependence of the axial ratios from negative to positive in any distorted rutile-type $M^3$OOH. In Figure 4, the pressure dependence of $a/c$ over the entire pressure range is slightly positive, but it is difficult to describe the accurate tendency due to its large uncertainty above 12 GPa. The pressure dependence of $b/c$ is negative within the investigated pressure range. Accordingly, neither $a/c$ nor $b/c$ exhibit a switching of their pressure dependence from negative to positive, which indicates that the transition to the disordered state would not occur.

The elasticity changes and neither the $a$ nor $b$ axes experience stiffening. Combining these two facts, we conclude that all our experimental conditions were within the pressure range for asymmetric proton distribution.

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