Infrared absorption spectra of δ-AlOOH and its deuteride at high pressure and implication to pressure response of the hydrogen bonds

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Abstract. Infrared absorption spectra of δ-AlOOH and its deuterated form (δ-AlOOD) were measured at high pressure using a diamond anvil cell under a quasi-hydrostatic pressure condition using helium as a pressure-transmitting medium. Two absorption bands at 1180 cm⁻¹ and 1330 cm⁻¹ involving vibrations of hydrogen and oxygen atoms shifted to higher frequencies with increasing pressure up to 10 and 12 GPa for δ-AlOOH and δ-AlOOD, respectively. In contrast, at higher pressures the two bands did not shift so much. The pressure-response on the infrared spectra has a close relationship to the symmetrization of the hydrogen bonds and change in the compressibility which was observed from X-ray diffraction measurements.

1. Introduction
Pressure-response of hydrogen bonds in hydrogen-bearing materials is one of the most important issues for understanding pressure-induced changes in properties and crystal structure of hydrous materials. In particular, a pressure-response of hydrous minerals is a hot issue in earth and planetary sciences for understanding the role of hydrogen into the mineral physics of deep part of the earth and planets. δ-AlOOH is a high-pressure polymorph of diaspore (α-AlOOH) and boehmite (γ-AlOOH). δ-AlOOH is thermodynamically stable in the wide P-T range (33-134 GPa and 1350-2300 K) and it is expected that δ-AlOOH can carry water into the lower mantle [1]. It is also noteworthy that a strong hydrogen bond is formed in its crystal structure. By squeezing such a material with strong hydrogen bonds, symmetrization can occur in the hydrogen-bond geometry at very high pressure. The most prominent example is the symmetrization of hydrogen bonds in ice VII, a high-pressure polymorph of

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The hydrogen-bond symmetrization can occur even in dense hydrous minerals. First principle calculations predicted that the symmetrization will accompany a considerable increase in the bulk modulus. A theoretical study revealed that δ-AlOOH will undergo the hydrogen-bond symmetrization at 28 GPa and approximately 20% increase in the bulk modulus will be associated with this transition [3]. Followed by the theoretical study, pressure-response of hydrogen bonds in δ-AlOOH was investigated with X-ray and neutron diffraction measurements. Neutron diffraction studies demonstrated the hydrogen position in the crystal structure of deuterated δ-AlOOH (hereafter δ-AlOOD) both at ambient pressure and high pressures up to 9 GPa [4, 5]. As a result, it was shown that the hydrogen (deuterium) site was not disordered in the crystal structure and the hydrogen bond aligns in the plane defined by the a- and b-axes. By extrapolating the pressure-dependence of hydrogen bond geometry obtained from the neutron diffraction measurements to higher pressures, it was suggested that the hydrogen-bond symmetrization of δ-AlOOD can occur at a pressure range (16-24 GPa) which is notably lower than that predicted by the theoretical approach [5]. Recent powder X-ray diffraction measurements under quasi-hydrostatic pressure condition revealed that pressure-response on the lattice constants of δ-AlOOH and δ-AlOOD drastically changed at pressures 10 GPa and 12 GPa, respectively [6]. The a- and b-axes where the hydrogen bond aligns, stiffen at these pressure conditions. Moreover, more than 20 percent increase was found in the bulk modulus at pressures higher than 10-12 GPa [6]. Similar compression behavior was also reported from a theoretical study [7].

Vibrational spectroscopy can be a direct indicator for hydrogen-bond symmetrization [2, 7]. For observing subtle pressure-induced phenomena, it is also essential to conduct high-pressure experiments under the quasi-hydrostatic condition. In this paper, infrared absorption spectra of δ-AlOOH and δ-AlOOD samples were measured and pressure-response of the hydrogen bond is discussed.

2. Experimental

δ-AlOOH and δ-AlOOD were synthesized at 18 GPa and 900-1000°C for 30-60 min using a Kawai-type high-pressure apparatus [6]. The starting materials of δ-AlOOH and δ-AlOOD were gibbsite (γ-Al(OH)₃) and deuterated bayerite (β-Al(OD)₃), respectively. Deuterated bayerite was precipitated from the mixture of D₂O and NaAlO₂. The detailed procedures were reported elsewhere [5, 6]. The sample of δ-AlOOD contained impurity hydrogen in the crystal structure and the isotopic composition was δ-AlOOH(D₀.744(2)H₀.256(2)) that was determined from Rietveld refinement analysis on the neutron diffraction patterns.

Infrared absorption spectra were measured at high pressure using a diamond anvil cell and a Fourier-transform infrared spectrometer (FTIR) equipped with an IR microscope. All spectra were obtained at room temperature with spectral resolution of 4 cm⁻¹. Type IIa (nitrogen-free) diamonds with the culet size of 300 µm were used as anvils. A rhenium gasket with the initial thickness of 250 µm was used after being pre-indenteted to approximately 60 µm thick. Helium was loaded to the cell as a pressure-transmitting medium to achieve a quasi-hydrostatic condition using a versatile loading system at NIMS [8]. Many of hydrous minerals intensively absorb infrared light because of the large dipole moment of OH ions. For obtaining reasonable absorbance in infrared absorption spectra without saturation, the powder samples are required to be diluted with KBr which is optically transparent in infrared region. A reference pellet (pure KBr pellet) and a sample pellet diluted with KBr were loaded in a single sample chamber in a metal gasket with the initial diameter of 150 µm [9]. This so-called “micro-pellet method” enabled us to measure infrared absorption spectra of a reference pellet and a sample pellet at a same pressure condition. Thus precise spectroscopic comparisons can be achieved under the quasi-hydrostatic condition. Generated pressure was determined by the ruby fluorescence technique.
3. Results and discussion
Representative infrared absorption spectra of $\delta$-AlOOH and $\delta$-AlOOD observed at high pressures are displayed in figure 1 and figure 2, respectively. Several absorption bands were observed in a frequency region lower than 1500 cm$^{-1}$. No obvious absorption peak was detected in the frequency region higher than 2500 cm$^{-1}$. As shown in figure 2, more absorption peaks were observed for $\delta$-AlOOD in comparison with those for $\delta$-AlOOH (see figure 1). This is because $\delta$-AlOOD contain 26 atomic percent hydrogen in the crystal structure, and both of O-H and O-D bonds gave rise to the infrared absorption bands for the deuterated sample. In other words, the absorption peaks which were observed exclusively for the deuterated sample are attributable to vibrational modes involving hydrogen atoms. For instance, two absorption bands at 850 cm$^{-1}$ and 990 cm$^{-1}$ were observed exclusively for $\delta$-AlOOD under the ambient pressure condition. By the isotope substitution with deuterium, these bands shifted from the two bands at 1180 cm$^{-1}$ and 1330 cm$^{-1}$ for $\delta$-AlOOH, respectively. The frequency ratio of 850 cm$^{-1}$ to 1180 cm$^{-1}$ is 0.72 and that of 990 cm$^{-1}$ to 1330 cm$^{-1}$ is 0.74. The frequency ratio of OH to OD vibrations is known to be the square root of reduced mass ratio ($\mu_{OD}/\mu_{OH}$), 0.73. These coincidences strongly support that these vibrational modes involve oxygen and hydrogen atoms.

With increasing pressure, most of the absorption peaks observed in this study shifted to higher frequency, but the pressure dependence is not so simple. Figure 3 plots the pressure dependences on the peak positions of the absorption bands for $\delta$-AlOOH which were observed at 1180 cm$^{-1}$ and 1330 cm$^{-1}$ at ambient pressure. The peak positions of the absorption bands shifted to higher frequency with increasing pressure. It is noteworthy that the pressure dependence showed a kink at approximately 10 GPa (see figure 3). Recent X-ray diffraction measurements at high pressure revealed that the $a$- and $b$-axes of $\delta$-AlOOH stiffen at 10 GPa, while the $c$-axis shows no marked change [6]. The boundary
Figure 3. Pressure dependence of peak positions of two infrared absorption bands of $\delta$-AlOOH. Each series of the plots has a kink at approximately 10 GPa.

Figure 4. Pressure dependence of infrared absorption peaks of $\delta$-AlOOH($D_{0.74}H_{0.26}$). Each series of the plots has a kink at approximately 12 GPa.
pressure is coincident with the pressure in which the pressure-dependence of infrared absorption bands of δ-AlOOH changed (see figure 3). Pressure dependence of peak positions in the infrared spectra of δ-AlOOD is plotted in figure 4. It was found that the pressure-dependence of the four absorption bands, which originated from vibrational modes involving OD and OH, showed a kink at approximately 12 GPa. According to the X-ray diffraction study, a behavior similar to δ-AlOOH was also found for δ-AlOOD, but the change in compressibility occurred at a slightly higher pressure of 12 GPa [6]. Also in the case of δ-AlOOD, the coincidence was found in the pressure where pressure dependence changed between the infrared absorption spectra and the X-ray diffraction measurements.

It was suggested that the change in the compressibility of δ-AlOOH reported from the X-ray diffraction measurements was induced by the symmetrization of the hydrogen bond [6]. The compression behavior of δ-AlOOH revealed by X-ray diffraction was in agreement with the previous theoretical studies [3]. A considerable disagreement remains in the transition pressures between the experimental results (10-12 GPa) and the theoretical estimation (28 GPa). This discrepancy can be reasonable because the theoretical studies on δ-AlOOH using first principles calculation were conducted at static 0 K condition. These calculations neglect the temperature and quantum effects of proton. These vibrational effects are suggested to lower the transition pressure of hydrogen bond symmetrization of δ-AlOOH [3]. The present study clearly showed that the vibrational modes involving hydrogen exhibited a significant change at a pressure in which the compressibilities changed. Furthermore, isotopic effects were also found in the transition pressure. More intensive studies on infrared absorption spectra and Raman spectra will be necessary to assign the vibrational modes more precisely and make a systematic comparison to the theoretical works.

4. Conclusions
Pressure dependence of hydrogen-bearing vibrational modes of δ-AlOOH and δ-AlOOD considerably changed at 10 GPa and 12 GPa, respectively. The isotope effect is presumably syngenetic to the change in the compressibilities observed by X-ray diffraction measurements. These experimental results suggest that the hydrogen-bonding symmetrization occurs at around 10 GPa and 12 GPa, which are extremely low pressure ever reported. The discrepancy with the theoretical estimation will be reconciled in future.

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