A possible existence of phase change of deuterated ice VII at about 11 GPa by X-ray and Raman studies

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Abstract. High pressure experiments were performed with deuterated ice VII using diamond anvil cell in a pressure range of 0.1 MPa to 60 GPa at room temperature in order to further understanding a long-argued issue of phase change in ice VII at approximately 11 GPa. In-situ X-ray diffractometry revealed splitting of diffraction lines of cubic ice VII above 11GPa, which were indexed as a tetragonal structure. The tetragonal structure survived at least up to 60 GPa. Pressure versus volume curves of cubic and tetragonal structures were obtained and the bulk moduli were calculated. Raman spectroscopy showed that the full width at half maximum of O-D vibrational mode decreased with increasing pressure, and showed minimum value at 11 GPa, and then it became broader again above this pressure. The squared vibrational frequency changed linearly with pressure, and the slope changed at about 14 GPa, indicating existence of phase change. All experimental results evidently supported the existence of phase change of ice VII at approximately 11 GPa.

1. Introduction

Ice exhibits a wide variety of forms consisting of tetrahedrally hydrogen-bonded water molecules due to molecular polarity. More than twenty forms including crystalline and amorphous phases have been reported, regardless stable or metastable [1]. Moreover, recently a few post-ice X phases with new dense packing at megabar pressures have been predicted by theoretical calculation studies, e.g., see [2]. Also, a lot of novel properties such as superionic conductivity have been proposed by theoretical studies [3, 4] and also investigated by experimental studies [5, 6]. Whereas, at moderate pressure condition of 10 GPa, where ice VII and VIII are stable above and below about 270 K, respectively, new phase change and property change have been uncovered for both ices. These phenomena have been also another long-argued issue in ices research [7-12].

For example, Pruzan et al., reported that the full width at half maximum (FWHM) value of the O-H and O-D stretching mode, ν1 (A1g), exhibited a minimum near 13 GPa for H2O ice VII and D2O ice VII [7]. Owing to its similarity to the spectrum of ice VIII, the phenomenon was attributed to partial proton ordering in ice VII at approximately 13 GPa even at room temperature [7]. Later, they explained the decrease in FWHM to be the result of a two-phonon decay process of the oxygen...
sublattice and the following increase to be due to anharmonic intermolecular coupling, resulting from hydrogen bond strengthening [8]. X-ray diffractometry (XRD) and Raman spectroscopy studies on H$_2$O ice VIII by Yoshimura et al. showed that the slope of the axial ratio, $a/c$, versus pressure changed at 14 GPa, and that the errors in lattice parameters, calculated assuming the same tetragonal structure, became larger [9]. In addition, a new low-frequency lattice-vibration mode appeared at 14 GPa [9]. According to high-resolution XRD, radial XRD, and single crystal XRD studies by Somayazula et al., a phase transition to a tetragonal structure was clearly detected for H$_2$O ice at 14 GPa at room temperature, and the tetragonal structure maintained up to 60 GPa before symmetrization of the hydrogen bonds occurred [10]. Synchrotron far-infrared spectroscopy of H$_2$O and D$_2$O ice VIII by Klug et al. showed a first-order transition, caused by a subtle phonon instability with an isostructural movement of molecules in the ice VIII structure [11]. Change in proton conductivity observed at 15 GPa was explained by ab initio calculations as a change in mechanism of proton conduction [12].

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Using deuterated water (D$_2$O), it is expected that isotopic effects, including mass and quantum effects, make the phase change easily visualize, because they affect phonon of oxygen sublattice and intramolecular vibration of water molecules. And, to elucidate the phase change, a combination of XRD and Raman spectroscopy is required: The former can catch structural changes while the latter can expose vibrational change in constituent molecules. In this study, high pressure XRD and Raman spectroscopy experiments were performed with deuterated water (D$_2$O) and light water (H$_2$O), for comparison, in order to clearly detect the phase change and to further the understanding of the nature of the phase change occurring near 10 GPa.

### 2. Experimental procedure

A lever-and-spring type diamond anvil cell (DAC) was used to generate the high-pressure. Rhenium and stainless steel gaskets were used. Pressure measurements were made by ruby fluorescence method. Superpure water (milli-Q) and deuterium oxide (100.0% D) were used for light water (H$_2$O) and deuterated water (D$_2$O), respectively. The pressure range of in-situ XRD for D$_2$O water was 0.1 MPa to 60 GPa, and that for H$_2$O water was 2.0 to 21 GPa. All experiments were performed at room temperature, 297 K. In order to reduce effect of strain due to non-hydrostatic stress, heating treatments, in which whole DAC was heated at 373 K and 473 K in an oven, were carried out at about 8, 20 and 30 GPa for tow D$_2$O samples. Samples were characterized by XRD and Raman spectroscopy. XRD studies were performed using synchrotron radiation at the BL-10XU of SPring8 and at the BL-18C of the Photon Factory of KEK. Monochromatized X-rays with wavelengths of 0.04163 nm and 0.06198 nm were used. XRD patterns were detected using an imaging plate. The diffraction images were translated to one-dimensional profiles using the IP-Analyzer data-analysis program [13] and diffraction peaks were fitted using fitting software, fityk. The Raman spectroscopy system used consisted of a diode laser ($\lambda = 473$ nm) and CCD-detectors. Thirteen experimental paths for eight D$_2$O samples and five paths for four H$_2$O samples were examined.

### 3. Results and discussion

Figure 1a shows representative Raman spectra of the O-D vibration mode $\nu_1 (A_{1g})$ with pressure change (black triangles on the red lines). Since O-D modes overlap with the two-phonon modes of the diamond anvil, the spectra obtained from the diamond anvil alone near the sample are indicated by grey lines at the bottom of the individual figures, for comparison. The FWHM of the O-D modes decreased with increasing pressure, reaching a minimum at approximately 11 GPa, and increased again above 11 GPa. Peak intensities reached maxima at approximately 11 GPa. Similar results were also observed for H$_2$O ice. FWHM values plotted in figure 1b were extracted by fitting the Raman spectra using fitting software, fityk. Red and blue marks indicate values for D$_2$O ice and H$_2$O ice, respectively. The FWHM values of D$_2$O ice were smaller than those of H$_2$O ice at all pressure ranges.
examined. The results presented in this study are consistent with those previously reported by Pruzan et al. [7, 8].

The squared vibrational frequencies of $\nu_1 (A_{1g})$ as a function of pressure for D$_2$O ice are given in figure 2. These values show a linear dependence on pressure, and at approximately 13–14 GPa there is an evident change in slope. According to previous Raman studies [8], the squared vibrational frequencies vary linearly with pressure for a given ice form. The change in the slope observed near 13–14 GPa in the present study demonstrated that a phase change occurred at that pressure. This is a new indication of the phase transition for D$_2$O ice VII.

A rough inspection of the XRD patterns revealed 110, 200, 211, and 220 diffraction lines of cubic ice VII above 2.0 GPa for both D$_2$O and H$_2$O samples (figure 3). When examined in detail, peak splitting was observed above 11 GPa. Below 11 GPa, the diffraction lines were exactly indexed as 110, 200, 211, and 220 of cubic ice VII. At approximately 11 GPa diffraction lines began to split with new diffraction lines appearing at higher angles of the original lines. These splitting diffraction lines were indexed as the 200 and 002, 211 and 112, and 220 and 202 lines of a tetragonal structure. After the

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**Figure 1.** a: Changes in O-D vibration mode of sample with pressures, shown in red. Two-phonon modes of diamond are shown in grey. b: Changes in FWHM of O-D and O-H vibration modes for D$_2$O and H$_2$O ice VII.

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**Figure 2.** Squared frequencies of $\nu_1 (A_{1g})$ with pressure. Difference in marks, triangles and circles, indicates difference in data sets for two samples.

**Figure 3.** Changes in XRD patterns with pressure.
heating treatment, the splitting remained and became sharper. The differences in d-values, consequently, lattice parameters and volumes were not evaluated between the before-heating data and after-heating one. Figure 4 shows XRD patterns before splitting at 10.3 GPa and after splitting at 36.7 GPa. Figures inserted display peak fitting results, indicating clear peak-separation at 36.7 GPa. The present results for D$_2$O ice VII agreed well with those of Somayazulu et al. for H$_2$O ice VII, which indicate a phase transition to a tetragonal structure near 14 GPa [10].

In the careful experiments by Somayazulu et al. [10], similar splitting of diffraction lines was observed. Since such splitting could have been derived from strain due to uniaxial compression, they made heat treatment to eliminate the effects. After heat treatment, splitting diffraction lines sharpened and the splitting itself clearly remained. From these results, they concluded that the splitting was caused by a phase transition and was not simply strain due to nonhydrostatic stress. In the present study, similar splitting of diffraction lines was observed for D$_2$O ice VII, and after the heating treatment the splitting diffraction lines also became sharper. Therefore, the formation of a tetragonal structure, characterized by peak splitting similar to Somayazulu et al.’s study, can be attributed to a substantial phase transition. As described above, previous comprehensive studies have argued the existence of a phase transition and/or property change between 11 and 14 GPa for ice VII and ice VIII. The present study provides additional evidence for the existence of a phase change at the pressure range for D$_2$O ice VII.

The lattice parameters were calculated for a cubic structure below 10 GPa and for a tetragonal structure above 11 GPa. At approximately 11 GPa, the $a$-axis of the cubic structure separated to an $a$-axis and a smaller $c$-axis. The difference between the $a$-axis and $c$-axis became larger with increasing pressure. Changes in lattice volume with pressure up to 40 GPa for D$_2$O ice and up to 20 GPa for H$_2$O ice, respectively, are shown in figure 5. A grey solid curve in figure 5 indicates the pressure versus volume curve (P-V curve) of ice VII reported by Hemley et al.[14]. Below 10 GPa, the volumes of cubic structure in the present study agree well with the Hemley et al.’s P-V curve. A black solid curve above 11 GPa indicates P-V curve obtained presently for the tetragonal structure of D$_2$O ice. The volumes of the tetragonal structure are a little smaller in the pressure range examined. This may be likely, because the tetragonal structure is a high-pressure phase. At the transition from cubic to the tetragonal structure, change in volume was not distinguished for H$_2$O ice and D$_2$O ice, which suggests the second order transition. As for transition pressure, there was no difference between H$_2$O and D$_2$O ice in this study.

For the cubic structure below 10 GPa the bulk modulus $K_0$ and $K_0'$ were calculated to be 22.7 GPa and 3.45, respectively using the Birch–Murnaghan equation of state. The calculated value, 22.7 GPa, is close agreement with value of 23.7 GPa reported by Hemley et al.’s [14]. While, the bulk modulus $K_6$ and $K_6'$ calculated for the tetragonal structure above 11 GPa were 26.2 GPa and 3.82, respectively. The absolute value of bulk modulus, 26.2 GPa may not be exact one, but the tetragonal structure is a substantially stiffer structure with a larger bulk modulus than the cubic structure.
In the present study, the transition of D$_2$O ice VII to a tetragonal structure at approximately 11 GPa was clearly observed by XRD, which is consistent with the transition reported for H$_2$O ice VII by Somayazulu et al. [10]. Moreover, the change in the slope of the squared vibrational frequencies, $v_1 (A_{1g})$, versus pressure plot was detected at almost the same pressure by Raman spectroscopy. The phase change can be characterized by formation of a tetragonal structure for D$_2$O ice, however, the reason for forming the tetragonal structure has not yet been inferred in this study.

The tetragonal structure of D$_2$O ice observed in this study survived up to 60 GPa, similar to the result for H$_2$O ice reported [10]. Contrary to this result, changes in the FWHM of $v_1 (A_{1g})$ were observed in the limited pressure range of 10 to 25 GPa. A previous study by Pruzan et al. attributed the change in the FWHM of $v_1 (A_{1g})$ to a partial proton ordering [7] or a change in the phonon modes [8]. And, Somayazulu et al. described that the transition involved change in the character of the proton order/disorder [10]. The relationship between the forming tetragonal structure and the proton order/disorder is subject to be clarified. Further experimental and theoretical studies should be performed.

References
[1] Hemley R J 2010 High Press. Res. 30 581
[2] Militzer B and Wilson H F 2010 Phys. Rev. Lett. 105 195701
[3] Cavazzoni C, Chiarotti G L, Scandolo S, Tosatti E, Bernasconi M and Parrinello M 1999 Science 283 44
[4] Goldman N, Fried L E, Kuo I F W and Mundy C J 2005 Phys. Rev. Lett. 94 217801
[5] Goncharov A F, Goldman N, Fried L E, Crowhurst J C, Kuo I F W, Mundy C J and Zaug J M 2005 Phys. Rev. Lett. 94 125508
[6] Lin J F, Gregoryanz E, Struzhkin V V, Somayazulu M, Mao H K and Hemley R J 2005 Geophys. Res. Lett. 32 L11306
[7] Pruzan Ph, Chervin J C and Gaythie M 1990 Europhys. Lett. 13 81
[8] Pruzan Ph, Chervin J C, Wolanin E, Canny B, Gauthier M and Hanfland M 2003 J. Raman Spectrosc. 34 591
[9] Yoshimura Y, Stewart S T, Somayazulu M, Mao H K and Hemley R J 2006 J. Chem. Phys. 124 024502
[10] Somayazulu M, Shu J, Zha C S and Goncharov A F 2008 J. Chem. Phys. 128 064510
[11] Klug D D, Tse J S, Liu Z, Gonze X and Hemley R J 2004 Phys. Rev. B 70 144113
[12] Iitaka T 2012 Abstract SMP48-01 presented at JpGU Meeting, Chiba, Japan, 20-25 May
[13] Seto Y 2012 Rev. High Press. Sci. Tech. 22 145 (in Japanese)
[14] Hemley R J, Jephcoat A P, Mao H K, Zha C S, Finger L W and Cox D E 1978 Nature 330 737