BL-18C/2012G509

Phase change of D_2O ice VII at approximately 11 GPa

Hirokazu Kadobayashi, [1,*] Hisako Hirai,[1] Michika Ohtake,[2] Yoshitaka Yamammoto,[2]
Satoshi Nakano,[3] and Takumi Kikegwa[4]
[1] Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan
[2] National Institute of AIST, Tsukuba, 305-8569, Japan
[3] National Institute for Material Science, Tsukuba, Ibaraki 305-0044, Japan
[4]Photon Factory, Tsukuba 305-0801, Japan

1 Introduction

The H_2O ice exists in a wide variety of forms. Twenty different stable and metastable forms have been reported as a function of pressure, temperature, and P–T path for their formation. In addition, many novel properties such as symmetrization of hydrogen bonds at high pressure, proton ordering at low temperature, and superionic property at high-P and high-T have been investigated. Whereas, at a moderate pressure of 10 GPa, where ice VII and VIII are stable above and below approximately 270 K, respectively, new phase changes and property changes have been uncovered for both ices [e.g.1-3]. For example, Pruzan et al. attributed their Raman data to partial proton ordering in ice VII at approximately 13 GPa even at room temperature [1]. X-ray study of H_2O ice VIII by Yoshimura et al. suggested a phase change at 14 GPa from the change in axial ratio, *a*/*c*, versus pressure [2]. According to high-resolution XRD, radial XRD, and single crystal XRD studies by Somayazulu et al., a phase transition to a low symmetry structure was clearly detected for H_2O ice at 14 GPa at room temperature [3]. As described above, the existence and nature of this phase change have become increasingly well understood by many studies. In this study, high pressure X-ray experiments were performed on deuterated water (D_2O) and light water (H_2O), for comparison, to clearly detect the phase change and to further the understanding of the nature of the phase change occurring near 10 GPa [4, 5].

2 Experiment

A lever-and-spring type diamond anvil cell (DAC) was used. Pressure measurements were carried out using the ruby fluorescence method and diamond Raman method. Super pure water (milli-Q) and deuterium oxide (100.0 % D) were used. The pressure range of *in-situ* XRD for D_2O water was 2.0 to 60 GPa, and that for H_2O water was 2.0 to 21 GPa. All experiments were performed at room temperature, 297 K. Three sample-preparation methods were tried. Among them, the best one was as follows: the gasket hole was filled with deuterated water, and the entire DAC was rapidly cooled in a liquid nitrogen bath, then the pressure was loaded up to 2 GPa. The powder patterns obtained exhibited very smooth and homogeneous diffraction lines along Debye rings. In order to reduce strain due to non-hydrostatic stress, heating treatments were given for D_2O samples prepared. The heating was performed at pressures from 8 to 35 GPa by heating the entire DAC in an oven at 373, 423, and 473 K for 2 to 4 hours. Samples were characterized by XRD at the BL-18C beamline of the Photon Factory of KEK. The diffraction peaks obtained were fitted using the fitting software, Fityk.

3 Results and Discussion

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. Especially in the XRD patterns of the samples prepared by the best method, clear splitting was observed up to 40 GPa, which was the highest pressure limit for these samples. The 110, 211, and 220 diffraction lines clearly split, whereas the 200 line did not split. Since such splitting could have been derived from strain due to uniaxial compression, a heating treatment of the samples were performed at pressures before and after splitting from 8 to 35 GPa to reduce such effects. After heating treatment, splitting diffraction lines sharpened and the splitting itself clearly remained. The effect of non-hydrostatic stresses should have been reduced because of the observed peak sharpening. Therefore, the observed splitting was inferred

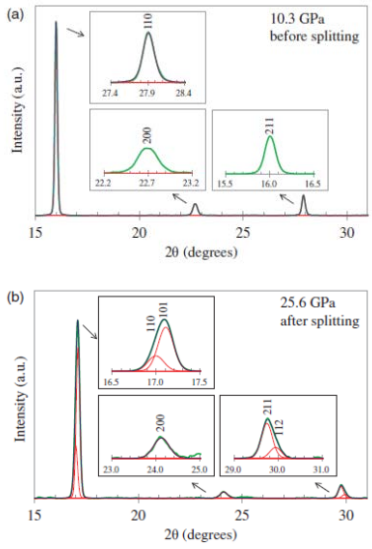

Fig.1 Representative XRD patterns before and after splitting. The wavelength of X-ray is 0.06198 nm.

to be intrinsic phenomenon, i.e. the lowering of the symmetry occurred for D_2O samples. These splitting diffraction lines were indexed as the 110 and 101, 211 and 112, and 220 and 202 lines of a tetragonal structure. The magnitude of split increased with increasing 2θ. Fig. 1 shows representative XRD patterns before splitting at 10.3 GPa and after splitting at 25.6 GPa. The inserted figures display peak separation results by the peak fitting software. The 111 diffraction line was not observed due to weak intensity, and the 200 line did not split though the 110, 211, and 220 lines split. The existence or absence of splitting for the cubic lines in the present results agreed well with the previous study for H_2O ice [3].

Although the structure and symmetry of the transformed phase could not be determined, an attempt to calculate the volume of the low symmetry phase was made, assuming that the phase had a tetragonal structure. Changes in the lattice volume calculated with pressures up to 40 GPa for D_2O ice and those up to 20 GPa for H_2O ice, respectively, are shown in Fig. 2. The grey solid curve in Fig. 2 indicates the pressure versus volume curve (*P-V* curve) of ice VII reported as an entirely cubic structure by Hemley et al. [6]. Below 10 GPa, the volumes calculated as an exact cubic structure in this study closely coincided with their curve [6]. The volumes calculated as a tetragonal structure above 11 GPa showed values slightly smaller than those reported by that study, which may be conceivable because the low symmetry structure is a high-pressure phase. The black solid curve indicates a P-V curve presently estimated as a tetragonal structure. As for lattice volume and transition pressure, there was no difference between H_2O and D_2O ice in this study.

The bulk modulus K_0 and K_0' of the cubic structure below 10 GPa were calculated as 22.7 GPa and 3.45, respectively, using the Birch–Murnaghan equation of state. The value of 22.7 GPa was close to the value of 23.7 GPa reported by Hemley et al. [6], while those for a tetragonal structure above 11 GPa were 26.2 GPa and 3.82, respectively. The absolute value of bulk modulus, 26.2 GPa, might not be exact; however, the transformed structure might have a substantially stiffer structure with a bulk modulus larger than that of the cubic structure.

As described above, previous comprehensive studies have argued the existence of a phase transition and/or property change at pressure range between 11 and 14 GPa for ice VII and ice VIII. In the present study, the transition of D_2O ice VII to a low symmetry structure at approximately 11 GPa was clearly observed by XRD study. Thus, in this study, the additional evidence for the existence of a phase change for D_2O ice VII was provided; however, the reason for the formation of the low symmetry structure was not inferred.

The low symmetry structure of D_2O ice was retained at least up to 40 GPa in the present study. Somayazulu et al. reported that the low symmetry structure of H_2O ice was maintained before hydrogen bond symmetrization transition near 60 GPa [3]. They explained the transition as ferroelastic with the appearance of the spontaneous strain, and proposed that a change in

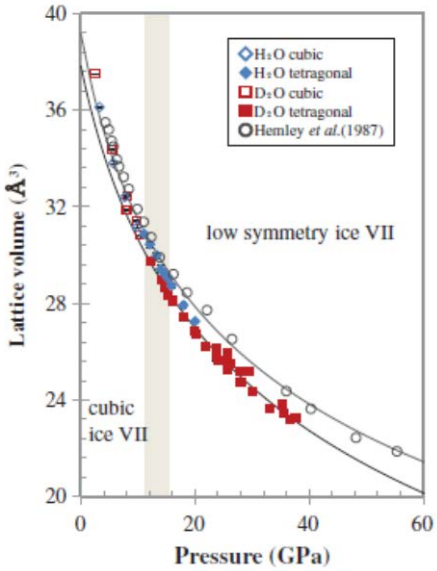

Fig.2: Changes in lattice volumes with pressure for cubic ice VII and the low symmetry ice VII. Solid grey curve indicates the *P-V* curve determined as an entirely cubic structure by Hemley et al. [6]. Solid black curve indicates a P-V curve calculated by assuming that the low symmetry phase has a tetragonal structure. Error bars are hidden by individual marks.

the character of proton order/disorder is associated with the phase transition [3]. Pruzan et al. also explained the phase transition as a phenomenon relating to proton order/disorder behaviour based on the change in the FWHM of OD-modes [1]. These studies suggested the involvement of proton behaviour with the phase transition. A recent neutron diffraction study demonstrated that protonic species were localized on octahedral interstitial sites of oxygen sublattice above about 13 GPa, however, the form did not exhibit low symmetry but cubic one [7]. In any case, the neutron study pointed out that one should take into account protonic species existing at sites and/or states different from conventional network structure of ice VII even at moderate pressures. Further experimental and theoretical studies are required to elucidate the nature of phase transition at about 11 GPa and to understand still hidden properties of ice VII.

References

[1] Ph. Pruzan et al., *Europhys. Lett.* **13, 81** (1990).
[2] Y. Yoshimura et al., *J. Chem. Phys.* **124**, 02450 (2006).
[3] M. Somayazulu et al., *J. Chem. Phys.* **128**, 064510 (2008).
[4] H. Kadobayashi et al., *Journal of Physics: Conference Series* **500**, 182017 (2014).
[5] H. Hirai et al., *High Pressure Research* **34**, 289 (2014).
[6] R. J. Hemley et al., *Nature* **330**, 737 (1987).
[7] M. Guthrie et al., *PNAS* **110**, 10552 (2013).

* kadobayashi@sci.ehime-u.ac.jp