

Elastic properties of ice VII and its high-pressure polymorphs

Ice shows rich polymorphism under various pressure and temperature conditions due to the variation of hydrogen bonds linking the H₂O molecules. This is one reason why the properties of H₂O ice under pressure are of great interest in a broad range of fields including physics, chemistry, and earth and planetary sciences. At room temperature, compressed liquid water transforms to tetragonal ice VI at 1.05 GPa and with further compression, ice VI transforms to cubic ice VII at 2.1 GPa. The structure of ice VII consists of a body-centered cubic (bcc) lattice of oxygen and each oxygen atom covalently bonded to two hydrogen atoms occupying two of four tetrahedral sites (see Fig. 1). The phase X, in which the proton is at the center position between two oxygen atoms with a bcc framework of oxygen, was predicted as a following phase of ice VII by Holzapfel (1972) [1]. Infrared and Raman spectroscopic studies suggest that a sluggish transition of ice VII with pressure to the atomic phase X starts at approximately 60 GPa and ends at approximately 100 GPa. The possible existence of intermediate phases, in which protons distribute dynamically into double potential wells along the axis of hydrogen bond, has been suggested from theoretical studies (e.g., [2]).

In this study [3], longitudinal and transversal velocities in polycrystalline ice were measured at room temperature and a pressure range of 6–60 GPa by Brillouin scattering method. Synchrotron X-ray diffraction measurements were also conducted simultaneously with Brillouin scattering measurements at the pressure range from 40 to 60 GPa to clarify the change in elastic properties across the expected transitions of ice. Experiments were conducted with the Brillouin scattering measurement system equipped with a CO₂ laser heating system installed at beamline BL10XU [4].

Polycrystalline ice directly frozen from water by compression usually consists of several anisotropic large grains and it is difficult to obtain precise aggregate acoustic velocity for material using such samples because the acoustic velocity is sensitively affected by crystallographic orientation. Therefore, we quenched

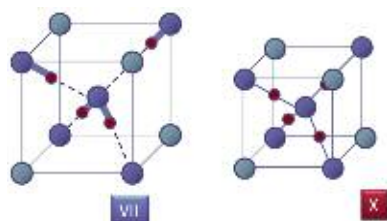


Fig. 1. Crystal structures of high-pressure dense ice: Oxygen atoms are represented by large blue spheres and hydrogen atoms by small red spheres.

ice VII from water using a CO₂ laser in a diamond anvil cell at 14 GPa to obtain an isotropic aggregate of ice VII. We could obtain nearly isotropic spectra from the polycrystalline ice by this quenching process. Then, we compressed the sample with a pressure interval of 2–3 GPa and collected Brillouin spectrum at room temperature and each pressure up to 60 GPa. Measurements were also taken along a decompression path until reaching 6 GPa. Measured acoustic velocities for longitudinal and transversal modes of ice are plotted as a function of pressure in Figs. 2(a) and 2(b), respectively. Velocities collected along compression and decompression paths were in good agreement with each other except the pressures between approximately 40 GPa and 55 GPa. The pressure dependence of the longitudinal acoustic velocity of ice above 58 GPa is clearly different from that below 50 GPa, although an intermediate pressure region was hidden by the transversal mode of a single-crystal diamond. We conducted measurements with the χ angles of upper and lower velocity limits for the transversal mode of a single-crystal diamond, at 40–63 GPa. Therefore, the longitudinal velocities of ice should be in the shadow range of Fig. 2(a) at 48–57 GPa. Figure 3 shows the volumes of ice against pressure obtained in this study in the pressure range of

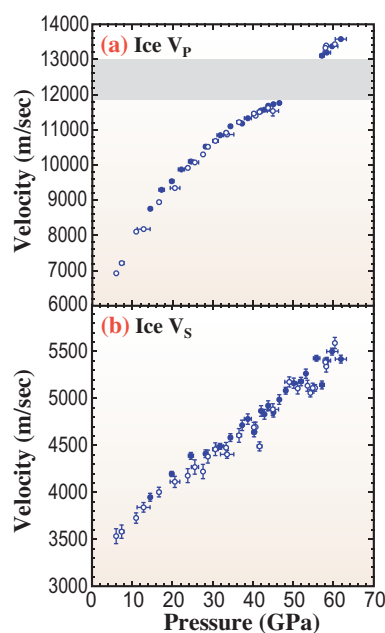


Fig. 2. Acoustic velocities in polycrystalline H₂O ice measured in this study as a function of pressure: (a) Transversal velocities, (b) longitudinal velocities. Filled and open circles represent acoustic velocities measured along compression and decompression paths, respectively. The velocity region is shadowed in which the spectrum of transversal mode for single-crystal diamond hides other spectra.

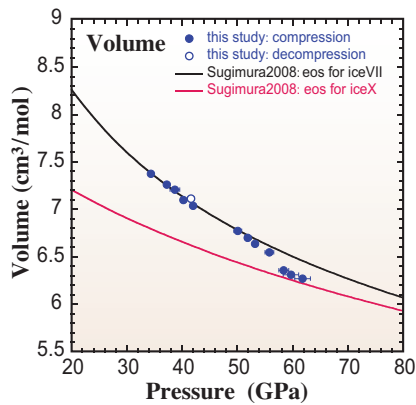


Fig. 3. Measured volumes of ice as a function of pressure: Filled and open blue circles represent volumes measured in this study along compression and decompression paths, respectively. A black line and a red line are predicted with the equations of state of ice VII and ice X, respectively, proposed by [5].

40–60 GPa. Volumes of ice seem that they were on the line predicted using the equation of state of ice VII suggested by a density-functional calculation combined with synchrotron X-ray diffraction measurements [5] until 58 GPa and approached that of ice X above 58 GPa.

It has been debated whether the compression behavior of bcc ice should be expressed with one equation of state. In this study, we could calculate the adiabatic elastic moduli of bcc-structured ice from a set of longitudinal and transversal velocities and volume, which are measured simultaneously in the pressure range of 40–60 GPa, independent of the debate. The slope of the shear modulus against pressure changes at approximately 35–40 GPa, and we also observed that there is a small discontinuity of the shear modulus against pressure at approximately 55–60 GPa (see Fig. 4(a)). There is no distinct discontinuity in bulk modulus at 40 GPa, but the pressure dependence is clearly different below 50 GPa and over 58 GPa (see Fig. 4(b)). It is plausible that the pressure dependence of the bulk modulus changes at approximately 58 GPa accompanied by discontinuities of shear modulus and other vibration properties, which have been observed in previous studies. We consider that these observed changes at approximately 58 GPa are comparable to the transition from a statically disordered state to a dynamically disordered state of the hydrogen bond in bcc-structured ice, which is proposed by theoretical studies. This change in pressure dependence of the bulk modulus could support the argument that bcc-structured ice is expressed better with two sets of thermodynamic parameters.

We demonstrated that a change in the hydrogen bonding state clearly affects the elastic properties of the bcc-structured ice. A temperature effect on the change of elastic properties was not clarified in this study, but the discontinuous change of thermodynamic properties across the transition should exist at a whole

temperature range of the transition. The high-temperature bcc-structured ice could exist in cold subducting slabs of the Earth and in interiors of icy planets and satellites. The elasticity difference between ice VII and the dynamically disordered ice X may affect the dynamics of the interiors of these planets. Further investigation in a wide range of temperature is required for more detailed modeling; however, the thermoelastic properties of high-pressure polymorphs of ice obtained in this study could contribute to clarifying the dynamics and evolution of the Earth and icy planets and satellites.

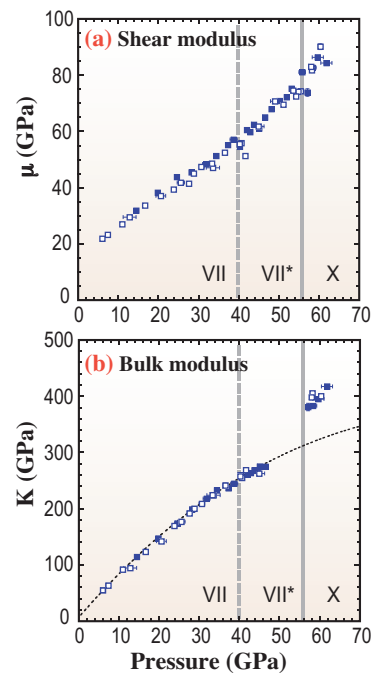


Fig. 4. Pressure dependence of the elastic moduli obtained from measured velocity: (a) shear moduli and (b) bulk moduli as functions of pressure: Filled and open blue squares represent elastic moduli measured in this study along compression and decompression paths, respectively. The estimated boundary between ice VII and the transitional state of ice VII (VII*) and that between the transitional phase to the dynamically disordered ice X (X) are shown as a bold grey dashed line and a bold grey solid line, respectively. Black dotted lines in (b) are predictions from specific heats obtained in this study and an isothermal equation of state for ice VII.

Yuki Asahara

Department of Earth and Space Science, Osaka University

E-mail: asaharay@anvil.ess.sci.osaka-u.ac.jp

References

- [1] W.B. Holzapfel: J. Chem. Phys. **56** (1972) 712.
- [2] M. Benoit *et al.*: Phys. Rev. Lett. **89** (2002) 145501.
- [3] Y. Asahara, K. Hirose, Y. Ohishi, N. Hirao, M. Murakami: Earth Planet Sci. Lett. **299** (2010) 474.
- [4] M. Murakami *et al.*: Phys. Earth Planet. Int. **174** (2009) 282.
- [5] E. Sugimura *et al.*: Phys. Rev. B **77** (2008) 214103.