Japan Geoscience Union Meeting 2012
(May 20-25 2012 at Makuhari, Chiba, Japan)

SMP48-01 Room:102A Time:May 23 13:45-14:00

Proton dynamics in ice VII

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Proton dynamics in the hydrogen bonds, in particular, dissociation and recombination of water molecules is a basic process of physical and chemical phenomena in many chemical systems and life systems [1]. In this talk, we study the proton conductivity of ice VII [2], which may exist in astronomical icy bodies, from the view point of the transport theory of ionic defects and rotation defects in ice, and from view point of molecular dynamics simulation of the hydrogen and oxygen atoms. The figure shows the temperature-pressure dependence of conductivity obtained by the two methods. The peak of conductivity is interpreted from the view point of (A) collaboration of conduction of ion defects and rotation defects and (B) transition from ”plastic phase”[3] to ”crystalline phase”. On the basis of these viewpoints, we discuss the measurement of electric conductivity [4] and possible effects on the proton chemistry in ice VII.

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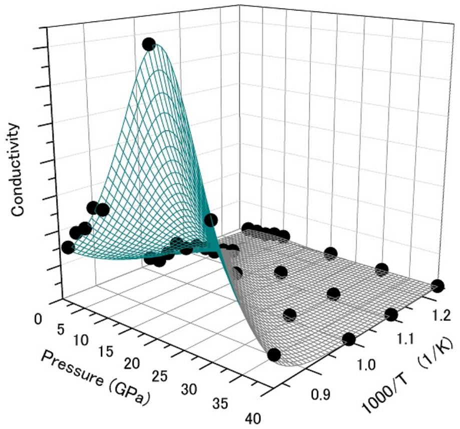
http://www2.jpgu.org/meeting/2011/yokou/SMP045-18.pdf

Figure: Temperature and pressure dependence of the electrical conductivity Ice VII: the filled circles are the result of molecular dynamics, and the surface represents the fit by transport theory.

Keywords: ice, high pressure phase, proton dynamics, electric conductivity, point defect, plastic phase



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SMP48-02 Room:102A Time:May 23 14:00-14:15

Pressure and temperature response of proton conductivity of ice VII and VIII, and their phase relations

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1. Introduction

Between ˜2 and ˜60 GPa, it has generally been accepted that only two solid H2O phases-a high temperature, proton disordered, cubic ice VII and a low temperature, proton ordered, tetragonal ice VIII are stable. However, based on X-ray diffractions and spectroscopic studies, it was pointed out that a phase transition or some structural change occurs at around 14 GPa [1-5]. In this study, we measured pressure and temperature responses of proton resistance of ice VII and VIII at 2-40 GPa and 263-300 K by using an AC impedance analysis method. We discuss the cause of the obtained P-T responses of proton conductivity and the phase relations of solid H2O.

2. Experimental

Platinum or gold electrodes were placed around a hole of a rhenium gasket combined with cubic boron nitride powder. Distilled and deionized H2O was loaded into the hole and pressurized by diamond anvils having flats of 0.35 mm in diameter. The electrodes were connected to a LCR meter. In our impedance spectroscopy measurements, an 1 V ac voltage signal was introduced into the system and the response of the system to this signal is expressed by complex impedance Z = R + Xi, where R and X are the real part and imaginary part of Z, respectively. The frequency ranged from 20 Hz to 1 MHz. We fitted the R-X plot with a fuction of a semicircle and obtained a bulk proton resistance of the sample at different pressures and temperatures. By use of size of the sample between electrodes measured at each pressure, the resistance value was converted into conductivity. Pressure at room temperature was determined based on a Raman shift of the diamond anvil. At target pressure, temperature was controlled by putting the whole cell into a freezer. Sample temperature was determined based on a type K thermocouple stuck on the table side of the anvil. Powder X-ray diffraction patterns were also obtained at a KEK-PF-AR-NE1 beamline on some runs.

3. Results and discussion

During increasing pressure at room temperature, the proton conductivity became smaller by the one order of magnitude at 2.2 GPa due to VI-VII transition. After taking a local minimum at ˜3 GPa, it increased with pressure and took a local maximum at ˜10GPa, which is greater by the one order of magnitude of that at 3 GPa. Then, it decreased with pressure. At 20 GPa, it was almost identical to that at 3 GPa. Then, it was almost constant up to 40 GPa. By powder XRD measurements at high pressure and room temperature, a slight splitting of diffraction lines of cubic VII was observed above 10 GPa, which is almost consistent with [4]. Therefore, the anomaly of high conductivity at ˜10 GPa should be caused by the pressure induced structural change of VII [4].

Low temperature experiments at constant load revealed that the lower temperature it was, the lower conductivity the sample had. The conductivity of proton ordered VIII was lower than that of proton disordered VII. This indicates that proton concentration variation rather than proton mobility (mean free path) variation is dominant in the conductivity variation with temperature. Thus, we cannot interpret the high conductivity state due to appearance of modulated incommensurate phases [1], which have the degree of order higher than proton disordered VII.

On VII-VIII boundary with temperature at constant load, we did not observe a clear discontinuity and large variation of temperature dependency of the conductivity. Namely, the anomaly of high conductivity at ˜10 GPa exists also in the VIII stable region. This is consistent with anomaly of pressure variation of c/a ratio of VIII [2, 3] and some structural change suggested from pressure variations of Raman spectra of VIII [2, 5], which were observed at 10-15GPa and lower temperature than that of this study.

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Keywords: ice, proton conductivity, high pressure, low temperature, phase transition

SMP48-03 Room:102A Time:May 23 14:15-14:30

Phase change of hydrogen hydrate under low temperature and high pressure

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Low temperature and high pressure experiments of filled ice Ic structure of hydrogen hydrate were performed using diamond anvil cell and He-refrigerator cryostat. The temperature and pressure ranges were at 30 to 300K and 5 to 55GPa, respectively. X-ray diffractometry revealed that the cubic structure changed to a tetragonal structure at high pressure and low temperature region as expected by a theoretical study. Phase boundary between cubic and tetragonal structures was estimated. Raman spectroscopy also showed change in frequency of vibron of hydrogen molecules at the phase boundary.

Keywords: hydrogen hydrate, phase change, low temperature, high pressure

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SMP48-04 Room:102A Time:May 23 14:30-14:45

Investigation of compressional mechanism of hydrous magnesium silicate by first-principles calculations

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It is widely accepted that the atmosphere and the oceans of the Earth are formed by degassing of the Earth's mantle. Most of the water may have been lost or it may still be stored in the Earth's mantle. If considerable amounts of water are present in the Earth's mantle, such water plays a key role in the geodynamics of the Earth's interior, because it affects the melting temperature and the transport properties of minerals as well as their elastic properties. Recent high pressure experiments suggested that main components of the transition zone of the mantle, wadsleyite and ringwoodite, can store significant amount of water [1-4], and the lower mantle minerals, consisting of Mg-perovskite, magnesiowustite and Ca-perovskite, can potentially store considerable amounts of water [5]. More recently, the substitution mechanism of protons in wadsleyite was studied experimentally by using neutron diffraction technique [6] and theoretically by the first-principles calculations [7] within the density functional theory (DFT) [8]. However the effects of water solution on their physical properties have not yet been fully understood. Then the first principles DFT calculations are performed here to investigate change in compression mechanism of hydrous Mg_2SiO_4, $MgSiO_3$ and MgO, and influence of proton incorporation on the phase transitions between three polymorphs of Mg_2SiO_4, i.e, forsterite, wadsleyite and ringwoodite, and partitioning of Mg_2SiO_4 into $MgSiO_3$ and MgO. Calculated bulk moduli of hydrous Mg_2SiO_4 have become significantly lower than that of water-free one, in which the calculated result of ringwoodite supports the high pressure experiment [9]. Calculated bulk moduli of hydrous Mg-perovskite and periclase are also much lower (-10%~) than that of anhydrous one. Our free energy calculations suggest that partitioning pressure from hydrous ringwoodite to perovskite and hydrous periclase become significantly larger than that for anhydrous case. If water remains considerable amounts of water in the lower mantle, there has still been possibility that 660 km seismic discontinuity is derived from the partitioning between hydrous minerals.

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Keywords: first principles calculation, magnesium silicate, phase transition, elastic modulus, bulk modulus

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SMP48-05 Room:102A Time:May 23 14:45-15:00

Behavior of hydrogen isotopes in brucite at high pressures and temperatures

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Hydrogen plays important roles in chemical and physical properties of hydrous minerals such as rheology, electrical conductivity, and diffusivity. Brucite $Mg(OH)_2$ is one of the representative hydrous minerals occurring in the earth's crust and mantle. It has a CdI_2 structure (S.G. P-3m1), which is consisted of edge-sheared MgO_6 octahedra where OH-bonds are bound along c-axis (Zigan and Rothbauer 1967). The brucite layer is a fundamental building unit of hydrous phyllosilicate including micas, serpentines, clay minerals and dense magnesium hydrous silicates (DMHS). OH-bond possibly largely affects the nature of interlayer forces and the stability of such hydrous phases under geological pressure and temperature conditions. In the present study, we have performed X-ray powder diffractometry, micro-Raman spectroscopy and high pressure-temperature interdiffusion experiments of hydrogen isotopes in brucite to understand their behaviors at high pressures and high temperatures.

Protonated and deutriated water were mixed to be desired D/H ratios, and then added to MgO powder. The starting materials encapsulated in an autoclave were heat at 250 degC and under autogenic pressure as high as 40 bars for 168 h. The grain size of recovered brucite is smaller than 10 micron in diameter. In order to determine isotope effects on lattice parameters, the brucite powders were examined by X-ray powder diffractometer. In diffusion experiments, two semi-circular disks of pure $Mg(OH)_2$ and $Mg(OD)_2$ were compressed in a diamond anvil cell and heated at 300 degC for ˜40 hours in a furnace in argon atmosphere. The pressures of the samples after cooling were ˜1-2 GPa. H-D diffusion profiles of recovered samples were obtained on the basis of the intensity ratios of OH and OD stretching peaks by a micro-Raman spectroscopy.

An isotope effect on lattice parameters of brucite could be successfully recognized by precise XRD measurements in the present study. The a-axis of brucite is nearly constant with respect to the D/H ratio. However, the c-axis of $Mg(OH)_2$ linearly decreases down to 99.7 % with increasing deuterium content. This tendency suggests that the OH- and OD-bonds oriented along c-axis constrain the spacing of basal plane of the brucite structure. Smaller amplitude of the stretching vibration of OD than that of OH causes the shrinkage of d_{0001}. Diffusion profile measurements of the recovered sample from 1.8 GPa and 300 degC tentatively clarified that the H-D interdiffusion coefficient (D_{H-D}) is 10^{-15} m^2/s order. This value tends to be much larger than those of other cations in silicates. For instance, the D_{H-D} of brucite is more than ten orders of magnitude larger than the Si-self diffusion coefficient in forsterite estimated considering the same temperature and grain size with those in the present study (Brady 1983, Hallwig et al. 1982). It was also clarified that the D_{H-D} in $Mg(OH)_2$ is faster than that in $Mg(OD)_2$. This fact is inconsistent with that small distance between nearest-neighboring hydrogen isotopes in $Mg(OD)_2$, which is deduced from its c-axis length, could enhance exchange of hydrogen isotopes. The width of hydrogen-bearing layers is not simply related to the D_{H-D}. Higher frequency (3650 cm^{-1}) of OH stretching vibration than that of OD (2693 cm^{-1}) is a plausible explanation of high D_{H-D} in proton-rich brucite. OH-bond which is a majority of hydroxyl bonds in proton-rich brucite would cause high probability of hydrogen isotope exchange.

Keywords: brucite, hydrogen isotopes, diffusion, diamond anvil cell, lattice parameters

SMP48-06 Room:102A Time:May 23 15:00-15:15

Pressure-induced phase transition and high-pressure response of hydrogen bonds in portlandite

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$Ca(OH)_2$, portlandite, belongs to brucite-type layered hydroxides, which is considered to be a model structure of hydrous minerals. This has hydrogen bonds within the interlayer of CaO_6 octahedral sheets. According to previous neutron diffraction studies of $Ca(OD)_2$, repulsive D...D interaction and hydrogen bonds in portlandite becomes much stronger under high pressure up to 4.5 GPa. Recently, it is said that portlandite undergoes a phase transition to a high-pressure phase at 6-8 GPa, at room temperature. However, the crystal structure of the high-pressure phase and the role of hydrogen bonds are still unknown. In the present study, the crystal structure of the high-pressure phase was clarified for the first time from powder and single crystal X-ray diffraction measurements. The crystal structure was determined to be monoclinic. In the structure, octahedral layers shift close each other, and some of the oxygen atoms become close enough to form the bondings with two neighboring Ca atoms. Based on the clarified structure of high-pressure phase accompanying the displacements of CaO_6 layers and Ca atoms, it is suggested that hydrogen bonds are closely related to the phase transition. In addition, several plausible positions of the hydrogen atoms in the structure are estimated in the high-pressure phase. Preliminary neutron diffraction experiments were also carried out using the new high-pressure cell. The high-pressure phase of $Ca(OD)_2$ was observed for the first time by the neutron diffraction. Further advanced experiments using much stronger neutron flux will allow us to acquire structural information of hydrogen bonds and the hydrogen positions in portlandite.

Keywords: Paris-Edinburgh cell, high pressure, neutron diffraction, hydrous minerals, phase transition, hydrogen bond

SMP48-07 Room:102A Time:May 23 15:30-15:45

X-ray diffraction study of vitreous hydrous silica

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Water changes the properties of magma such as viscosity, density, and sound velocity, when it is dissolved into magma. Therefore, it is interested how dissolution of water affects structure of silicate melts. We have studied the hydrous silica glass, which was quenched from 200 MPa and 1500 C, by the X-ray diffraction analysis using synchrotron radiation.

Keywords: amorphous, hydrous magma

SMP48-08 Room:102A Time:May 23 15:45-16:00

Melting of transition metal-hydrogen systems under high pressure

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Hydrogen reacts with many kinds of metals and forms metal hydrides. Early transition metals such as Ti and V form hydrides while solubility of hydrogen in other transition metals such as Fe and Ni is low at ambient pressure. However, Fe and Ni absorb hydrogen under high pressure conditions. To study liquid state of transition metal-hydrogen systems, we have performed x-ray diffraction measurements under high-pressure high-temperature conditions for Ti, V, Mn, Fe, Co and Ni.

Experiments were performed using a cubic-type multi-anvil press installed on BL14B1 at SPring-8. Stating materials are TiH_2 and VH_2 for Ti and V, and pure metals for Mn, Fe, Co and Ni. It was inserted in a high pressure assembly together with hydrogen source. A NaCl capsule was used to keep hydrogen. The sample was heated at about 4 GPa. We did not observed clear melting for TiH_2 and VH_2 while we measured x-ray diffraction of liquid transition-hydrogen alloy for Mn, Fe, Co and Ni. The results showed that the nearest distance between metal atoms elongated by hydrogenation.

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Keywords: High Pressure, Hydrogen, Metal, Liquid, X-ray Diffraction, Structure

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Take Off of the J-PARC High-Pressure Neutron Diffractometer PLANET

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The high-pressure neutron diffractometer PLANET is the new spectrometer dedicated for high-pressure experiments, which is now being constructed in MLF at J-PARC. The main purpose is to investigate the effect of the water on the Earth's dynamics with the help of the neutron. One of the most characteristic features is the huge 6ram 6axes press with the maximum centric load to 3000 tonf, which enables us to investigate the structure of crystals, liquids and amorphous solids under high-pressure and high-temperature conditions of 20GPa and 2000K. We have installed the high-pressure press, ATSUHIME, and the construction of the spectrometer was almost finished. After the last big earthquake, we successfully received the neutron beam again in the last Janually. We introduce the state of the comissioinning and the future plan.

Keywords: high pressur, neutron, J-PARC