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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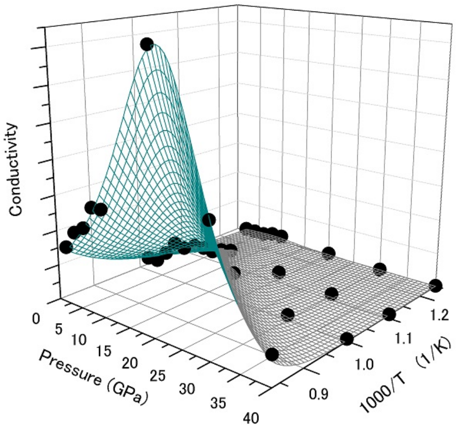
Proton dynamics in the hydrogen bonds, in particular, dissociation and recombination of water molecules is a basic process of physical and chemical phenomena in many chemical systems and life systems [1]. In this talk, we study the proton conductivity of ice VII [2], which may exist in astronomical icy 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.

[1] M. Eigen and L. de Maeyer, Proc. R. Soc. Lond. A 247, 505 (1958).
[2] E. Sugimura et al., Phys. Rev. B 77, 214103 (2008).
http://www.iitaka.org/
[3] Y. Takii et al., J. Chem. Phys. 128, 204501 (2008).
[4] T. Okada et al., Abstract of Japan Geoscience Union Meeting 2011, SMP045-18.
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



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.

[1] Loubeyre et al. (1999) Nature
[2] Pruzan et al. (2003) J. Raman Spectrosc.
[3] Yoshimura et al. (2006) J. Chem. Phys.
[4] Somayazulu et al. (2008) J. Chem. Phys.
[5] Yoshimura et al. (2011) J. Phys. Chem. B

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.

References

[1] Inoue, T., Yurimoto, H. & Kudoh, Y., Geophys. Res. Lett. 22, 117-120 (1995).
[2] Kohlstedt, D.L., Keppler, H. & Rubie, D.C., Contrib. Mineral. Petrol. 123, 345-357 (1996).
[3] Yusa, H., Inoue, T. & Ohishi, Y., Geophys. Res. Lett. 27, 413-416 (2000).
[4] Ohtani, E., Mizobata, H. & Yurimoto, H., Phys. Chem. Minerals. 27, 533-544 (2000).
[5] Murakami, M., Hirose, K. Yurimoto, H, Nakashima, S. & Takafuji, N., Science 295, 1885-1887 (2002).
[6] Sano-Furukawa, A., Kuribayashi, T., Komatsu, K., Yagi, T., and Ohtani, E., Phys. Earth Planet. Interiors 189, 56-62 (2011).
[7] Tsuchiya, J., and Tsuchiya, T., J. Geophys. Res. 114, B02206 (2009).
[8] Payne, M.C., Teter, M.P., Allan, D.C., Arias, T.A. & Joannopoulos, J.D. Rev. Mod. Phys. 64, 1045-1097 (1992).
[9] Inoue, T, Weidner, D.J., Northrup, P.A. & Parise, J.B., Earth Planet. Sci. Lett. 160, 107-113 (1998).

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

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

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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.

This work is partly supported by NEDO under ”Advanced Fundamental Research on Hydrogen Storage Materials”

[1] Y. Fukai, Butsuri, 55 (2000) 685(in Japanese).
[2] Y. Katayama, et al., J. Phys.: Conf. Ser., 215 (2010) 012080.

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

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SMP48-09 Room:102A Time:May 23 16:00-16:15

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

HATTORI, Takanori[1*], Asami Sano-Furukawa[1], Hiroshi Arima[2], Wataru Utsumi[1], Toru Inoue[3], Hiroyuki Kagi[4], Takehiko Yagi[4]

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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

SMP48-P01 Room:Convention Hall Time:May 23 17:15-18:45

High pressure NMR of high density liquid molecular hydrogen

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Microscopic dynamics of molecular hydrogen in liquid state is important for understanding its transport properties. Nuclear magnetic relaxation times of compressed liquid molecular hydrogen were measured at room temperature using a diamond anvil cell. We determined spin relaxation times of molecular hydrogen at pressures up to 1.8 GPa at 294+/-1 K temperature, where active dynamics of the molecules are quantitatively described from the observed results [1]. The dynsmics of molecules in highly-compressed hydrogen is in reasonable agreement with the standard kinetic theory assuming hard-sphere molecules.

[1] T. Okuchi, J. Phys. Chem. C, 116, 2179 (2012)

SMP48-P02 Room:Convention Hall Time:May 23 17:15-18:45

First principles molecular dynamics study on filled ice hydrogen hydrate under pressure

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We present a study on the structural and vibrational properties of filled ice C2 hydrogen hydrate under compression by first principles molecular dynamics (FPMD). It is essential to note that the experimentally reported cubic Fd-3m (space group) C2 phase reflects the symmetry at high (room) temperature when the hydrogen bond network is disordered and the hydrogen molecules are orientationally disordered. In this sense, the "cubic" symmetry would definitely be lowered at low temperature where the hydrogen bond network is ordered and the hydrogen molecules are aligned. Indeed, we found tetragonal symmetry (P41212 and Pna21 space group) in our FPMD at low temperature. This finding demonstrates that the thermal effects play an essential role in stabilizing the structure to appear as cubic below 40 GPa. We also observed an indication of transition to an unknown high pressure phase above 40 GPa which is consistent with the experimental findings. Moreover, we extend our efforts to determine the phase boundary line between hydrogen bond ordered (disordered) phases and the H2 rotation and non-rotation phases at a rough approximation. The vibrational frequencies are extracted from Fourier analysis of the MD trajectories, which are in good agreement with experimental data. Hydrogen bond is predicted to symmetrize below 60 GPa based on the analysis of O-H stretching frequencies and radial distribution function g(OH). In comparison with the pure ice VII, the hydrogen bond symmetrization pressure in C2 hydrogen hydrate is much lower as reduced by a factor two.

(1) E. D. Sloan, Clathrate Hydrates of Natural Gases. (Marcel Dekker, New York, 1990).
(2) T. Iitaka and T. Ebisuzaki, Physical Review B 68 (17), 4 (2003).
http://www.iitaka.org/
(3) W. L. Mao, H. K. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Z. Guo, J. Z. Hu, J. F. Shu, R. J. Hemley, M. Somayazulu, and Y. S. Zhao, Science 297 (5590), 2247 (2002).
(4) W. L. Vos, L. W. Finger, R. J. Hemley, and H. K. Mao, Physical Review Letters 71 (19), 3150 (1993); W. L. Vos, L. W. Finger, R. J. Hemley, and H. K. Mao, Chemical Physics Letters 257 (5-6), 524 (1996).
(5) H. Hirai, S. Ohno, T. Kawamura, Y. Yamamoto, and T. Yagi, Journal of Physical Chemistry C 111 (1), 312 (2007); S. Machida, H. Hirai, T. Kawamura, Y. Yamamoto, and T. Yagi, Journal of Chemical Physics 129 (22) (2008).
(6) M. Benoit and D. Marx, Chemphyschem 6 (9), 1738 (2005).

Keywords: hydrogen, hydrate, high pressure, phase transition, molecular interaction, molecular dynamics

SMP48-P03 Room:Convention Hall Time:May 23 17:15-18:45

Changes in lattice parameters of filled ice Ih structure of methane hydrate under high pressure

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In our previous Raman study, orientaional ordering of guest methane molecules in a filled ice Ih structure of methane hydrate was observed above15 to 20GPa. Also, Sasaki's group reported clear change in lattice vibration mode of the structure at around 15GPa by Raman spectroscopy, showing a certain change in state of the structure. However, change in a fundamental structure has not yet been observed at the pressure range by X ray diffractometry. In this study, the lattice parameters of the filled ice Ih structure were carefully measured at room temperature up to 40GPa. The results showed that axes ratios changed at around 15 GPa, although the fundamental structure was maintained. The similar changes in the axes ratios were observed at low temperatures and also for denudated-water methane hydrate. The relationship of the axes-ratio change to the orientational ordering of methane molecules in the filled ice Ih structure was discussed.

Keywords: Methane Hydrate, X ray diffraction, high pressure, Raman spectroscopy

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SMP48-P04 Room:Convention Hall Time:May 23 17:15-18:45

Stabilities of filled ice II structure of hydrogen and helium hydrates at low temperatures and high pressures

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High pressure and low temperature experiments with filled ice II structures of hydrogen hydrate and helium hydrate were performed by using diamond anvil cells and a helium-refrigerator cryostat. The experimental conditions were in a region of 0.2 to 4.5 GPa and 130 to 300 K for the former hydrate and of 0.2 to 5.0 GPa and 200 to 300 K for the latter one, respectively. X-ray diffractometry for hydrogen hydrates revealed a series of phase change from sII to filled ice Ic via filled ice II. Change in a/c ratio was observed at approximately 2 GPa, and Raman spectroscopy also showed changes in frequencies of vibron and OH vibration mode at around 2 GPa within the filled ice II structure. For helium hydrate, X-ray diffractometry showed that the filled ice II structure did not transformed to filled ice Ic structure in this study, being contrary to the previous prediction, but decomposed into helium and ice VI or VIII. Difference in compressibility between both hydrates was examined in relation to their stabilities.

Keywords: hydrigen hydrate, helium hydrate, filled ice II structure, stability

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SMP48-P05 Room:Convention Hall Time:May 23 17:15-18:45

Vibrational properties of hydrous ringwoodite, first principles investigation

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Wadsleyite and ringwoodite are primary constituent minerals in the Earth's transition zone. These phases can contain up to a few wt% H_2O in the crystal structure and are thought to be the most important water reservoirs in the Earth. We have investigated the high pressure protonation sites in hydrous wadsleyite using first principles calculation and found that the oxygen O_1 site is the most favorable for protonation in wadsleyite because of the electric imbalance of this site. On the other hand, the crystal structure of ringwoodite does not have such peculiar protonation sites and the reason of such high retention of water in ringwoodite has been unclear so far. In present study, I have calculated the vibrational properties of hydrous ringwoodite under pressure with various protonation models by first principles. Comparing with the IR and Raman measurements, I will discuss the protonation sites in hydrous ringwoodite.

Research supported in part by special coordination funds for promoting science and technology (Supporting Young Researchers with Fixed-term Appointments) and Grants-In-Aid for Scientific Research from the Japan Society for the Promotion of Science 20103005 and 21740380.

Keywords: hydrous ringwoodite, first principles, vibrational property

SMP48-P06 Room:Convention Hall Time:May 23 17:15-18:45

A high-temperature neutron difraction study on $Mg(OD)_2$

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The structure of deuterated brucite, $Mg(OD)_2$, was investigated by measuring neutron diffraction at high temperature and at atomospheric pressure to see the dynamic behavior of D atoms with increasing temperature. The neutron diffraction experiments from 202K to 600K were carried out at the beamline of Wide-Angle Neutron Difractometer (WAND) in the High Flux Isotope Reactor (HRIR), Oak Ridge National Laboratory, USA. Rietveld analysis was performed with both the single D site model and the three-site D model. D atom sits at a crystallographic $2d$ site on the 3-fold rotation axis in the single D site model and at a $6i$ site with occupation factor of 1/3 in the three-site D model. Analysis for 600 K data was not successful using the single D site model but was successfully converged using the three-site D model. This is possibly due to the strongly anisotropic D motion.

Keywords: brucite, Deuterium, high temperature, dynamic behavior, neutron diffraction

SMP48-P07 Room:Convention Hall Time:May 23 17:15-18:45

Hydrogen solubility into Fe-C and Fe-Si alloys at high pressure

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The most of the Fe-Ni cores of terrestrial planets are considered to contain light elements, such as S, Si, O, C and H. Hydrogen is considered to be one of the plausible light elements in the planetary cores. It is important to understand the effect of coexisting light elements, i.e. C and Si, on the solubility of H into Fe. Here, we have carried out in-situ X-ray diffraction experiments on the Fe_3C-H and FeSi-H systems to investigate the solubility of hydrogen into Fe-C and Fe-Si alloys under high pressure.

The experiments were performed up to 19 GPa and 2073 K for FeSi-H system and up to 17 GPa and 1973 K for Fe_3C-H system. Hydrogen dissolved in FeSi and $FeSiH_x$ hydride was formed above 10 GPa. This hydrogenation pressure is much larger than that of Fe, suggesting that presence of Si in Fe metal increases the minimal pressure for H incorporation. Hydrogen content (x) increases from 0.07 to 0.22 with increasing pressure for $P > 10$ GPa and the H content in $FeSiH_x$ is lower than that in FeH_x. The effect of carbon on hydrogenation pressure and H solubility will also be discussed.

Keywords: Hydrogen, hydride, Fe-alloy, diffraction

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

SMP48-P08 Room:Convention Hall Time:May 23 17:15-18:45

Hydrogen in the core inferred from high P-T reaction of Fe-Ni-Si-H2O

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Iron-nickel alloy containing some light elements is considered to be main constituent of the Earth core. We have reported the effect of nickel on iron-water reaction under high pressure and temperature at the Joint Meeting in 2010, which suggests a significant extending of oxyhydroxide phase to higher pressure than pure iron?water system. We have further studied the reaction of iron-nickel alloy and water by adding silicon which is one of the most plausible light elements of the core using a laser-heated diamond anvil cell combined with X-ray diffraction measurements at KEK-PF:AR-NE1A. The starting material of iron-nickel-silicon alloy was prepared in an arc furnace in a pure Ar atmosphere. The foiled iron-nickel-silicon alloy was loaded into the sample hole of Re gasket, with distilled water. Pressures were calculated using the equation of state of ice VII phase. The sample was heated with Nd:YAG laser using a double-sided heating techniques. The temperatures were determined by the thermal radiation from the heated sample. The experimental conditions were up to about 40GPa and 2000K. In situ observation at pressures and temperatures is essential to identify the reaction phase because the iron rich hydride produced in the reaction is unquenchable to the ambient condition. We observed the reaction between the iron-nickel-silicon alloy and water and phase transition of each phase at high pressure and temperature. In the present study, oxyhydroxide and metal hydride were stable to 38GPa and 1000K, while oxide and metal hydride was produced at higher pressure and 1650K. The stability field of oxyhydroxide expands more than Fe-Ni-water system to higher pressure of 42GPa. The produced hydride phase with a dhcp structure transformed to an fcc structure at higher temperature at 1900K 42GPa. The results indicate that hydrogen was much partitioned to mantle phase by silicon and nickel in the core material.

Keywords: Earth'S core, hydrogen, iron alloy, synchrotron X-ray, high pressure

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Developments of 6-6 type compression for high-pressure neutron diffraction at PLANET

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NA

Keywords: high-pressure neutron diffraction, 6-6 type compression, J-PARC

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SMP48-P10 Room:Convention Hall Time:May 23 17:15-18:45

Developments of pressure and temperature controlling system for x-ray and neutron scattering experiments

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Some polymorphs or amorphous phase of ice, for example, ice II, HDA, LDA, etc,, could only be accessible by compressing under low-temperature, and metastable ice phases like ice Ic, IV, XII, VII' are formed through HDA. Therefore, it is essentially important for the study of ices to control pressure and temperature individually. For x-ray study, diamond anvil cells (DACs) with helium-gas driven membrane have been widely used in synchrotron facilities so far, and the DAC often attaches to a helium compressor-type cryogenic system. The problems of cryostat are 1) generally too large and heavy, and 2) having noise and oscillation so that it is difficult to set it to laboratory based x-ray diffractometer. We have developed liquid-nitrogen circulating type cryogenic system with newly designed DAC with very large opening angle. The considerably small cryostat and the specially designed DAC allow us to conduct single crystal or powder x-ray diffraction experiments under pressure from 80 K to 473 K, and of course, pressure and temperature are individually controllable. Moreover, there is no oscillation thanks to removing pulsate compressor from the system.

On the other hand, for neutron experiments, high pressure (up to 2000 bar) helium-gas driven Paris-Edinburgh cells have been used in ISIS and ILL. Although this technic has been quite sophisticated at the moment, some technical difficulties like helium gas leaking and safety problems have still remained. Therefore, we again adopt liquid nitrogen circulating system for 100 ton opposed-type press for high pressure and low/high temperature neutron scattering experiments.

The p-T controlling system for x-ray has been now nearly perfected and that for neutron is going to be completed until March/2012. We reported the details of the systems and briefly introduce some preliminary studies using them.

Keywords: Low temperature, High pressure, ice, x-ray diffraction, neutron diffraction

SMP48-P11 Room:Convention Hall Time:May 23 17:15-18:45

Performance of PLANET beamline

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The powder diffractometer dedicated to high-pressure experiments (PLANET) is now being constructed on BL11 at the spallation neutron source of J-PARC. PLANET aims to study structures of hydrogen-bearing materials including dense hydrous minerals of the Earth's deep interior, magmas and light element liquids.Here we present design of neutron delivery system of PLANET and first results of beam characterization.

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SMP48-P12 Room:Convention Hall Time:May 23 17:15-18:45

6-rams Multi Anvil Press installed in BL11

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Neutron diffraction is a powerful tool to investigate hydrogen in minerals and rocks. New neutron diffraction beamline ”PLANET” is currently under construction at BL11 of Materials and Life Science Experimental Facility (MLF) at J-PARC, at Tokai, Ibaraki. One of the unique features of this beamline is that 6-rams multi-anvil high-pressure apparatus (ATSUHIME) is installed, to generate high pressure and high temperature conditions of earth’s mantle. Maximum load of each hydraulic ram is 500-ton. Each rams are controlled independently by six plunger pumps. The press will be installed at experimental hutch at Feb. 2012. I will present the current status of the 6-rams multi-anvil apparatus.

Keywords: neutron diffraction, 6-rams press

SMP48-P13 Room:Convention Hall Time:May 23 17:15-18:45

Neutron Camera Installed in BL11 ”PLANET” Beamline in J-PARC

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The neutron camera of the custom-made product by Toshiba Corp. was introduced in J-PARC BL11 ”PLANET” beamline on December 22, 2011. Various examinations have been made from several years before for the introduction.

In this talk, we will present the outline of the neutron camera, and report the result of the preliminary experiment conducted using a 45MeV pulsed neutron source of Hokkaido University (Hokkaido LINAC). Although it has not realized yet to conduct neutron imaging experiment in J-PARC BL11 ”PLANET” beamline using this camera because of the way of the beamline construction, it should be possible to conduct preliminary neutron imaging experiment by the presentation day. So, in addition, we will introduce the preliminary results in our beamline.

By introduction of this camera, it becomes possible to observe the various sample images under high pressure and high temperature using large-volume high pressure apparatus. Especially neutron has an advantage to detect hydrogen and water in samples, which is much different from X-ray. So our target is to see hydrogen-bearing sample by this camera. Still more, we are considering to conduct three-dimensional neutron tomography using this camera. Especially, when we use the Paris Edinburgh press, it will be possible to do tomography under high pressure and high temperature. So we are also doing this kind of development.

Acknowledgements: We thank Koichi Nittoh in Toshiba Co., Ltd., Chikara Konagai in Toshiba Nuclear Engineering Services Co., Ltd. and Hironobu Kimura in Toshiba Power System Inspection Services Co., Ltd. for their cooperation for the introduction of our neutron camera.

Keywords: neutron imaging, water, the Earth’s interior, neutron camera