Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

SMP46-01 Room:106 Time:May 22 09:00-09:15

Hydrogen in enstatite: A density functional theory study

Moe Sakurai[1*], Hiroshi Sakuma[1], Noriyoshi Tsujino[2], Eiichi Takahashi[1], Katsuyuki KAWAMURA[3]

[1]Department of Earth and Planetary Sciences, Tokyo Institute of Technology, [2]Institute for Study of the Earth's Interior, Okayama University, [3]Graduate Schole of Environmental Sience, Okayama University

Water (or more precisely, hydrogen) has a profound influence on the physical properties of mantle such as viscosity, melting temperature, transmission of seismic waves, and electrical conductivity (e.g. Hirschmann and David Kohlstedt, 2012). The hosts for water would be nominally anhydrous minerals (NAMs) such as olivine, pyroxene, and garnets, which are major minerals in mantle.. In order to understand the effect of water on the physical properties of these NAMs, we have to investigate how hydrogen is incorporated in these NAMs. First-principles electronic state calculations based on density functional theory (DFT) have an advantage for understanding the positions of hydrogen in minerals. Recent first-principle study has revealed the configuration of H substitution for Mg and Si ions in forsterite (Fo; Mg_2SiO_4) (Umemoto et al., 2011). The lowest-energy structure involved four hydrogen atoms in a tetrahedral site by substituting for silicon. The calculated O-H stretching frequencies for the structure were in good agreement with experimental IR absorption spectra of Fo.

In this study, we focused on the water in orthopyroxene (Opx; $(Mg,Fe)_{2-x}Al_{2x}Si_{2-x}O_6$). The water solubility in Opx increased linearly with increasing Al_2O_3 content (Rauch and Keppler, 2002). Why does the water content of Opx increase with increasing Al_2O_3 content? The aim of this study is to understand the mechanism of hydrogen substitution in Opx.

We have calculated the electronic state in Enstatite (En; $MgSiO_3$) which is an end member of Opx using the DFT. Calculations were performed using the generalized gradient approximation (GGA-PBE) (Perdew et al., 1996). The pseudepotential method was employed. The optimized lattice constants of En without vacancies are a = 18.4556 A, b = 8.92120 A, and c = 5.24794 A (for the *Pbca* symmetry). The $1*2*4$ k-point mesh was used for this supercell. Dynamical matrices for hydrogen atoms were computed using density functional perturbation theory (Giannozzi et al., 1991). We substituted hydrogen and/or Al^{3+} for Si^{4+} in the *T2* site and Mg^{2+} in the *M1* site. Four types of the substitution $(4H)_{Si}$, $(2H)_{Mg}$, $(Al+H)_{Si}$ and $(4H)_{Si}$+$(Al+H)_{Si}$ were considered. Here the ions in parenthesis refer to added ions, the subscript ions refer to removed ions. Highly reactive site in En was evaluated from the lowest unoccupied molecular orbital (LUMO) distribution around various atoms. Stable positions of hydrogen in En were estimated from the direct comparison of the vibrational frequencies obtained by experimental FT-IR method and by the first-principles methods.

The calculated O-H stretching frequencies distributed from 3800 to 3000 cm^{-1} depending on the substitution types. The frequencies for the structures of $(4H)_{Si}$, whose frequencies were dominant at high frequencies, can explain the high-intensity experimental IR absorption spectra of En. The calculated O-H stretching frequencies for the structures of $(4H)_{Si}$+$(Al+H)_{Si}$ were in good agreement with the experimental band which appeared only for Al_2O_3-bearing En. In En with $(Al+H)_{Si}$ substitution, there was a remarkable change for the LUMO distribution around a Si ion in *T2* site compared to the Si ion in En without the substitution. This change of the LUMO distribution implied that the Al incorporation enhances the instability of Si ions in close *T2* site. This would be explain why the Al incorporation in En enhances its the water solubility.

Keywords: orthopyroxene, hydrogen position, frequency calculation, IR, density functional theory

SMP46-02 Room:106 Time:May 22 09:15-09:30

Influence of Al incorporation on the amount of protons in $MgSiO_3$ perovskite

Tomoyuki Yamamoto[1]*

[1]Faculty of Science and Engineering, Waseda University

Most of the geoscientists believe that olivine-based minerals form the major constituent in the upper mantle, which extends to a depth of 660 km. Major component of the upper mantle is Mg_2SiO_4 in which there are three phases depending upon the depth, i.e., Forsterite (alpha phase) , Wadleyite (beta phase) and Ringwoodite (gamma phase). Pressure induced phase transitions occur at about 10 GPa and 15 GPa under low temperature condition from alpha to beta and from beta to gamma phases, respectively. 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].

On the other hand, some experiments suggested that the pure Mg-perovskite, which is one of the major component of the Earth's lower mantle, can store tiny amount of water in its structure [5,6]. However, it was reported very recently that $MgSiO_3$ perovskite can store more water when the Al is incorporated [7]. In the present study, the first-principles calculations were carried out to investigate the influence of Al incorporation on the amount of water in $MgSiO_3$ perovskite. Our preliminary results show that the solution energy of protons in $MgSiO_3$ decreases when the Al ions are incorporated.

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] Inoue, T., Wada, T., Sasaki, R., & Yurimoto, H., Phys. Earth Planet. Inter. 183, 245 (2010)
[7] Inoue, T. & Yurimoto, H., DI13D-2451 presented at 2012 Fall Meeting AGU

Keywords: first-principles calculation, lower mantle, magnesium silicate perovskite, water storage, alminium

SMP46-03 Room:106 Time:May 22 09:30-09:45

Proton dynamics in ice VII

Toshiaki Iitaka[1]*

[1]RIKEN ASI

Proton dynamics in the hydrogen bond of water molecules is a basic process of physical and chemical phenomena in many chemical and life systems [1]. In the previous talk[2], we examined the proton conductivity of ice VII [3], which may exist in astronomical icy bodies, in terms of transport theory of defects and molecular dynamics simulation. In this talk, we will examine the details of defect motion by visualization as well as heat conductivity and the modulated structures[4]

[1] M. Eigen and L. de Maeyer, Proc. R. Soc. Lond. A 247, 505 (1958).
[2] T. Iitaka, Abstract of Japan Geoscience Union Meeting 2011, SMP048-01.
T. Okada et al., Abstract of Japan Geoscience Union Meeting 2011, SMP048-02.
[3] E. Sugimura et al., Phys. Rev. B 77, 214103 (2008).
[4] P. Loubeyre et al., Nature 397, 503 (1999).

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

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

SMP46-04 Room:106 Time:May 22 09:45-10:00

In-situ neutron scattering experiments of ice VI under high pressure and low temperature

Kazuki Komatsu[1*], Kazuya Nakayama[1], Tamami Koizumi[1], Hiroyuki Kagi[1]

[1]Geochemical Research Center, Graduate School of Science, The University of Tokyo

In-situ neutron scattering experiments for ice VI under high pressure and low temperature were carried out in order to investigate the long-standing problem of the order-disorder transition of ice VI. We used 99.9 % D_2O as sample, in contrast with the study of Salzmann et al. (2009) who used D_2O with 0.01 mol/L DCl. We also used the newly developed P-T variable cell (Komatsu et al., in press) which allows us to explore pressure and temperature individually; it is essentially important for this study because compression under low-temperature is necessary to make fine powdered iceVI. Cup-shaped WC anvils, TiZr encapsulating gaskets and duralumin support ring were used as anvils and gaskets, respectively. Their combination of anvils and gaskets has much less attenuation for both incident and scattered neutron; the intensity is 2.6-5.2 times more than the conventional single toroidal anvils. Another run which includes Pb as a pressure maker with D_2O was also conducted to find the anomaly in P-V-T relationship, which was reported by Mishima et al. (1979).

The neutron diffraction patterns taken at any P-T conditions we explored (0.6˜1.7 GPa, 100-240 K) were well explained by the disordered iceVI structure model, and no additional peaks were found in this study. The observed V-T relationships at 1.3 GPa have no clear anomaly, but seems normal, which means that no strong evidence to show the transition from disordered to ordered-state was observed.

References

B. Kamb, A. Prakash, W. C. Hamilton, and S. J. LaPlaca, quoted by B. Kamb, in Physics and Chemistry of Ice, edited by E. Whalley, S. Jones, and L. Gold (Royal Society of Canada, Ottawa, 1973).

Iizuka, R., Yagi, T., Gotou, H., Komatsu, K., and Kagi, H. (2012) High Press. Res., 32, 430-441.

Johari, G.P., and Whalley, E. (1976) Journal of Chemical Physics, 64, 4484-4489.

Komatsu, K., Moriyama, M., Koizumi, T., Nakayama, K., Kagi, H., Abe, J., and Harjo, S. (2013) High Pressure research, in press

Kuo, J.L., and Kuhs, W.F. (2006) Journal of Physical Chemistry B, 110, 3697-3703.

Mishima, O., Mori, N., and Endo, S. (1979) Journal of Chemical Physics, 70, 2037-2038.

Salzmann, C.G., Radaelli, P.G., Mayer, E., and Finney, J.L. (2009) Physical Review Letters, 103.

SMP46-05 Room:106 Time:May 22 10:00-10:15

High resolution neutron powder diffraction of methane hydrate at high pressure

Takuo Okuchi[1*], Shigeo Sasaki[2], Satoshi Takeya[3], Masashi Yoshida[2], Naotaka Tomioka[1], Narangoo Purevjav[1]

[1]ISEI, Okayama University, [2]Faculty of Engeneering, Gifu University, [3]REEF, National Institute of Advanced Industrial Science and Technology

Neutron plays complementary role to x-ray in material science at high pressure, especially as the most powerful probe for structural analysis of hydrogen-bearing compounds. J-PARC (Japan Proton Accelerator Research Complex) now becomes one of the strongest pulsed neutron sources which give us such a probe. Here we present our recent high-resolution neutron powder diffraction result of fully-deuterated methane hydrate at high pressure, which was measured at TAKUMI beamline (BL19) at J-PARC MLF (Materials and Life Science Experimental Facility), using compact high-pressure anvil cells. For this purpose we have developed a new-type cell design suitable for time-of-flight neutron diffraction.

Keywords: methane hydrate, neutron diffraction, high pressure

SMP46-06 Room:106 Time:May 22 10:15-10:30

Phase changes of hydrogen- and methane-hydrates under low temperature and high pressure

Hisako Hirai[1*], KAGAWA, Shingo[1], TANAKA, Takehiko[1], MATSUOKA, Takahiro[2], OHISHI, Yasuo[3], YAGI, Takehiko[1], OHTAKE, Michika[4], YAMAMOTO, Yoshitaka[4]

[1]GRC Ehime University, [2]KYOKUGEN, [3]JASRI, [4]AIST

One type of hydrates (referred to HH) has recently received significant interest as a clean hydrogen storage material, and methane hydrate (referred to MH), called 'fiery ice' is expected an useful natural resource. Both hydrates have been thought to be potentially ubiquitous in space objects such as icy satellites of the solar system and extrasolar planets. At lower pressures these hydrates have clathrate structures which consist of host cages formed by hydrogen-bonded water molecules with encapsulated guest species. At higher pressures, MH and HH transform to a filled ice Ih structures (MH-FIIhS) and filled ice Ic structure (HH-C2), respectively. These filled ice structures consist of a host ice framework and guest molecules contained in the voids of the host ice framework. Comprehensive studies performed under room temperature for MH and HH provided interesting properties, however, low temperature and high pressure behaviors have rarely been known except a few studies. In this study, low-temperature and high-pressure experiments were performed to clarify the phase changes of MH-FIIhS and HH-C2 in the previously unexplored region.

Clamp-type diamond anvil cells and a helium-refrigeration cryostat were used in this study. The pressure and temperature ranges for HH-C2 were 5.0 to 50.0 GPa and 30 to 300 K, and those for MH-FIIhS were 2.0 to 77 GPa and 30 to 300 K, respectively. Pressure measurements were made via a ruby fluorescence method and a diamond Raman method. Temperature measurements were made using a silicon semiconductor thermometer and chromel-alumel thermocouples. The initial samples of MH and HH were prepared by ice-gas interface method and gas-loading method, respectively. The samples were characterized via X-ray diffractometry (XRD) using synchrotron radiation at BL-10XU at SPring8 and BL-18C at the Photon Factory (KEK) and Raman spectroscopy.

In situ X-ray diffractometry revealed that the cubic HH-C2 transformed to tetragonal at low temperatures and high pressures, and that the axis ratio of the tetragonal phase changed depending on the pressure and temperature. These results were consistent with theoretical predictions performed via first principle calculations. The tetragonal phase was determined to be stable above 20 GPa at 300 K, above 15 GPa at 200 K, and above 10 GPa at 100 K. Further changes in the lattice parameters were observed from about 45 to 50 GPa throughout the temperature region examined, which suggests the transformation to another high-pressure phase above 50 GPa. Guest molecules have been known to rotate freely in both clathlate and filled ice structure under low pressure. The reasons for the transformation to the tetragonal structure can be explained as follows: the tetragonal structure might be induced due to changes in the vibrational or rotational modes of the hydrogen molecules from free-rotation state to orientational-ordered state under low temperature and high pressure.

In our previous studies of MH-FIIhS by Raman spectroscopy, orientational ordering of guest methane molecules, namely suppressing rotation, occurred at 15-20 GPa, although there was no clear change in the lattice parameters and volume by the XRD study. The present XRD study revealed clear changes in the axis ratios at 15 to 20 GPa at 300K. The Raman spectroscopy showed split of CH vibration mode of the methane molecules at the almost same pressure. These results indicated that the orientational ordering of the guest molecules resulted in deformation of the lattice. The change in rotational mode of the guest molecules is a phase change. Thus, the results demonstrate that there are guest-disordered phase and guest-disordered phase within same MH-FIIhS frame work structure. Similar changes in the axis ratios and split of CH vibration mode were observed at low temperature regions.

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

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

SMP46-07 Room:106 Time:May 22 11:00-11:15

A neutron diffraction study of phase transition in lawsonite at high pressure

Asami Sano[1*], Takaya Nagai[2], Riko Iizuka[3], Yusuke Seto[4], Takahiro Kuribayashi[5], Takanori Hattori[1]

[1]Quantum Beam Science Directorate, JAEA, [2]Department of Natural History Sciences, Faculty of Science, Hokkaido Univ., [3]Geochemical Laboratory, Graduate School of Science, Univ. of Tokyo, [4]Graduate School of Science, Kobe Univ., [5]Institute of Mineralogy, Petrology and Economic Geology, Graduate School of Science, Tohoku Univ.

Lawsonite is a hydrous mineral which is considered as a main carrier of hydrogen in the subtucting slab. It has a wide stability field at the pressures from 3.5 GPa to 10 GPa, and up to 1000 C. Previous single crystal X-ray diffraction and neutron diffraction studies indicate that there exist two phase transitions at low temperature. A property of low temperature is sometimes considered to be equivalent to the behavior at high pressure, and some studies pointed out the possibility of transition at high pressure. To investigate the pressure response of hydrogen bond and phase transition in lawsonite, neutron diffraction experiment was conducted.

Lawsonite was deuterated by D-H exchange reaction in the furnace under deuterated nitrogen atmosphere. High pressure and high temperature neutron diffraction experiment was conducted by 6-ram press at J-PARC MLF. Using 6-6 type anvil with TEL size of 10 mm, neutron diffraction pattern was corrected up to 6 GPa and 800 C. In addition, hydrostatic experiment at ambient pressure was conducted using Paris-Edinburgh press. New peak was observed at 1.83 Angstrom that indicates phase transition at high pressure. Detail of the result will be presented at the talk.

Keywords: Lawsonite, neutron diffraction, hydrous mineral, subducting slab

SMP46-08 Room:106 Time:May 22 11:15-11:30

In-situ neutron diffraction observation of hydrogen positions in portlandite under high pressure and temperature

Riko Iizuka[1*], Takaya Nagai[3], Asami Sano[2], Yusuke Seto[4], Takahiro Kuribayashi[5], Takanori Hattori[2], Hiroyuki Kagi[1]

[1]GCRC, The University of Tokyo, [2]Japan Atomic Energy Agency, [3]Hokkaido University, [4]Kobe University, [5]Tohoku University

$Ca(OH)_2$, 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. Among the other isostructual hydroxides, Ca ion in portlandite has the largest cation size, which might cause unique pressure-induced phase transitions. Previous high-pressure studies reported that portlandite undergoes a phase transition to a high-pressure (high-P) phase at 6-8 GPa and room temperature [1-3], and it transforms into another high-pressure and high-temperature (high-PT) phase at $>$6 GPa, $>$200C [4,5]. The crystal structures of these unquenchable high-P and -PT phases have been determined to be different monoclinic phases by X-ray and/or neutron diffraction measurements. 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. However, there was no in-situ neutron observation on portlandite under much higher pressure and temperature conditions, where the high-P and -PT phases are stable. Therefore, hydrogen positions in the crystal structures of portlandite under corresponding such high-PT conditions are still unknown. In the present study, in-situ neutron diffraction studies under high-PT conditions were performed in order to clarify the hydrogen positions in these portlandite polymorphs.

An initial sample of powder $Ca(OD)_2$ was synthesized from a mixture of CaO powder and stoichiometrically excess D_2O in an autoclave at 220C for 4 days. High-PT experiments were conducted using a 6-ram press called ”Atsuhime” at a new high-PT beamline ”PLANET” combined with a pulsed-neutron source at MLF, J-PARC. The neutron diffraction patterns were measured at 8.3 GPa and 400C, 200C, RT during decreasing temperature. The obtained diffraction peaks were originated from only the high-PT phase of portlandite. The crystal structure parameters and atomic positions were refined by Rietveld analytical method using GSAS software. For a model structure of the high-PT phase, the parameters, of which structure was determined by neutron diffraction data at 10 K, 0.1 MPa by Leineweber et al., 1997 [5], were used.

The structure of the high-PT phase obtained at 8.3 GPa, 400C was a = 5.076(1)A, b = 5.985(1)A, c = 5.763(1)A, and *beta* = 100.37(7). Each lattice parameter of a, b, c was larger than that of [5] by 6, 2, and 4%, respectively. The *beta* angle was smaller by 3%. In contrast, among the current results, the lattice parameters and atomic positions including hydrogen was not largely fluctuated by temperature (400C, 200C, and RT) at 8.3 GPa. The isotropic temperature factor (U_{iso}) gradually increased with increasing temperature. Based on the obtained structure of the high-P phase accompanying the displacements of CaO_6 layers and Ca atoms from the original structure of portlandite. Comparing the structure of the high-PT phase to that of the high-P phase, the phase transition mechanism can be inferred. There might be at least two positions for hydrogen in the high-P phase, one of which changed from the original position to keep stable even after the formation of new Ca-O bondings. These results agree well with those from our previous Raman and IR absorption spectroscopy measurements of OH-bonds. Therefore, it is suggested that the hydrogen bonds in portlandite are strongly affected by the phase transitions, for which the role of hydrogen bonds might be a driving force.

References
[1] Ekbundit et al., J. Solid State Chem., 126, 300-307 (1996)
[2] Catalli et al., Geophys. Res. Lett., 35, L05312 (2008)
[3] Iizuka et al., Phys. Chem. Minerals, 38, 777 (2011)
[4] Kunz et al., High Press Res., 14, 311-319 (1996)
[5] Leinenweber et al., J Solid State Chem., 132, 267-273 (1997)
[6] Xu et al., Phys. Chem. Miner., 34, 223-232 (2007)
[7] Xu et al., J. Solid State Chem., 180, 1519-1525 (2007)

Keywords: portlandite, hydrogen bond, phase transition, neutron diffraction, PLANET, high pressure

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

SMP46-09 Room:106 Time:May 22 11:30-11:45

Hydrogen in portlandite -Neutron diffraction measurements at high pressure and high temperature-

Takaya Nagai[1*], Asami Sano[2], Riko Iizuka[3], Hiroyuki Kagi[3], Yusuke Seto[4], Takahiro Kuribayashi[5], Takanori Hattori[2]

[1]Faculty of Science, Hokkaido Univ., [2]JAEA, [3]Univ. of Tokyo, [4]Kobe Univ., [5]Tohoku Univ.

$Ca(OH)_2$ is one of the simplest hydrous minerals. Because this type of structure is a component unit in complex hydrous phases such as chondrodite, it is important to understand structural behaviors at high pressure and high temperature. However, only a few previous researches can be found on crystallography of $Ca(OH)_2$ in the conditions of simultaneously high pressure and high temperature, although there were quite a few studies on EOS, phase relation, melting and so on, which were performed by using X-ray diffraction technique. Last year a brand-new TOF neutron beamline (PLANET) dedicated for high pressure and high temperature measurements started to operate in J-PARC, Japan. $Ca(OH)_2$ was selected as one of the first targeted materials measured at the PLANET.

Deuterated samples were prepared via hydrothermal treatment with CaO fine powders and excess D_2O water in a Teflon lined stainless steel autoclave at 493 K for 4 days. After the hydrothermal treatment was completed, precipitates were filtered out, washed with D_2O water, and then dried at 383 K under vacuum for 3 hours. The products were confirmed to have the CdI2-type structure by conventional powder X-ray diffraction measurements and were checked to be deuterated by IR absorption spectra. TOF neutron powder diffraction measurements of $Ca(OH)_2$ were carried out from 300 to 773 K at about 3 GPa at the PLANET beamline in J-PARC, Japan. At first, temperature was increased to 773 K at about 3 GPa for annealing and then data acquisition was carried out at each temperature condition to lower temperature. The measurement time at each targeted P-T conditions was about 8 hour after the temperature reached equilibrium. Generation of high pressure and high temperature can be performed by using the 6-ram big press (Atsuhime) installed at PLANET.

Quality of diffraction patterns is surprisingly superior and only diffraction peaks from $Ca(OH)_2$ could be observed owing to radial collimators equipped with Atsuhime, although powder sample of $Ca(OH)_2$ was loaded into a cylindrical graphite furnace in ZrO_2 pressure medium cube. The detailed structure parameters such as lattice parameters and atomic coordinates were refined by the Rietveld method by using a program GSAS.

Keywords: hydrogen, portlandite, high pressure and high temperature, neutron diffraction, Atsuhime, PLANET

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

SMP46-10 Room:106 Time:May 22 11:45-12:00

High pressure neutron diffraction of anhydrous and hydrous albite glasses and preliminary neutron imaging in PLANET

Toru Inoue[1*], Akihiro Yamada[1], Satoru Urakawa[2], Akio Suzuki[3], Hiroshi Arima[4], Hidenori Terasaki[5], Osamu Ohtaka[5], Takanori Hattori[6], Asami Sano[6]

[1]Geodynamics Research Center, Ehime University, [2]Department of Earth Sciences, Okayama University, [3]Department of Earth and Planetary Materials Science, Faculty of Science, Tohoku University, [4]Institute for Materials Research, Tohoku University, [5]Graduate School of Science, Osaka University, [6]Japan Atomic Energy Agency

We, magma group, have conducted neutron diffraction experiment under high pressure first time on February 15-21, 2012. Samples were anhydrous and deuterated-hydrous albite glasses. We used semi-sintered ZrO2 with a dimension of 17 mm cubic as pressure medium, and enclosed the samples which diameter were 4.6 mm in the center of the cell. The anvil truncation was 10 mm. We used Ni-doped WC anvil, and adopted 6-6 type compression system. The diffraction data were collected at 2.3 and 5.5 GPa in both anhydrous and deuterated-hydrous albite glasses, respectively. The measurement times at 2.3 and 5.5 GPa were 14 and 22 hours at the live times, respectively. In this experimental period, the beam intensity was about 290 kW; this intensity was about 1/3 of the expected intensity in J-PARC in the future. Moreover, the empty and the vanadium cells under each condition were also measured, and the sample diffraction pattern were corrected by those data. Details of the results will be presented.

Moreover, the exploratory experiment of neutron imaging was also conducted. Details of the results will be also presented.

Keywords: J-PARC, PLANET, neutron diffraction, amorphous material, neutron imaging, high pressure

SMP46-11 Room:106 Time:May 22 12:00-12:15

Measurements of silica glass and water using a high-prssure diffractometer in J-PARC/MLF

Yoshinori Katayama[1*], HATTORI, Takanori[1], YAGAFAROV, Oscar[1], SAITOH, Hiroyuki[1], SANO, Asami[1], SUZUYA, Kentaro[1], CHIBA, Ayano[2]

[1]JAEA, [2]Keio Univ.

Neutron diffraction measurements at ambient conditions and at pressures of 2.3 GPa and 5.5 GPa at room temperature were carried out using a high-pressure neutron diffractometer, PLANET, installed in J-PARC/MLF. We compressed a sample in a ZrO2 cube using a six-axis press by a 6-6 method. The size of the sample was 4.6mm in diameter and 6.7mm in height. The size of the incident beam was 2.5mm in width and 4.5mm in height. The pressure was estimated from the applied load. Clean diffraction patterns without diffraction lines from surrounding materials were obtained. Measurements on heavy water at ambient conditions were also carried out. We will try to measure heavy water at high pressures. The results will be also reported.

Keywords: neutron diffraction, glass, water, high pressure

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

SMP46-12 Room:106 Time:May 22 12:15-12:30

Performance and the Current Status of the High-Pressure Neutron Diffractometer PLANET

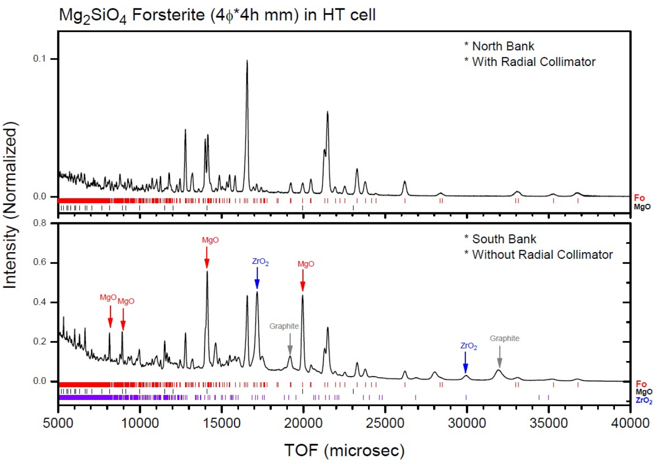
Takanori Hattori[1*], Asami Sano[1], Hiroshi Arima[5], Kazuki Komatsu[4], Akihiro Yamada[3], Takaya Nagai[2], Yoshinori Katayama[1], Toru Inoue[3], Wataru Utsumi[1], Hiroyuki Kagi[4], Takehiko Yagi[3]

[1]JAEA, [2]Hokkaido Univ., [3]Ehime Univ., [4]Univ. of Tokyo, [5]Tohoku Univ.

The PLANET is the world's first neutron beamline specialized for high-pressure and high-temperature experiments. The most characteristic feature is the capability to investigate the state of the matter at high-pressure and high-temperatures up to 20GPa and 2000K with the multi-anvil high-pressure apparatus. The construction was started in 2008. The beamline was commissioned in the first half year of JFY 2012 and the new data is being taken by project members. This year, the beamline is reborn to a public beamline of J-PARC. In this talk, the performance of the PLANET and the typical results are introduced.

The resolution of the diffraction pattern (Delta d/d=0.6%) was found to be almost equal to the designed value(0.5%). The elimination of the background from the sample surrounding materials, which is the most important feature of the high-pressure experiments, was found to be accomplished with the use of the severe incident collimator and radial receiving collimator system. The beamline is opened for general users since the last half year of JFY2013 (from Feb.).

Keywords: high pressure, neutron



SMP46-P01 Room:Convention Hall Time:May 22 18:15-19:30

Ideal Strength of Nano-polycrystalline diamond under High Temperature and High Pressure using MD Simulation

Waka Uchida[1]*, Shinichiro Nakamura[2], Toshiaki Iitaka[3]

[1]Tokyo Institute of Technology, Graduate School of Bioscience and Biotechnology, [2]RIKEN, Research Cluster for Innovation, [3]RIKEN, Advanced Science Institute

The aim of this work is to study the hardness of nano-polycrystalline diamond. Nano-polycrystalline diamond is a nanosized artificial diamond. It has diamond crystalline structure [1] and the same physical property as natural diamond, strong hardness, high thermal conductivity, and excellent electrical insulators. It is also harder than natural diamond, because it has various kinds of crystal planes. That is why it is applied for the Diamond Anvil Cell used in the high pressure experiment. It is important to synthesize nano-polycrystalline diamond and study its physical properties.

Ideal strength is the limit value of elasticity before the solid gets above the limit of elasticity and irreversible deformation occurs when the infinite, defect-free solid are gradually put more load on [2,3]. For the preparative simulation, we performed Molecular Dynamics (MD) simulations for studying ideal strength of crystalline diamond. The LAMMPS codes [4] with Tersoff potential [5] (SiC.tersoff) were used in all simulations. Temperature and time steps were set at 300 K and 0.001 ps, respectively. After constant pressure and constant temperature (NPT) simulation was performed for 1 ps, constant volume and constant temperature (NVT) simulation was performed for 210 ps. The share strength was evaluated at the {010} slip plane in the <100> slip direction, at the {110} in the <-110>, and at the {111} in the <1 1 -2> by performing NVT simulations with strain increasing at every 1000 steps. Our simulation data showed the ideal shear strength 202.0 (GPa) at critical strain of 0.39, 93.4 (GPa) at 0.33, and 87.9 (GPa) at 0.16 of the {010} slip plane in the <100> slip direction, of the {110} in the <-110>, and of the {111} in the <11-2>, respectively.

In the main simulation we study whether or not Hall-Petch behavior [6,7] are applied for nano-polycrystalline diamond. We will perform MD simulations for larger grain size of nano-polycrystalline diamond than 4.1 nm that was reported by Branicio et al. [8]. We study also hardness of nano-polycrystalline diamond with the ideal strength. We will perform MD simulations for nano-polycrystalline diamond with the same method as preparative simulation.

[1] T. Irifune, A. Kurio, S. Sakamoto, T. Inoue, H. Sumiya, Nature 421, 6923 (2003).
[2] A. Kelly and N. H. Macmillan, Strong Solids (Clarendon, Oxford, 1986).
[3] J. W. Morris, Jr., C. R. Krenn, D. Roundy, and M. L. Cohen, in Phase Transformations and Evolution in Materials, edited by P. E. A. Turchi and A. Gonis (The Minerals, Metals and Materials Society, Warrendale, PA, 2000), p. 187.
[4] S. Plimpton, J. Comp. Phys. 117, 1 (1995).
[5] J. Tersoff, Phys. Rev. B 39, 5566 (1989).
[6] Hall, E. O. The deformation and ageing of mild steel: III Discussion of results. Proc. Phys. Soc. Lond. B 64, 747 (1951).
[7] Petch, N. J. The cleavage of polycrystals. J. Iron Steel Inst. 174, 25 (1953).
[8] Z.D. Sha, P.S. Branicio, V. Sorkin, Q.X. Pei, Y.W. Zhang, Diamond & Related Materials. 20, 1303 (2011).

Keywords: nano-polycrystalline diamond, ideal strength

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

SMP46-P02 Room:Convention Hall Time:May 22 18:15-19:30

A possible reason for forming tetragonal phase of hydrogen hydrates under low-T and high-P by Raman spectroscopy

Shingo Kagawa[1*], Hisako Hirai[1], Takehiko Tanaka[1], Takahiro Matsuoka[2], Yasuo OHISHI[3], Takehiko Yagi[1], Michika Ohtake[4], Yoshitaka Yamamoto[4]

[1]Geodynamics Researcch Center Ehime University, [2]KYOKUGEN, Center for Quantum Science and Technology under Extrem Conditions, Osaka University, [3]Japan Synchrotron Radiation Research Institute, [4]Advanced Industrial Science and Technology

Hydrogen hydrates are composed of hydrogen-bonded host water molecules forming cages or ice frameworks that include guest hydrogen molecules. One type of hydrogen hydrate, filled-ice Ic structure (HH-C2), is thought to have cubic structure. High pressure experiments of HH-C2 at room temperature revealed that HH-C2 survived from 2.3 GPa up to at least 80.3 GPa with structural changes at around 40 and 60 GPa. The structural change at around 40 GPa was explained to be relating to symmetrization of the hydrogen bond in the host water molecules. Another experiment reported that the structure of HH-C2 persisted to 11 K at about 4 GPa.

An ab initio calculation predicted that the cubic structure of HH-C2 transforms to a tetragonal structure under high-pressure and low-temperature. Such phenomenon has not yet been experimentally examined. Recently, in situ X-ray diffractometry (XRD) confirmed that the cubic structure of HH-C2 transforms to a tetragonal structure at low-temperatures and high-pressures. So, in this study, in order to estimate the reasons for the transformation to the tetragonal structure, Raman measurements were performed for the vibrational and rotational modes of the guest hydrogen molecules under low-temperature and high-pressure.

Clamp-type diamond anvil cells (DAC) made of copper-beryllium was used. The DAC was cooled by liquid nitrogen in an open-flow DAC holder. The pressure and temperature ranges were 5.0 to 33.0 GPa and 90 to 300 K, respectively. For pressure measurements, a ruby ?uorescence method was used. For temperature measurements, alumel-chromel thermocouples were used. Initial samples were prepared by gas-loading method at ISSP, Tokyo University. The samples were characterized by optical microscopy and Raman spectroscopy manufactured by Photon Design.

The transformation of HH-C2 to a tetragonal structure was inferred to be produced by changes in the rotational or vibrational modes of the guest hydrogen molecules (referred as roton and vibron, respectively). At room temperature the vibron obtained from 5 to 33 GPa was consistent with the previous study. At lower temperatures, the slope of wavenumber of the vibron versus temperature was slightly changed at around 210 to 230 K in the case of 16 GPa. On the other hand, distinct split of roton S0(0) was observed at 173 K, 8 GPa. At 300 K the split of the roton S0(0) was expected to occur at around 20 GPa from the XRD study, but it was unclear possibly because of thermal disturbance. The pressure and temperature conditions at which the roton split occurred in the present Raman study were good agreement with those of phase boundary between the cubic and the tetragonal phase determined by the XRD study.

Hydrogen molecules in the cubic HH-C2 structure are thought to be rotationally disordered at lower pressure and higher temperature. The single roton peaks indicate disordered rotating state of hydrogen molecules. The splitting roton observed suggested that the rotational mode changed from the disordered (spherical) mode to ordered (ellipsoidal) one, which induced the deformation of the lattice, namely transformation to a tetragonal structure.

Keywords: hydrogen hydrate, Diamond Anvil Cells, low-temperature and high-pressure, Raman spectroscopy, rotational ordering

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

SMP46-P03 Room:Convention Hall Time:May 22 18:15-19:30

Axis-ratio change induced by guest ordering of filled ice Ih methane hydrate under high pressure and low temperature

Takehiko Tanaka[1*], Hisako Hirai[1], MATSUOKA Takehiro[2], OHISHI Yasuo[3], Shingo Kagawa[1], YAGI Takehiko[1], OHTAKE Michika[4], YAMAMOTO Yoshitaka[4]

[1]Geodynamics Research Center, Ehime University, [2]Center for Quantum Science and Technology under Extreme Conditions, Osaka University, [3]Japan Synchrotron Radiation Research Institute, [4]The National Institute of Advanced Industrial Science and Technology

In our previous Raman study, We reported that the orientaional ordering of guest methane molecules in a filled ice Ih structure of methane hydrate was observed above 15 to 20GPa. And, by Raman spectroscopy, Sasaki's group reported clear changes in lattice vibration mode of the structure at around 15GPa. That means a certain change in state of the structure. However, by X ray diffractometry, the change in a fundamental structure has not been observed at that pressure range. In this study, the lattice parameters of the filled ice Ih structure were carefully measured at room to low temperature. The results showed that the axis-ratio changed at around 15 GPa, while the fundamental structure was maintained. The similar changes in the axis-ratio were observed for denudated-water methane hydrate. Furthermore, by Raman spectroscopy at low temperature, it is suggested that these changes of the axis-ratio will be induced by the orientaional ordering of guest methane molecules in a filled ice Ih structure of methane hydrate.

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

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

SMP46-P04 Room:Convention Hall Time:May 22 18:15-19:30

Hydrogen in the core under the co-existence of sulfur and oxygen

Tomoya Yamashita[1], Tadashi Kondo[1*], Hidenori Terasaki[1], Takumi Kikegawa[2]

[1]Earth and Space Sci., Osaka Univ., [2]IMSS, KEK-PF

Hydrogen, oxygen and sulfur are important candidates of light elements in the Earth's core for considering reaction between metallic iron and water in the early earth. In this study, we investigated direct reaction between FeS and water to constrain the scenario in the core formation and the abundance of light elements in the core. Starting materials of FeS was confined with pure water in the hole of rhenium gasket. In-situ X-ray diffraction experiments under pressures and temperatures using laser-heated diamond anvil cell (LHDAC) were performed at KEK-AR-NE1A station, Tsukuba, Japan. After the sample was compressed to the nominal pressure at room temperature, it was heated to around the melting temperature of water ice. Pressures were determined using the equation of state of water ice VII (Somayazulu et al., 2008). The X-ray diffraction pattern at each condition was collected on an imaging plate. No ruby was used to avoid forming hydrous aluminous phase. High temperatures generate by a Nd:YAG laser driven in multimode were measured based on the emission spectra from the heated area. We performed the high P-T experiments up to 65GPa and 1700K and found that FeS reacts with H2O to form FeS2, FeH and FeO. No significant volume change was observed in high-pressure polymorphs of FeS and FeS2 indicating most hydrogen is preferentially incorporated into iron-hydride, FeHx, under the presence of FeS and FeO. This result is contrasted to the previous study on FeS-H2 system (Shibasaki et al., 2011) The recovered sample was examined by SEM-EDS and we found the sulfur rich portion than starting composition on the contact surface between water and FeS. This is consistent with X-ray observation of sulfur-rich phase. Furthermore, the stability field of delta-MOOH phase was significantly extended to higher pressure region comparing to that of Fe-H2O system (Ohtani et al., 2005). The delta phase eventually decomposed to hydride and oxide(s) around 35GPa. Hydrogen abundance X in the FeHx phase is 0.80-0.90 which is comparable to the Fe-H2O system. The results suggest that hydrogen in the FeS and its high pressure polymorphs were reduced under the co-existence FeO and FeH.

Keywords: light elements in the core, high pressure and high temperature, synchrotron experiments