

SMP045-01

Room:301B

Time:May 24 14:15-14:30

Pressure-induced intermolecular interactions in crystalline silane-hydrogen

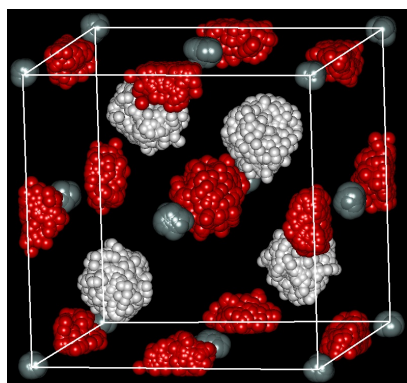
Wai-Leung Yim¹, John S. Tse², Toshiaki Iitaka^{3*}

¹Institute of High Performance Computing, ²University of Saskatchewan, ³RIKEN ASI

The structure and dynamics of a recently discovered solid silane-hydrogen complex under high pressure are elucidated with first-principles molecular dynamics calculations. A structure with orientationally disordered silane and hydrogen with their centers of mass arranged in a distinctive manner are found. Natural bond orbital analysis reveals that perturbative donor-acceptor interactions between the two molecular species are enhanced by pressure. The experimentally observed anticorrelated pressure-frequency dependency is a consequence of these novel interactions. Possibility of finding such solid silane-hydrogen complex inside of Jupiter is discussed.

<http://www.iitaka.org/~neutron/theory.html>

<http://www.rikenresearch.riken.jp/eng/research/6495>



Keywords: hydrogen, silane, high pressure, intermolecular interaction, vibron, molecular dynamics

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SMP045-02

Room:301B

Time:May 24 14:30-14:45

Dynamic behavior of D atoms in Mg(OD)₂ at high temperature

Takaya Nagai^{1*}, Hiroyuki Kagi³, Asami Sano², Riko Iizuka³

¹Hokkaido University, ²JAEA, ³The University of Tokyo

We are now constructing a new beam line (PLANET) specially dedicated to neutron diffraction measurements at high pressure and high temperature in J-PARC under a Grant-in-Aid for Scientific Research on Innovative Areas from the MEXT (proposal: Earth Science Based on the High Pressure and Temperature Neutron Experiments). We hope to obtain the first data measured at PLANET in this fall. Before that, we measured neutron diffraction at high temperature and at atmospheric pressure to see the dynamic behavior of D atoms at the temperature just below the dehydration reaction. The neutron diffraction experiments from 202K to 600K were carried out at the Wide-Angle Neutron Diffractometer beamline (WAND) in the High Flux Isotope Reactor (HRIR), Oak Ridge National Laboratory, USA. In addition, we measured IR spectra on Mg(OD)₂ from room temperature to a dehydration temperature to obtain some complementary data to neutron diffraction data.

Keywords: brucite, hydrogen atom, high temperature, dynamic behavior, IR measurement, neutron diffraction

SMP045-03

Room:301B

Time:May 24 14:45-15:00

D/H isotope effects in distorted rutile type hydrous minerals

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delta-AIOOH, distorted rutile type oxyhydroxide is an important hydrous mineral in the deep earth that is stable at the lower mantle condition. Theoretical studies have pointed out that hydrogen would locate at the center between two oxygen atoms at high pressure, which is so called symmetrization of the hydrogen bond. X-ray diffraction study found the difference in the pressure where compression behavior change, suggests there is D/H isotope effect. To investigate D/H isotope effect in the pressure response of strong hydrogen bond in delta-AIOOH, Neutron diffraction experiment is conducted at SNAP in SNS, Oak Ridge.

High pressure was obtained using a Paris-Edinburgh high-pressure cell with BN anvils. About 100 mg of powder sample was loaded into a null-scattering TiZr alloy encapsulating gasket. Deuterated methanol-ethanol was used as a pressure medium. The diffraction pattern was collected by the detector at the angle of 90 degrees. Pressure was calculated using an equation of state of delta-AIOOH determined by X-ray diffraction study. The structure was refined by means of Rietveld method using GSAS and EXPGUI software package. The data was collected at 0, 2.5, 4.1, 5.6, 6.7, 7.1 GPa.

The intensity of 120 reflection continues to decrease at high pressure and become almost zero intensity at 6.7 GPa, suggesting the transition from P21nm to Pnnm as a precursor of symmetrization. This pressure condition is slightly lower than the pressure where the change in compressibility was observed. Strong D/H isotope effect was found in hydrogen bond geometry; O-H distances are longer than O-D, and H...O distances are shorter than D...O at the same pressure condition, whereas O...O distances do not show significant discrepancies. Present result is consistent with the previous study that found the change in compressibility of delta-AIOOH at high pressure than deuterated delta-AIOOD.

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SMP045-04

Room:301B

Time:May 24 15:00-15:15

Magma Studies towards Pulse Neutron Utility

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The proposal of Grant-in-Aid for Scientific Research on Innovative Areas "Neutron Earth Science" was succeeded in the autumn of 2008, and one of the scientific research group "Magma group" is doing efforts for various exploratory experiments to make it possible to do coming Neutron experiment under high pressure and high temperature. The aim of our group is to understand magma activity in the earth interior through the understanding of the structure and physical properties of the magma with and without water. Our target material includes iron melt. Through these studies, we would like to establish "High P&T Neutron Magma Science". The scientific target is mainly divided into three groups; 1) structure of magma, 2) physical properties of magma, and 3) state observation of magma. In the present stage, the preliminary experiments and the development of the experimental technique are necessary. So we are conducting these studies by divided into two technical groups; 1) "Neutron scattering experiment" group and 2) "Neutron imaging experiment" group. In this talk, we will introduce our recent developments for the above issues.

Keywords: magma, water, neutron scattering, neutron imaging

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SMP045-05

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Time:May 24 15:15-15:30

Exploratory studies on state observation of magma by neutron imaging

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¹Japan Atomic Energy Agency, ²GRC, Ehime Univ.

Water is one of the important volatile components of the Earth. In low pressure condition, the silicate component bearing liquid and water bearing fluid can be distinguished by the existence of the immiscible region, and hydrous solidus can define clearly. In higher pressure, however, the immiscible region should be disappeared to form miscible region.

Main obstacle to observing such a phenomenon is weak contrast difference between magma and fluid. The main advantage of neutron imaging technique is that light elements can be detected in silicate melt such as magma. In this presentation, we report preliminary results of neutron imaging method at BL11 of MLF/J-PARC, which is a neutron beamline dedicated for neutron science under high pressure and high temperature conditions.

Keywords: high pressure and high temperature, silicate melt, neutron imaging

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SMP045-06

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Neutron scattering experiment on water under high pressure and temperature

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¹QuBS/JAEA

We plan to carry out neutron scattering experiments on liquid water under high pressure and temperature using a high pressure neutron diffractometer, PLANET, which will be available in fall this year, at J-PARC. Our previous synchrotron x-ray diffraction experiments and molecular dynamics simulation studies have revealed that structure of liquid water changes drastically under high pressure and temperature. But experimental observation of hydrogen is limited and neutron experiments are necessary to understand pressure and temperature dependence of hydrogen bonds in water. In this presentation, scientific background and the present status of target, design of an high-pressure assembly, methods for data analysis will be shown.

[1] Y. Katayama, T. Hattori, H. Saitoh, T. Ikeda, K. Aoki, H. Fukui, and K. Funakoshi, Phys. Rev. B 81, 014109 (2010)

[2] T. Ikeda, Y. Katayama, H. Saitoh, and K. Aoki, J. Chem. Phys. 132, 121102 (2010).

Keywords: water, neutron, high temperature, high pressure, structure, liquid

SMP045-07

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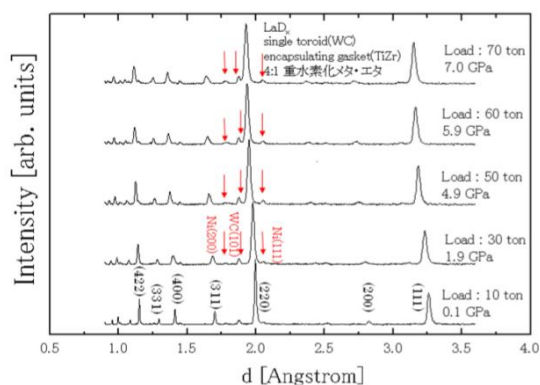
Time:May 24 15:45-16:00

High-pressure neutron diffraction study on metal hydrides at total scattering diffractometer NOVA in J-PARC

Takanori Hattori^{1*}, Mitsunori Honda¹, Akihiko Machida¹, Kazuki Komatsu², Asami Sano¹, Hiroshi Arima¹, Yoshinori Katayama¹, Katsutoshi Aoki¹, Toshiya Otomo³

¹JAEA, ²University of Tokyo, ³KEK

Now, high-pressure structural changes in rare-earth hydrides $\text{La}(\text{H}/\text{D})_2$ is being investigated by neutron diffraction under the program of Advanced Fundamental Research on Hydrogen storage materials (Hydro-star). The preceding investigation by synchrotron diffraction revealed that the rare-earth hydrides (LaX_2) commonly shows spontaneous dissociation into two phases with different hydrogen contents under pressure. In this transformation, metal sub lattice keeps the macroscopic crystallinity, suggesting that hydrogen diffuses in metal sublattice. To investigate the hydrogen behavior in high hydrogen-density states is indispensable for generating new functional materials. The aforementioned behavior is speculated only from the lattice parameter of the metal sublattice due to the insensitivity of x-ray to hydrogen. To confirm the behavior, it is indispensable to investigate by diffraction using neutron, which is sensitive to hydrogen. Therefore, we developed the device to realize high-pressure neutron diffraction. For the prescription, we coupled a compact but heavy load applicable Paris-Edinburgh cell with total scattering diffractometer NOVA, which has world-quickest data-acquisition performance. Through the various developments, we succeeded in obtaining the high quality data sufficient to apply Rietveld analysis at the highest pressure in Japan. The details will be introduced in this talk.



Keywords: high-pressure, neutron, metal hydride

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SMP045-08

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Time:May 24 16:00-16:15

High-pressure neutron diffraction experiments of ice at TAKUMI in J-PARC using Palm cubic anvil apparatus

Masashi Arakawa^{1*}, Hiroshi Fukazawa², Hiroyuki Kagi¹, Kazuki Komatsu¹, Riko Iizuka¹, Jun Abe², Hiroshi Arima², Takanori Hattori², Asami Sano², Wataru Utsumi², Takuo Okuchi³, Yoshiki Ohno⁴, Shigeo Sasaki⁴

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In-situ neutron diffraction measurements of hydrogen-ordered phase of ice VI were performed at J-PARC using a clamp-type high-pressure device, palm cubic anvil apparatus. The results indicate that the hydrogen-ordered phase of ice VI would be ferroelectric. This might be a new phase of ice. Not only in icy grains and icy bodies' surface, but also in icy bodies' interior, ferroelectric ice, which possesses the ability to carry a charge, might exist.

Keywords: ice, high pressure, hydrogen ordering, neutron diffraction

SMP045-09

Room:301B

Time:May 24 16:30-16:45

High-pressure Raman and powder neutron diffraction studies of methane hydrate up to 1.2 GPa

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Gas clathrate hydrates are inclusion compounds which consist of a crystalline host cage-like framework of hydrogen-bonded water molecules in which small guest gas molecules are enclosed. Methane hydrate (MH) is the most common gas hydrate, and has attracted attention as a promising natural resource to replace fossil fuels for the next generation. At room temperature, the initial structure I of methane hydrate (MH-sI) successively transforms to MH-II (sH) and MH-III (sO, filled ice) at 0.9 GPa and 1.9 GPa, respectively. The cubic MH-sI is composed of two different host water cages of 12-hedra (S1) and 14-hedra (M), and the hexagonal MH-II (sH) has three 12-hedra (S1), two other small 12-hedra (S2), and one large 20-hedron (LL) [1]. On the other hand, the MH-III (sO) is the channel or the filled ice structure which is no longer cage structure [2].

The methods of x-ray diffraction (XRD), neutron diffraction (ND), nuclear magnetic resonance (NMR) and Raman spectroscopy are effective in estimation of the cage occupancy of guest molecule. In our laboratory, we adopted the Raman spectroscopy for studying the cage occupancy of gas hydrates, because the Raman frequency shift of guest molecular vibration is sensitive to the environment by the host water cage.

High-pressure Raman measurements of synthesized MH-II (sH) grown in a diamond anvil cell (DAC) show that each host LL cage encloses one guest methane molecule in the pressure region of 0.9 - 1.3 GPa, and two or three methane molecules occupy each LL cage above 1.3 GPa [3,4]. These results implied the existence of phase transformation by the change of cage occupancy at 1.3 GPa. However, there is an inconsistency between our Raman results and the previous XRD and ND results [5] which suggested that five methane molecules occupy each LL cage.

In the present study, we performed Raman scattering and the neutron diffraction measurements for the identical sample of MHII (sH) in order to clarify the cage occupancy. The full deuterated MH ($\text{CD}_4\text{-D}_2\text{O}$) sample was synthesized in a high-pressure vessel at 263 K and 8 MPa. The obtained fine powder of MH was put in a sample chamber of a high-pressure moissanite anvil cell, and then was loaded up to 1.2 GPa (sample volume: 6 mm³). The Raman spectra from the present sample show that MH is the low pressure phase, MH-II (sH). Powder neutron diffraction studies were carried out on the Takumi beam line in MLF at J-PARC. We obtained the fine neutron diffraction patterns. We will present the Raman and powder neutron diffraction studies of methane hydrate up to 1.2 GPa.

[1] E.D. Sloan Jr., Clathrate hydrates of Natural Gases, 2nd ed., Marcel Dekker, Inc., New York, (1998).

[2] J.S. Loveday *et al.*, Phys. Rev. Lett. 87, 215501 (2001).

[3] H. Shimizu *et al.*, J. Phys. Chem. B 106, 30 (2002).

[4] T. Kumazaki *et al.*, Chem.Phys. Lett. 388, 18 (2004).

[5] J.S. Loveday *et al.*, Can. J. Phys. 81, 539 (2003).

Keywords: Methane hydrate, Raman scattering, High-pressure, Opposite anvil cell, Neutron diffraction

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SMP045-10

Room:301B

Time:May 24 16:45-17:00

Neutron powder diffraction at high pressure using compact opposed anvil cell

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Current status of technical developments for time-of-flight powder neutron diffraction at high pressure using compact opposed anvil cells were reported [1,2]. We conducted the diffraction experiments at J-PARC MLF BL19 "TAKUMI". Neutron diffraction patterns up to 8 GPa has been successfully obtained using the compact cell.

References: [1] T. Okuchi et al., J. Phys. Conf. Ser., 215 (2010) 012188; [2] T. Okuchi et al., Rev. High Press. Sci. Tech., 20, 175-178, 2010.

Keywords: Powder neutron diffraction, opposed anvil cell

SMP045-11

Room:301B

Time:May 24 17:00-17:15

Technical improvements on Paris-Edinburgh high-pressure cell for neutron diffraction and ruby fluorescence measurements

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Neutron is a complementary probe to X-ray for material sciences in determining crystal structures. In particular, neutron diffraction is powerful to locate hydrogen positions in hydrogen-bearing compounds. The spallation neutron source of new generation is now being constructed in Tokai, Ibaraki Pref. as a part of the J-PARC facility. In the history of high-pressure neutron science, the most crucial technical progresses would be the developments and uses of Paris-Edinburgh (P-E) presses in strong neutron sources in European countries and US. In order to use practically a P-E press in J-PARC in future, it is necessary to improve these conventional techniques for achieving higher pressure with larger sample volume. We especially redesigned the parts of anvils and gaskets surrounding samples acquiring higher intensities for the same initial sample volume as original anvils. There are two main points for our improvements; a new anvil made of Ni-WC with a wide conical aperture for getting higher signal intensity and an optical window for monitoring ruby fluorescence spectra, a hybrid gasket made of TiZr and Al-alloy for reducing absorption of incident neutron beam.

High-pressure generation tests have been performed several times using Bi as a pressure calibrant and measurements of ruby fluorescence spectra at the same time. In-situ and high-quality X-ray diffraction experiments were also carried out using synchrotron radiation at PF-AR, KEK, with NaCl pellets as pressure calibrants. The sample volume was 50 mm³ and the highest pressure obtained was above 13 GPa. The neutron diffraction measurements were carried out at BL19, MLF, J-PARC. As a result, 3 times higher intensities of neutron scattering from Pb pellet were obtained using our improved anvils than conventional single toroidal anvils. This suggests that our new anvils are expected to give sufficient intensity for crystal structure analysis from smaller amount of sample in a shorter measurement time even under higher pressure. Our study indicates that some important improvements were produced by the development of new cell assemblies. Furthermore, the required improvements and future prospects to the technique will be proposed.

Keywords: Paris-Edinburgh cell, high pressure, neutron diffraction, hydrous minerals, J-PARC, hydrogen bonding

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SMP045-12

Room:301B

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Attenuation correction for the Paris-Edinburgh cell using path-length calculation

Kazuki Komatsu^{1*}, Riko Iizuka¹, Jun Abe², Asami Sano², Hiroshi Arima², Takanori Hattori², Hiroyuki Kagi¹

¹The Univ. of Tokyo, ²JAEA

In order to obtain structural information, attenuation corrections using path-length calculation were carried out for the Paris-Edinburgh cell. Attenuation factors can be calculated using both neutron path-length and neutron transparency for anvils, gasket etc. We also obtained the observed attenuation factors by using a vanadium pellet. The calculated attenuation factor is well consistent with the observed one.

SMP045-13

Room:301B

Time:May 24 17:30-17:45

Development of high pressure cell for neutron diffraction experiment

Asami Sano^{1*}, Kazuki Komatsu², Takuo Okuchi³, Takanori Hattori¹

¹JAEA, ²Univ. of Tokyo, ³Okayama Univ.

In PLANET, which is now under construction in J-PARC, 6-axis high pressure apparatus will be installed to conduct high pressure neutron diffraction experiment. Paris-Edinburgh press and Palm cubic press are also available, which have a capability to reach low temperature. High pressure generation is significantly affected by the material and design of gasket and cell. We are developing cell to generate high pressure using these presses and the result of test experiment will be presented.

1. Paris-Edinburgh (PE) press

PE press is widely used in neutron facility since it has a wide window. We have succeeded to generation to 6.6 GPa at 60 ton using single toroid WC anvils, and to 14.4 GPa at 130 ton using double toroid sintered diamond anvils.

2. Sintered Diamond (SD) Anvil for 6-8 type multi anvil press

To use 6-8 type cell for neutron diffraction, absorption by anvil is a problem since neutron diffraction requires wide window. SiC-binder SD has a potential for generate high pressure if it is used as anvil material for 6-8 type anvil press, and it absorbs less neutron compared to Co-binder SD. We conduct test experiment at ARNE7, in KEK, Tsukuba. High pressure was generated using multi anvil apparatus (MAX-III), using SD cube with 9.5mm on edge and TEL of 1.5 mm. The result shows that it can reach over 30 GPa at 300 ton, suggesting the ability for pressure generation. Future development of cell for large volume sample cell and high temperature is necessary.

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SMP045-14

Room:301B

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Developments of large-volume 6-6 type technique for high-pressure neutron diffraction

Akihiro Yamada^{1*}, Takaaki Kawazoe¹, Nishiyama Norimasa¹, Toru Inoue¹, Takehiko Yagi²

¹GRC, Ehime Univ., ²ISSP, Univ. of Tokyo

NA

Keywords: high-pressure neutron diffraction, 6-6 type compression, multi-anvil apparatus

SMP045-15

Room:301B

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Neutron guide at PLANET in MLF of J-PARC

Hiroshi Arima^{1*}, Takanori Hattori¹, Asami Sano¹, Kazuki Komatsu², Hiroyuki Kagi²

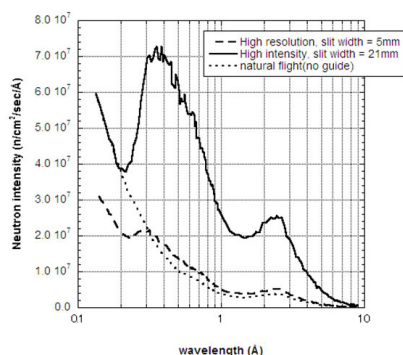
¹Japan Atomic Energy Agency, ²The University of Tokyo

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.

The performance for the instrument required by users vary according to their research fields such as earth and space science, material science, and high-pressure physics and chemistry. Therefore, the instrumental design should incorporate wide Q range and have the flexibility for intensity-resolution optimization to improve versatility and efficiency in structure analysis of crystal and liquid at high pressure.

Key requirements for the guide at the beamline are as follows: (i) focus neutrons of wavelength between 0.45 to 10 Å, especially below 1 Å, to achieve accurate crystal structure analysis; (ii) generate a small focal spot size to reduce background noise from a complicated sample environment; and (iii) provide a homogeneous phase space distribution at the sample position to maintain relatively high beam flux without sacrificing resolution of the diffraction profile. To fulfill these requirements, we designed an elliptical-shaped guide, which has rectangular cross-section and consists of four walls coated with supermirror.

The instrument commissioning has been started from March 2011 parallel with the final stage of the construction. Here we present design of neutron delivery system of PLANET and first results of beam characterization.



The simulation results of incident neutron fluxes on the sample position.

Keywords: neutron diffraction, supermirror, high pressure and high temperature

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SMP045-16

Room:301B

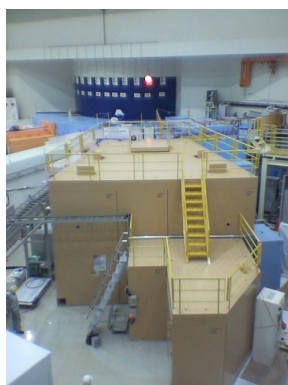
Time:May 24 18:15-18:30

Here comes first beam in high-pressure neutron diffractometer PLANET

Takanori Hattori^{1*}, Hiroshi Arima¹, Asami Sano¹, Jun Abe¹, Wataru Utsumi¹, Takaya Nagai², Hiroyuki Kagi³, Toshiaki Iitaka⁴, yoshinori katayama¹, Toru Inoue⁵, Takehiko Yagi⁶

¹JAEA, ²Hokkaido University, ³University of Tokyo, ⁴RIKEN, ⁵Ehime University, ⁶ISSP

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 6m 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 30GPa and 2000K. We have installed several optical devices, such as choppers, supermirror guides, 4-dimensional slit, and data acquisition system. On the last March, we received FIRST NEUTRON BEAM. In the talk, we overview the spectrometer and introduce the current construction state.



Keywords: High Pressure, Neutron, High-Pressure Diffractometer

SMP045-17

Room:301B

Time:May 25 08:30-08:45

Densified silica glass study by RMC simulation using X-ray and neutron diffraction data

Oscar Yagafarov^{1*}, Shinji Kohara², Laszlo Temleitner³, Yasuhiro Inamura⁴, Yoshinori Katayama⁵

¹QuBS, JAEA; HPPI RAS, Russia, ²JASRI, ³JASRI; HAS RISSPO, Hungary, ⁴J-PARC Center, JAEA, ⁵QuBS, JAEA

In the nearest future it will be possible to complement high pressure x-ray measurements at synchrotron with neutron diffraction study at J-PARC. Analyzing both experimental data in combination may have a synergistic effect. One possible method is to use the Reverse Monte Carlo (RMC) algorithm [1] to derive structures of disordered materials from both diffraction data. In order to gain experience we analyze previously measured X-ray and neutron diffraction data on normal and densified silica glass SiO₂ [2,3].

High pressure study of this archetypal glass, formed by SiO₄ tetrahedrons with network structure, is still challenging. One of the main issues is understanding of permanent densification mechanism (at $p > 10$ GPa at room temperature). It is known that densification is occurred mostly with modification in the intermediate range order rather than in short-range order. The fact that heating induces the structural change in the intermediate range order suggests that a thermally activated process such as rebonding (breaking of the original bonds and forming of new ones) should accompany the changes.

In order to verify topological changes by analyzing structures directly, we used RMC simulation to build 3D structural models of normal and densified glass. RMC derived a set of coordinates of the 6000 atoms of the configurations that are in good agreement with the experimental data.

RMC model reproduces the experimental data accurately and gives reasonable bond angle distributions. The O-Si-O angle distributions peak around 109 deg, only a slight broadening is seen in the densified glass. The intertetrahedral Si-O-Si angle distribution in the densified silica glass slightly shifts to lower values. Overall not much difference is seen in the other bond angles distributions. As for network topology study, RMC modeling should be done carefully. In usual way denser model is created by compacting of normal one. But in this case it is impossible to model rebonding process, since due to coordination number constraints RMC cannot change the connectivity pattern much. Therefore proper model of densified silica glass should be started from different (independent) initial configurations. To provide better understanding of densification mechanism further analysis (e.g. void space distribution) is in progress.

[1] O. Gereben et. al., J. Optoe. Adv. Mater. **9**, 3021 (2007).

[2] Y. Inamura et. al., Spring-8 User Exp. Rep. N0259(2001A) P.47.

[3] Y. Inamura et. al., J. Non-Cryst. Solids **293-295**, 389 (2001).

Keywords: silica glass, RMC, neutron diffraction, X-ray diffraction, high pressure

Pressure response of ionic resistance and refractive indices of ice VII

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¹ISSP, Univ. of Tokyo, ²Max-Planck-Institut für Chemie

Introduction

Ice VII is the stable form of ice at ambient temperature between 2.2 and ~40 GPa. Loubeyre et al. (1999) has detected spatially modulated phases between 2.2 and 25 GPa by single-crystal X-ray diffraction. However, the inducement mechanism remains unknown. Cavazzoni et al (1999) has theoretically predicted a superionic phase of H₂O with fast hydrogen diffusion between solid phase and fluid phase above 20 GPa and 2000 K. In this study, we attempted to measure ionic conductivities and refractive indices of H₂O directly at high pressures and temperatures by using diamond anvil cells (DAC).

Experimental methods

We performed the experiments using a DAC with type I diamonds having flats of 0.35 mm in diameter. A rhenium gasket combined with cubic boron nitride powder as insulation material was used to contain the sample. Distilled and deionized H₂O was loaded into ~0.1 mm diameter and ~0.03 mm thick sample chamber in the DAC. The pressure at room temperature was determined by the Raman spectrum of diamond-anvil. The central area of the sample of about 0.05 mm in diameter was subsequently heated from one side with a laser. The size of the heating spot was larger than the distance between the electrodes. Temperature was measured by a spectroradiometric method above 900 K and interpolated below 900 K from the relationship between the laser power and the temperature, respectively. We measured ionic resistance, namely, ac electrical resistance with an LCR meter (Agilent 4284A) and the platinum electrodes in configuration of a quasi four-probe microcircuit at high pressure and temperature. In our impedance spectroscopy (IS) measurement, 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. During IS measurement, we kept the sample temperature by controlling the laser power. Optical path length of the sample was also measured at high pressure and ambient temperature.

Results and discussion

We observed ideal impedance arcs in comparative high frequency region. We fitted the R-X plot with a function of a semicircle and obtained a bulk resistance of the sample at different pressures and temperatures. At 2.2 GPa, the bulk resistance of ice VII was greater by the one order of magnitude of that of Ice VI. At ice VII stable region, the bulk resistance decreased with increasing pressure. At 10 GPa, it was minimum value and smaller by the one order of magnitude of that of ice VII at 2.2 GPa. Then, it increased with increasing pressure. At 20 GPa, it was almost identical with that at 2.2 GPa. Above 20 GPa, it decreased slightly with increasing pressure. The change with pressure at ambient temperature is very reproducible between the all five experimental runs. The pressure region of anomaly of the bulk resistance of ice VII is consistent with that of the modulated phases reported by Loubeyre et al. (1999). At around 45 GPa, the bulk resistance decreases gradually with increasing temperature and some discontinuous changes were observed. High temperature experiments to check the reproducibility of the observed results and to clarify the behavior at different pressures are now in progress.

SMP045-19

Room:301B

Time:May 25 09:00-09:15

Synthesis and characterization of D-bearing piemontite

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Ca₂Al_{3-p}Mn³⁺_pSi₃O₁₂(OH)-piemontites were synthesized at 0.3-0.4 GPa and 500 C using hydrothermal equipment. The run products were analyzed using electron microprobe analyzer and infrared absorption spectral method, and refined using X-ray and neutron powder diffraction methods. The starting materials (s.m.s) of oxide mixture of stoichiometric compositions with $p = 0.75, 1.0$ and 1.1 and D₂O were used for hydrothermal synthesis experiments at 0.3-0.4 GPa and 500 deg.C. Starting materials: Oxide mixtures heated at 850 deg.C, and excess D₂O. Capsule systems: 1) Ag outer capsule with MnO₂-Mn₂O₃ buffer + H₂O; Ag90Pd10 inner capsule with charge + D₂O; 2) Au outer capsule with MnO₂-Mn₂O₃ buffer + D₂O; Ag90Pd10 inner capsule with charge + D₂O.

In the present synthesis experiments of deuterium-bearing piemontite using Ag-outer capsule with solid buffer + H₂O, deuterium was considerably or completely replaced by hydrogen. On the other hand, in the experiments using Au-outer capsule with solid buffer + D₂O, D-bearing piemontite was synthesized successfully. However, even in this case, seal of Au-outer capsule should be perfect, because hydrogen moves in and out inner Ag90Pd10 capsule.

There is no essential difference for Mn³⁺ distributions among octahedral M1, M2 and M3 sites between D-bearing piemontite and H-bearing piemontite: the Mn³⁺ occupancies at M1 and M3 in D-bearing piemontite refined using X-ray powder diffraction data are close to those of H-bearing piemontite (Nagashima and Akasaka, 2004). In this study, neutron diffraction data of a D-bearing piemontite synthesized from $p = 1.0$ starting material at 0.3 GPa and 500 deg.C were measured. Although D in this piemontite was considerably replaced by H because of the use of Ag-outer capsule with solid buffer + H₂O, D-positions could be refined. Neutron diffraction study of D-bearing piemontite synthesized successfully in this study will give us useful information for the relations between cation substitutions and hydrogen bond.

Keywords: piemontite, hydrothermal synthesis, infra-red, Rietveld analysis, deuterium

SMP045-20

Room:301B

Time:May 25 09:15-09:30

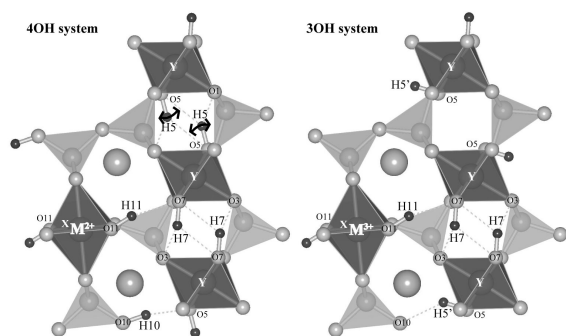
Close relationship between oxidation state of transition elements and hydrogen-bonding system

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The behavior of hydrogen in minerals is one of the prominent topics in Earth Science. The numbers of hydroxyl groups in minerals are not necessarily fixed. In some cases, the exact number of hydroxyl groups depends on the concentration of divalent and trivalent cations in the octahedral sites. In pumpellyite-group minerals with the simplified formula of $^{VII}W2^{VI}X^{VI}Y_2^{IV}Si_3O_{14-n}(OH)_n$ ($Z = 4$), the Y site is generally only occupied by trivalent cations, and the X site is occupied by both divalent and trivalent cation. The $M^{2+}/(M^{2+} + M^{3+})$ at X varies in a range of ca. 0.4-0.6. Thus, the number of OH, n in the formula, is 3-4. It means that pumpellyite with only divalent cations at the X site has four hydroxyl groups in the formula unit, but the number of hydroxyl groups will be three if only trivalent cations occupy the X site, as suggested by the substitutional scheme of $M^{2+} + 4OH^- \leftrightarrow M^{3+} + 3OH^- + O^{2-}$. It has been known that, in pumpellyite structure, hydroxyl groups are located at four oxygen positions, O5, O7, O10 and O11, and the hydrogen-bonding system in pumpellyite structure has been realized based on those hydroxyl groups. However, Nagashima et al. (2009, 2010) recently found two different hydrogen-bonding systems in pumpellyite and sursassite. Such situation that OH-bearing minerals have two or more different hydrogen-bonding systems can be also expected in other hydrous minerals containing transition elements.

In this presentation, I review and summarize the close relationship between oxidation state of transition elements and hydrogen-bonding systems in hydrous silicate minerals, and clarify the importance of further studies using neutron diffraction.



Hydrogen-bonding systems in pumpellyite (Nagashima et al. 2010)

Keywords: Hydrogen bond, Hydrous mineral, Transition element

SMP045-21

Room:301B

Time:May 25 09:30-09:45

Water partitioning between nominally anhydrous mantle minerals: experimental study with FT-IR analysis

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Water affects physical property of minerals, such as elemental diffusion rates, melting points, etc. Even a small amount of water plays a key role in mantle rheology, so the presence of water is very important in understanding the earth dynamics. Although the solubility of hydrogen in minerals, such as olivine has been well studied, experiments those determine water partitioning between coexisting mantle minerals are still limited.

In order to investigate the partitioning of water between nominally anhydrous minerals in mantle phases, we performed high-temperature and high-pressure experiments using Kawai-type multi-anvil apparatus (SPI-1000, SAKURA-2500) and piston-cylinder apparatus at the Magma Factory, Tokyo Institute of Technology. Starting materials are olivine, orthopyroxene and clinopyroxene separated from a spinel peridotite (KLB-1). Powdered minerals were set in Au or Au₇₅Pd₂₅ capsules to form monomineralic layers with more than 200 micron meters in thickness each. Trace amount of moisture was added by breathing in some capsules. Otherwise, water was not added. Experimental conditions were that equivalent at the topmost mantle and that at mantle transition zone. The topmost mantle conditions are pressures of 1-2 GPa and temperatures of 1200-1300C. The mantle transition zone condition is 17 GPa and 1650C. The water contents were obtained from a vacuum type Fourier transform infrared spectroscopy (JASCO-FT-IR6100). Detection limit in the IR spectra in 3000-4000 cm⁻¹ is typically less than 1 ppm due to very low back ground.

In all experiments at the topmost mantle conditions, $D_{(opx/oliv)}$ and $D_{(cpx/oliv)}$ are 10-30. These partition coefficients are much smaller than those reported by Grant et al., (2007) who analyzed coexisting minerals in mantle xenoliths. The difference might be explained by excess hydrogen solubility in our experimental olivine by oxidation effect. Alternatively, the difference might be due to the hydrogen loss in mantle xenolith olivines during transportation. $D_{(cpx/opx)}$ in our experiments are 2-4 which are in excellent agreement with those values in mantle xenoliths.

In some run products oxygen fugacity was controlled by NNO buffer. In unbuffered runs, however, oxygen fugacity becomes much higher than NNO due to absorption of iron into Au₇₅Pd₂₅ capsule. In the oxidized samples, IR spectra of clinopyroxene, orthopyroxene and especially olivine showed 3700cm⁻¹ band. This band is similar to those in talc and serpentine but neither is stable at our experimental conditions. It is suggested that the IR spectra at 3700cm⁻¹ are due to OH stretching vibration without hydrogen bonding. The excess hydrogen may be OH in defects coupled with Fe³⁺ formed by oxidation.

At the mantle transition zone condition, we obtained $D_{(maj/wads)}$ to be 1.6. The fact that majorite garnet contains greater amount of water than coexisting wadsleyite seems surprising, because wadsleyite is known to be one of the major reservoir of water in the Earths transition zone. However, the same tendency was already experimentally reported in MgO-SiO₂-H₂O system by Bolfan-Casanova et al. (2000). Because our partition data were obtained in very low water concentration level (usually less than 100ppm) concentration dependence of the partition coefficients must be studied in future works.

Keywords: water, anhydrous mineral, FT-IR, partitioning, mantle

SMP045-22

Room:301B

Time:May 25 09:45-10:00

Phase diagram of Fe-H system at high pressure: In-situ X-ray experiments using single crystal diamond capsule

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Earth's outer core is approximately 10% less dense than pure iron. Hydrogen is considered to be one of the light elements which cause the density deficit of Earth's core. Fukai (1984) suggested that hydrogen can dissolve into metallic iron under high pressure. We have determined the melting temperature of FeH between 10 and 20 GPa under hydrogen saturated condition and proposed that the melting temperature is more than 1773K lower than that of pure Fe at CMB condition (Sakamaki et al., 2009). In this study, we performed Hydrogenation experiments of Fe that coexists with hydrous ringwoodite. The amount of hydrogen x in FeH_x was calculated by X-ray diffraction pattern using multi anvil apparatus SPEED-Mk2 installed at BL-04 in SPring-8, Japan. Single crystal diamond and rhenium composite capsule were used as sample container. The amounts of hydrogen x (FeH_x) were estimated by X-ray diffraction pattern. Hydrogen concentration in FeH_x coexisting with hydrous ringwoodite is between 0.4 and 0.6 at 1273K and 14~23 GPa. This value is significantly lower than those reported (x=1~1.2) by Shibazaki et al (2009). The difference may be due to the difference in amount of water in the system. Our experiments were conducted under water under saturated condition while those of Shibazaki et al (2009) were probably water saturated. Although Shibazaki et al (2009) reported experimental results only at 1273K, we will show results between 1273K and 1823K at pressures between 14 and 23 GPa. In our experiments, for example at 16GPa, FeH_x coexisted with FeH_x melt above 1773K, and gamma-FeH_x melted completely at 1823K. The amount of hydrogen in gamma-FeH_x coexisted with FeH_x melt should be plotted on solidus line. Using these result, melting temperature of pure iron and that of FeH, the phase diagram of Fe-H system are constructed.

Keywords: iron, hydrogen, phase diagram, core, hydrogenation