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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.

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Keywords: nano-polycrystalline diamond, ideal strength

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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

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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

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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