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高温高圧下におけるナノ多結晶ダイヤモンドの ideal strength に関する分子動力学シミュレーションによる研究
Ideal Strength of Nano-polycrystalline diamond under High Temperature and High Pressure using MD Simulation

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ナノ多結晶ダイヤモンドは、ナノサイズのダイヤモンド結晶構造を持った人工ダイヤモンドであり、天然のダイヤモンドと同様な物性を持っている [1]。すなわち、硬度が高く、高い熱伝導性、絶縁性を持つ。また、多数の結晶面が重なり合った構造であるため、天然のダイヤモンドより硬い。そのことより、高圧実験で用いられているダイヤモンドアンビルセル (DAC) への応用が考えられている。このため、ナノ多結晶ダイヤモンドの作製及び物理的性質を観察することは非常に重要な課題となっている。そこで本研究では、ナノ多結晶ダイヤモンドの硬さを調べることを目的とした。

準備計算として、ダイヤモンドの結晶構造を用いて ideal shear strength を求めた。ソフトウェアは LAMMPS [2] を用い、Tersoff potential [3] (SiC.tersoff) を用いた。温度は 300 K、Time step は 0.001 ps に設定した。構造最適化を NPT 条件下で 1 ps 行った後、210 ps の MD シミュレーションを NVT 条件下で行った。この際、1 ps 経過する度に、各結晶面の各方向に strain を増加させた。その結果、すべり面が {010} ですべり方向が<100>の時、ideal share strength は 202.0 (GPa) でその時の critical strain は 0.39 であった。すべり面が {110} ですべり方向が<-110>の時は、ideal share strength は 93.4 (GPa) でその時の critical strain は 0.33 であった。また、すべり面が {111} ですべり方向が<11-2> の時、ideal share strength は 87.9 (GPa) でその時の critical strain は 0.16 であった。

今後、ナノ多結晶ダイヤモンドに Hall-Petch [5,6] の関係があるか否かを詳しく調べる。Branicio らによって報告されている [4]、grain size 4.1 nm より大きな grain size の計算を行い、ナノ多結晶ダイヤモンドの硬さを調べる。その際、そのナノ多結晶ダイヤモンドの、あるすべり面におけるあるすべり方向の ideal strength を求める。ideal strength とは、無限に欠陥のない固体に徐々に負担をかける際、その固体が弾性限界を超え、形が完全に変化する直前の弾性の限界の値をいう [7,8]。この計算も、準備計算と同様に分子動力学シミュレーションを行う。

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キーワード: ナノ多結晶ダイヤモンド, ideal strength
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低温高圧下における水素ハイドレート低対称化のラマン分光による原因推定
A possible reason for forming tetragonal phase of hydrogen hydrates under low-T and high-P by Raman spectroscopy

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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.

キーワード: 水素ハイドレート, ダイヤモンドアンビルセル, 低温高圧実験, ラマン分光分析, 配向秩序化
Keywords: hydrogen hydrate, Diamond Anvil Cells, low-temperature and high-pressure, Raman spectroscopy, rotational ordering

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高圧・低温下におけるメタンハイドレート Filled Ice Ih 構造の軸比変化とその誘因
Axis-ratio change induced by guest ordering of filled ice Ih methane hydrate under high pressure and low temperature

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ラマン分光法により 15〜20GPa の圧力領域において、タンハイドレート FilleIce Ih 構造は、ゲストメタン分子の配向が秩序化することが著者らのグループにより報告されている。さらに 15Gpa 付近では、格子振動に変化が観察され、その状態変化が起きることを Sasaki らのグループが報告している。しかし、同様な圧力領域における X 線回折では、明瞭な変化の報告はされていない。今回、室温〜低温下において、フレームワークに軽水・重水を用いたメタンハイドレート FilledIce Ih 構造の格子定数を X 線回折により精密に測定した。その結果、15〜20GPa の圧力領域において、その軸比の傾きに明瞭な変化が観察された。さらに、低温下でのラマン分光法による実験結果とから、この、軸比変化はゲストメタン分子の配向の秩序化によるものと推測される。

キーワード: メタンハイドレート, X 線回折, 高圧, ラマン分光
Keywords: Methane Hydrate, X ray diffraction, high pressure, Raman spectroscopy

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硫黄と酸素の存在下における核中の水素
Hydrogen in the core under the co-existence of sulfur and oxygen

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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.

キーワード: 核の軽元素, 高温高圧実験, 放射光実験
Keywords: light elements in the core, high pressure and high temperature, synchrotron experiments