

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.

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