Japan Geoscience Union Meeting 2010
(May 23-28 2010 at Makuhari, Chiba, Japan)

SMP057-18 Room: 101 Time: May 24 09:45-10:00

Cage occupancy of methane molecule in structure-H methane hydrate

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Gas clathrate hydrates are inclusion compounds which consist of a crystalline host framework of hydrogen-bonded water molecules forming cages in which small guest 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 hydrate 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 use the Raman spectroscopy for studying the cage occupancy of gas hydrates. The Raman frequency shift of guest molecular vibration is sensitive to the environment by the host water cage.
High-pressure Raman measurements were performed for investigating the pressure-induced phase transformations and the cage occupancy of synthesized MH-II (sH) grown in a diamond anvil cell (DAC), As a result, we found that each host LL cage enclosed one guest methane molecule in the pressure region of 0.9 - 1.3 GPa, on the other hand 2 or 3 methane molecules occupied each LL cage at pressures from 1.3 GPa to 1.9 GPa [3,4]. These results implied the existence of phase transformation by the change of cage occupancy at 1.3 GPa. However, there is inconsistency between our Raman study and the previous XRD and ND experiments [5] which suggests that five methane molecules occupy each LL cage.
At present, we are developing the new high-pressure diamond anvil cell (DAC) for the neutron diffraction and Raman scattering measurements in order to clarify the cage occupancy in MH-II (sH) phase. We will present the state of development of new DAC.

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