P154-033 Room: 201B Time: May 17 9:52-10:05

Exploring a Post Filled-ice Ih Structure of Methane Hydrate under high pressure and its implications of the icy planets

Shin-ichi Machida[1]; Hisako Hirai[2]; Takehiko Yagi[3]

[1] Life and Environmental Sci., Tsukuba Univ; [2] Geoscience, Tsukuba Univ.; [3] Inst. Solid State Phys, Univ. Tokyo

Methane hydrate is expected as a new energy resource of the next generation. At the same time, methane gas is an effective greenhouse gas and methane hydrate has been related to environmental change. In addition, methane hydrate is thought to be one of the major components of outer planets and their moons. Therefore, understanding on the stability and phase changes of methane hydrate under high pressure is required from on the wide view points.

The previous high pressure studies showed that methane hydrate took structure I up to 1GPa, and that transformed to a hexagonal structure which was stable up to 2GPa, and that finally transformed to a filled ice Ih structure (FIIhS). Recently the high pressure studies carried out showed the retention of the FIIhS up to 40GPa, and above 40GPa experiment further has not been performed. According to theoretical study using first-principle calculation, the FIIhS can survive up to 100GPa and symmetrization of hydrogen bond proceeds in step wise at 50GPa and 70GPa. Therefore, this study is intended (1)to examine whether the FIIhS can exist above 40GPa, dissociates into solid methane and iceVII, or transforms to a post-FIIhS. (2)to examine the stability of the FIIhS under such high pressure by characterizing vibration modes of methane and water molecules. (3)to infer the states of methane hydrate within the interiors of outer planets and their moons.

A lever-spring type diamond anvil cell was used in the high-pressure experiments. The optical microscopy, X-ray diffractometry (XRD) and Raman spectroscopy were performed for characterization. CO2-laser heating in high-temperature experiment was used. High-pressure experiments were made in the pressure range from 2 to 86GPa.

In the XRD patterns, a new diffraction lines were observed above 40GPa, indicating that the FIIhS transformed to a new structure. Because the number of the diffraction lined was limited, the detail of the new structure was not determined, but lowering symmetry was clearly indicated.

In the Raman spectra, the symmetric stretching vibration modes of methane molecules(n1 and n3) were changed at approximately 15GPa and 40GPa. The change in the Raman spectra about 15GPa might be resulted from the following reason. The distances between the methane molecules were shorter than van der Waals radius in the FIIhS even at 2GPa just after the transition. With increasing pressure, these distances became further shorter consequently, some interaction might occur between the methane molecules. This causes the change in intermolecular vibration mode. And also, this interaction might substantiate the stability of FIIhS under such high pressure. The change at 40GPa was thought to be related to the step-wise symmetrization of the hydrogen bonds.

High-temperature experiments were carried out under the conditions (several hundred K, 50-80GPa) comparing to those of interior of outer planets, Uranus and Neptune. Methane hydrate survived under these conditions, suggesting that the filled ice structure or post filled ice structure is possibly present within the interiors of these bodies.