

Phase changes of hydrogen- and methane-hydrates under low temperature and high pressure

Hisako Hirai^{1*}, KAGAWA, Shingo¹, TANAKA, Takehiko¹, MATSUOKA, Takahiro², OHISHI, Yasuo³, YAGI, Takehiko¹, OHTAKE, Michika⁴, YAMAMOTO, Yoshitaka⁴

¹GRC Ehime University, ²KYOKUGEN, ³JASRI, ⁴AIST

One type of hydrates (referred to HH) has recently received significant interest as a clean hydrogen storage material, and methane hydrate (referred to MH), called 'fiery ice' is expected an useful natural resource. Both hydrates have been thought to be potentially ubiquitous in space objects such as icy satellites of the solar system and extrasolar planets. At lower pressures these hydrates have clathrate structures which consist of host cages formed by hydrogen-bonded water molecules with encapsulated guest species. At higher pressures, MH and HH transform to a filled ice Ih structures (MH-FIIhS) and filled ice Ic structure (HH-C2), respectively. These filled ice structures consist of a host ice framework and guest molecules contained in the voids of the host ice framework. Comprehensive studies performed under room temperature for MH and HH provided interesting properties, however, low temperature and high pressure behaviors have rarely been known except a few studies. In this study, low-temperature and high-pressure experiments were performed to clarify the phase changes of MH-FIIhS and HH-C2 in the previously unexplored region.

Clamp-type diamond anvil cells and a helium-refrigeration cryostat were used in this study. The pressure and temperature ranges for HH-C2 were 5.0 to 50.0 GPa and 30 to 300 K, and those for MH-FIIhS were 2.0 to 77 GPa and 30 to 300 K, respectively. Pressure measurements were made via a ruby fluorescence method and a diamond Raman method. Temperature measurements were made using a silicon semiconductor thermometer and chromel-alumel thermocouples. The initial samples of MH and HH were prepared by ice-gas interface method and gas-loading method, respectively. The samples were characterized via X-ray diffractometry (XRD) using synchrotron radiation at BL-10XU at SPring8 and BL-18C at the Photon Factory (KEK) and Raman spectroscopy.

In situ X-ray diffractometry revealed that the cubic HH-C2 transformed to tetragonal at low temperatures and high pressures, and that the axis ratio of the tetragonal phase changed depending on the pressure and temperature. These results were consistent with theoretical predictions performed via first principle calculations. The tetragonal phase was determined to be stable above 20 GPa at 300 K, above 15 GPa at 200 K, and above 10 GPa at 100 K. Further changes in the lattice parameters were observed from about 45 to 50 GPa throughout the temperature region examined, which suggests the transformation to another high-pressure phase above 50 GPa. Guest molecules have been known to rotate freely in both clathrate and filled ice structure under low pressure. The reasons for the transformation to the tetragonal structure can be explained as follows: the tetragonal structure might be induced due to changes in the vibrational or rotational modes of the hydrogen molecules from free-rotation state to orientational-ordered state under low temperature and high pressure.

In our previous studies of MH-FIIhS by Raman spectroscopy, orientational ordering of guest methane molecules, namely suppressing rotation, occurred at 15-20 GPa, although there was no clear change in the lattice parameters and volume by the XRD study. The present XRD study revealed clear changes in the axis ratios at 15 to 20 GPa at 300K. The Raman spectroscopy showed split of CH vibration mode of the methane molecules at the almost same pressure. These results indicated that the orientational ordering of the guest molecules resulted in deformation of the lattice. The change in rotational mode of the guest molecules is a phase change. Thus, the results demonstrate that there are guest-disordered phase and guest-ordered phase within same MH-FIIhS frame work structure. Similar changes in the axis ratios and split of CH vibration mode were observed at low temperature regions.

Keywords: hydrogen hydrate, methane hydrate, phase change, low temperature, high pressure