

Mechanisms of phase transitions of methane hydrate under high pressure

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Methane hydrate (MH), called as “ burning ice ”, is expected to be a fruitful natural resource, at the same time, methane is rather effective greenhouse gas than carbon dioxide. It is also thought to be a major constituent of icy bodies in and outside the solar system. MH is composed of hydrogen-bonded host water molecules forming cages or frameworks that include guest methane molecules. Three phases of MH have been known so far. The low-pressure phase, sI, is stable below 0.8 GPa and it transforms into a hexagonal structure, sH, at 0.8 GPa and further transforms to a filled ice Ih (FIIhS) at 1.8 GPa at room temperature. At these phase transitions, release of water content is accompanied. As described above, the existence of phase transitions and the structures of transformed high-pressure phases have been clarified by the previous studies. However, transition mechanisms from the lower-pressure phase to individual high-pressure phases have been unresolved issue. In this study, high-pressure experiments were performed to investigate mechanisms of the phase transitions of MH at high pressures.

Clamp type and lever-spring type diamond anvil cells were used in this study. The pressure and temperature conditions were from 0.2 to 3.0 GPa and 300 K, respectively. Pressure measurements were made via a ruby fluorescence method. The initial samples of MH were prepared by ice-gas interface method. The samples were characterized via time-resolved X-ray diffractometry using synchrotron radiation at BL-10XU, SPring-8, and time-resolved Raman spectroscopy at GRC, Ehime University.

As for sI-sH phase transition, Raman spectroscopy revealed that 5^{12} cages of sI survived during the transition and that the 5^{12} cages remained as same 5^{12} cages of sH structure. And, $5^{12}6^2$ cages of sI changed to $4^35^66^3$ and $5^{12}6^8$ cages of sH. The results suggested that the sI-sH transition may follow a martensitic-like mechanism because of being maintaining 5^{12} cages unchanged in sH structure. On the other hand, at sH-FIIhS transitions, Raman spectroscopy detected abrupt collapse of all constituent cages in sH and release of fluid or solid methane molecules. And then, the framework of FIIhS was gradually reconstructed, absorbing the released methane molecules into the FIIhS structure. The results indicated that the sH-FIIhS transition follows reconstructive mechanism. The explanations may be reasonable, because the former transition is from a cage to another cage structure, and the latter one is from a cage structure to different framework of a filled ice structure.

Keywords: methane hydrate, mechanisms of phase transitions, high-pressure, X-ray diffractometry, Raman spectroscopy