

Phase transition mechanisms of methane hydrate under high pressure by time-resolved XRD and Raman spectroscopy

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Methane hydrate, called “fiery ice,” is expected to be a clean energy resource, whereas methane is a greenhouse gas even more potent than carbon dioxide. Also, methane hydrate is thought to be an important constituent of icy planets and their satellites, such as Neptune and Titan. Gas hydrates are clathrate compounds composed of hydrogen-bonded water cages (host), with molecules or atoms (guests) included in the cages [1]. A lot of studies of methane hydrate under high-pressure has revealed that sI structure of methane hydrate transforms sH [one at about 0.8 GPa and further transforms a filled ice Ih structure at about 1.8 GPa at room temperature [e.g.2,3]. However, the transition mechanism from one structure to another one has been little studied except for a study of kinetics under dynamic loading conditions [4]. Gas hydrates exhibit unique structures consisting of a water-network host and freely rotating guests, and so a characteristic transition mechanism different from an exclusively martensitic or reconstructive one is expected to exist.

In this study, the phase transition mechanisms of methane hydrate from an sI to an sH structure and from an sH to a filled ice Ih structure were examined using a combination of time-resolved X-ray diffractometry, time-resolved Raman spectroscopy, and simultaneous charge-coupled device (CCD) camera observation under fixed pressure conditions [5].

The X-ray study of the sI–sH transition at 0.8 GPa revealed an inverse correlation of the relative intensities between sI and sH during the transition, suggesting that the structure of sI was replaced in turn with sH structure. The Raman study showed that the 12-hedra of sI were maintained in the sH structure and that the 14-hedra of sI were replaced sequentially with additional 12-hedra, modified 12-hedra, and 20-hedra cages of sH. The wavenumber of the 14-hedra was unchanged before and during the transition and those of the newly formed cages of sH were comparable to those of the completed sH. The fractions of these cages exhibited inverse correlation. These results suggest that upon replacing the cages, methane molecules simultaneously migrated into the cages of sH from the 14-hedra. In other words, the transition is characterized by partly retaining the former structure and replacing the cages with a short-range-order migration of atoms. On the basis of these observed characteristics, the mechanism from the sI to sH transition is perhaps best described using an analogy from genetic recombination as “a cage-recombination mechanism.”

As for the sH filled ice Ih transition at 1.8 GPa, the X-ray study showed that the sH structure collapsed suddenly, releasing solid methane. The filled ice Ih structure formed in a relatively short period of time and the solid methane gradually disappeared, perhaps by being incorporated into the filled ice Ih structure. The Raman study showed the abrupt collapse of sH and the release of fluid methane. It also showed that the framework of filled ice Ih formed in a short period. Then fluid methane was gradually incorporated into the filled ice Ih to complete its structure. The simultaneous CCD camera observation showed that the samples turned suddenly to brown or gray, which indicated the collapse of sH and the release of methane. The CCD camera observation also showed that the brown patches were gradually absorbed in the filled ice structure. From these results, the transition mechanism is explained as a typical reconstructive one.

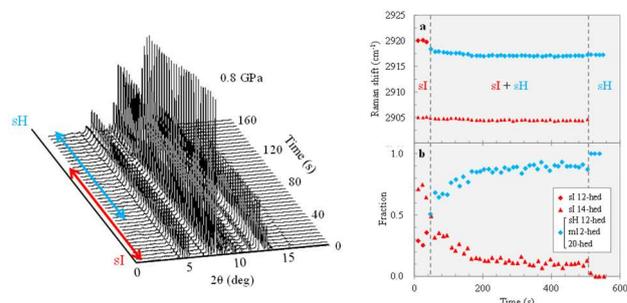


Figure 1. left: Representative time-resolved XRD patterns during the sI–sH transition at a fixed pressure of 0.8 GPa. Right: a: Variation of wavenumbers of C–H vibration modes for the 12-hedra (red rhombuses) and 14-hedra (red triangles) of sI and of the 12-hedra + modified 12-hedra + 20-hedra (blue rhombuses) of sH as a function of time. b: Variations of fractions of those cages. The label “m 12-hed” in the index stands for “modified 12-hedra.”

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