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Transition mechanism of sH to filled-ice Ih structure of methane hydrate under fixed pressure condition

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Abstract. The phase transition mechanism of methane hydrate from sH to filled-ice Ih structure was examined using a combination of time-resolved X-ray diffractometry (XRD) and Raman spectroscopy in conjunction with charge-coupled device (CCD) camera observation under fixed pressure conditions. Prior to time-resolved Raman experiments, the typical C-H vibration modes and their pressure dependence of three methane hydrate structures, fluid methane and solid methane were measured using Raman spectroscopy to distinguish the phase transitions of methane hydrates from decomposition to solid methane and ice VI or VII. Experimental results by XRD, Raman spectroscopy and CCD camera observation revealed that the structural transition of sH to filled-ice Ih occurs through a collapse of the sH framework followed by the release of fluid methane that is then gradually incorporated into the filled-ice Ih to reconstruct its structure. These observations suggest that the phase transition of sH to filled-ice Ih takes place by a typical reconstructive mechanism.

1. Introduction

Methane hydrate, called “fiery ice,” is expected to be a clean energy resource, although methane is, on the other hand, a greenhouse gas even more potent than carbon dioxide. It is also 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]. Many guest species can be incorporated into clathrate structures, which have three types of varieties, sI, sII, and sH structures depending on the guest sizes at ambient to relatively low pressures [1]. At higher pressures, more varieties of structures are formed [2–6]. With increasing pressure, a cage structure is compressed and forced to change to one that can accommodate more guests per mole of water [7, 8]. At further higher pressures, the cage structures are no longer retained, and consequently well-designed structures, called filled-ice structures, are formed [9]. The filled-ice structures consist of an ice or icy framework and guests filling the voids between them [9–11]. Almost all filled-ice structures decompose at pressures below 6–7 GPa [12–14]. Among them, methane and hydrogen hydrates exhibit notable stability up to 86 GPa at room temperature and low temperatures according to previous experimental and theoretical studies [15, 16]. Methane hydrate (hereafter denoted as MH) has an sI structure composed of two 12-hedra and six 14-hedra components



in a unit cell at low (< 0.8 GPa) pressures and room temperature, but transforms to an sH cage structure formed by three 12-hedra, two modified 12-hedra, and a 20-hedra at approximately 0.8–1.0 GPa. A further transformation to a filled-ice Ih structure (hereafter denoted as FIhS), which consists of a framework of ice (similar to ice Ih) and methane molecules that fill the channels running along the a- and c-axes [14]. Water is released through each of the transitions and subsequently crystallizes as either ice VI or VII depending on the pressure. Thus, MH increasingly becomes methane-rich as it transitions from one structure to another. The sequence of these phase transitions of MH with pressure have been studied [7, 13, 17], and the structural details including the precise positions of the host oxygen atoms, multi-occupancies, and site disorders of guests have been determined by neutron diffraction [14, 18]. In contrast, there are only a few studies about the essential mechanism of the phase transitions [19, 20].

A recent work by Hirai *et al.* [19] studied the mechanism of sI to sH phase transition using time-resolved in-situ X-ray diffraction and Raman spectroscopy at a constant pressure. They revealed that although the 12-hedra of sI are retained, the 14-hedra are replaced sequentially by additional (newly formed) 12-hedra, modified 12-hedra, and 20-hedra cages of sH, which suggests that the cage-recombination is responsible for the sI–sH transition mechanism [19]. On the other hand, in-situ observation under a dynamic loading condition [20] and that at a fixed pressure [19] both showed that the sH-FIhS transition occurs by a reconstructive mechanism, but their signatures are quite different [19, 20]. In the dynamic loading experiment, the sH-FIhS transition was detected by the rapid pressure decreased and low-frequency shift of the C–H vibration mode [20], while in the static pressure experiment such low-frequency shift of the C–H mode was interpreted as a result of the decomposition to solid methane and ice [21]. It is also noted that the phase transition kinetics is greatly influenced by the rate of compression [19, 20]. Therefore, to understand the essential mechanism of the phase transition an experiment where the pressure is carefully and precisely controlled from beginning to end of the transition is required.

The C–H stretching modes of methane molecules, ν_1 and ν_3 , are very sensitive to the surrounding conditions and the vibrational frequency of these modes vary in response to changes in the cage framework [1, 2, 21]. In this study prior to time-resolved measurements of the MH transition, the C–H vibration modes of the each MH phase (sI, sH and FIhS) as well as solid and fluid methane, which are produced through decomposition of the hydrate structure, were collected as a function of pressure, in which the each structure was simultaneously confirmed by XRD. We then use those data as reference for the assignment of Raman peaks and identified the cage structure of MH and phase state of the decomposition product.

This study employs in-situ, time-resolved observations using synchrotron XRD and Raman spectroscopy to understand the essential mechanism of sH-FIhS phase transition.

2. Experimental procedure

A clamp-type and a lever-spring-type of diamond anvil cells (DAC) were used to generate high pressures. A pair of anvils with a culet size of 600 μm and a stainless steel gasket were used for each run. Pressure (0.2–6.0 GPa) was measured using the ruby fluorescence method and carefully controlled so as to have a constant pressure distribution across the sample chamber. All the experiments were performed at room temperature (297 K). The initial methane hydrate sI sample was synthesized by a conventional ice–gas interface method at the National Institute of Advanced Industrial Science and Technology (AIST). The powdered sample (2–3 μm in average grain size) was loaded together with a few ruby balls for pressure measurement in a sample hole in a gasket in a cryogenic vessel cooled by liquid nitrogen. The initial pressure was carefully adjusted to below 0.2 GPa at low temperature to seal the MH sample in the cell without being transformed to the sH structure. In-situ XRD observations were performed by using synchrotron radiations at BL-10XU beamline of SPring-8 and at BL-18C beamline of the Photon Factory of the High Energy Accelerator Research Organization (KEK). Monochromatic X-rays with wavelengths of 0.04134 and 0.06198 nm with a beam size of 100 μm were used in SPring-8 and KEK, respectively. Raman spectroscopy was conducted by using a highly

confocal Raman system (PhotonDesign, RSM 800) equipped with a diode laser ($\lambda = 473$ nm). For time-resolved measurements, diffraction patterns and Raman spectra were collected every 4.3 and 8 seconds using an X-ray CCD detector and the Raman system, respectively.

Prior to time-resolved XRD measurements, we collected a series of XRD patterns using an imaging plate detector during pressure increase by 0.1 GPa step in order to precisely determine the phase transition pressure. As the result, the transition pressure of the sH–FIIhS transition was determined to be 1.8 GPa, which is consistent with previous studies [2, 4]. The sample pressure was finely controlled by an automatic gas flow system by adjusting the flow rate and pressure of helium gas flowing into a membrane in the DAC. The helium gas pressure was increased very slowly at a rate of 1.0 bar/min until the sample pressure reached to just below the transition pressure of the sample, and the pressure was kept constant for approximately 1 h to make sure no phase transition occurred before starting time-resolved measurements. Helium gas was then re-introduced to the membrane at the same flow rate to provide a driving force for the phase transition, although the absolute pressure would not change in this process (i.e. the pressure in the sample chamber was kept constant throughout the time-resolved measurements). The time-delay of the phase transition was 40 to 160 s after the gas introduction in the present runs. The pressure was also kept constant during the time-resolved Raman spectroscopy measurements in which a driving force for the transition was introduced by slightly rotating the clamp screw by less than 1 deg.

3. Results and discussion

Figures 1a and 1b show typical Raman spectra of C-H vibration modes for sI, sH and FIIhS and variation of Raman shift as a function of pressure from 0.2 to 6.0 GPa, respectively. The open circles show the variation of Raman shift of sI below 0.9 GPa, sH between 0.9 and 1.8 GPa and FIIhS above 1.8 GPa. The crosses indicate the data points in which the structure was also identified as FIIhS by XRD. The solid triangles and solid squares are liquid and solid methane, respectively, which were obtained from a separate run where MH was decomposed to water and fluid methane at 0.7 GPa and 423 K. The C-H vibration modes of both liquid and solid methane increased almost linearly with increasing pressure, and the observed Raman shift values are in good agreement with those of the previous study [21, 22]. Two C-H vibration modes observed below 1.8 GPa are assigned to the small and large cages of sI and sH, respectively and linearly increase with pressure. The abrupt changes at about 1.0 GPa are attributed to the phase transition from sI to sH. Note that the Raman shift values obtained from FIIhS are about 10 cm^{-1} higher than those of solid methane. The Raman shifts observed in this study are well comparable to those reported by Hirai *et al.* (2001) [2] and Bezacier *et al.* (2014) [21], but are not consistent with those by Kumazaki *et al.* (2004) [23]. The result of the latter study [23] seems to be explained more reasonably by solid methane.

Figures 2a and 2b show the time-resolved Raman spectra and the typical Raman spectra of the C-H vibration modes observed during the transition from sH to FIIhS. Although the C–H modes from the three types of cages were almost superimposed just after the formation of sH at 0.9 GPa, that from the 20-hedra appeared as a shoulder peak at the higher frequency side of the main peak just before the transition to FIIhS at 1.8 GPa (Figs. 2a, 2b bottom). In the sH structure, the cage occupancy of the 20-hedra increases with increasing pressure to maintain such large cages [13, 18]. This leads to changes in the vibration mode of the 20-hedra, as observed in the present and previous studies [2, 23]. Thus, the spectrum collected after 8 s (Figs. 2a and 2b) shows the typical C–H modes of sH at 1.8 GPa. After approximately 100 s, the peaks of sH cages suddenly broadened and a fluid methane peak appeared together with the peak characteristic of FIIhS. The relative intensity of fluid methane then gradually decreased, whereas that of FIIhS became intense and sharp (Figs. 2a and 2b). At the beginning of the FIIhS formation (between 100 and 160 s), its Raman shift was slightly lower by $5\text{--}6\text{ cm}^{-1}$ than that of typical FIIhS (Fig. 2b), but became comparable ($\sim 2945\text{ cm}^{-1}$) after 160 s (Fig. 2b).

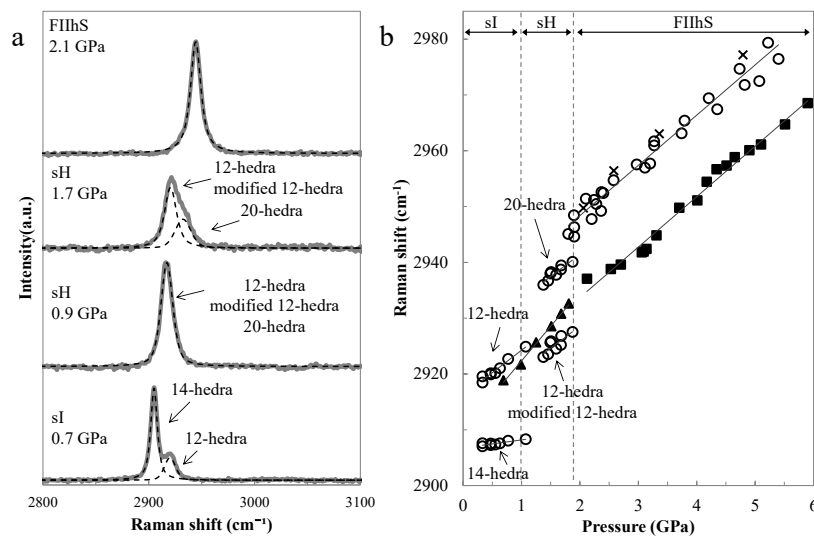


Figure 1. (a) Typical Raman spectra of C-H vibration modes for methane molecules included in sI, sH, and FIhS. (b) Variations of Raman shift of C-H vibration modes as a function of pressure. The open circles indicate Raman shift of MH. The crosses in the FIhS region show data of which structure is confirmed to be FIhS by XRD. The solid triangles and solid squares are fluid and solid methane, respectively.

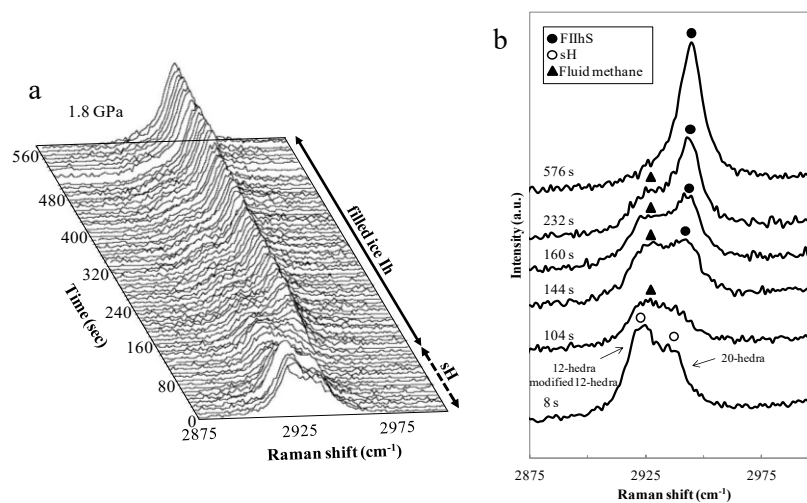


Figure 2. (a) Time-resolved Raman spectra and (b) typical Raman spectra obtained during sH–FIhS transition at a fixed pressure of 1.8 GPa. The black circles, black triangles and open circles indicate the C-H vibration modes of FIhS, fluid methane and sH, respectively.

Figures 3a and 3b show the time-resolved XRD patterns and typical XRD patterns during the transition from sH to FIhS at 1.8 GPa. Up to ~160 s, the observed diffraction peaks were indexed with sH and ice VI. After 160 s, the sH peaks suddenly disappeared and instead, peaks of FIhS appeared. This means that the construction of the FIhS framework requires a relatively short time period of 50–60 s. In addition to FIhS peaks, small peaks of solid methane also appeared (Fig. 3b). The Raman observation clearly shows that fluid methane was released during the transition to FIhS. It is most likely that a part of such formed methane crystallized during the XRD measurement, since the pressure condition was very close to its solidification pressure (1.7 GPa at room temperature [22]).

Figure 4 shows the CCD camera images that were taken simultaneously with the XRD measurements. Drastic changes in color and transparency were observed during the sH–FIHs transition: the transparent sH suddenly turned to brown to dark gray, which probably indicated the release of fluid or solid methane, according to a previous study reporting the decomposition of MH [19]. The release of solid and fluid methane was also detected by the Raman and XRD observations, as described above. After the drastic color change (i.e., collapse of the sH framework), the sample became gradually transparent again, suggesting that methane was being consumed for the construction of FIHs.

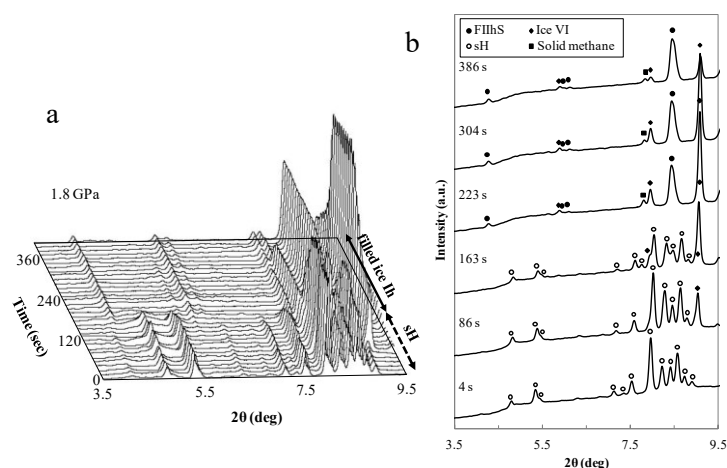


Figure 3. (a) Time-resolved XRD patterns and (b) typical XRD patterns obtained during sH–FIHs transition at a fixed pressure of 1.8 GPa. Black circles, black diamonds, black squares and open circles indicate the diffraction lines of FIHs (Imcm, $a=4.7960$, $b=8.1159$, $c=7.9691$ Å), Ice VI ($P4_2/nmc$, $a=6.0959$, $c=5.6177$ Å) and sH ($P6/mmm$, $a=11.8135$, $c=9.9958$ Å), respectively.

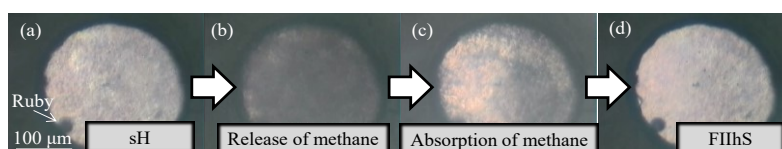


Figure 4. Optical changes in the sample chamber observed during the sH-FIHs transformation by CCD camera.

The present in-situ observations using XRD, Raman spectroscopy, and CCD imaging demonstrates that the sH–FIHs transition occurs through a sudden collapse of sH structure followed by the release of fluid or solid methane that are then gradually incorporated into the FIHs to reconstruct its structure. This clearly shows that the phase transition takes place by a typical reconstructive mechanism, which seems to be reasonable taking into account the large difference in crystal structure and chemical composition between the two phases.

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