Changes in structure and preferential cage occupancy of ethane hydrate and ethane-methane mixed gas hydrate under high pressure

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Abstract. Structural changes and preferential cage occupancies were examined for ethane hydrate and ethane-methane mixed gas hydrates with five compositions in a pressure range of 0.2 to 2.8 GPa at room temperature. X-ray diffractometry and Raman spectroscopy showed the following structural changes. The initial structure, structure I (sI), of ethane hydrate was retained up to 2.1 GPa without any structural change. For the mixed hydrates, sI was widely distributed throughout the region examined except for the methane-rich and lower pressure regions, where sII and sH appeared. Above 2.1 GPa ethane hydrate and all of the mixed hydrates decomposed into ice VI and ethane fluid or methane-ethane fluid, respectively. The Raman study revealed that occupation of the small cages by ethane molecules occurred above 0.1 GPa in ethane hydrate and continued up to decomposition at 2.1 GPa, although it was thought that ethane molecules were contained only in the large cage.

1. Introduction

Gas hydrate, a clathrate compound, consists of cages formed by hydrogen-bonded host water molecules, with guest molecules or atoms included in the cages [1]. The structure and cage occupancy of gas hydrates containing a single guest species under ambient pressure to gigapascal order pressures has been widely studied, whereas gas hydrates containing two guest species, so-called mixed gas hydrate, have not been fully studied under such high pressure. In the case of the methane-ethane system, structural changes of methane hydrate, an end-member hydrate of the system, have been comprehensively studied by X-ray diffractometry (XRD) and Raman spectroscopy; i.e., the initial structure I (sI) transformed to a hexagonal structure (sH) at about 1 GPa, sH further transformed to a filled ice Ih structure at about 2 GPa [2-5], and this structure survived up to 86 GPa at room temperature [6-10]. In contrast, the structural change of ethane hydrate, another end-member, has not been clarified in a pressure range of gigapascal order, although the initial structure at ambient pressure is known to be sI. For methane–ethane mixed hydrate, interesting phenomena have been reported. Both methane and ethane form sI at ambient pressure. However, Raman and NMR studies showed the existence of sII, and theoretical calculations proposed structural changes from sI to sII depending on the composition under a pressure range below 4.5 MPa [11, 12]. Later, the relationship between initial synthetic gas composition and synthesized hydrate composition, as well as structural change between...
sl and sII, was examined by Raman and XRD studies [13, 14, 15]. Selection of the structure type, sl or sII, was sensitive to the composition. Thus, it is fascinating to know whether structural selection depends on the ethane content under a pressure region higher than 1 GPa, or whether other structural changes occur.

It was thought that ethane molecules were accommodated only in the large cage of ethane hydrate because of the large molecular size. However, small cage occupation by ethane molecules was displayed for ethane hydrate in the relatively higher pressure range from 20 to 479 MPa by a Raman study [16]. Such small cage occupation was termed “pressure-induced small cage occupation” [16]. It is also of interest to assess whether the pressure-induced small cage occupation is maintained under very high pressure, and how two individual guests can occupy and leave large and small cages in the mixed hydrate. In this study, the structural changes, as well as the cage occupancies of the small and large cages by each guest, were examined.

2. Experimental
A lever-and-spring type diamond anvil cell (DAC) was used in the high-pressure experiments. Pressure measurements were made by the ruby fluorescence method. The accuracy of this measurement system is 0.1 GPa. The pressure range examined for ethane hydrate and mixed hydrates were from 0.1 to 4.3 GPa and from 0.1 to 2.8 GPa, respectively. Starting powder hydrates were synthesized using a conventional ice-gas interaction technique. The initial gas compositions used for the syntheses were 3mol % ethane-97mol % methane (hereafter compositions are described by ethane molar composition), 10, 15, 25, 50 and 100% ethane. Syntheses were carried out three to five times for each composition. The gas pressures applied to the syntheses were 2.5, 2.2, 2.0, 1.8, 1.5 and 2.0 MPa for the initial gas compositions of 3, 10, 15, 25, 50 and 100%, respectively. The temperature during the syntheses was 270 ± 1K. The composition of the synthesized hydrates measured by gas-chromatography was 22, 30, 34, 53, 73 and 100% for initial gas composition of 3, 10, 15, 25, 50 and 100%, respectively. The ethane content of synthesized hydrate is known to be higher than that of the initial gas [11,13] mainly due to differences in the Langmuir constant [1]. The measured compositions were almost similar to those reported previously [13,15]. In the starting materials, ice Ih, 5 to 10 wt%, remained, which was difficult to remove completely from the starting materials. Therefore, the present experiments were those in a system in which excess water existed. Cage occupancy was estimated by peak areas of the vibration modes in Raman spectra. The XRD experiment was performed using synchrotron radiation on a BL-18C at the Photon Factory, High Energy Accelerator Research Organization (KEK). A monochromatized X-ray with a wavelength of 0.6940Å was used.

The experiments were made under room temperature, namely, the temperatures were not strictly controlled. As for rate of compression, the lowest possible one was applied, for example, it took about 4 hours for compression of 0.2 GPa. Thus, the experiments performed were not those under complete equilibrium conditions without any kinetic disturbance. However, the results obtained were coincident for three to five experiments with good reproducibility.

3. Results
The initial structures of the synthesized hydrates at ambient pressure were examined by Raman spectroscopy at 140 ± 2 K prior to examining the structural changes under high pressure (Fig. 1). In the region of the C-C vibration mode (ν3), for pure ethane hydrate and the 73% sample a vibration mode was observed at 1001 cm⁻¹ assigned to the large cage of sl, for the 53% sample doublet modes were observed at 1001 and 991 cm⁻¹ assigned to the large cages both of sl and sII, respectively, and for the 34, 30 and 22% samples a mode was observed at 991 cm⁻¹ assigned to the large cage of sII. In the region of C-H vibration modes (ν1 and 2 ν11) the same structural changes, depending on the composition, were observed. Selection of the initial structures were consistent with those reported previously [13, 15].

For pure ethane hydrate, XRD revealed that the structure of sl was retained from ambient pressure up to 2.1 GPa (Fig. 2a). Above 2.1 GPa, sl of ethane hydrate decomposed into ice VI and
fluid ethane. With decreasing pressure after decomposition, sI was reproduced from ice VI and fluid ethane at about 2.0 GPa. A hexagonal structure (sH) [17] and filled ice Ih structure [18], which exist in methane hydrate, were not observed. Some amount of water was released from the hydrate with increasing pressure despite the structure of sI being unchanged. The released water crystallized to ice VI above 1 GPa. Raman spectroscopy did not detect a vibration mode of fluid ethane but only of sI, which indicated that only water was released. This indicated that the composition (ethane/water ratio) of the hydrate changed. The release of water will be discussed later. Raman spectra of pure ethane hydrate clearly showed both large and small cage occupation of ethane molecules in C-C and C-H regions. Both cage occupations continued until decomposition at 2.1 GPa. Above 2.1 GPa, vibration modes assigned to fluid ethane were observed. Fig. 3 shows variations of the C-C and C-H vibration modes with pressure change for the large and small cage, respectively. The vibration modes from the small cage were higher than those of the large cage by about 20 to 30 cm\(^{-1}\), and the slope with pressure of the small cages was larger.

For the 73 and 53% mixed hydrates, the structure at 0.2 GPa was sI, although at ambient pressure the former hydrate showed sI and the latter one showed the coexistence of sI and sII. Above 0.2 GPa, both hydrates showed the same behaviour as that observed in pure ethane hydrate. Water was released from both hydrates with increasing pressure. Fig. 2b shows the XRD patterns after freezing of the released water for the 73% sample. The Raman study showed that ethane molecules for the 73 and 53% samples were contained solely in the large cages, and that methane molecules were contained both in the large and small cages. At 0.2 GPa, most methane molecules were contained in the small cage for the 73% sample, while almost half the number of molecules was contained in the large and small cages for the 53% sample. These observed occupancies of methane molecules were quite reasonable, assuming that the ethane molecules occupied the large cage by priority, because the ratio of the large to small cage in sI is 3:1. The degree of these occupations by ethane and methane molecules changed with pressure. A detailed description will be provided elsewhere.

For the 34 and 30% hydrates, the structure at 0.2 GPa was sI, although at ambient pressure the structure was sII. Until about 1.0 GPa only sI was observed. sH appeared in addition to sI at 1.3 GPa for the 34% sample and at 1.1 GPa for the 30% sample (Fig. 2c). sH and sI coexisted up to 2.1 GPa. At 2.1 GPa, both sH and sI decomposed into ice VI and a fluid ethane-methane mixture. With decreasing pressure, sH and sI were reproduced again from ice VI and the mixed fluid. Water was released with increasing pressure.
other five cages in sH are small, i.e. sH is a structure dominated by small cages. Therefore, sI prefers the large cage. Although sH has a very large 20-hedral cage, there is only one per unit cell that sI possesses more large-cages than the other structures. The ratios of large cage to small cage are up to 2.1 GPa. The main reason for the retention of sI of ethane hydrate might be attributed to the fact molecule is 5.5Å, thus it may be too large to form a filled ice Ih structure.

For the 22% hydrate, only sII was observed at 0.2 GPa, as in ambient pressure. At 0.3 GPa, sI appeared in addition to sII. The coexistence of sI and sII continued to 0.6 GPa. At 0.7 GPa, only sI remained. Above 1.2 GPa sH appeared, and sH and sI coexisted up to 2.1 GPa. At 2.1 GPa, sH and sI decomposed to ice VI and ethane-methane fluid. These phase changes were reversible. Water was released with increasing pressure. Reabsorption of the released water into sI was observed with decreasing pressure. For a sample which was left at 0.3 GPa for 2 days, two large single crystals of sI and a few crystals of sII grew in the DAC. Thus, Raman spectra were obtained separately from sI and sII crystals. The Raman spectra show that ethane molecules were contained in the large cages of the existing structures, while methane molecules were both in the small and large cages of the structures.

4. Discussion
The structural changes observed in the present experiments are summarized in Fig. 4, which is not an equilibrium phase diagram. The present system was one under excess water, thus water or ice VI existed in all regions, which are not shown below 2.1 GPa in Fig. 4. At ambient pressure the structure changed from sI to sII depended on the composition similarly as reported [13, 15], but at 0.2 GPa sI was formed for all samples except for the 22% sample. For pure ethane hydrate, the initial structure at ambient pressure was sI, which was retained up to 2.1 GPa. For the mixed hydrates, sI was distributed widely throughout the region examined except for the methane-rich and lower pressure regions. Above 2.1 GPa pure ethane hydrate and all of the mixed hydrates decomposed into ice VI and ethane fluid or ethane-methane fluid, respectively. A filled ice Ih structure was not formed for all the compositions examined, which was different from the behaviour of methane hydrate. The guest size of an ethane molecule is 5.5Å, thus it may be too large to form a filled ice Ih structure.

For methane hydrate, sI transformed to sH at about 1 GPa, while for ethane hydrate sI survived up to 2.1 GPa. The main reason for the retention of sI of ethane hydrate might be attributed to the fact that sI possesses more large-cages than the other structures. The ratios of large cage to small cage are 3:1 for sI, 1:2 for sII and 1:(3+2) for sH [1,17]. Since the size of an ethane molecule is 5.5Å, it prefers the large cage. Although sH has a very large 20-hedral cage, there is only one per unit cell. The other five cages in sH are small, i.e. sH is a structure dominated by small cages. Therefore, sI, in
which the large cage is dominant, is of great advantage for ethane molecules rather than sH. Thus, sI might be retained up to decomposition at 2.1 GPa instead of a structural change to sH.

It was believed that ethane molecules were contained only in the large cage. However, pressure-induced small cage occupation was reported in pure ethane hydrate at pressures from 20 to 479 MPa [16]. The present study revealed that this small cage occupation by ethane molecules continued until the decomposition of ethane hydrate at 2.1 GPa, while it was not detected at ambient pressure. It might be disadvantageous to leave small cages open against compression of the structure. The small cage occupancy might accompany the release of water. If ethane molecules only move to small cages without the release of water, it results in leaving the large cages open. It is greater disadvantage than leaving small cages open under high pressures.

The release of water with increasing pressure implies that the hydrate composition (guest/water ratio) changes with pressure, i.e. the total cage occupancy of the hydrate increases with pressure. It is known that gas hydrates change their structures into guest-rich ones by releasing water under high pressure [7, 18]. For example, in the structural change of methane hydrate from sI to sH, water is released [3, 4, 8], consequently, the cage occupancy of sH increases by multi-occupancy in the large 20-hedron cage [18]. Also in the case in which there is no structural change, cage occupancy increases by releasing water within the same structure. Clathrate structures consisting of cages are sustained by guest species which hold the cage voids [1, 7], thus to increase total cage occupancy withstands effectively against compression of structure under high pressure. The release of water may be caused by this reason, and the compositional change with pressure is also required from the phase rule. The release of water resulting in an increase of total cage occupancy might be an effective way to stabilize the clathrate hydrate structures, just as preferential cage occupancy and structural selection are ways to survive under high pressure.

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Figure 4. (a) Summary of structural changes of ethane hydrate and methane-ethane mixed hydrate. The structures at ambient pressure are those at 140 K, while the structures above 0.2 GPa are those at room temperature. Water or ice VI exists in all regions below 2.1 GPa, because of excess water system.

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