High-Pressure Phase Equilibrium and Raman Microprobe Spectroscopic Studies on the Methane Hydrate System

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The three-phase coexistence curve of methane hydrate + saturated water + saturated fluid CH_4 was investigated in the temperature range from 305 to 321 K and pressure range from 98 to 500 MPa. The equilibrium curve increases monotonically on a $T-p$ diagram at these experimental conditions. The Raman spectra of the C−H symmetric vibration mode in the methane hydrate split into two peaks, while a single peak is detected in the fluid CH_4 and water phases. The split of the Raman peak indicates that two kinds of hydrate cages are occupied by the CH_4 molecules. The peak intensity ratio of two types of CH_4 molecules is almost independent of pressure in the range up to 500 MPa; that is, the cage occupancy ratio is constant. The Raman spectrum for the intermolecular vibration mode (O−O stretching) of the water molecules changes linearly with pressure from 207 to 228 cm^{-1}, and the Raman shifts of the C−H vibration mode in the S-cage and in the water phase vary linearly with pressure from 2915 to 2919 cm^{-1} and from 2910 to 2916 cm^{-1}, respectively. On the other hand, the Raman shift of C−H vibration in the M-cage is nearly constant at the lower frequency. That is, the hydrate cage shrinkage is caused by a pressure increase; however, the M-cage contains adequate vacant volume for the CH_4 molecule.

Introduction

Gas hydrates are crystalline substances which are constructed of water and many types of gas molecules. Under certain conditions, the water molecules form open network structures which have cavities that are several angstroms in diameter. The gas molecules are entrapped in these cavities. The structures of major gas hydrates are basically expressed with three types of cages, which are S-, M-, and L-cages. The lattice structure of methane hydrate of interest to us in the present study is called structure-I and constructed of two S-cages and six M-cages (von Stackelberg, 1949). Gas hydrates themselves have attracted the attention of many investigators in the past several decades. Recently, attention has been paid to the possibility of natural gas exploitation in linkage with CO_2 isolation under the deep ocean floor by use of gas hydrates (Ohgaki et al., 1996, 1997).

Several papers have reported the phase equilibrium data of methane hydrate, which are compiled in the texts of Berecz and Balla-Achs (1983) and Sloan (1990). However, most of them are concerned with the low-pressure region up to 30 MPa except the measurement by Marshall et al. (1964), which is up to 400 MPa. In the present study, we measured the three-phase coexisting relations of gas hydrate (H) + saturated water (L_1) + saturated fluid CH_4 (F_2) for the methane hydrate system in the pressure range up to 500 MPa to ascertain the stability boundary of methane hydrate as we did in the study of the carbon dioxide hydrate system (Nakano et al., 1998). In addition, in situ Raman microprobe spectroscopy is applied to investigate the intramolecular vibration of the gas molecule and the intermolecular vibration of water both in the hydrate crystal and coexisting fluid phases.

Materials

Research grade CH_4 (purity 99.95 mol %) was obtained from Takachiho Trading Co., Ltd., and used without further purification. The distilled water was obtained from Yashima Pure Chemicals Co., Ltd.

Experimental Apparatus and Procedures

The experimental apparatus used in the present study consists of an optical high-pressure cell, a high-pressure pump, an intensifier, pressure gauges, a temperature control system, a charge-coupled device (CCD) camera, and a laser Raman microprobe spectrometer. The optical high-pressure cell (inner volume, 0.2 cm^3; maximum working pressure, 500 MPa; made of stainless steel) has sapphire windows on the upper and lower sides. A stainless steel ball of 2 mm in diameter was set in the cell for agitation by the vibration generated from the outside. The behavior of the cell was observed by a CCD camera through the sapphire window. The temperature was controlled by thermostated water flowing into a jacket attached to the cell. The equilibrium temperature was measured within an accuracy of ± 0.02 K by use of a thermometer stuck into a hole of the cell wall. The estimated accuracy of the pressure measurement was within ± 1 MPa.

The single crystal of methane hydrate was analyzed by in situ Raman spectroscopy by use of a laser Raman microprobe spectrometer with a multichannel CCD detector. The laser beam for the object lens irradiated the sample through the sapphire window. The Raman ray of the opposite direction was taken in with the same lens.

A known amount of CH_4 was supplied to the cooled (approximately 280 K) and vacuum-pumped cell. Then the contents were pressurized to the desired pressure by successively charging water with an intensifier. Immediately methane hydrate started to form. After the pressurization, the system temperature was increased gradu-

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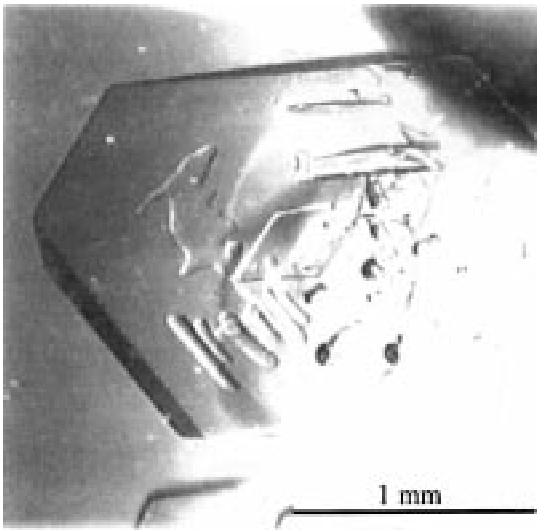

Figure 1. Single crystal of methane hydrate aged at 321 K and 493 MPa.

ally, and consequently, the three-phase coexistence of H + L_1 + F_2 was attained. The contents were agitated intermittently for 24 h in order to establish the three-phase equilibrium. To avoid a hysteresis effect, the three-phase coexistence was measured with an annealing method. The gas hydrate generated in the above experiment was annealed with a temperature cycle method (±0.05 K one cycle per day) during a few days in the present experiment.

Clear single crystals of gas hydrates were obtained by an annealing method described in the previous paper (Nakano et al., 1998). A typical single crystal of methane hydrate annealed at approximately 321 K and 493 MPa is shown in Figure 1. Keeping the temperature and pressure constant, the single crystal of methane hydrate in equilibrium was put into the laser Raman microprobe spectrometer. The argon ion laser beam (514.5 nm and 100 mW) condensed to 2 μm in spot diameter was irradiated from the object lens to the sample through a sapphire window, and the Raman ray of the opposite direction was taken in with the same lens. The spectral resolution was about 1 cm^{-1}. The integration time was varied within the range of 10−300 s, depending on the intensity of the light scattering. More detailed information about the experimental apparatus and procedure are described in the previous paper (Nakano et al., 1998).

Results and Discussion

The three-phase coexistence curve of H + L_1 + F_2 for the methane hydrate system is shown in Figure 2, and the data are listed in Table 1. The methane hydrate system does not have the quadruple point of H + L_1 + L_2 (saturated liquid guest molecules) + G (saturated gas) which was observed in the carbon dioxide hydrate system because the three-phase coexistence curve of H + L_2 (saturated liquid CH_4) + G originating from the quadruple point of H + S_2 (solid CH_4) + L_2 + G terminates at the critical end point near the CH_4 critical point of approximately 190 K and 4.6 MPa. The three-phase coexistence curve of H + L_1 + F_2 monotonically increases in the temperature−pressure (logarithm) diagram, and then at pressures greater than 400 MPa, the pressure increases sharply. The data obtained in the present study agree well with the published data (Marshall et al., 1964; McLeod and Campbell, 1961; Kobayashi and Katz, 1949; Ohgaki et al., 1996). Dyadin et al. (1997) have reported that the equilibrium curve reaches a temperature maximum (320.9 K) at 550 MPa. Also they have pointed out that the methane hydrate crystal becomes structure-II in the pressure range from 620 MPa to 1.5 GPa.

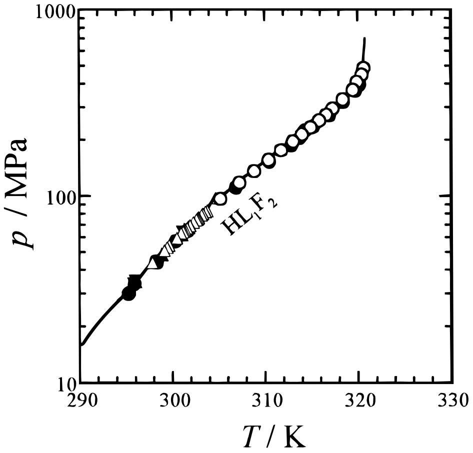

Figure 2. Three-phase coexisting curve of methane hydrate + water + fluid CH_4: ○, present study; ●, Marshall et al. (1964); ▲, McLeod and Campbell (1961); ▼, Kobayashi and Katz (1949); △, Ohgaki et al. (1996).

Table 1. Phase Equilibrium Data for Three-Phase Coexistence of Methane Hydrate + Water + Fluid CH_4 up to 493 MPa

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
305.08	98	313.88	217	319.17	376
307.13	119	314.83	237	319.80	414
308.74	138	315.74	258	320.33	455
310.29	158	316.50	277	320.54	493
311.64	178	317.20	299		
312.92	199	318.29	335		

The CH_4 molecule has four Raman active vibration modes; that is, they are C−H symmetric stretching (ca.. 2900 cm^{-1}), double degenerated bending (ca.. 1500 cm^{-1}), triple degenerated stretching (ca.. 3000 cm^{-1}), and triple degenerated bending vibrations (ca.. 1300 cm^{-1}) (Wu et al., 1995). However, the Raman intensities of the second and the third ones are very weak, and the last one was not detected in the spectrum. Therefore, only the C−H symmetric stretching vibration mode was given attention in the present work. Typical Raman spectra of the C−H symmetric stretching vibration mode of the CH_4 molecule in the fluid CH_4 (saturated with water), methane hydrate, and water (saturated with CH_4) phases are shown in Figure 3. In the case of methane hydrate, the spectrum splits into two peaks, while a single peak is detected around 2911 cm^{-1} for the fluid CH_4 and the water phases. The split of the Raman peak indicates that CH_4 molecules are entrapped in both S- and M-cages. The larger peak corresponds to the CH_4 entrapped in the M-cage and the smaller one corresponds to the S-cage, considering the intensity ratio of the two peaks. The energy difference between the two peaks is caused by the characteristic volume of each cage. That is, the small space around the CH_4 molecule in the S-cage causes the C−H bond to become short, while the CH_4 molecule in the M-cage occupies a larger space than the compressed fluid CH_4. The peak intensity of C−H vibration in each cage is defined by the peak height. The average intensity ratio (M-cage/S-cage) is about 4.3, and the value does not change in the pressure range up to 500 MPa. At least we can say that the cage occupancy ratio is independent of pressure, although the exact value of the occupancy ratio cannot be calculated directly from the intensity ratio.

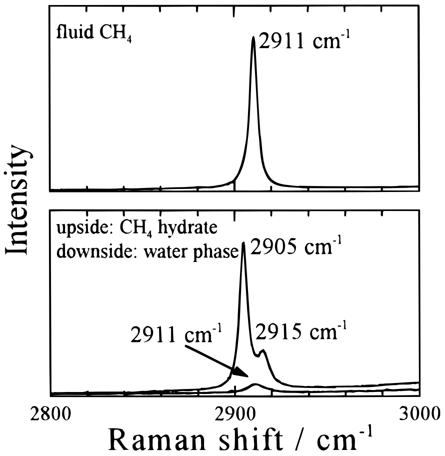

Figure 3. Raman spectra of intramolecular vibration mode of CH_4 molecule in the fluid CH_4, methane hydrate, and water phase at 100 MPa.

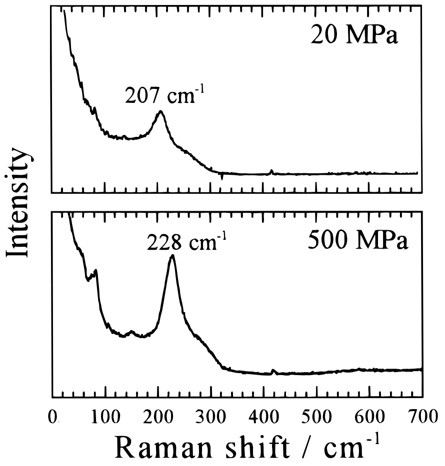

Figure 4. Raman spectra of the intermolecular vibration mode of water in the methane hydrate crystal at 20 and 500 MPa.

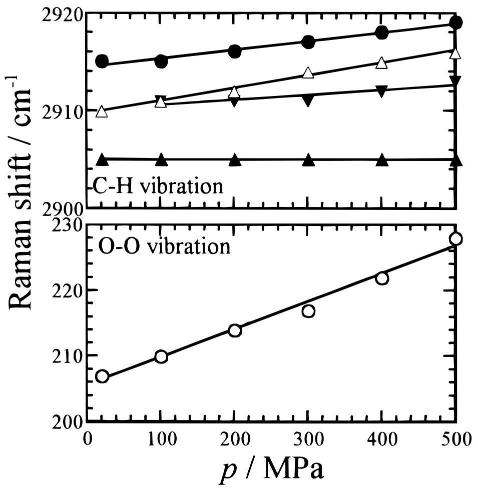

Figure 5. Pressure effect on C−H and O−O vibration modes: ●, S-cage; ▲, M-cage; ▼, fluid CH_4 phase; △, water phase; ○, O−O vibration in the methane hydrate.

The Raman spectrum of the intermolecular (O−O) vibration mode of water is observed in the methane hydrate crystal, as shown in Figure 4, although no peak is detected in the aqueous solution because the number density of the hydrogen-bonded oxygen is very small in the water phase and the spectrum is hidden in the Rayleigh scattering. The Raman peak around 200 cm^{-1} which corresponds to the hydrogen bonds of the hydrate cage is a peculiar spectrum of methane hydrate lattice. Although similar spectra were obtained in the carbon dioxide hydrate system (Nakano et al., 1998), the Raman peak becomes somewhat clearer in the methane hydrate than in the carbon dioxide hydrate. The difference would be caused by the crystal characteristics; however, it is still unclear now. The tendency is more notable at 500 MPa than at 20 MPa, as shown in Figure 4. Moreover, two small peaks which would indicate the libration of the CH_4 entrapped in the S-cage are detected at about 80 and 150 cm^{-1}.

The pressure effect on the C−H symmetric stretching vibration in each phase and O−O vibration in the methane hydrate crystal is shown in Figure 5. The C−H stretching vibration energies in the S-cage of methane hydrate and the water phase increase monotonically with pressure. The vibration energy in the fluid CH_4 also increases slightly with a gentle slope. However, only the vibration energy in the M-cage is almost constant. These findings suggest that the hydrogen-bonded water cage shrinks gradually by pressurization, and then, the space for the CH_4 molecules in the aqueous solution and the S-cage becomes smaller. Finally, the libration of the CH_4 molecule in the S-cage can be detected. On the other hand, the vibration energy of CH_4 in the M-cage is almost constant because the space around the CH_4 molecule is large enough to keep the C−H vibration energy constant even if the hydrate cage shrinks with a pressure increase.

Conclusions

The three-phase coexistence curve of methane hydrate + water + fluid CH_4 was obtained up to approximately 500 MPa by use of an optical high-pressure cell with sapphire windows. The equilibrium pressure increases monotonically with temperature for the present experimental conditions. The single crystal of methane hydrate was analyzed in situ by use of laser Raman microprobe spectroscopy. The Raman spectra of the C−H symmetric vibration mode of CH_4 in the methane hydrate split, and that indicates the CH_4 molecules are entrapped in two different types of hydrate cages. The Raman spectrum of the intermolecular vibration mode of water is obtained clearly around 200 cm^{-1}, and its pressure dependence reveals the compressibility of methane hydrate. The C−H vibration energies of CH_4 in the S-cage, water, and fluid phases increase with pressure, although the vibration energy of CH_4 in the M-cage is constant.

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