Thermodynamic and Raman Spectroscopic Studies of Ar Hydrate System

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Abstract: The three-phase coexisting curve of Ar hydrate + water + gas has been investigated in a pressure range up to 485 MPa and a temperature range of (279.57 to 305.32) K. The Raman spectrum of intermolecular O-O stretching vibration mode has been measured for Ar hydrate crystal along the stability boundary curve. Both the discontinuity of slope of the three-phase coexisting curve and the pressure dependence of the Raman shift reveal that two structural phase transition points exist at (281 ± 1) MPa and (302.7 ± 0.1) K, (456 ± 1) MPa and (304.6 ± 0.1) K in a pressure range up to 485 MPa for the Ar hydrate system.

INTRODUCTION

Ar hydrate was found out by Villard in 1896 [1], and it has been widely studied by many investigators. It is well known that Ar hydrate belongs to structure-II hydrate [2] as well as Kr, O_2, and N_2 hydrates. Structure-II hydrate is composed of the two types of hydrogen-bonded water cages. We have called S-cage (pentagonal dodecahedron, 5^{12}) and L-cage (hexakaidecahedron, $5^{12}6^4$), and its crystal type is cubic ($Fd3m$).

Thermodynamic stability boundary for the Ar hydrate system at high pressures has been reported by several investigators. Dyadin, Larionov, Mirinski, Mikina, and Starostina [3] have reported the stability boundary of hydrate formation in the Ar-H_2O system under pressure up to 1500 MPa. They have indicated that two structural transition points are located at 720 MPa and 960 MPa. Lotz and Schouten [4] have claimed that structure-II Ar hydrate changes to structure-I around 620 MPa from the decomposition curve originated from new quadruple point (620 MPa and 304.6 K). Manakov, Voronin, Kurnosov, Teplykh, Larionov, and Dyadin [5] measured the stability boundary in a pressure range up to 1000 MPa. They have claimed that there are three structural phase transition points from the discontinuity of dp/dT on the stability boundary, and discovered that the structure-II Ar hydrate changes to the structure-H type hydrate ($P6/mmm$) at 460 MPa, which is similar to the low-pressure's one discovered by Ripmeester, Tse, Ratcliffe, and Powell [6]; the structure-H is composed of three S-cages, two S'-cages ($4^35^66^3$), and one U-cage ($5^{12}6^8$). The most important finding by Kurnosov, Manakov, Komarov, Voronin, Teplykh, and Dyadin [7] is that the tetragonal hydrate structure ($P4_2/mmm$) consists of two 14-hedral cavities ($4^25^86^4$) in the unit lattice and two Ar atoms occupy a 14-hedral cavity in a pressure range of (770 to 960) MPa. Hirai, Uchihara, Nishimura, Kawamura, Yoshimoto, and Yagi [8] confirmed the tetragonal structure by X-ray diffraction studies at room tempera

ture, but they couldn't find structure-H Ar hydrate around 500 MPa. Loveday, Nelmes, Klug, Tse, and Desgreniers [9] support those findings of Manakov, Voronin, Kurnosov, Teplykh, Larionov, and Dyadin [5] and Kurnosov, Manakov, Komarov, Voronin, Teplykh, and Dyadin [7], and they clarify that the Ar hydrate changes to so called "filled-ice" above 960 MPa.

Shimizu, Hori, Kume, and Sasaki [10] have reported that the Raman spectra of interatomic Ar-Ar interaction are detected around 150 cm^{-1} in the pressure range from (160 to 970) MPa at room temperature. They have claimed that this Raman spectrum corresponds to the multioccupancy of Ar atoms in the L-cage of structure-II. The double occupancy of Ar hydrate system has been predicted by many simulation approaches [11-13]. Based on the neutron diffraction experiments at 293 K, Manakov, Voronin, Kurnosov, Teplykh, Komarov, and Dyadin [14] have reported the multioccupancy of the structure-II Ar hydrate in the pressure range from (340 to 430) MPa.

Many investigators have studied the Ar hydrate system, but the most of them have carried out by use of Diamond Anvil Cell at room temperature, which is away from three-phase coexisting conditions (hydrate + water + gas). Unless the investigation is carried out along the three-phase coexisting condition, any varied structure might emerge depending on the composition. We have already reported other two noble gas hydrate systems (Kr and Xe) in the pressure range up to approximately 500 MPa under three-phase coexisting conditions [15]. Based on the slope change of the boundary curve and the pressure dependence on the Raman O-O shifts for the Kr hydrate crystal, a structural phase transition point exists at 414 MPa and 319.20 K, while the Xe hydrate crystal of structure-I does not exhibit any phase transition in the pressure range up to 500 MPa. In the present study, the three-phase coexisting curve (hydrate + water + gas) for Ar hydrate system in a temperature range of (279.57 to 305.32) K and a pressure range up to 485 MPa has been investigated precisely. The pressure dependence of the intermolecular O-O vibration along the three-phase coexisting curve has been analyzed by use of laser Raman spectroscopy.

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EXPERIMENTAL SECTION

Materials

Research grade Ar was purchased from the Neriki Gas Co. Ltd., having a stated minimum purity of 99.9999 mol %. Distilled water was obtained from Yashima Pure Chemicals Co. Ltd. Both were used without further purification.

Experimental Apparatus

Two types of high-pressure cell that are appropriate for the experimental pressure region were used in the present study. The experimental apparatus were essentially the same as that used previously [16, 17]. It consisted of a high-pressure cell having a couple of sapphire windows (inner volume, 1 cm^3 and 0.2 cm^3; maximum working pressure was 75 MPa and 500 MPa, respectively; Both were made of stainless steel, SUS630), a mixing ball, a high-pressure pump for supplying and/or pressurizing the samples, an intensifier, pressure gauges, a temperature control system, and, a charge-coupled device (CCD) camera. The high-pressure cell (500 MPa) was designed and manufactured to establish the equilibrium conditions for measuring the three-phase coexisting curve and to prepare the hydrate single crystal for performing in situ laser Raman spectroscopic analysis, simultaneously.

Procedures

A desired amount of Ar was introduced into the evacuated and cooled cell. A mixing ball in the cell was vibrated from the outside for agitation. The contents were pressurized up to the desired pressure by successive supply of water. After the formation of Ar hydrate, in order to establish the three-phase (hydrate + water + gas) equilibrium, the system temperature was gradually increased and the contents were agitated intermittently. The phase behavior of the system was observed by the CCD camera through the sapphire window. The equilibrium temperature was measured within a reproducibility of 0.02 K using a thermistor probe (Takara D-641) calibrated by a Pt resistance thermometer (25 Ω) into the water bath or a hole in the cell wall. For pressure measurement, two different pressure gauges were used according the working pressure. Up to 75 MPa, a pressure gauge (Valcom VPRT) calibrated by a Ruska quartz Bourdon tube gauge was used with an estimated maximum uncertainty of 0.02 MPa. Over 75 MPa, a pressure transducer (NMB STD-5000K) and digital peak holder (NMB CSD-819) was used with an estimated maximum uncertainty of 2 MPa.

After the preparation of single crystal at the three-phase coexisting equilibrium under several pressure conditions, the Raman spectra were measured. A typical photograph of Ar hydrate crystals is shown in Fig. (**1**). The largest single crystal (the preparation procedures were described elsewhere [17]) was aged more than a couple of weeks. In several equilibrium conditions, Ar hydrate crystals were analyzed using a laser Raman microprobe spectrometer with a multichannel CCD detector (Jobin Yvon Ramanor T64000). The laser beam from the object lens irradiated the sample through the upper sapphire window. The backscatter of the opposite direction was taken in with the same lens. The argon ion laser beam of 514.5 nm and 100 mW was condensed to 2 μm spot diameter. The spectral resolution was about 1 cm^{-1}.

RESULTS AND DISCUSSION

The three-phase coexisting data obtained in the present study for the Ar hydrate system are listed in Table **1**. Fig. (**2**) shows the pressure temperature relations of Ar hydrate system accompanied with the literature values [3, 18]. In the low-pressure region (up to 200 MPa), our data are in good agreement with Marshall's ones [18]. Moreover, except less than 20 MPa, the present data are in almost agreement with Dyadin's ones [3].
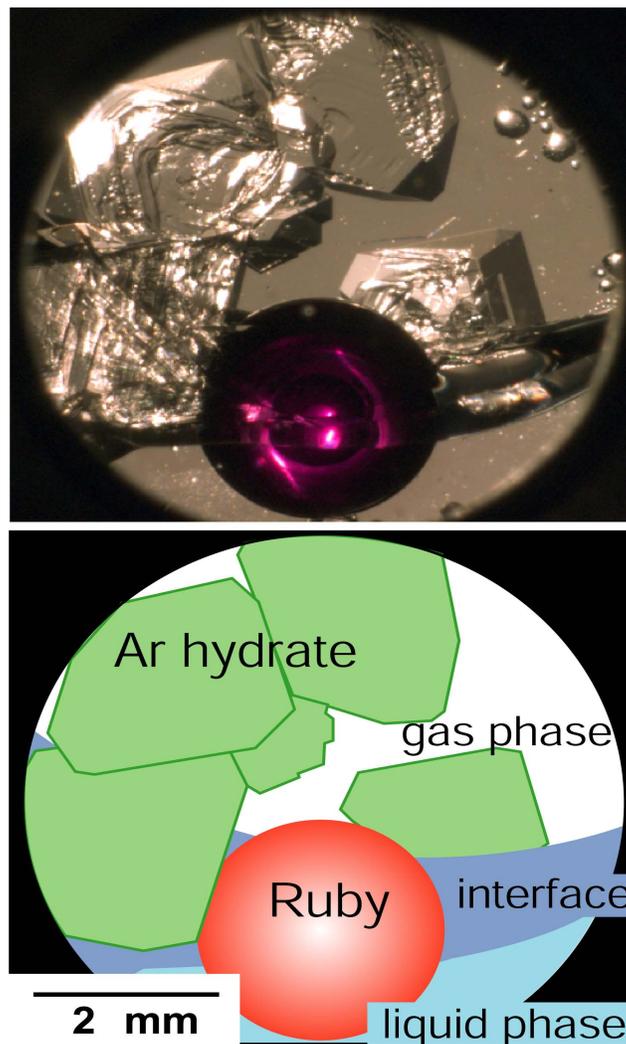

Fig. (1). Photo (upper) and schematic drawing (bottom) of single crystals of Ar hydrate under three-phase coexisting condition of hydrate + liquid (water) + gas at 284 MPa and 302.75 K. A spherical ruby of 2.5 mm in diameter is trapped in the high-pressure cell in order to stir the contents.

Fig. (**3**) shows the extended figure (the pressure ranges from 200 MPa to 500 MPa) of the thermodynamic stability boundary for the Ar hydrate system in the present study. The stability boundary changes greatly in the slope at (281±1) MPa and (302.7±0.1) K, and (456±1) MPa and (304.6±0.1 K) respectively. Generally, the large slope change of dp/dT means the structural phase transition point as previously described [15, 19] (Kr and SF$_6$ hydrate systems). Manakov, Voronin, Kurnosov, Teplykh, Larionov, and Dyadin [5] have reported the structural change (structure-II to structure-H)

around 460 MPa. On the other hand, no investigator has reported about the structural change point around 280 MPa. We have divided the three-phase coexisting curve to the three regions. The region A corresponds to the pressure range up to 281 MPa. The pressure range from 281 to 456 MPa is region B, and over 456 MPa defined as region C. Especially, in the region B, the present data show the large discrepancies with the literature [3, 18].

Table 1.   Three-Phase Coexisting Data for the Ar Hydrate System

T / K	p / MPa	T / K	p / MPa
279.57	17.72	293.95	98
280.55	19.81	294.70	108
281.64	22.23	296.10	129
282.64	24.44	297.17	147
283.95	28.17	297.99	169
284.72	31.93	299.44	199
284.84	32.38	300.39	226
285.25	32.60	301.65	258
286.15	38.29	302.75	284 (s-I)
287.16	42.86	303.09	322 (s-I)
288.16	48.82	303.60	358 (s-I)
288.66	51.70	304.10	409 (s-I)
289.65	57.96	304.57	447 (s-I)
290.68	66.22	305.05	464 (s-H)
291.06	69.40	305.19	474 (s-H)
292.07	77	305.21	476 (s-H)
293.18	89	305.32	485 (s-H)

(s-I), structure-I; (s-H), structure-H.

The Raman spectrum of intermolecular O-O stretching vibration mode of water molecules was detected around 210 cm^{-1} in the structure-II gas hydrate systems; we have already reported about N_2 and SF_6 hydrate systems [19, 20]. The peak corresponding to the hydrate cage structured by hydrogen bonds is a peculiar to the structure of hydrate lattice. In the present study, the Raman shift of the O-O stretching vibration for the Ar hydrate crystal at 46 MPa and 288 K is detected at 209 cm^{-1}. The typical Raman spectra of the intermolecular O-O vibration mode in the Ar hydrate crystals in each region of Fig. (**3**) are shown in Fig. (**4**). The O-O vibration energy increases with pressure (along the three-phase coexisting curve), that is, the hydrate cage shrinks gradually by pressurization.

Fig. (**5**) shows the pressure dependence of the Raman shift corresponding to the O-O stretching vibration for the Ar hydrate system, which measured along the three-phase coexisting curve. For comparison, the previous results of the Kr (structure-II) and Xe (structure-I) hydrate crystals measured along the three-phase coexisting curves [15] are also shown in Fig. (**5**). We have already speculated that the structure-II

Kr hydrate changes to structure-H at 414 MPa by the slope change of three-phase coexisting curve and the Raman spectrum.
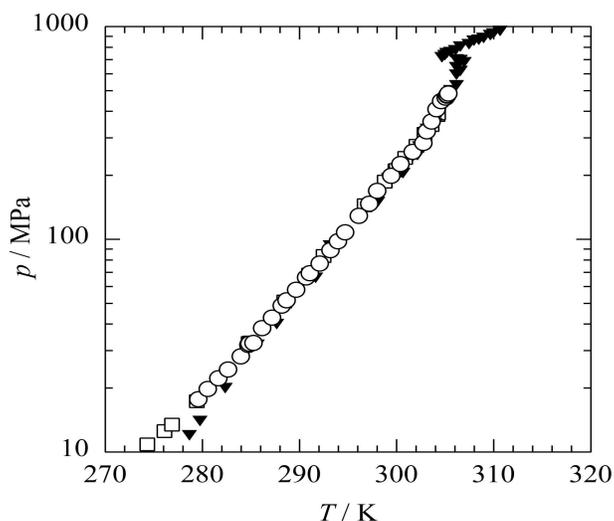

Fig. (2). Pressure - temperature relations of Ar hydrate stability boundaries: ○, three-phase coexisting curve of Ar hydrate (present study); □, Marshall, Saito, and Kobayashi [18]; ▼, Dyadin, Larionov, Mirinski, Mikina, and Starostina [3]. From our experimental data (up to 485 MPa), Ar hydrate has two structural transition points located at 281 MPa and 456 MPa. Dyadin, Larionov, Mirinski, Mikina, and Starostina [3] have claimed that the discontinuous slope changes around 460 MPa and 770 MPa are caused by structural transitions to structure-H [5] and to tetragonal structure [7], respectively.
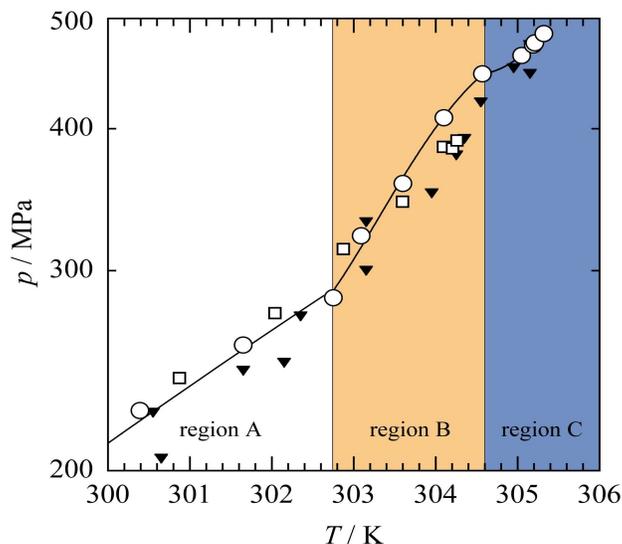

Fig. (3). Enlarger data (the pressure ranges from 200 MPa to 500 MPa) of Fig. **2**: ○, present study; □, Marshall, Saito, and Kobayashi [18]; ▼, Dyadin, Larionov, Mirinski, Mikina, and Starostina [3]. The stable structure in each region is as follows; region A, structure-II; region B, structure-I; region C, structure-H.

The pressure dependence of the O-O vibration in the Ar hydrate system up to 281 MPa (correspond to region A of Fig. (**3**)) agrees well with the structure-II Kr hydrate system. Therefore, the structure-II Ar hydrate is stable in the region A.
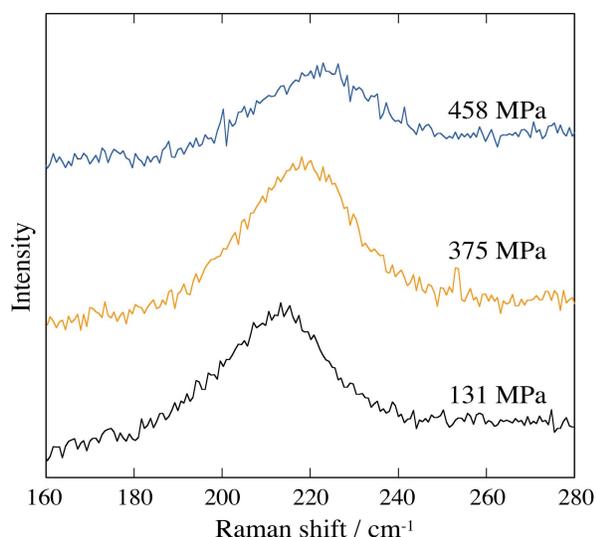
Fig. (4). Raman spectra of the intermolecular O-O vibration mode in the Ar hydrate crystals at 131 MPa (structure-II), 375 MPa (structure-I), and 458 MPa (structure-H).
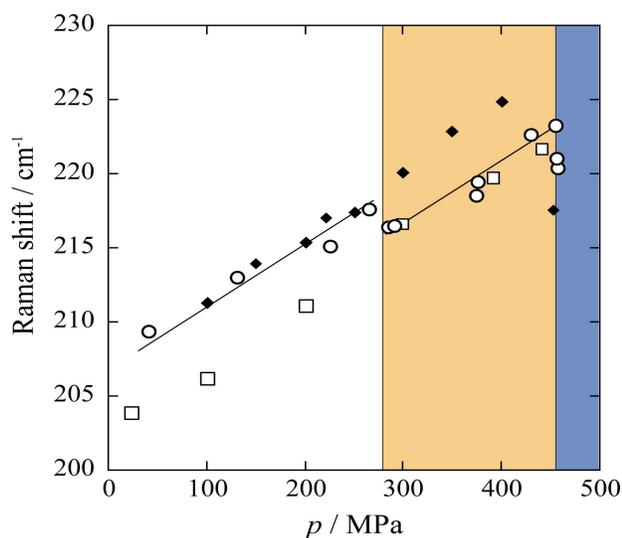

Fig. (5). Pressure dependence of the Raman shift corresponding to the O-O stretching vibration for the Ar hydrate system along the three-phase coexisting curve: ○, Ar hydrate; ◆, Kr hydrate (structure-II: up to 414 MPa; structure-H: over 414 MPa) [15] ; □, Xe hydrate (structure-I) [15].

From the pressure range from (281 to 456) MPa (correspond to region B), the results of the O-O vibration are almost same tendency of the Xe hydrate system [15]. The fact suggests that Ar hydrate crystal may be the structure-I lattice in the region B. Moreover, the slope change of the stability boundary (Fig. (**3**)) also supports structural phase transition of Ar hydrate crystal. However, Shimizu, Hori, Kume, and Sasaki [10] have evaluated the multi occupancy of Ar atoms by the Raman spectra of Ar-Ar interatomic stretching vibration around 150 cm^{-1}. Manakov, Voronin, Kurnosov, Teplykh, Komarov, and Dyadin [14] have suggested the double occupancy of the structure-II Ar hydrate in the pressure region from (340 to 440) MPa based on neutron diffraction experiments at 293 K. Tanaka, Nakatsuka, and Koga [11] reported that double occupancy dominated over single occu-

pancy above 270 MPa from van der Walls Platteuw theory. In the present study, those were not taken up because it was difficult to clarify the meaning Raman peak from noises on the shoulder of Rayleigh scattering. Therefore, we cannot discuss about the double occupancy of Ar atoms in the Ar hydrate system by the Raman peaks of the present study. On the other hand, Lotz and Schouten [4] suggested that structure-II Ar hydrate changes to structure-I at the high-pressure region. Thus, it might be thought that there are the following two possibilities about the phenomenon around 280 MPa; the structural phase transition of Ar hydrate and/or the change of cage occupancy. We speculate as follows. Around 280 MPa, the one Ar atom occupied in the one large cage (M-cage) of structure-I may be more comfortable than two Ar atoms occupied in the one L-cage (double occupancy) of structure-II. And as a result, the structural change from structure-II Ar hydrate to structure-I has occurred in the region B.

At 459 MPa (correspond to region C), the O-O vibration energy of Ar hydrate becomes lower than that of structure-I hydrate [15] (Xe hydrate system). The similar discontinuity of the pressure dependence has shown in the Kr hydrate system (Fig. (**5**)); the Raman shift of Ar hydrate is slightly (3 cm^{-1}) higher than that of the Kr hydrate at almost same pressure; in this pressure range, the Kr hydrate is structure-H [15]. Moreover, there is a drastic slope change of three-phase coexisting curve of Ar hydrate around 456 MPa in the present study (Fig. (**3**)). They show good agreement with Manakov, Voronin, Kurnosov, Teplykh, Larionov, and Dyadin [5] (460 MPa). Those facts strongly support that the structural phase transition in the Ar hydrate crystal occurs around 456 MPa, and that the structure of Ar hydrate observed over 456 MPa (region C) would be structure-H as reported by Manakov, Voronin, Kurnosov, Teplykh, Larionov, and Dyadin [5] and Manakov, V. I. Voronin, A. V. Kurunosov, A. E. Teplykh, V. Y. Komarov, and Y. A. Dyadin [14] and Loveday, Nelmes, Klug, Tse, and Desgreniers [9]. Additionally, in the high-pressure region (760 to 960 MPa), the tetragonal Ar hydrate would be stable as Kurnosov, Manakov, Komarov, Voronin, Teplykh, and Dyadin [7] have reported.

CONCLUSIONS

The three-phase coexisting curve of Ar hydrate system was obtained up to 485 MPa. Single crystals of Ar hydrate were analyzed in situ by use of laser Raman spectroscopy along the three-phase coexisting curve. The slope changes of dp/dT on the boundary curve and the pressure dependence of the intermolecular O-O stretching vibration mode of the Ar hydrate system reveal that two structural phase transition points exist at (281±1) MPa and (302.7±0.1) K, (456±1) MPa and (304.6±0.1) K, respectively. For the Ar hydrate system, the structure-II hydrate crystal exists up to 281 MPa and changes to structure-I in the pressure region from 281 to 456 MPa. Finally, Ar hydrate changes to structure-H around 456 MPa.

ACKNOWLEDGEMENTS

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