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Phase changes of methane hydrate induced by guest orientational ordering under low temperature and high pressure

Hisako Hirai,[1,*] Takehiko Tanaka,[1] Takahiro Matsuoka,[2] Yasuo Ohishi,[3] Michika Ohtake,[4] Yoshitaka Yamamoto,[4] Satoshi Nakano,[5] and Takumi Kikegwa[6]

[1] Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan
[2] KYOKUGEN, Osaka University, Toyonaka, Osaka 560-8531, Japan
[3] Japan Association of Synchrotron Radiation Institution, Harima 679-5198, Japan
[4] National Institute of AIST, Tsukuba, 305-8569, Japan
[5] National Institute for Material Science, Tsukuba, Ibaraki 305-0044, Japan
[6] Photon Factory, Tsukuba 305-0801, Japan

1 Introduction

A high pressure phase of methane hydrate above 2 GPa is a filled ice Ih structure (hereafter referred to as MH-FI). The host framework of MH-FI resembles ice Ih, and the guest methane molecules fill the tunnel-like voids of the framework. Previous studies by the present authors reported that the fundamental structure of MH-FI was retained at least up to 90 GPa at room temperature, with phase changes occurring at 40 GPa and 15–20 GPa [1,2]. The phase change at 40 GPa detected by changes in the X-ray diffraction (XRD) patterns was inferred to be related to the symmetrization of the hydrogen bonds of the host framework. The other phase change at 15–20 GPa due to splitting of C-H vibration modes of methane molecules detected by the Raman spectroscopy was explained to be caused by the orientational ordering of the guest methane molecules. However, changes of lattice parameters and volume at around 20 GPa have not yet been observed in any XRD study. And, other phase changes at low temperatures and high pressures have yet to be explored. In this study, in order to clarify the phase changes of MH-FI under high-pressure and low-temperature conditions, the lattice parameters of the host framework and vibration modes of the guest molecules were examined by the XRD study and Raman spectroscopy.

2 Experiment

Clamp-type diamond anvil cells (DAC) and a helium-refrigeration cryostat were used to generate high pressure (2.0–77.0 GPa) and low temperature (30–300 K) conditions, respectively. The pressure was measured via the ruby fluorescence method and diamond Raman method. The temperature was measured by a chromel–alumel thermocouple and a silicon semiconductor thermometer. The initial samples of MH-FI were synthesized by the conventional ice–gas interface method, and those of MD-FI (deuterated-water host methane hydrate) were did by the ice–gas interface method and gas-loading one. XRD measurements were performed at BL-18C. A monochromatized X-ray with a wavelength of 0.06198 nm was used. The Raman spectroscopy was also performed at high pressures and low temperatures.

3 Results and Discussion

The XRD data revealed the changes in the axial ratios for MH-FI and MD-FI. Splits of the C–H vibration modes were also found. The temperature and pressure conditions of the splits agreed closely with those of the changes in the axial ratios. Therefore, the experimental results show that orientational ordering of the guest methane molecules occurs over a wide range of temperatures and pressures. The guest ordering induced anisotropic contraction of the host framework, which in turn resulted in changes in the axial ratios within the same fundamental structure [3].

All phase changes observed by the XRD study are summarized in Fig. 1. Both the MH and MD samples possess three phases: (i) the original FI phase with a guest-disordered state (blue rhombuses), (ii) a guest-ordered state (green ones, labelled as GOS-phase in Fig.1), and (iii) the HP phase (red ones) developed at low temperatures and high pressures above 2 GPa. The grey belts in Fig.1 denote the boundaries between the phases. For the MD samples, the boundaries shifted towards a higher pressure regime, indicating the influence of the isotopic effect [3].

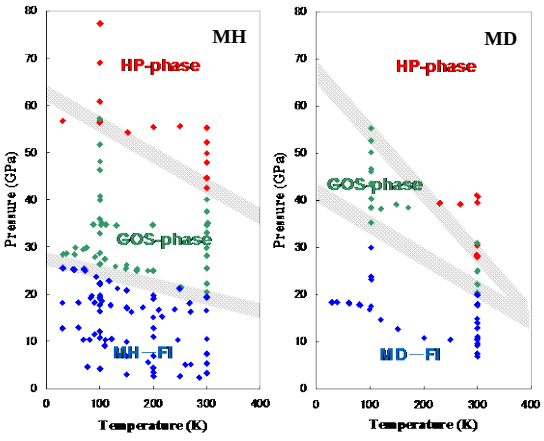

Fig. 1: Summary phase changes of methane hydrate.

References

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* hirai@sci.ehime-u.ac.jp