BL-18C/2018G524

Retention of filled-ice structure of methane hydrate up to 134 GPa

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1 Introduction

Methane hydrate (MH) is one of the well-studied clathrate hydrates, which consist of host cages formed by hydrogen-bonded water molecules and guest methane molecules included in the cage structures [1]. It presents an sI cage structure (MH-sI) below 0.8 GPa and at room temperature [1]. At 0.8 GPa, the sI cage structure of MH becomes an sH cage structure (MH-sH), and at 1.8 GPa, a filled-ice Ih cage structure (MH-FI) is formed [2–5]. MH-FI presents an ice framework with a structure similar to that of ice Ih in which guest methane molecules can be entrapped [2]. At higher pressure, the fundamental structure of MH-FI is retained up to at least 86 GPa, with some phase transitions occurring at 15–20 GPa and 40–50 GPa [6–9]. The 15–20 GPa transition, from MH-FI to MH-GOS (GOS: guest-ordered state), was detected via Raman spectroscopy and X-ray powder diffraction (XRD) and interpreted to be caused by the orientational ordering of guest methane molecules within the framework [9]. The 40–50 GPa transition, from MH-GOS to a high-pressure phase (MH-HP), was accompanied by the appearance of new XRD lines whose d-values were close to those of MH-GOS [7,9], suggesting that the structure of MH-HP may be related to that of MH-GOS. The transition from MH-FI to MH-GOS is well understood [9]. On the other hand, that from MH-GOS to MH-HP has not yet been comprehensively investigated although its existence was detected from the appearance of new diffraction lines [6–9]. That is mainly because the latter transition is significantly slow, and both MH-GOS and MH-HP coexist under wide pressure ranges. Thus, the diffraction lines originating exclusively from MH-HP have not yet been identified owing to the superimposition of lines from both phases. Therefore, to understand the mechanism of MH-GOS to MH-HP transition, it is firstly required to identify the characteristic diffraction lines of MH-HP. In this study, high-pressure experiments (up to 134 GPa) were performed in order to clarify the changes in the host framework during individual transitions.

2 Experiment

High pressure was generated by using diamond anvil cells with culet sizes of 100 to 350 μm. Rhenium was used as the gasket material. The sample pressure was estimated based on the diamond Raman shift [10] and the ruby fluorescence methods [11]. The starting material, MH-sI sample, was synthesized via the conventional ice–gas interface reaction method [12] at the National Institute of Advanced Industrial Science and Technology. The powdered MH-sI sample (average grain size of 2–3 μm) was loaded into the sample chamber in a cryogenic vessel cooled by liquid nitrogen together with a few ruby balls (ca. 2–10 μm) used as pressure markers. XRD experiments were performed using beamline BL-10XU at SPring-8 and beamline BL-18C at Photon Factory, High Energy Accelerator Research Organization (KEK), where monochromatic X-rays with wavelengths of 0.04424 and 0.06121 nm were used, respectively. The pressure range for XRD was 1.8–134 GPa. All experiments were performed at room temperature (298 K).

3 Results and Discussion

In order to clearly distinguish the diffraction lines of MH-GOS from those of MH-HP, the transition from MH-GOS to MH-HP under increasing pressure was carefully investigated. Figs. 1(a) and 1(b) show the representative XRD patterns during MH-GOS to MH-HP transition and the variations of the *d*-values from the individual phases with pressure, respectively.

In Fig. 1(a), the XRD spectrum at 26.1 GPa exhibits a typical MH-GOS pattern; all diffraction lines were indexed as MH-GOS and ice VII (indicated with green circles and blue rhombi, respectively). With increasing pressure, three new diffraction lines (indicated with red circles) that belonged to neither MH-GOS nor solid methane began to appear at 33.8 GPa. The intensities of these new diffraction lines gradually increased, and, in contrast, those of MH-GOS gradually decreased and remained visible in the spectrum up to 53.7 GPa. At 53.7 GPa, two additional diffraction lines appeared. Finally, the diffraction lines of MH-GOS were totally replaced by five new diffraction lines when pressure reached 57.7 GPa. The *d*-values of the new diffraction lines were close to those of MH-GOS at 33.8–53.7 GPa (Fig. 1(b)). The *d*-values of the new diffraction lines were different from those for solid methane reported in previous studies [13,14]. By analyzing the transition process using the approach proposed herein, five typical diffraction lines of MH-HP could be identified.

These new lines were in excellent agreement with those for a structure with space group *Pmcn* predicted recently by a theoretical study [15]. The identification of the diffraction lines exclusive to MH-HP allowed us to identify the start of the transition more accurately, which was found to occur at approximately 34 GPa (6 GPa lower than the previously reported value) [6–9]. To explore the possibility of MH-HP undergoing a further transition, XRD experiments up to 134 GPa were performed. No changes such as diffraction line splitting or new diffraction line appearance were observed above 57.7 GPa after the transition to MH-HP was completed; i.e., MH-HP is stable up to at least 134 GPa without presenting any assessable change (Fig. 1 (a)).

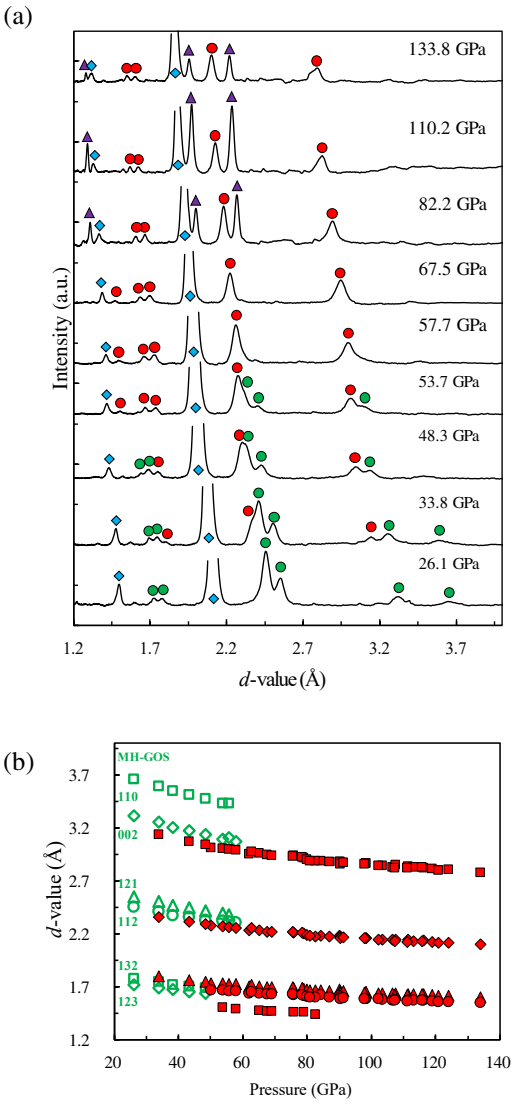

FIG. 1. (a) Typical XRD patterns of MH and ice VII coexisting in the sample chamber. Red circles, green circles, blue rhombi, and purple triangles indicate MH-HP, MH-GOS, ice VII, and Rhenium, respectively. (b) Variation of *d*-values with pressure. Open green and solid red symbols indicate the *d*-values of MH-GOS and MH-HP, respectively.

Acknowledgement

This research was partly supported by a Grant-in-Aid for JSPS Fellows (grant no. 19J01467) and Early-Career Scientists (grant no. 19K14815) from the Japan Society for the Promotion of Science. This research was also supported by the Joint Usage/Research Center PRIUS, Ehime University, Japan.

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