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# High-pressure X-ray diffraction study on the phase transition of methane hydrate in water-methane-ammonia system

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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-I) 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-II), and at 1.8 GPa, a filled-ice Ih structure (MH-III) is formed [2–5]. MH-III presents an ice framework with a structure similar to that of ice Ih in which guest methane molecules can be entrapped [2].

MH is thought to be ubiquitous in space and to be an important constituent of outer icy planets and their moons owing to its significant high-pressure stability. In the case of Saturn's largest moon, Titan, recent experimental studies suggested that the icy mantle of this moon contains MH, where it acts as an essential supply source of atmospheric methane [6,7]. Therefore, understanding the high-pressure behavior of MH under the mantle conditions of icy planets and their moons is important to estimate their internal structure. In this study, therefore, high-pressure (up to approximately 20 GPa) experiments were performed using synchrotron X-ray powder diffraction (XRD) combined with diamond anvil cells to understand the high-pressure behavior of MH in a water–methane–ammonia system.

## 2 Experiment

High pressure was generated using diamond anvil cells. The sample pressure was estimated using the ruby fluorescence method [8]. The methane hydrate sample (powdered MH-I) was synthesized via the conventional ice–gas interface reaction method [9] at the National Institute of Advanced Industrial Science and Technology. Aqueous ammonia (12.5 wt% $NH_3$) was freeze-crushed using a mortar and pestle cooled with liquid nitrogen before mixing it with powdered MH-I. The starting powder sample was prepared by mixing powdered MH-I and freeze-crushed aqueous ammonia at a mass ratio of 1:1. A few ruby balls (ca. 5–10 μm) were added to the powdered samples as pressure markers before loading the samples into the sample chamber in a cryogenic vessel cooled with liquid nitrogen. XRD observations were performed using beamline BL-18C at Photon Factory, High Energy Accelerator Research Organization. Monochromatic X-rays with wavelengths of 0.06125 nm and beam sizes of 60 to 100 μm were used. The pressure range during XRD was 0.2 to 19.4 GPa; all experiments were performed at room temperature (298 K).

## 3 Results and Discussion

Figure 1 shows representative XRD patterns of the samples containing MH + aqueous ammonia under increasing pressures at room temperature. Red squares, blue rhombi, and orange circles indicate MH-I, MH-II, and MH-III, respectively; blue arrows

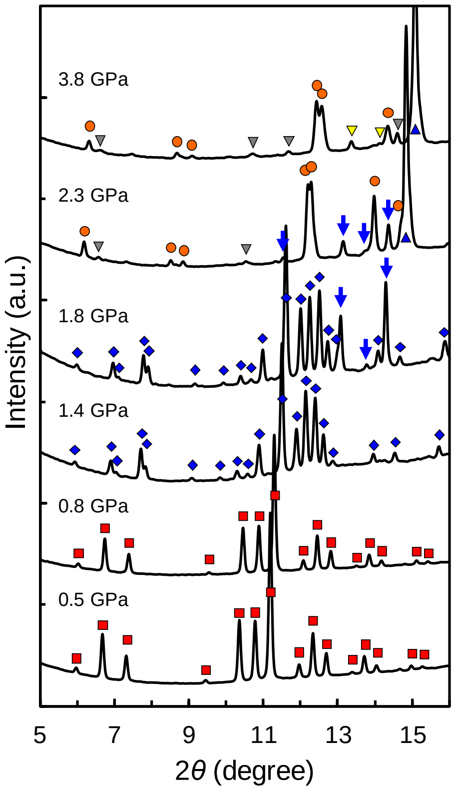

Figure 1. Typical XRD patterns of the samples containing MH + aqueous ammonia under increasing pressures at room temperature.

and triangles indicate ice VI and ice VII, respectively; and inversed yellow and gray triangles indicate ammonia hemihydrate phase-II (AHH-II) and an unknown phase, respectively. The diffraction lines shown as an unknown phase might have corresponded to ammonia-related phases and not to high-pressure ices, solid methane, MH, the rhenium of the gasket material, or the corundum of the pressure markers.

At 0.5 GPa, typical diffraction lines of MH-I were observed (bottom of figure 1); these survived up to 0.8 GPa. The diffraction lines of MH-I disappeared above 0.8 GPa and those of MH-II appeared at 1.4 GPa. The phase transition from liquid water into ice VI in a pure $H_2O$ system occurs at approximately 1 GPa at room temperature. However, ice VI, indicated by blue arrows in Figure 1, was observed above 1.8 GPa in the present experiments. The increase in the crystallization pressure of liquid water in the present system can be attributed to ammonia acting as a water crystallization inhibitor. At higher pressures, changes in diffraction lines were observed owing to phase transitions from MH-II to MH-III and from ice VI to ice VII at 2.3 GPa and the appearance of AHH-II at 3.8 GPa. The diffraction lines of MH-III were observed up to at least 19.4 GPa. Thus, our XRD measurements in a water–methane–ammonia system revealed that MH-I transforms into MH-II at pressures above 0.8 GPa, MH-II further transforms to MH-III at pressures above 1.8 GPa, and MH-III survives up to at least 19.4 GPa without decomposing into water and methane.

The transition pressures of MH and the transition pressure of ice VI to ice VII were close to those reported in previous studies for water–methane system [10,11]. This indicates that ammonia affects the crystallization of liquid water into ice VI, but does not affect the solid–solid transitions of MH and high-pressure ices. Our results also revealed that, under pressures up to 2.3 GPa, ammonia exists as aqueous ammonia in the sample chamber and, above 3.8 GPa, phase transition to AHH-II occurs. It is therefore considered that MH can coexist with aqueous ammonia below 2.3 GPa and coexist with AHH-II above 3.8 GPa. A previous experimental study reported that aqueous ammonia crystallizes into AHH-II at ~3.5 GPa [12]. Although the starting material used in this study presented a significantly higher $H_2O$ content than that used in previous studies focused on the high-pressure behavior of water–ammonia system, we also observed the appearance of AHH-II at pressures close to those used in previous studies [12]. This suggests that the formation pressure of AHH-II at room temperature may not depend on the ammonia concentration of the starting material.

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