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In-situ X-ray diffraction studies of the stability of methane hydrate under high pressure and high temperature

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1 Introduction

Methane hydrate is thought to be an important constituent of icy planets and their satellites, such as Neptune, Uranus and Titan. It is a clathrate compound composed of hydrogen-bonded water cages and methane molecules included in the cages. Methane hydrate has an sI cage structure composed of two 12-hedral and six 14-hedral components in a unit cell at low pressures (< 0.8 GPa) and room temperature. It transforms to an sH cage structure composed of three 12-hedral, two modified 12-hedral, and a 20-hedral at approximately 0.8 GPa, which further transforms to a filled-ice Ih structure at approximately 1.8 GPa[1-3]. Although the sequence of the phase transitions with pressure have been studied well at room temperature, there are only a few studies that addressed the stability of methane hydrate under high pressure and high temperature[4, 5]. In addition, the pressure range of these previous studies is only limited to < 5 GPa. Therefore, a further investigation is needed to understand the stability and physicochemical behavior of methane hydrate under extreme conditions corresponding to the mantle of giant icy planets.

2 Experiment

Lever-spring-type diamond anvil cell was used for high pressure generation. Pressure was estimated by using the ruby fluorescence method. High temperature generation was achieved by an electric furnace. Temperature was measured with an accuracy of ±1 K by a chromel-alumel thermocouple. The starting material, methane hydrate sI sample, was synthesized by the conventional ice–gas interface reaction method at a fixed P-T condition of 15 MPa and 271 K at the National Institute of Advanced Industrial Science and Technology. The powdered sample of methane hydrate was loaded together with a few ruby balls as a pressure marker in a sample hole in a Re gasket in a cryogenic vessel cooled by liquid nitrogen. In-situ XRD observations were performed at BL-18C beamline of the Photon Factory of the High Energy Accelerator Research Organization (KEK), where monochromatic X-rays with wavelength of 0.06198 nm was available.

3 Results and Discussion

Fig. 1 shows the typical XRD patterns before and after heating at around 20 GPa. All diffraction lines observed were indexed with the filled ice Ih (orange circles), solid methane (purple cross) and ice VII (blue triangle). Before heating, the typical XRD patterns of filled ice Ih and ice VII were observed at 298 K and 18.3 GPa. After heating, the XRD patterns of filled ice Ih survived at least 423 K and 20.0 GPa, but the diffraction patterns of filled ice Ih disappeared and were replaced by those of solid methane at 503 K and 15.5 GPa. This means that filled ice Ih decomposes into solid methane and ice VII above 423 K at around 20.0 GPa. The results of high P-T experiments showed that filled ice Ih decomposes into solid methane and ice VII at temperatures considerably lower than the melting curves of solid methane and ice VII at around 20 GPa. This suggests that methane hydrate is unlikely to be stable in the mantle of giant icy planets such as Neptune and Uranus.

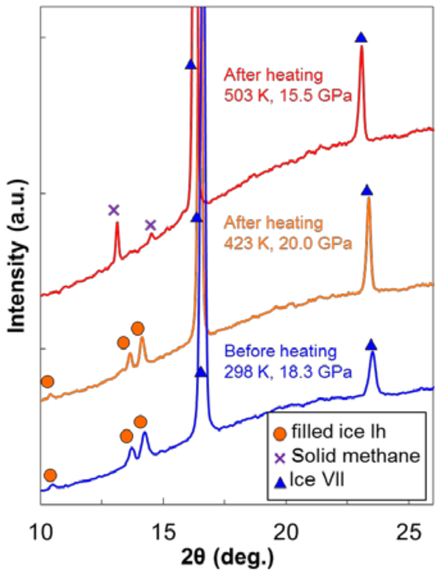

Fig. 1: Representative XRD patterns before and after heating at around 20 GPa. Orange circles, purple cross and blue triangle indicate the diffraction lines of filled ice Ih, solid methane and Ice VII, respectively.

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