Phase transition mechanism of sH to filled-ice Ih of methane hydrate under fixed pressure condition

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1 Introduction

Gas hydrates are clathrate compounds composed of hydrogen-bonded water cages (host) with molecules or atoms (guests) included in the cages [1]. Many guest species can be incorporated into clathrate structures, which have three types of varieties, sI, sII, and sH structures depending on the guest sizes at ambient to relatively low pressures [1]. At higher pressures, more varieties of structures are formed [2-5]. With increasing pressure, a cage structure is compressed and forced to change to one that can accommodate more guests per mole of water [6]. At further higher pressures, the cage structures are no longer retained, and consequently well-designed structures, called filled-ice structures, are formed. The filled-ice structures consist of an ice or icy framework and guests filling the voids between them [7].

Methane hydrate (hereafter denoted as MH) has an sI structure composed of two 12-hedra and six 14-hedra components in a unit cell at low (< 0.8 GPa) pressures and room temperature, but transforms to an sH cage structure formed by three 12-hedra, two modified 12-hedra, and a 20-hedra at approximately 0.8–1.0 GPa. A further transformation to a filled-ice Ih structure (hereafter denoted as FIIhS), which consists of a framework of ice (similar to ice Ih) and methane molecules that fill the channels running along the a- and c-axes [8]. The sequence of these phase transitions of MH with pressure have been studied [9, 10], and the structural details including the precise positions of the host oxygen atoms, multi-occupancies, and site disorders of guests have been determined by neutron diffraction [8, 11]. In contrast, there are only a few studies about the essential mechanism of the phase transitions [12, 13]. Therefore, this study employs in-situ, time-resolved observations using synchrotron XRD to understand the essential mechanism of sH-FIIhS phase transition.

2 Experiment

A clamp-type and a lever-spring-type of diamond anvil cells (DAC) were used to generate high pressures. A pair of anvils with a culet size of 600 μm and a stainless steel gasket were used for each run. Pressure (0.2-6.0 GPa) was measured using the ruby fluorescence method and carefully controlled so as to have a constant pressure distribution across the sample chamber. All the experiments were performed at room temperature (297 K). The initial methane hydrate sI sample was synthesized by a conventional ice–gas interface method at the National Institute of Advanced Industrial Science and Technology (AIST). The powdered sample (2–3 μm in average grain size) was loaded together with a few ruby balls for pressure measurement in a sample hole in a gasket in a cryogenic vessel cooled by liquid nitrogen. In-situ XRD observations were performed by using synchrotron radiations at BL-18C beamline of the Photon Factory of the High Energy Accelerator Research Organization (KEK) and at BL-10XU beamline of SPring-8. Monochromatic X-rays with wavelengths of 0.06198 and 0.04134 nm with a beam size of 100 μm were used in KEK and SPring-8, respectively. The sample pressure was finely controlled by an automatic gas flow system by adjusting the flow rate and pressure of helium gas flowing into a membrane in the DAC.

3 Results and Discussion

Fig. 1a and 1b show the time-resolved XRD patterns and typical XRD patterns during the transition from sH to FIIhS at 1.8 GPa. Up to ~160 s, the observed diffraction peaks were indexed with sH and ice VI. After 160 s, the sH peaks suddenly disappeared and instead, peaks of FIIhS appeared. This means that the construction of the FIIhS framework requires a relatively short time period of 50– 60 s. In addition to FIIhS peaks, small peaks of solid methane also appeared (Fig. 1b). It is most likely that a part of such formed methane crystalized

during the XRD measurement, since the pressure condition was very close to its solidification pressure (1.7 GPa at room temperature [14]). The present in-situ observations using XRD demonstrate that the sH-FIIhS transition occurs though a sudden collapse of sH structure followed by the release of fluid or solid methane that are then gradually incorporated into the FIIhS to reconstruct its structure. This clearly shows that the phase transition takes place by a typical reconstructive mechanism, which seems to be reasonable taking into account the large difference in crystal structure and chemical composition between the two phases.
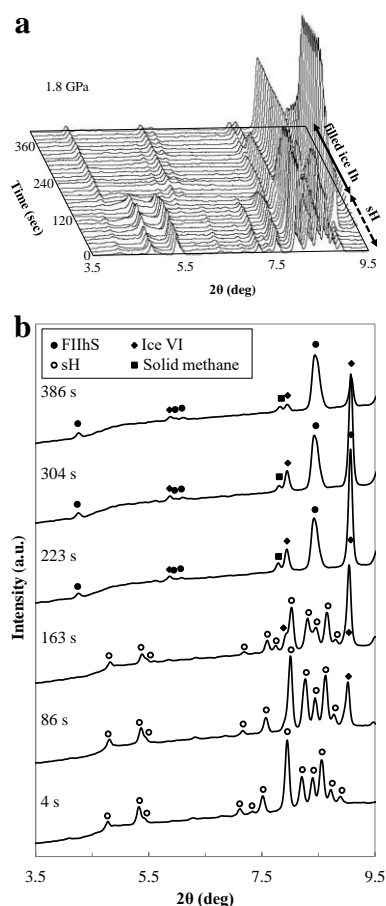

Fig.1: (a) Time-resolved XRD patterns and (b) typical XRD patterns obtained during sH–FIIhS transition at a fixed pressure of 1.8 GPa. Black circles, black diamonds, black squares and open circles indicate the diffraction lines of FIIhS, Ice VI and sH, respectively.

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