

## Phase changes of filled ice Ih methane hydrate induced by the orientational ordering of the guest molecules

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Oriental ordering of guest methane molecules in a filled ice Ih structure of methane hydrate (MH) was observed above 15 to 20 GPa at room temperature in a previous Raman study. However, the change in the fundamental structure was not observed at the pressure region by X-ray diffractometry. In this study, low-temperature and high-pressure experiments were performed with filled ice Ih structure of methane hydrate under pressure and temperature conditions of 2.0 to 77.0 GPa and 30 to 300 K, respectively, using diamond anvil cells and a helium-refrigeration cryostat. Distinct changes in the axial ratios of the host framework were revealed by In-situ X-ray diffractometry. Splitting in the CH vibration modes of the guest methane molecules, which was previously explained by the orientational ordering of the guest molecules, was observed by Raman spectroscopy. The pressure and temperature conditions at the split of the vibration modes agreed well with those of the axial ratio changes. The results indicated that orientational ordering of the guest methane molecules from orientational disordered-state occurred at high pressures and low temperatures, and that this guest ordering led to the axial ratio changes in the host framework. Existing regions of the guest disordered-phase and the guest ordered-phase were roughly estimated by the X-ray data. In addition, above the pressure of the guest-ordered phase, another high pressure phase was developed at a low-temperature region.

Keywords: Methane Hydrate, X ray diffraction, high pressure, Raman spectroscopy