

A stabilizing mechanism of carbon dioxide hydrate under low-temperature and high-pressure

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1 Introduction

CO₂ hydrate consists of cages formed by hydrogen-bonded host water molecules with guest CO₂ molecules in the cages [1]. CO₂ hydrate takes sI structure similar to many other gas hydrates, but it exhibits characteristic behaviors different from those of other gas hydrates. For most gas hydrates, the slopes of the phase boundaries between gas hydrates and gas + water are positive in temperature versus pressure field. On the other hand, for CO₂ hydrate the phase boundary turned from a positive slope to a negative one at an inflection point (294K, 328 MPa) [1]. Recently, the authors determined phase changes of CO₂ hydrate in a region from 80 to 300 K and from 0.2 to 3.0 GPa [2]. However, it has not been known why the sI structure of CO₂ hydrate survives at such conditions. In this study, high-pressure and low-temperature experiments were performed to clarify a stabilizing mechanism under low-temperature and high-pressure.

2 Experiment

A clamp-type diamond anvil cell (DAC) and a helium-refrigeration cryostat were used. Pressure measurements were made by using the ruby fluorescence method. Temperature measurements were made with Si-diode thermometer and chromel-alumel thermocouples. The initial materials were prepared using a conventional ice-gas interface method, of which conditions were 271 K and 2.0 MPa. The occupancies for large and small cages of the initial samples were estimated to be 98% and 94%, respectively, by Rietveld analysis. X-ray diffractometry (XRD) was performed using synchrotron radiation at BL-18C at the Photon Factory, KEK. A monochromatized beam with a wavelength of 0.06198 nm was used.

3 Results

Changes in the lattice parameter with temperature were measured at a few fixed pressures of approximately 0.2 GPa and 0.4 GPa (Fig. 1a and 1b). A peculiar behavior was observed as follows. With decreasing temperature, the lattice parameters decreased, which is normal behavior. However, at approximately 210 K, the lattice parameter abruptly increased, and after that the lattice parameter reduced again with decreasing temperature. Fig. 1c and 1d show XRD patterns before and after the

expansions of the lattice. Before the expansion, only sI, as a matter of course, existed, whereas ice Ih appeared and continued to exist after the expansion at both pressures. It is noteworthy that dry ice was never observed with these expansions. This means that sI was not simply decomposed, but only H₂O molecules was released to form ice Ih. The release of ice Ih indicates an increasing degree of guest occupancy.

The lattice expansion accompanied by a release of ice Ih was observed at 210 K. Release of H₂O molecules indicates increasing cage occupancies, i.e. becoming a denser structure. Transforming into a denser structure by releasing H₂O molecules is an effective way to sustain the cages structure, therefore this can be recognized as a stabilizing mechanism under high pressure and low temperature.

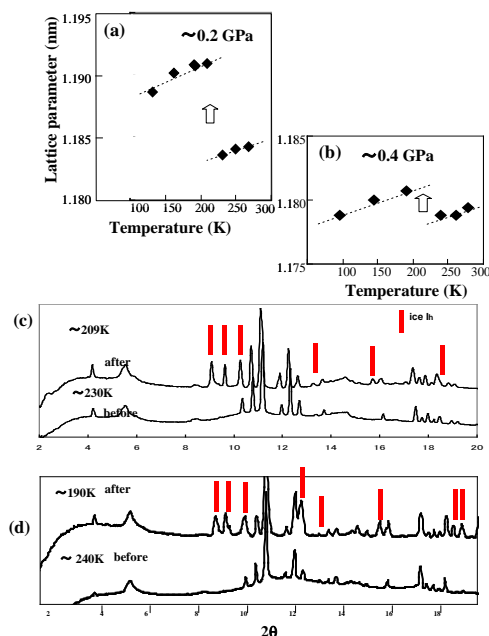


Fig. 2 a and b: Variations of lattice parameter, c and d: XRD patterns before and after the lattice expansion.

References

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