Phase changes and instability of carbon dioxide hydrate under high-pressure and low-temperature

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High-pressure and low-temperature experiments of CO_2 hydrate were performed in order to determine the stability field and also to detect a characteristic interaction between the guest and the host molecules in CO_2 hydrate. The temperature regions were 269K˜257K and 278K˜64K. In the former experiment, a lever-spring type diamond-anvil cell and a refrigerant-circulation device were used. Pressures were changed from 0.3 to 3.3GPa at two fixed temperatures of approximately 269K and 257K. Characterizations of phase changes were made by X-ray diffractometry and Raman spectroscopy. CO_2 hydrate synthesized by a contact-reaction method showed sI structure. Decomposition of CO_2 hydrate (sI) to ice VI and solid-CO_2 was observed between 0.9GPa and 1.3GPa at about 269K and 1.1GPa and 1.2GPa at about 257K. In addition, the phase transition of ice VI to ice VIII, a hydrogen-ordered phase of ice VII, was observed between 2.6GPa and 2.9GPa. From the experimental results of the phase boundary between CO_2 hydrate and dry ice-ice VI was extended into a high-pressure and low-temperature region from the previously reported one.

Raman spectroscopy was carried out in a pressure range from 0.3 to 1.5GPa at approximately 265K. With increasing pressure, decrease of the intramolecular C-O vibration modes were observed. Such behavior of the intramolecular vibration mode with pressure was not observed in other gas hydrates such as methane hydrate. The result suggests that a characteristic interaction exists between the guest CO_2 molecules and the host water molecules in CO_2 hydrate. This might relate to the instability of CO_2 hydrate under high pressure.

In the latter experiment, a high-pressure cryostat system was used. The experiment was carried out to observe phase changes of CO_2 hydrate at the extremely low temperature predicted by a theoretical calculation. The samples were characterized by X-ray diffractometry during lowering the temperature from the room temperature to 64K at two pressure conditions of 0.3˜0.5GPa and 2.1˜2.8GPa. At the pressures of 0.3 to 0.5GPa, the sI of CO_2 hydrate was kept without phase transition through the temperature range.