

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 CO₂ 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 CO₂ hydrate. In the relatively higher temperature region, approximately 250~270K, a lever-spring type diamond-anvil cell and a coolant circulation device were used. Pressures were changed from 0.3 to 3.3GPa at four fixed temperatures of approximately 269, 260, 257 and 252K. Characterizations of phase changes were made by X-ray diffractometry and Raman spectroscopy. Decomposition of CO₂ hydrate sI to ice VI and solid-CO₂ was observed between 0.9GPa and 1.3GPa at 269K, 0.6 and 1.1GPa at 260K and 1.1GPa and 1.2GPa at 257K. The phase transition of ice VI to ice VIII, a hydrogen-ordered phase of ice VII, was observed between 2.6GPa and 2.9GPa at 257K. On the basis of the present results, the phase boundary between CO₂ hydrate and dry ice-ice VI was extended into a high-pressure and low-temperature region from the previously reported one. Moreover a new phase of CO₂ hydrate was discovered within the range from 0.7 to 1.0GPa at 252K observation.

In order to examine phase changes of CO₂ hydrate at the extremely low temperature predicted by a theoretical calculation, further low-temperature (64~300K) experiment was carried out using a cryostat system. 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 CO₂ hydrate was kept without phase transition through the temperature range. While, at the conditions of 0.6~0.9GPa 134~267K, the similar new phase was observed.

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 works between the guest CO₂ molecules and the host water molecules in CO₂ hydrate. This might relate to the instability of CO₂ hydrate under high pressure.