

Phase changes of CO₂ hydrate under high pressure and low temperature

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Introduction

CO₂ hydrate is a clathrate compound and the crystal structure type is sI at low pressure. CO₂-reduction in the atmosphere is one of the most urgent subjects for mankind. Some technical developments to seclude CO₂ as CO₂ hydrate in ocean floor have been proceeded. Looking around the solar system, existence of CO₂ hydrate in and beneath Martian permafrost has been predicted from spacecraft probes and theoretical studies [1]. Thus, its stability and properties under high pressures and low temperatures are of great interest for fundamental understanding of clathrate hydrate, for the ocean sequestration technology, and for planetary science.

Experimental

A clamp-type diamond anvil cell (DAC) and a helium-refrigeration cryostat were used in these high-pressure and low-temperature experiments. The pressure and temperature ranges were 0.2 to 3.0 GPa and 80 to 300 K, respectively. Pressure measurements were made using the ruby fluorescence method. The accuracy of this measurement system is 0.1 GPa, taking both the resolutions of the spectrometer and the analytical procedure into account. Ruby balls were put both in the sample chamber and on the opposite side of the diamond anvil locker at ambient pressure. Temperature measurements were made with chromel-alumel thermocouples. One thermocouple was in contact with a diamond anvil very close to the sample chamber, and the other one was in contact with the locker close to the ruby balls described above. XRD patterns were measured at more than 100 points by changing the pressure at several fixed temperatures and by changing the temperature at several fixed pressures.

Results and Discussion

X-ray diffractometry clearly revealed several phase changes under high pressure and low temperature. For instance, at approximately 230 K, all diffraction lines were indexed as those of sI at 0.4 GPa, several new diffraction lines started to appear in addition to those of sI at 0.6 GPa. Those of sI disappeared, and new lines and those from ice VI were observed at 0.9 GPa, but here those of dry ice did not appear. The new diffraction lines were not indexed by the known gas hydrate structures, sI, sII, sH, and sT. At 1.0 GPa, those of dry ice started to

appear and the intensity of the ice VI lines became stronger, but the new lines still remained. At 1.2 GPa, the new lines disappeared, and only those of dry ice and ice VI were observed. Ice VI transformed to ice VIII above 1.8 to 2.0 GPa. Similar phase changes were observed with good reproducibility at the more than hundred P-T points examined. The phase changes observed are summarized in Fig. 1.

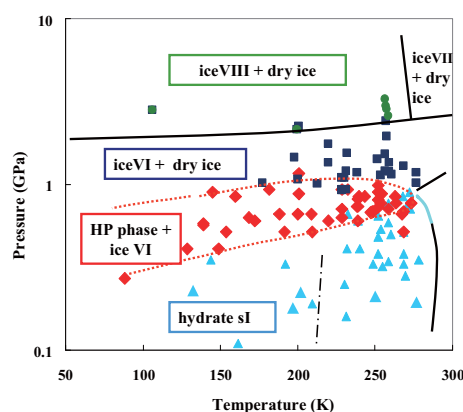


Fig.1 A reaction diagram showing phase changes of CO₂ hydrate under low temperature and high pressure.

In the present study, the phase boundary between CO₂ hydrate and water + CO₂ described previously [2] was extended towards the higher-pressure and low-temperature region. Below about 0.6 GPa only sI was observed, which was consistent with previous work. The results also showed the existence of a new high-pressure phase (called tentatively HP-phase in the paper) in a range from approximately 0.6 GPa to 1.0 GPa below 270 K.

The limitations to the stable region may be related to characteristic interactions in CO₂ hydrate, because CO₂ molecules have hydrophilic oxygen atoms both sides. Such interaction may be enhanced by compressing cages, and finally the cages may collapse under high pressure.

References

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