

## Phase transition of CO<sub>2</sub> clathrate hydrate

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The presence of CO<sub>2</sub> clathrate hydrate in comets has been suggested. The water molecules in comets exist as amorphous ice at large distances from the sun. The amorphous ice includes many molecules such as CO<sub>2</sub>, CO, and NH<sub>3</sub>. With decrease in distance from the sun, the water molecules in the amorphous ice rearrange and transform into clathrate hydrates by warming. Clathrate hydrates are inclusion compounds consisting of water molecules and guest molecules. The water molecules form cage-like structures and accommodate guest molecules.

CO<sub>2</sub> clathrate hydrate forms a cubic in space group Pm $\bar{3}$ n. The unit cell contains 46 water molecules in a framework of two dodecahedral and six tetrakaidecahedral cages. If the cages are fully occupied, the composition is CO<sub>2</sub> / 5.75H<sub>2</sub>O. The oxygen atoms are classified to three crystallographically nonequivalent sites, and hydrogen atoms are classified to six crystallographically nonequivalent sites. The hydrogen atoms are equally distributed among the two possible sites on each O-O bond according to the ice rules: (1) there is only one hydrogen atom on each bond, and (2) there are two hydrogen atoms close to each oxygen atom. Thus, CO<sub>2</sub> clathrate hydrate has the disorder arrangement of the hydrogen atoms.

At very lower temperature, clathrate hydrates might be transferred into a thermodynamically stable phase. However, phase transition is not attained over laboratory time scale; because the reorientational motion of the water molecules is significantly slow at low temperature below the glass transition temperature. Therefore, the arrangement of the water molecules is frozen in the structure at the high temperature phase.

The reorientational motion of the water molecules are accelerated by impurity doping, because point defects are occurred in the lattice (H.Fukazawa et al.,2005). It was found that the KOD-doped crystals of THF and acetone clathrate hydrates change into a structure (low temperature phase) at temperatures below 100K (O.Yamamuro et al., 1995). Since the change does not occur in clathrate hydrates with rare gases as guest molecules, we suppose that the mechanism of the phase transition depends on shape and motion of guest molecules.

It is expected that CO<sub>2</sub> clathrate hydrate also has a low temperature phase. The CO<sub>2</sub> molecules rotate anisotropically about a symmetry axis inside the cages (T.Ikeda et al., 1998&2000). The surrounding hydrogen atoms are temporarily attracted and released by the oxygen atoms of the rotating CO<sub>2</sub> molecule and so the reorientational motions of the water molecule are enhanced. In order to investigate whether CO<sub>2</sub> clathrate hydrate has a low temperature phase or not, we measured neutron powder diffraction data of deuterated CO<sub>2</sub> clathrate hydrate.

A powder sample of deuterated CO<sub>2</sub> clathrate hydrate was prepared in following manner. The powder ice was made from the solution with mole fraction of KOD to D<sub>2</sub>O,  $2.43 \times 10^{-4}$  using an atomizer. The powder ice of about 12 g was loaded into a pressure cell and pressurized with CO<sub>2</sub> gas to about 3 MPa. To accelerate the formation of clathrate hydrate, the sample temperature was cycled between 272 and 278 K.

The powder neutron diffraction data of the sample was measured with powder neutron diffractometer HERMES installed at the Japan Atomic Energy Research Institute. The structure parameters were refined by the Rietveld method using intensity data of the scattering angle between 20 and 140 degree.

The results show that the diffraction profiles at 50K have peaks which are not observed in the high temperature phase. The intensities of the peaks increase with increase in the annealing time. In addition, the lattice constants of KOD-doped CO<sub>2</sub> clathrate hydrate are about 0.1% larger than that of crystal without KOD at 50K. The CO<sub>2</sub> clathrate hydrate without KOD keeps the structure at high temperature even in 50K. The results suggest that the CO<sub>2</sub> clathrate hydrate has a low temperature phase.