

# In situ neutron diffraction study of formation and decomposition process in clathrate hydrate

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The neutron diffraction measurements were carried out on HERMES installed at JRR-3. A single-crystal sapphire cell was used as a high-pressure sample cell. The Bragg peaks of the sapphire cell were excluded by Cd Blade of HERMES.

Figure 1 (a) shows time resolved diffraction patterns of methane hydrate (MH). Each measurement was done for 14 min. Analysis was based on the previous crystal structure data [1, 2]. The temperature and pressure dependence of mass fraction was obtained as shown in Figure 1 (b).

The CH<sub>4</sub> gas was gradually applied D<sub>2</sub>O ice until 6 MPa at 216 K as isothermal process. The diffraction peaks of MH were observed in this condition and the mass fraction of MH was 0.05. The pressure was kept at ca. 6 MPa for 18.5 hours. However, the mass fraction of MH did not change. We changed temperature from 216 K to 240 K and then the pressure increased to 6.7 MPa. The CH<sub>4</sub> gas was applied until 7 MPa at 240 K. And the pressure was kept at ca. 7 Pa for 18.5 hours. The mass fraction of MH slightly increased to 0.07. Following, temperature increased to 260 K and the pressure changed to 7.5 MPa. The mass fraction of MH increased until 0.13.

Next, we released the pressure and decrease temperature. The mass fraction of MH decreased to 0.07. We repeated to change temperature in the same way although the pressure was only applied up to 6 MPa at a maximum. In this case, the mass fraction of MH increased until 0.1 at 240 K. Here,  $0.13/7.5 \times 6 = 0.104$ . Accordingly, it is clarified that the mass fraction of MH was proportional to the CH<sub>4</sub> gas pressure. Finally, temperature was increased at 6 MPa as isobaric process. The D<sub>2</sub>O ice did not melt at 277 K. When temperature in-

creased to 282 K, the D<sub>2</sub>O ice melted and the Bragg peak of MH grew rapidly. There was no Bragg peak of D<sub>2</sub>O ice (Ih) at 282 K. However, when temperature decreased to 240 K, the Bragg peak of D<sub>2</sub>O ice appeared and the mass fraction of MH was 0.6. Accordingly, methane hydrate covered D<sub>2</sub>O ice and D<sub>2</sub>O water did not flow out. In addition, it is proposed that unreacted water remained because we used coarse-grained powder of D<sub>2</sub>O ice (<400 micrometer).

As a result, it is clarified that the growth rate depends on the pressure of CH<sub>4</sub> gas, although we considered that the growth rate didn't depend on the pressure under the sufficient pressure for the growth.

## References

- 1) A. Hoshikawa, N. Igawa, H. Yamauchi, and Y. Ishii: *J. Phys. Chem. Solid.*, 66, 1810-1814 (2005).
- 2) A. Hoshikawa, N. Igawa, H. Yamauchi, and Y. Ishii: *J. Chem. Phys.*, 125, 034505 (2006).

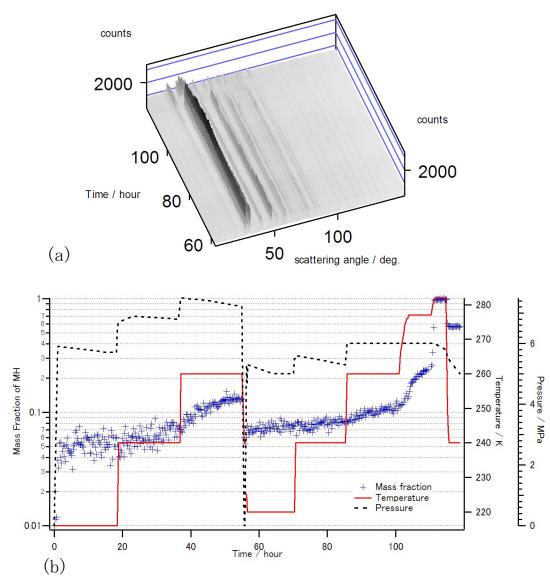


Fig. 1.