MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2010B0039 実験課題名 Title of experiment Occupancy of guest molecules in hydrocarbon hydrate 実験責任者名 Name of principal investigator Akinori Hoshikawa 所属 Affiliation Ibaraki University	装置責任者 Name of responsible person Toru Ishigaki 装置名 Name of Instrument/(BL No.) iMATERIA / BL20 実施日 Date of Experiment 2011/2/16

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

(1) mixed gas hydrate, $8(0.7\ CH_4\ 0.3CO_2)\cdot 46(D_2O)$

(2) ethane hydrate, $8(C_2H_6)\cdot 46(D_2O)$

(3) propane hydrate, $8(C_3H_8)\cdot 136(D_2O)$

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

We prepared three samples which were mixed gas hydrate, ethane hydrate, and propane hydrate. These samples were packed into the vanadium holder with an Al flange and an In-seal at liquid N_2 temperature. The samples were kept under 100 K. Each sample was set to the cold head of the refrigerator and cooled down. The neutron measurements were done at 10 K with double frame mode. After measurement, the sample environment was changed. At the outside of the vacuum chamber, the refrigerator was heated up and another sample was set to the cold head and the sample was cooled down.

Figure 1 shows the Rietveld refinement pattern of mixed gas hydrate. There are 5 phases, which are

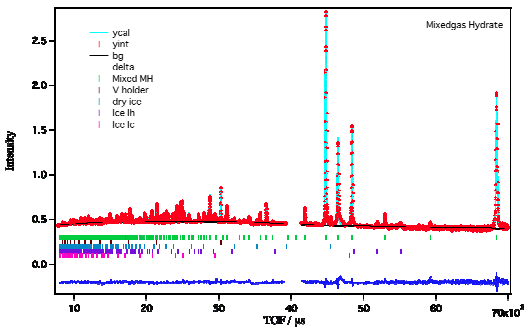

Figure 1. Powder neutron diffraction pattern of mixed gas hydrate

mixed gas hydrate, vanadium (holder), dry ice (CO_2), Ice Ih, and Ice Ic. It was clarified that the mixed gas hydrate had Structure I. There are two types of cage structure in Structure I. One is dodecahedron and another is tetrakaidecahedron. Usually, a guest molecule occupies in each polyhedron. In our analysis of mixed gas hydrate, the guest molecules, which were mixed gas of CO_2 and CH_4, occupied in only tetrakaidecahedra. Moreover, CO_2 and CH_4 occupied approximately half and half. The carbon dioxide has a lower freezing point than methane. It is possible that the carbon dioxide is selectively condensed when the sample is cooled down by liquid nitrogen in order to pack into the holder. It is considered that the mixture ratio was changed. Because the clathrate hydrate is non-stoichiometric inclusion compounds, the occupancy of the guest molecule can be variable.

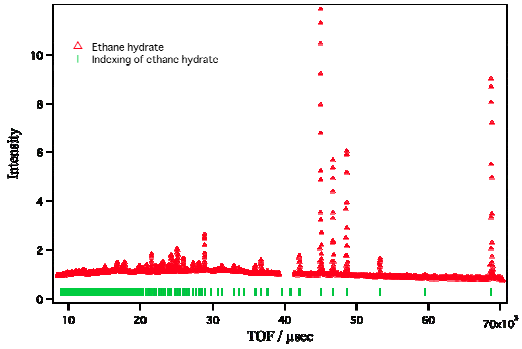

Figure 2. Powder neutron diffraction pattern of ethane hydrate

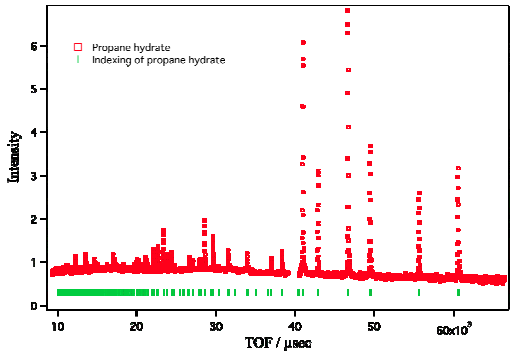

Figure 3. Powder neutron diffraction pattern of propane hydrate

Figure 2 shows diffraction pattern of ethane hydrate. In rough analysis, we could confirm that the crystal structure of ethane hydrate was Structure I. The guest molecule occupied in each polyhedral cage. It seems that there is no major impurity in the diffraction pattern. We succeeded in the synthesis of pure ethane hydrate.

Figure 3 shows diffraction pattern of propane hydrate. In rough analysis, it was confirmed that the crystal structure of propane hydrate was Structure II as shown in the previous reports. There are two types of cage structure in Structure II. One is dodecahedron and another is hexakaidecahedron. There are 16 dodecahedra and 8 hexakaidecahedra in the unit cell of Structure II. The propane molecule cannot occupy in the dodecahedron because of large molecular size. The propane molecules as the guest molecule occupied in the hexakaidecahedra. It was successful that we synthesized pure propane hydrate because impurity peaks hardly can be confirmed. Further, we need to analyze by improving structure model with hydrogen atoms. And we have a plan for using maximum entropy method with developing software.

In summary, the crystal structure of hydrocarbon hydrate was investigated by powder neutron diffraction at low temperature. We measured 3 samples (mixed gas hydrate, ethane hydrate, and propane hydrate) with powder neutron diffractometer. We confirmed that the crystal structure of both mixed gas hydrate and ethane hydrate was Structure I and that the one of propane hydrate was Structure II. Moreover, we succeeded in the synthesis of both ethane hydrate and propane hydrate because the sample was high purity from powder neutron diffraction pattern.