MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2014A0322 実験課題名 Title of experiment Guest storage capacity into dense methane hydrate 実験責任者名 Name of principal investigator Shigeo Sasaki 所属 Affiliation Dept. of Electrical, Electronic & Computer Engineering, Gifu University	装置責任者 Name of responsible person Kazuya Aizawa, Stefanus Harjo 装置名 Name of Instrument/（BL No.） TAKUMI/BL19 実施日 Date of Experiment 12 June 2014 – 15 June 2014

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. Fully deuterated methane hydrate powder in a diamond anvil cell, CD_4-$n$$D_2O$
2. Fully deuterated methane hydrate powder in a sapphire anvil cell, CD_4-$n$$D_2O$
3. Vanadium bulk 1.5 mmϕ x 2.0 mm, V
4. Vanadium bulk 1.5 mmϕ x 1.5 mm, V
5. Vanadium rod 5 mmϕ, V
6. NIST lanthanum hexaboride powder in V can, LaB_6

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.

In the previous experiments (2012A0059, 2012B0223), we have carried out the high pressure neutron diffraction measurements for fully deuterated methane hydrate (CD_4-$n$$D_2O$) and methane deuterohydrate (CH_4-$n$$D_2O$), in order to determine the cage occupancy of methane molecules in the large water cage of structure H (sH) methane hydrate. Although we obtained the excellent and unprecedented neutron powder diffraction pattern up to 5 Å in *d*-value for sH phase of CD_4-$n$$D_2O$, the existence of diffractions of ice-VI which invariably appears at the sI to sH phase transformation disturbed the detailed Rietveld analysis. The aim of this continuing proposal is, therefore, to obtain the neutron diffraction pattern of ice-VI-free sH CD_4-$n$$D_2O$ and to determine the precise storage capacity of methane molecules in the large cage of sH by fully utilizing the advantages of high resolution and low background of BL19 “TAKUMI”. In addition, the results of the proposed experiments will contribute to the more detailed Rietveld analysis for the neutron diffraction patterns previously obtained at “TAKUMI”.

In this experiment, we prepared two CD_4-$n$$D_2O$ samples as follows: (a) D_2O ice powder with ~5 μm in diameter was put into a sample chamber (2.0 mmϕ x 1.5 mm) of a diamond anvil cell (DAC) (Fig. 1), and then

2. 実験方法及び結果（つづき） Experimental method and results (continued)

liquefied deuterated methane (CD_4) was loaded into the chamber by spraying CD_4 gas on it cooled at ~80 K near the liquid nitrogen temperature. The sH CD_4-$n$$D_2O$ was synthesized at 1 GPa and room temperature over several days, and then was pressurized up to 1.65 GPa. (b) The sI CD_4-$n$$D_2O$ powder and liquid CD_4 were loaded into a sample chamber (2.0 mmϕ x 2.0 mm) of a sapphire anvil cell (SAC) in the same manner of (a). After loading, the sample was warmed to room temperature and was pressurized up to 1.30 GPa.

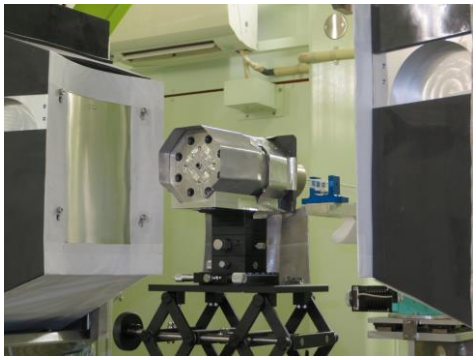

Fig. 1. Diamond anvil cell (DAC) including fully deuterated methane hydrate powder at TAKUMI.

The high intensity mode Neutron diffraction measurements were performed for the above two samples of sH CD_4-$n$$D_2O$ at "TAKUMI", using the focusing device and the 2 mm radial collimator. Figure 2 shows the obtained diffraction patterns as a function of TOF, which are roughly normalized by the incoherent scattering spectrum from V-Ni rod (5 mmϕ). The intensities of the diffraction peaks from ice-VI are obviously diminished in comparison with the previous results. Especially for the sample (CD_4-$n$$D_2O$ + liq. CD_4) in SAC [Fig. 2 (b)], we can estimate the pure diffraction peaks from sH CD_4-$n$$D_2O$ by comparing with the previous experiments, because the peaks from ice-VI are very weak. However, we could not fully remove the ice-VI peaks. Moreover, the very broad peak which probably comes from liquid CD_4 appears at around 47000 μs. These results suggest that the excess water generated at the sI to sH transformation of CD_4-$n$$D_2O$ does not sufficiently react with liquid CD_4 at ~1.3 GPa within several days.

Furthermore, the neutron diffraction measurements for NIST LaB_6 powder in V can, vanadium bulk chips, and empty anvil cells were also performed for the *d*-value calibration, normalizing the intensity of diffraction patterns, and the absorption and background corrections for anvils, gaskets, and other surroundings. The Rietveld analysis of guest methane storage capacity in large cages of sH CD_4-$n$$D_2O$ is now in progress, taking account of the above calibrations and the previous neutron diffraction patterns.

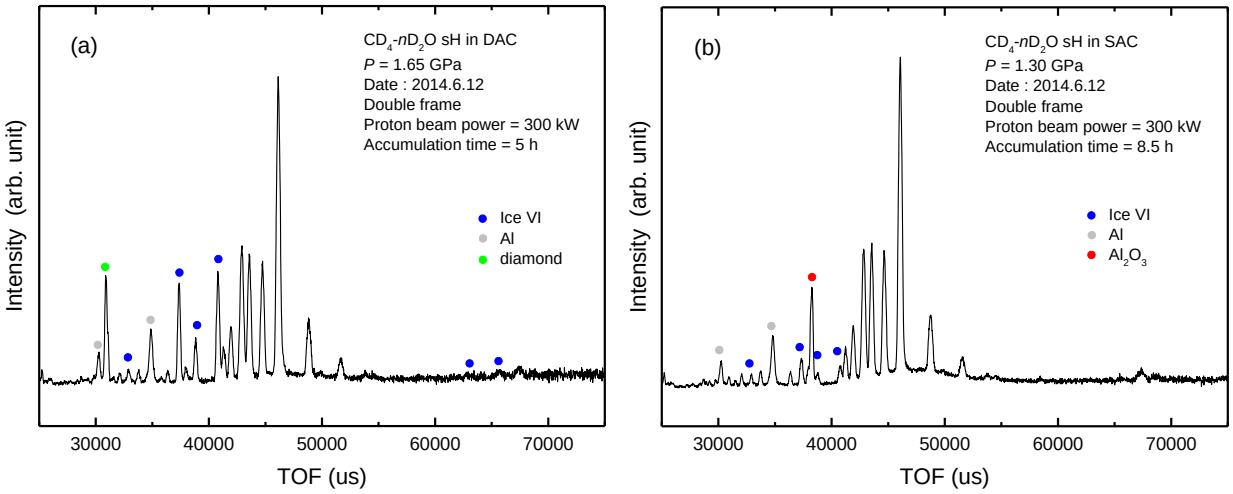

Fig. 2. Neutron powder diffraction patterns of fully deuterated methane hydrate (CD_4-$n$$D_2O$) (a) in a diamond anvil cell (DAC) at P = 1.65 GPa and (b) in a sapphire anvil cell (SAC) at P = 1.30 GPa. Blue, grey, green, and red solid circles stand for the diffraction peaks from ice-VI, aluminum gasket, diamond anvils, and sapphire anvils, respectively.