J-PARC **MLF Experimental Report**	提出日 Date of Report
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課題番号 Project No.	装置責任者 Name of responsible person
2012B0046	Toru Ishigaki
実験課題名 Title of experiment	装置名 Name of Instrument/（BL No.）
Detailed Crystal Structures of Na5/6[Li1/4Mn3/4]O2 as High-Energy Manganese-Based Electrode Materials for Li/Na Batteries	iMATERIA/BL-20
	実施日 Date of Experiment
	2012.11.23-2012.11.24
実験責任者名 Name of principal investigator	2013.3.5-2013.3.6
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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. Sodium manganese oxide containing lithium: P2-type layered $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$ with a space group of $P6_3/mmc$.

2. Sodium manganese oxide containing lithium: P2-type layered $Na_{2/3}[Li_{1/6}Mn_{5/6}]O_2$ with a space group of $P6_3/mmc$.

3. Lithium-rich manganese oxide: O2-type layered $Li_x[Li_{1/4}Mn_{3/4}]O_2$ with a space group of $P6_3/mc$.

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.

Experimental method: Neutron diffraction data of samples were collected at room temperature using a time-of-flight (TOF) neutron powder diffractometer at iMATERIA (BL20). The samples were put in a cylindrical vanadium cell (6 mm in inner diameter and more than 30 mm in height), which was sealed with indium metal in a helium-filled glove box. The neutron diffraction data were analyzed by the Rietveld method using the Rietveld analysis program, Z-Rietveld that was developed in J-PARC.

Results: Figure 1 shows a Rietveld refinement pattern of $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$. The neutron diffraction pattern can be indexed with a space group of $P6_3/mmc$. $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$ consists of two $[Li_{1/4}Mn_{3/4}]O_2$ layers that are stacked alternately along c-axis direction. Na ions are located at two different prismatic sites sandwiched in between the $[Li_{1/4}Mn_{3/4}]O_2$ layers. Supperlattice peaks were not observed on the neutron diffraction pattern because the difference of scatter length between lithium and manganese is quite small. Structural parameters refined by the Rietveld method for $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$ are summarized in Table 1. Although occupancy of lithium and oxygen was refined, deficiency at lithium and oxygen sites was not evidenced. The refinement

results clearly indicate a good agreement between the structural model and observed pattern. Isotropic atomic displacement parameters for the sodium sites that are located at two different sites were also refined. Relatively high displacement parameters are found as shown in Table 1, which is a consistent with the X-ray Rietveld refinement on a synchrotron X-ray diffraction pattern. Now, detailed analyses by Fourier synthesis and/or MEM analysis on the neutron diffraction data of the samples, including a Na^+/Li^+-exchanged product, are in progress.
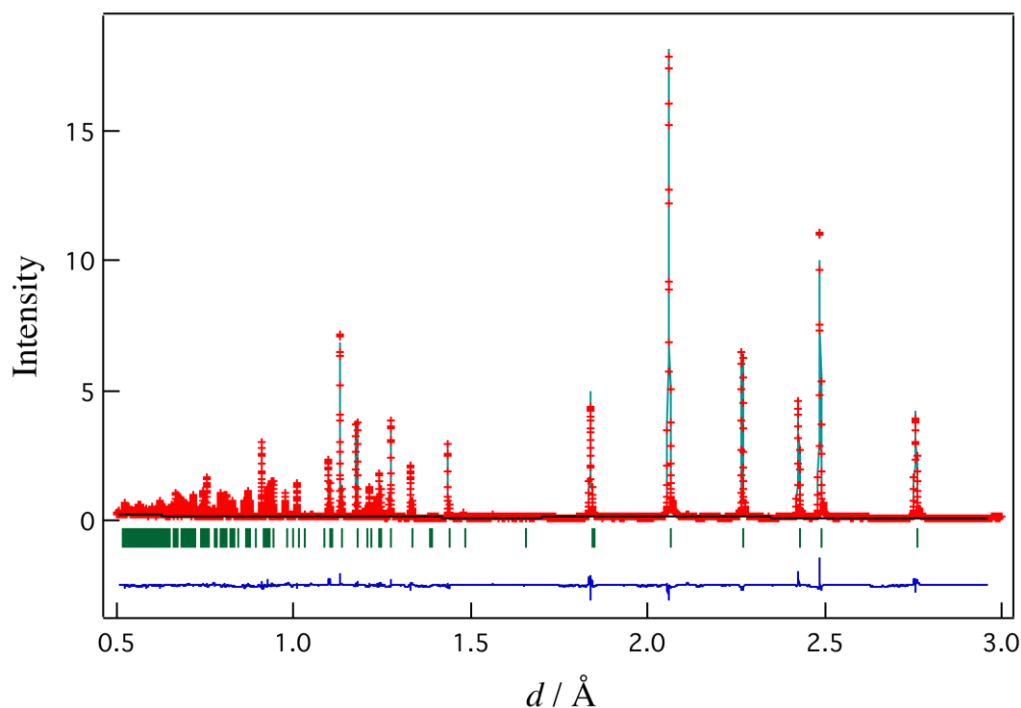

Fig. 1. Rietveld refinement on the neutron diffraction data of $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$: A comparison of observed (crosses) and calculated (black line) patterns with its difference (blue line). The short vertical green lines indicate the peak positions of all the possible Bragg reflections.

Table 1. Structural parameters obtained by the Rietveld refinement on the neutron diffraction data of $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$. Unit cell: $P6_3/mmc$ (194); a = 2.8711(3) Å, c = 11.028(15) Å; R_{wp} = 8.00 %, R_p = 6.21 %, R_e = 1.24, R_B = 4.86 %, R_F = 6.74, S^2 = 4.15.

Atom	Wyckoff positions	x	y	z	Occupancy	B
Na1	2b	0	0	1/4	0.33	5.395(18)
Na2	2d	1/3	2/3	3/4	0.50	2.77(2)
Li	2a	0	0	0	0.24	0.21(2)
Mn	2a	0	0	0	0.76	= B(Li)
O	4f	1/3	2/3	0.093(2)	1.000(6)	0.679(11)