MLF Experimental Report	提出日 Date of Report 2010/5/11
課題番号 Project No. 2009B0013 実験課題名 Title of experiment Crystal structure of xLi_2MnO_3-(1-x)$LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ as a cathode active material for lithium ion battery 実験責任者名 Name of principal investigator Yasushi Idemoto 所属 Affiliation Tokyo University of Science	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/（BL No.） SuperHRPD/BL08 実施日 Date of Experiment 2010/1/28-1/29, 2010/2/1-2/2

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.

yLi_2MnO_3-(1-y)$LiMn_{1/3-x/2}Ni_{1/3-x/2}Co_xO_2$ (x=1/3, 2/9; y=0.5, 0.6)
powder

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

We prepared yLi_2MnO_3-(1-y)$LiMn_{1/3-x/2}Ni_{1/3-x/2}Co_xO_2$ by means of a solution method using each metal acetate aqueous solution as starting materials. The precursor obtained from the solution was heat-treated in air at 650 ^oC for 15 h and the at 950 ^oC for 15 h. The phase of the product was identified by a powder X-ray diffraction and its metal composition was determined by an ICP. The cathode property was evaluated by CV and charge-discharge cycle tests.

The crystal structure was investigated by the Rietveld analysis using neutron diffractions, which were measured with Super HRPD. The about 1 gram of the sample powder was loaded in a vanadium can and then mounted in the apparatus. The experiment was performed in vacuum at room temperature, and the measurement time was 5~5.5 hours. The Rietveld analysis was carried out by using Z-Code package.

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

Results

Figure 1 shows a Rietveld refinement pattern of a solid solution of $0.6Li_2MnO_3$-$0.4LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ measured with Super HRPD. In the analysis, we assumed that the sample had a single phase of a layered rock-salt structure (S. G.; *R-3m*). As a result, it was found that diffraction peaks except for those around *d*=0.22 nm could be attributed to the layered structure. From the simulation and other previous works, it can be considered that the extra peaks were caused by a Li_2MnO_3 domain within the layered structure. Table 1 shows the refined structure parameters of the sample. As shown in this table, the Li site (3a site) was occupied partially by Ni — about 3 % — in the same way as $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$, and the occupancy at the oxygen site (6c site) was almost unity, indicating that an oxygen vacancy was negligible. The larger atomic displacement parameter of Li than the other elements may reflect that the sample could conduct Li ion. Similar results were also observed in the other solid-solutions of yLi_2MnO_3-$(1-y)LiMn_{1/3-x/2}Ni_{1/3-x/2}Co_xO_2$, although Ni at the Li site tended to increase with increasing the Ni content. From the quadratic elongation and the bond angle variance, it was also found that the distortion of the (Mn,Ni,Co,Li)-O_6 octahedron became smaller with increasing the Mn content. Since a sample with higher Mn content exhibited better cycle performance, Mn may play an important role in the cathode property from the viewpoint of the crystal structure.

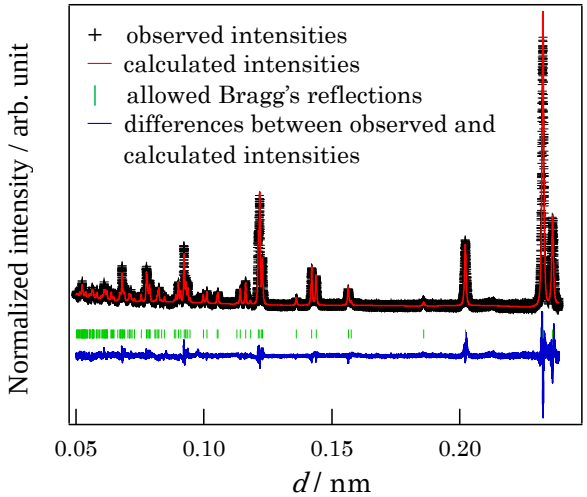

Fig. 1 The Rietveld refinement patterns of $0.6Li_2MnO_3$-$0.4LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$.

Table 1 The refined structure parameters of $0.6Li_2MnO_3$-$0.4LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ (S. G.; *R-3m*). R-factors were R_{wp}=11.89, R_p=10.05 and *S*=1.43. The lattice constants were *a*=*b*=0.28427(2) nm and *c*=1.418(2) nm.

Atom	Site	*x*	*y*	*z*	$10^2 \times B(nm^2)$	Site occupancy
Li1	3a	0	0	0	2.00(9)	0.965(1)
Ni1	3a	=Li1(*x*)	=Li1(*y*)	=Li1(*z*)	=Li1(*B*)	0.034(1)
Ni2	3b	0	0	0.5	0.41(7)	0.099(1)
Li2	3b	=Ni2(*x*)	=Ni2(*y*)	=Ni2(*z*)	=Ni2(*B*)	0.241(1)
Mn	3b	=Ni2(*x*)	=Ni2(*y*)	=Ni2(*z*)	=Ni2(*B*)	0.528
Co	3b	=Ni2(*x*)	=Ni2(*y*)	=Ni2(*z*)	=Ni2(*B*)	0.132
O	6c	0	0	0.240717(2)	0.570(6)	0.999(3)