MLF Experimental Report	提出日 Date of Report 2013/08/11
課題番号 Project No. 2012A0047 実験課題名 Title of experiment Structural analysis of new-type layered oxides $Li_{1-y}(Mn_aNi_bCo_c)O_2$ with Li de-intercalation/intercalation 実験責任者名 Name of principal investigator Hironori KOBAYASHI 所属 Affiliation National Institute of Advanced Industrial Science and Technology (AIST)	装置責任者 Name of responsible person Toru Ishigaki 装置名 Name of Instrument/（BL No.） BL20 実施日 Date of Experiment 2012/6/6-8, 2012/10/24-25

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.

We used the layered oxides $Li_{1.20}Mn_{0.53}Ni_{0.17}Co_{0.10}O_2$ for neutron diffraction (ND) measurements.

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.

Neutron diffraction data was taken in the range of $0.5 < d < 5.3$ and at room temperature on a time-of-flight (TOF) neutron powder diffractometer of iMATERIA (BL20). The sample of ca. 3g was contained in a vanadium cell. Figure 1 shows the ND and XRD patterns for $Li_{1.20}Mn_{0.53}Ni_{0.17}Co_{0.10}O_2$. The super structure peaks around d = 4.3 Å observed in XRD data were not observed in ND data, as shown in Fig. 1. The structure was refined using the ND data, the initial model being that of $LiNi_{1/2}Mn_{1/2}O_2$ [1], with space group $R\bar{3}m$ and atomic positions Li1/Ni1 at 3*a* (0, 0, 0), Li2/Ni2/Co/Mn at 3*b* (0, 0, 0.5), and O at 6*c* (0, 0, *z*) where $z \sim 0.25$. We clarified that the 3*a* site is occupied by a small proportion of Ni and attempted to accurately determine both the distribution of cations at the 3*a* and 3*b* sites [1]. Therefore, the occupation parameters of Co and Mn at the 3*b* site were fixed and that of Ni2 at the 3*b* site was refined. The total occupancies of both the 3*b* sites containing Li2/Ni2/Co/Mn and the 3*a* sites containing Li1/Ni1 were constrained to be unity [Li2(*g*)+Ni2(*g*)+Co(*g*)+Mn(*g*)=1 and Li1(*g*)+Ni1(*g*)=1]. Further constraints were introduced such that the sum of the Li and Ni occupancies over the two sites was constrained to be that of the value corresponding to the composition [Li1(*g*)+Li2(*g*)=1.2] and [Ni1(*g*)+Ni2(*g*)=0.17], respectively. Figure 2 shows the observed, calculated, and difference diffraction profiles of $Li_{1.20}Mn_{0.53}Ni_{0.17}Co_{0.10}O_2$ after Rietveld refinements. We confirmed that our refined structural model was good fitting with relative low *R* value and clarified that the lattice parameters were a = 2.854940(7) Å and c = 14.25393(7) Å and occupation parameter of Ni1(*g*) was 0.0380(3).

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

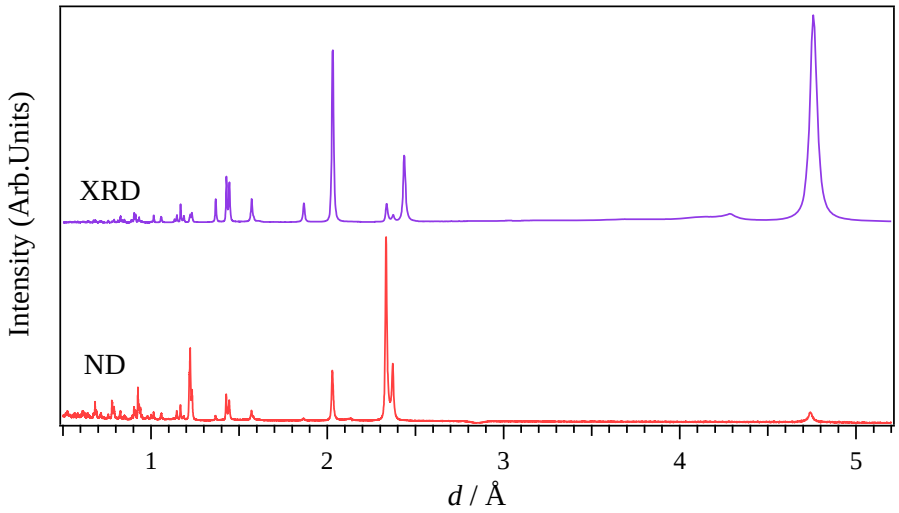

Figure 1　ND and XRD patterns for $Li_{1.20}Mn_{0.53}Ni_{0.17}Co_{0.10}O_2$

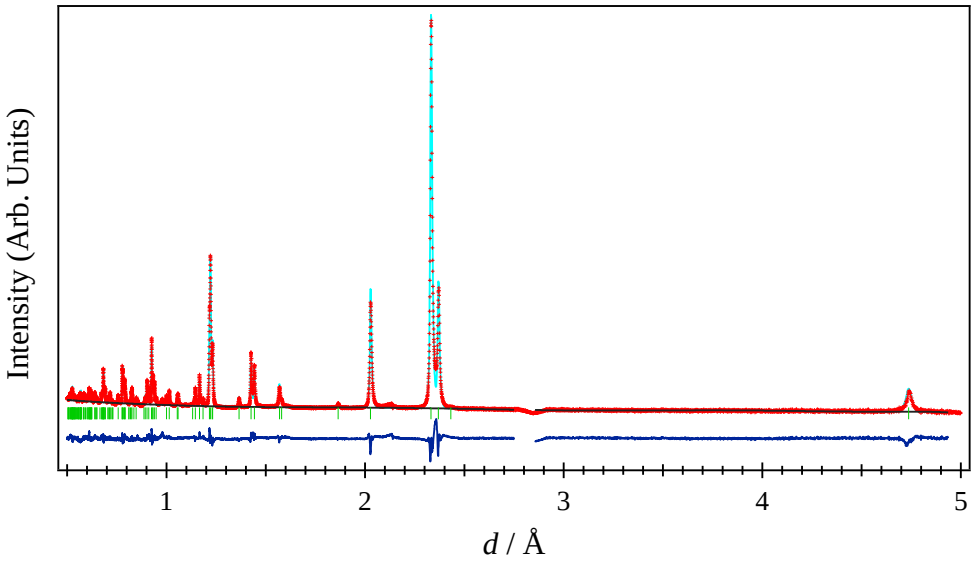

Figure 2　Observed, calculated, and difference diffraction profiles of $Li_{1.20}Mn_{0.53}Ni_{0.17}Co_{0.10}O_2$ after Rietveld refinements

Reference

[1]　H. Kobayashi, H. Sakaebe, H. Kageyama, K. Tatsumi, Y. Arachi, T. Kamiyama, J. Mater. Chem., 13 (2003) 590-595.