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 MLF Experimental Report	提出日 Date of Report 11/06/21
課題番号 Project No. 2010B0024 実験課題名 Title of experiment Crystal Structure Analyses of Li-Fe-Mn Silicates Synthesized by Soft Chemical Routes 実験責任者名 Name of principal investigator Shinichi Komaba 所属 Affiliation Tokyo University of Science	装置責任者 Name of responsible person Toru Ishigaki 装置名 Name of Instrument/(BL No.) iMATERIA/(BL No.20) 実施日 Date of Experiment Jan, 25 th , 2011

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.
Lithium iron silicate, $\text{Li}_2\text{FeSiO}_4$ Lithium iron-manganese silicate, $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_4$ Lithium manganese silicate, $\text{Li}_2\text{MnSiO}_4$

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.
<p>Lithium iron-manganese silicates, $\text{Li}_2\text{FeSiO}_4$, $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_4$, and $\text{Li}_2\text{MnSiO}_4$, have been prepared by a hydrothermal method at 150 °C. Time-of-Flight neutron scattering experiments of the samples have been carried out in iMATERIA at J-PARC. It is found that broad background profile for the all three samples, because adsorbed water at the materials surface cannot be eliminated by drying. The collected diffraction data have been analyzed after the background removal. Figure 1 compares synchrotron and neutron diffraction patterns of the samples. Since the iron and manganese have the similar X-ray scattering factors, the identical X-ray diffraction patterns are obtained in these samples. In contrast to the XRD, clear difference is noted in the neutron diffraction patterns, because the iron and manganese have quite different neutron scattering length. From the data of both XRD and ND, the structural details are summarized below; (1) the crystal structures can be assigned to the ordered $\beta\text{-Li}_3\text{PO}_4$-type structure. (2) $\text{Li}_2\text{FeSiO}_4$ has a non-negligible amount of twin defect as previously reported (N. Yabuuchi, S. Komaba et al., <i>Dalton Trans.</i>, 2011, 40, 1846-1848), whereas the $\text{Li}_2\text{MnSiO}_4$ crystallizes into the ordered $\beta\text{-Li}_3\text{PO}_4$-type structure without the twin defects. (3) A few percent of cation intermixing between Li / Me sites exists in all samples, which are not influenced by the difference in the</p>

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

transition metal species. From these results, we conclude that the difference in the role between the iron and manganese ions in the lithium silicates framework is mainly attributed to the formation of the twin defects. It is expected that the existence of defects would accelerate the lithium conduction in the bulk as the electrode materials for the rechargeable lithium batteries.

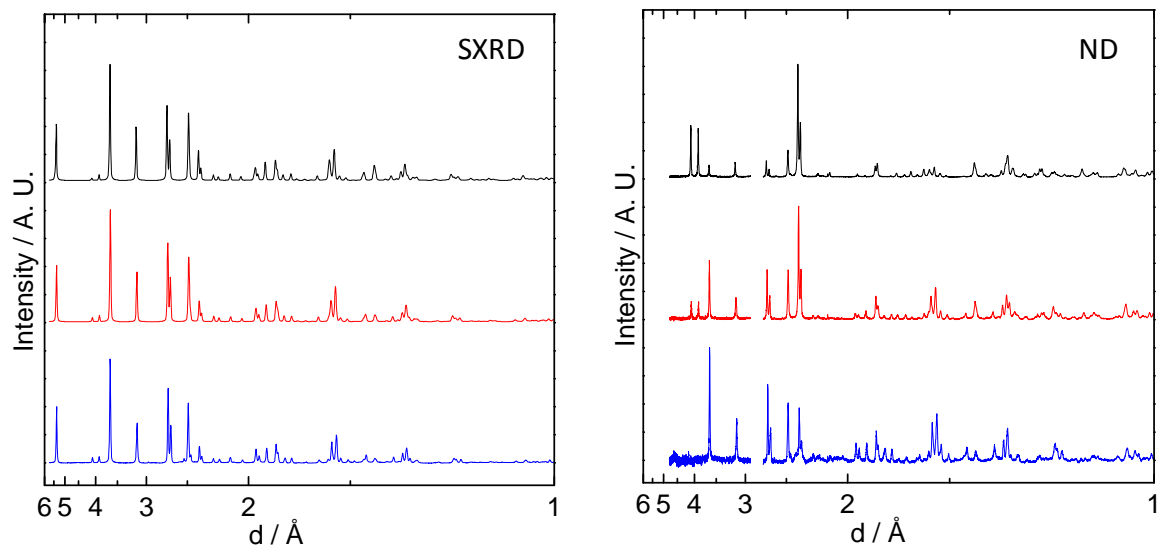


Figure 1 A comparison between synchrotron X-ray diffraction patterns and neutron diffraction patterns: (bottom) $\text{Li}_2\text{FeSiO}_4$, (middle) $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_4$, and (top) $\text{Li}_2\text{MnSiO}_4$. Neutron diffraction clearly reveals that iron and manganese ions similarly distribute in the rigid lithium silicate framework structure.

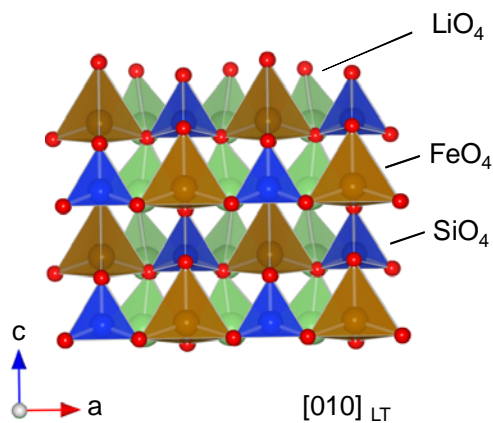


Figure 2 A schematic illustration of the low-temperature phase of Li_2MeO_4 (Me = Fe and / or Mn) synthesized by the hydrothermal method at 150°C , which is the related structure of the $\beta\text{-Li}_3\text{PO}_4$ -type structure. Though $\text{Li}_2\text{MnSiO}_4$ crystallizes into the defects-free phase, substitution of Fe for Mn results in the formation of the twin defects in the host structure.