Experimental Report

Proposal: **5-21-1075** **Council:** 10/2012

Title: Structural study of Nax(M,M')O2 layered oxides with M=Fe and M'=Mn

This proposal is resubmission of: 5-21-1069

Researh Area: Chemistry

Main proposer: **CARLIER Dany**

Experimental Team: MORTEMARD DE BOISSE Benoit

Local Contact: SUARD Emmanuelle

Samples: Nax(M,M')O2 (4 samples)

Instrument	Req. Days	All. Days	From	To
D2B	2	2	20/03/2013	22/03/2013

Abstract:

The study of the properties of sodium layered oxides started in the 1970s with the discovery of their electrochemical properties for sodium batteries. These systems were also studied for interesting physical properties: a high figure of merit for thermoelectric investigations for the P2-Na~0.7CoO2 phases and a superconductive behavior for the hydrated P2-Na0.35CoO2 phase.In our group, we recently reinvestigated the P2-NaxCoO2 and the P2-Na(Co,Mn)O2 phases as positive electrode in Na-batteries. We also focused on the Nax(Fe,Mn)O2 phases as they could exhibit good cycling properties and the advantage of being non-toxic and inexpensive. We recently synthesized some pure P2 and O3-Nax(Fe,Mn)O2 phases, using the combustion method, varying the Fe/Mn ratio and the Na content. To our knowledge, the P2-NaxMn2/3Fe1/3O2 and the Na-deficient O3 phases were not reported yet. In the opposite, the synthesis and the electrochemical properties of the P2 and O3-NaxFe1/2Mn1/2O2 with x=0.67 and 1 respectively, were very recently reported by Yabuuchi et al., but no detailed structural study was performed. Thus, neutron diffraction would be really helpful to investigate Na/vacancies or Mn/Fe ordering.

Structural study of $Na_x(M,M')O_2$ layered oxides with M=Fe and M'=Mn

Layered oxides A_xMO_2 (A=Li, Na and M=transition metal) were intensively studied during the 1980's for their electrochemical properties of reversible (de)intercalation of lithium/sodium. Then, for the next 20 years, most of the researches were focused on lithium batteries. Since the 2000's, the Na_xMO2 phases have been studied for potential replacement of the Li-ion technology for stationary batteries, where the prevailing parameters are the life time, the low price and the material availability. In this purpose, non-toxic and low-price $Na_xMn_{1-y}Fe_yO_2$ phases are being intensively studied by many laboratories [2-4] but these studies focus more on the electrochemical properties than on the structural ones. The important ionic radius of the Na^+ ion (0.76 Å) leads to a rich chemistry as several Na_xMO_2 polytypes (denominated as P2, P3 and O3) can be obtained.[1] In this structural designation, the letter P or O indicates the Prismatic or Octahedral environment of the alkali ion and the figure 2 or 3 gives the number of MO_2 slabs needed to describe the hexagonal cell. In order to get a better comprehension of these materials, ^{57}Fe Mössbauer spectroscopy was carried out on the O3-$Na_{0.82}Mn_{1/3}Fe_{2/3}O_2$ phase in our laboratory and highlighted two different Fe^{3+} environments, that could be explained by some local Mn/Fe ordering around the Fe^{3+} ion or a periodic ordering of the Mn and Fe ions in the MO_2 slabs. The very similar electronic configuration for the Mn^{3+}, Mn^{4+} and Fe^{3+} ions prevents any characterization of this possible ordering by X-Ray diffraction. On the contrary, it was possible to study this feature using Neutron Diffraction, as the bound coherent scattering lengths associated to the Mn and Fe atoms are very different (-3.75 fm and +9.93 fm respectively). Four phases showing different Mn : Fe ratios were studied: P2-$Na_{0.65}Mn_{2/3}Fe_{1/3}O_2$, P2-$Na_{0.67}Mn_{1/2}Fe_{1/2}O_2$, (O3+O'3)-$Na_{0.8}Mn_{1/2}Fe_{1/2}O_2$ and O3-$Na_{0.82}Mn_{1/3}Fe_{2/3}O_2$. The Neutron Diffraction patterns are shown on Fig. 1 along with the refinement of the structures, and corresponding cell and atomic parameters are reported on Table 1. As it can be seen in Fig. 1, all patterns are successfully fitted using the conventional space groups and no extra peaks are observed, i.e. we do not observe any evidence of a long-range ordering between the Mn and Fe cations, whatever their ratio is. The results concerning the O3-$Na_{0.82}Mn_{1/3}Fe_{2/3}O_2$ phase will be part of a soon to be submitted paper. The results concerning the other phases will be part of forthcoming publication(s).

[1] C. Delmas et al., Solid State Ionics 3/4 (1981) 165.
[2] N.Yabuuchi et al., Nature Materials 11 (2012) 512.
[3] J.S. Thorne et al., Journal of the Electrochemical Society 160 (2013) A361.
[4] B. Mortemard de Boisse et al., Journal of the Electrochemical Society 160 (2013) A569.

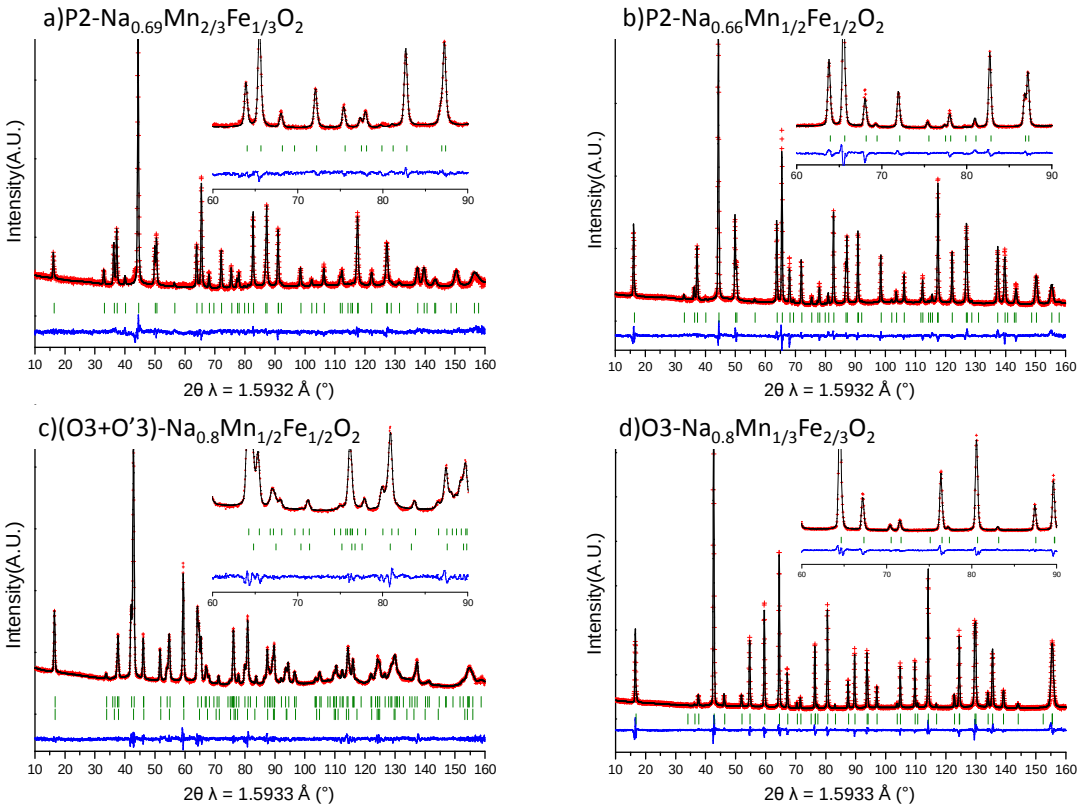

Figure 1: Observed and calculated Neutron Diffraction patterns for the (a) P2-$Na_{0.69}Mn_{2/3}Fe_{1/3}O_2$, (b) P2-$Na_{0.66}Mn_{1/2}Fe_{1/2}O_2$, (c) (O3+O'3)-$Na_{0.8}Mn_{1/2}Fe_{1/2}O_2$ and (d) O3-$Na_{0.8}Mn_{1/3}Fe_{2/3}O_2$ phases: (red) observed; (black) calculated; (blue) lower trace: difference plot; bar: Bragg reflections.

a) P2-$Na_{0.69}Mn_{2/3}Fe_{1/3}O_2$

Space group : $P6_3/mmc$
a = 2.93913(4) Å, c = 11.1648(3) Å from XRD
λ = 1.5932(2) Å

Atom	Site	Wyckoff positions			Occupancy	B_{iso}
Na_f	2b	0	0	1/4	0.25(2)	3.8(7)
Na_e	2d	2/3	1/3	1/4	0.44(2)	3.8(7)
Mn	2a	0	0	0	0.67	0.5
Fe	2a	0	0	0	0.33	0.5
O	4f	1/3	2/3	0.0909(4)	1	1.3(1)

Rwp = 3.49%; R_B = 3.88%

b) P2-$Na_{0.66}Mn_{1/2}Fe_{1/2}O_2$

Space group : $P6_3/mmc$
a = 2.93859(4) Å, c = 11.1886(2) Å from XRD
λ = 1.5932(2) Å

Atom	Site	Wyckoff positions			Occupancy	B_{iso}
Na_f	2b	0	0	1/4	0.23(1)	2.52(8)
Na_e	2d	2/3	1/3	1/4	0.43(1)	$=B_{iso}$ Na_e
Mn	2a	0	0	0	0.5	0.38(2)
Fe	2a	0	0	0	0.5	$=B_{iso}$ Mn
O	4f	1/3	2/3	0.0922(2)	1	1.05(5)

Rwp = 4.32%; R_B = 3.96%

c) (O3+O'3)-$Na_{0.8}Mn_{1/2}Fe_{1/2}O_2$ (Profile refinement only)

O3 phase
Space group : R-3m
a = 2.9731(6) Å, c = 16.377(6) Å from XRD
O'3 phase
Space group : C2/m
a = 5.2176(8) Å, b = 2.9453(4) Å, c = 5.752(2) Å et β = 108.224°(4) from XRD
λ = 1.5933(3) A

Rwp = 2.93%

d) O3-$Na_{0.8}Mn_{1/3}Fe_{2/3}O_2$

Space group : R-3m
a = 2.98045(6) Å, c = 16.3264(5) Å from XRD
λ = 1.5933(3) A

Atom	Site	Wyckoff positions			Occupancy	B_{iso}
Na	3b	0	0	1/2	0.80(2)	1.5(1)
Mn	3a	0	0	0	0.33	$=B_{iso}$ Fe
Fe	3a	0	0	0	0.67	0.32(5)
O	6c	0	0	0.2691(1)	1	0.83(3)

Rwp = 4.72%, R_B = 2.20%

Table 1: Structural parameters obtained from the refinements by the Rietveld method for (a) P2-$Na_{0.69}Mn_{2/3}Fe_{1/3}O_2$, (b) P2-$Na_{0.66}Mn_{1/2}Fe_{1/2}O_2$, and (d) the O3-$Na_{0.8}Mn_{1/3}Fe_{2/3}O_2$. For the (c) (O3+O'3)-$Na_{0.8}Mn_{1/2}Fe_{1/2}O_2$ phase, the refinement was performed using LeBail method.