

Crystal Structure and Electrochemical Properties of $\text{Li}_2\text{-xNa}_x\text{M}[\text{PO}_4]\text{F}$ ($M = \text{Mn, Fe, Co, Ni, and Mg}$)

Hamdi Ben Yahia, Masahiro Shikano, Hikari Sakaebe, Shinji Koike, Mitsuharu Tabuchi, Kuniaki Tatsumi, Hironori Kobayashi.

Research Institute for Ubiquitous Energy Devices, AIST, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan.

e-mail: benyahia.hamdi@aist.go.jp

During the last decade, the $(\text{Li,Na})_2\text{M}[\text{PO}_4]\text{F}$ ($M = \text{Mn-Ni}$) fluorophosphates have attracted much attention due to their potential use as positive electrode material in either Li-ion or Na-ion cells. Recently, our research group started systematic studies on the crystal/electronic-structures and the magnetic/electrochemical properties of the intermediate phases $\text{LiNaM}[\text{PO}_4]\text{F}$ (Fig. 1).¹⁻⁵

Table I. Crystallographic data of our new compounds.

Formula	S. G.	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	Ref.
$\text{Li}_{1.3}\text{Na}_{0.7}\text{Ni}[\text{PO}_4]\text{F}$	<i>Pnma</i>	10.7874	6.2196	11.1780		749.97	1
$\text{LiNaCo}[\text{PO}_4]\text{F}$	<i>Pnma</i>	10.9334	6.2934	11.3556		781.36	2
$\text{LiNaFe}[\text{PO}_4]\text{F}$	<i>Pnma</i>	10.9851	6.3686	11.4343		799.94	3
$\text{Li}_{1.65}\text{Na}_{0.35}\text{Fe}[\text{PO}_4]\text{F}$	<i>Pnma</i>	10.5108	6.4996	11.0504		754.92	4
$\text{LiNaFe}_{0.75}\text{Mn}_{0.25}[\text{PO}_4]\text{F}$	<i>Pnma</i>	10.9719	6.3528	11.4532		798.31	5
$\text{Li}_2\text{Mg}[\text{PO}_4]\text{F}$	<i>Pnma</i>	10.5773	6.2378	10.9297		721.10	*
$\text{LiNaMg}[\text{PO}_4]\text{F}$	$P2_1/c$	6.8179	11.2234	5.0222	90.00	384.30	*
$\text{LiNaNi}[\text{PO}_4]\text{F}$	$P2_1/c$	6.7720	11.1540	5.0210	90.00	379.26	1
$\text{Na}_2\text{Mn}[\text{PO}_4]\text{F}$ -new	$P2_1/c$	6.8654	11.8753	5.30702	90.00	432.70	*
$\text{Na}_2\text{Ni}[\text{PO}_4]\text{F}$	$P2_1/c$	13.4581	5.1991	13.6978	120.58	825.14	1

*: to be published

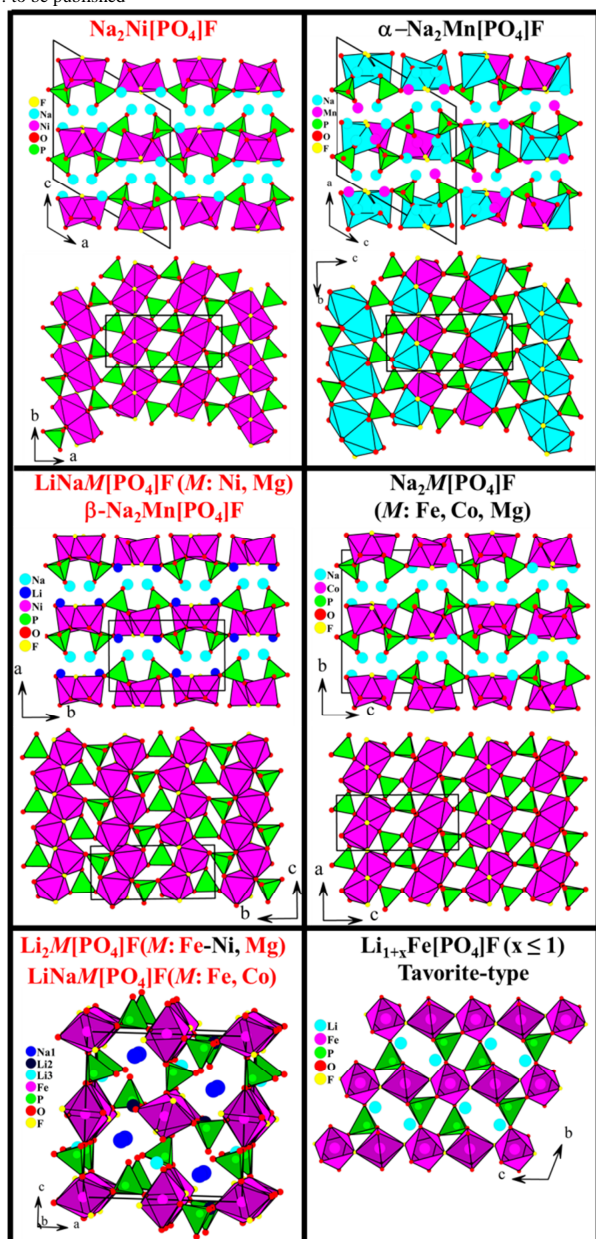


Fig. 1. Crystal structures of the $\text{A}_2\text{M}[\text{PO}_4]\text{F}$ compounds ($A = \text{Li, Na}$ and $M = \text{Mn-Ni, Mg}$). Those highlighted in red have been discovered in our research group [1-5].

$\text{LiNaFe}[\text{PO}_4]\text{F}$ ($M = \text{Fe}$), is the most attractive because of its electrochemical activity as an electrode material. As shown in Fig. 2, three oxidation peaks at 3.6 V, 3.9 V, and 4.37 V appear on the cycle voltammogram and they correspond to $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couples because the alkali metal atoms occupy three different crystallographic sites. To our knowledge, the 4.37 V is the highest value observed for $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. It does not correspond to $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox couple, since the ^{57}Fe Mössbauer data collected at 4.5 V shows the presence of 90% of Fe^{3+} and 10% of Fe^{2+} .

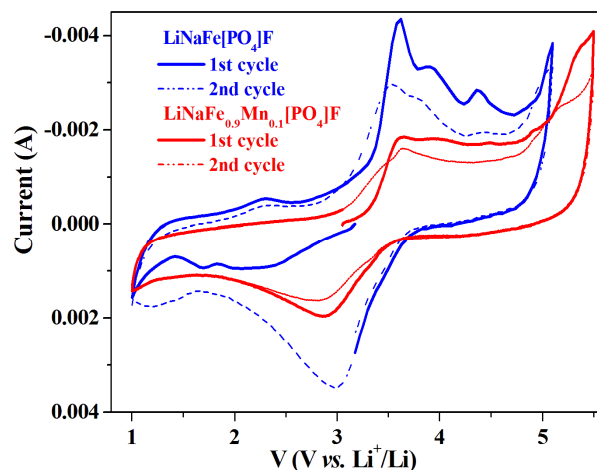


Fig. 2. Cyclic voltammogram curves of $\text{LiNaFe}[\text{PO}_4]\text{F}$ and $\text{LiNaFe}_{0.9}\text{Mn}_{0.1}[\text{PO}_4]\text{F}$ recorded at room temperature, between 1.0 V and 5.1 or 5.5 V vs. Li^+/Li , with a scanning rate of 5 mV/s.

The new compounds $\text{LiNaFe}_{1-x}\text{Mn}_x[\text{PO}_4]\text{F}$ ($x \leq 1/4$, $M = \text{Fe}_{1-x}\text{Mn}_x$) synthesized by solid state reaction route are isostructural to $\text{LiNaFe}[\text{PO}_4]\text{F}$ however, strong differences in the electrochemical behaviors have been observed. Indeed, the substitution of Mn for Fe induces a severe decrease of the electrochemical performances (Fig. 2), that is, three peaks of $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple drastically decrease. This behavior is attributed to the electrochemically inactive manganese.

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