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$\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3$: First Alluaudite-type Iron Phosphate Containing only Li^+ as Alkaline Ions

Khiem Trad ^{a,b}, Aurore Castets ^a, Alain Wattiaux ^a, Claude Delmas ^a, Mongi Ben Amara ^b, Dany Carlier ^{a*}

^a CNRS, Université de Bordeaux I, ICMCB, 87 avenue du Dr. A. Schweitzer, Pessac, F-33608, France.

^b UR Matériaux Inorganiques, Faculté des Sciences, Université de Monastir, 5019- Monastir, Tunisie.

*To whom correspondence should be addressed.

E-mail: dany.carlier@icmcb.cnrs.fr

Abstract:

A new iron phosphate $\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3$ has been prepared by the flux method and its structure was characterized from single crystal X-ray diffraction data. It crystallizes as an alluaudite type structure, characterized by the $A(2)A(2)'A(1)A(1)'A(1)''M(1)M(2)_2(\text{PO}_4)_3$ general formula with $a = 12.002(9) \text{ \AA}$, $b = 12.509(9) \text{ \AA}$, $c = 6.404(7) \text{ \AA}$, $\beta = 115.07(7)^\circ$ in the monoclinic $C2/c$ space group. The 3D framework consists of infinite chains of edge-sharing $M(2)_2\text{O}_{10}$ dimers and $M(1)\text{O}_6$ octahedra connected by phosphate tetrahedra leading to two sets of hexagonal tunnels. The Li^+ and Mn^{2+} ions partially occupy one of them, the other tunnel being empty. The Mössbauer spectroscopy confirmed the occurrence of only Fe^{3+} ions in octahedral environment. Electrochemical cycling tests in Li cells were performed using $\text{Li}_{0.75}\text{Mn}^{\text{II}}_{1.50}\text{Fe}^{\text{III}}_{1.75}(\text{PO}_4)_3$ powder as electrode material. Only a small amount of Li^+ ions can be reversibility deintercalated/intercalated corresponding to a capacity as low as 30 mAh/g with a 3.2 V average voltage. Moreover, a strong polarization due to low electronic and ionic conductivities is observed. The presence of Mn^{2+} ions in the same tunnel as Li^+ probably hinders a good Li^+ ionic diffusion.

1. Introduction:

Iron phosphates are among the most studied phosphate materials due to their complex and rich structural chemistry owing to the possible +2/+3 mixed valence of iron and its tendency to form various complex frameworks with the phosphate groups [1]. The interest devoted to these materials has been accentuated since the discovery, by Padhi et al., in 1997 of LiFePO_4 as a promising electrode material for Li-ion batteries [2]. Compared to the previously used LiCoO_2 oxide, this material has the advantages of low cost, low toxicity, high thermal stability, high capacity (170 mAh.g^{-1}), good cycling stability, and a flat discharge plateau (at 3.4 V). Besides LiFePO_4 , other iron phosphates were tested as electrode materials for rechargeable batteries [3]. Among polyanionic positive electrode materials, the alluaudite-type compounds are attracting much attention for sodium and/or lithium batteries due to their interesting open framework. Some phosphates phases were investigated as $\text{Li}_x\text{Na}_{2-x}\text{FeMn}_2(\text{PO}_4)_3$ [4] $\text{NaMnFe}_2(\text{PO}_4)_3$ [5], $\text{Li}_x\text{Na}_{(1-x)}\text{MnFe}_2(\text{PO}_4)_3$ [6], $\text{Li}_{0.47}\text{Na}_{0.2}\text{FePO}_4$ [7], $\text{Na}_2\text{Fe}_{1.96}\text{V}_{0.96}(\text{PO}_4)_3$ [8] and $\text{Na}_{1.702}\text{Fe}_3(\text{PO}_4)_3$ [9]. Recently the group of Yamada showed very high operating voltages for $\text{Na}_{2+2x}\text{Fe}_{2-x}(\text{SO}_4)_3$ sulfates compounds in sodium batteries [10-12]. Subsequently, analogous alluaudite-type sulfates Mn-based [13] and Co-based [14] were also studied as positive electrodes for Na-ion batteries. Very recently, a molybdate compound has also been reported: $\text{Na}_{2.67}\text{Mn}_{1.67}(\text{MoO}_4)_3$ as candidate for Na-ion batteries [15]. Although the alluaudite family encloses a large number of isostructural phosphates and arsenates either natural or synthetic, no alluaudite type materials containing only Li^+ ions as alkaline ions have been reported so far to the best of our knowledge. During our investigation of the $\text{Li}_x\text{Na}_{(1-x)}\text{MnFe}_2(\text{PO}_4)_3$ solid solution, no pure phase with x higher than 0.75 could be prepared [6]. K. Kang and co-workers, actually aimed to prepared an alluaudite-type LiFePO_4 , by ion-exchange from the analogous Na-alluaudite, but finally synthetized $\text{Li}_{0.47}\text{Na}_{0.2}\text{FePO}_4$ with remaining Na^+ in in the lattice acting as pillars. Stronger ion-exchange conditions resulted in the collapse of the structure [7].

The alluaudite structure has been first reported by Moore who proposed the $X(2)X(1)M(1)M(2)_2(PO_4)_3$ structural formula where $X(2)$, $X(1)$, $M(1)$ and $M(2)$ are cationic sites arranged in decreasing size [16]. Hatert et al., based on detailed structural refinements reported that $X(1)$ has three distinct positions labeled $A(1)$, $A(1)'$ and $A(1)''$, in the tunnel 1 and that $X(2)$ has two distinct positions labeled $A(2)$ and $A(2)'$ in tunnel 2 [17]. The structural formula of Moore was then reformulated as $A(2)A(2)'A(1)A(1)'A(1)''M(1)M(2)_2(PO_4)_3$. The structure can be described as a 3D skeleton structure $[M(1)M(2)_2(PO_4)_3]$ with two types of tunnels parallel to the c direction as shown in Figure 1a. All the existing alluaudite phases contain atoms only on $A(1)$, $A(2)'$, $M(1)$ and $M(2)$ sites [18-27] except for the following three phases: (i) $Cu_{1.35}Fe_3(PO_4)_3$ in which copper is distributed on the $A(2)$, $A(1)'$, $A(1)''$ sites and iron is located at the $M(1)$ and $M(2)$ sites [28], (ii) $K_{0.53}Mn_{2.37}Fe_{1.24}(PO_4)_3$ in which potassium occupies the $A(2)'$ site, manganese occupies $A(1)''$ and $M(1)$, it also shares the $M(2)$ site with iron [29] (iii) the solid solution $Li_xNa_{(1-x)}MnFe_2(PO_4)_3$ in which lithium and sodium are distributed over the $A(1)$ and $A(1)'$ sites while manganese and iron are distributed over the $M(1)$ and $M(2)$ sites [6].

In this paper, we report the synthesis of a new lithium iron phosphate $Li_{0.75}Mn_{1.50}Fe_{1.75}(PO_4)_3$ with an alluaudite-type structure prepared as single crystals by a flux method. The structural characterization was performed by single crystal X-ray diffraction. Then by classical solid state chemistry this material was obtained as a powder for further characterization (Mössbauer spectroscopy, 7Li MAS NMR). The electrochemical properties of this material were also studied vs Li.

2. Experimental

Single crystals of the title phase were isolated during an attempt to grow $LiMnFe_2(PO_4)_3$ in a flux of lithium dimolybdate $Li_2Mo_2O_7$. A starting mixture of $LiNO_3$, MnO , $Fe(NO_3)_3 \cdot 9H_2O$,

$(\text{NH}_4)_2\text{HPO}_4$ and MoO_3 corresponding to a molar ratio of $\text{LiMnFe}_2(\text{PO}_4)_3 : \text{Li}_2\text{Mo}_2\text{O}_7 = 2:1$ was dissolved in nitric acid, then the resulting solution was evaporated by heating at 353 K. The obtained dry residue was ground in an agate mortar, and then progressively heated in an open platinum crucible up to 873 K to expel NH_3 and CO_2 . The sample was then reground, melted for 1h at 1173 K and subsequently cooled slowly down to room temperature at $10^\circ\text{C}\cdot\text{h}^{-1}$ rate. Brown and hexagonally shaped crystals were obtained by washing the whole product with hot water in order to dissolve the flux.

A single crystal of dimensions $0.06 \times 0.07 \times 0.16$ mm was chosen for the structure determination. Data were collected with an Enraf-Nonius CAD4 diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). The unit cell parameters (monoclinic) and the orientation matrix were determined from a least squares fit of 25 intense reflections in the range $9.72^\circ \leq \theta \leq 14.74^\circ$. Among a total of 1269 unique reflections collected using the $(\omega-2\theta)$ scan mode ($2\theta_{\text{max}} = 29.96^\circ$), only 1180 were considered as observed according to the statistic criterion $[F_o^2 > 4\sigma(F_o^2)]$. No detectable decay was observed during the data collection, according to the intensities of two standard reflections measured every two hours.

The data were corrected for Lorentz and polarization effects, and for the absorption by ψ -Scan ($T_{\text{min,max}}: 0.57, 0.72$).

A pure powder sample with a composition close to the $\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3$ single crystals was synthesized by the conventional solid state reaction starting from a stoichiometric mixture of LiNO_3 , MnO , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$. After an initial treatment, similar to that undertaken for the synthesis of the single crystals until 873 K, the sample was subjected to final calcinations at 1113 K for 48 h with intervening grinding. A light brown powder was obtained by quenching in air. Its purity was checked from the examination of its X-ray powder diagram (Fig. 2) collected in the range $5^\circ \leq 2\theta \leq 80^\circ$ on a PANalytical diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). This pattern was refined by the Full profile matching, using the

Fullprof program [30]. The refined parameters $a = 12.004(1) \text{ \AA}$, $b = 12.484(1) \text{ \AA}$, $c = 6.389(1) \text{ \AA}$ and $\beta = 115.00(1)^\circ$ are in a good agreement with those obtained from single crystal X-ray data. The ICP measurements lead to the following composition: $\text{Li}_{0.8(1)}\text{Mn}_{1.4(1)}\text{Fe}_{1.8(1)}(\text{PO}_4)_3$. The particles size was analyzed by Scanning Electron Microscopy : the aggregates size ranges between 10 and 60 μm in diameter and consisted of 2 to 5 μm primary particles.

^{57}Fe Mössbauer measurements were performed using a constant acceleration Halder-type spectrometer operating in transmission geometry with a room temperature ^{57}Co source (Rh matrix). The velocity scale was calibrated according to the ^{57}Fe Mössbauer spectrum of a pure $\alpha\text{-Fe}^0$ foil recorded at room temperature. The polycrystalline absorbers were prepared in order to contain about 10 mg/cm^2 of iron and thus, to avoid saturation effects. The refinement of Mössbauer hyperfine parameters (δ isomer shift, Δ quadrupole splitting, Γ signal linewidth and relative areas) was performed using both homemade programs and the WinNormos software. Distributions of hyperfine parameters (quadrupole splitting) have been considered for overlapped components presenting apparent linewidth higher than 0.30 mm/s, following the method described by Hesse and Rübartsch [31].].

^7Li MAS NMR spectrum was recorded at 38 MHz respectively using a Bruker Avance solid state spectrometer with a Wide Bore Bruker magnet activated to 2.35 T. The spinning speed was varied up to 30 kHz using a standard 2.5 mm Bruker MAS probe. Single pulse and Hahn echo type experiments at 30 kHz (one rotor period as echo delay) were used with a 1.2 μs 90° pulse. The spectra were referenced to a 1 M aqueous solution of LiCl. The recycle time used for ^7Li NMR, $D_0 = 1 \text{ s}$, is long enough to avoid T_1 saturation effects for the studied nuclei in a paramagnetic phase.

The positive electrode was made of 80% active material, 15% carbon black conductive additive and 5% PTFE binder. The mixture was homogenized by ball milling for 15 min then dried under vacuum at 100°C overnight. Into an argon filled glove box, the mixture was finally

crushed into a thin sheet and then was cut into a disk (14 mm diameter) and Swagelok® type cells were assembled. Metallic lithium was used as negative electrode and a 1 M LiPF₆ solution in a mixture of propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1:3)) was used as electrolyte. Two Celgard® 2400 separators and a Viledon® polypropylene foil were used as separators. The electrochemical tests were carried out in the galvanostatic mode with a Bio-logic VMP system using a C/50 cycling rate.

3. Results and discussion

3.1. Structural characterization

The structure of the single crystal of Li_{0.75}Mn_{1.50}Fe_{1.75}(PO₄)₃ was solved by direct methods [32] and subsequently refined on F² by full matrix least squares techniques [33] using the C2/c space group. Crystallographic data and structural refinement conditions are summarized in Table I. All of the atoms were refined with anisotropic thermal parameters leading to $R_1 = 0.028$ and $wR_2 = 0.074$ and to the atomic coordinates given in Table II. Relevant interatomic distances are listed in Table III. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD- 434283.

The crystal data for Li_{0.75}Mn_{1.50}Fe_{1.75}(PO₄)₃ (i.e: Li_{3/4}Mn_{3/2}Fe_{7/4}(PO₄)₃) evidences its belonging to the alluaudite compounds characterized by the A(2)A(2)'A(1)A(1)'A(1)''M(1)M(2)₂(PO₄)₃ general formula [17]. The site occupancies indicate the following cationic distribution: 0.75 Li in A(1)' and 0.25 Mn in A(1)''; 1 Mn on M(1) and [0.25 Mn + 1.75 Fe] in M(2). The presence of lithium in the A(1)' site has already been observed in the solid solution Li_xNa_(1-x)MnFe₂(PO₄)₃ [6] and is in good agreement with the site stability study performed by DFT and DFT+U calculations on the LiMnFe₂(PO₄)₃ phase [6].

A polyhedral view of the structure as projected along the $[0\ 0\ 1]$ direction is shown Figure 1a. The structural units are $M(2)_2O_{10}$ dimers of edge-sharing $M(2)O_6$ octahedra, $M(1)O_6$ octahedra and PO_4 tetrahedra. The $M(2)_2O_{10}$ units share opposite edges with the $M(1)O_6$ octahedra to form zig-zag chains parallel to the $[1\ 0\ \bar{1}]$ direction (Fig. 1b). Such chains are connected by means of the phosphate groups to form a three-dimensional framework. This skeleton forms two sets of hexagonal tunnels at $(0, 0, z)$ and $(\frac{1}{2}, 0, z)$ respectively, in which the A sites are located.

The mean distance $\langle M(1)-O \rangle = 2.207(3)\ \text{\AA}$ is significantly larger than that $\langle M(2)-O \rangle = 2.045(3)\ \text{\AA}$ (Table III), which is in accordance with the exclusive presence of the Mn^{2+} ions in the M(1) site and the statistical occupancy of M(2) sites by the Mn^{2+} and Fe^{3+} ions. The octahedral environments of the M(1) and M(2) sites are highly distorted. In fact, in the M(1) site, the M-O distances range from 2.188(2) to 2.240(2) $\text{\AA}$. The M(2) site exhibits an extra-long M-O bond of 2.209(2) $\text{\AA}$, compared to the others (from 1.927(3) to 2.057(3) $\text{\AA}$) (Fig. 3a). Thus, its environment could be considered as a square pyramid (5+1 coordination). A similar behavior was previously observed in our study on $Na_{1-x}Li_xMnFe_2(PO_4)_3$ [6]. The average $\langle M(1)-O \rangle = 2.207(3)\ \text{\AA}$ distance is comparable to that (2.241(4) $\text{\AA}$) observed for the fully occupied M(1) site by Mn^{2+} in the alluaudite phosphate $Ag_2Mn_2Fe(PO_4)_3$ [24].

As usually observed in the alluaudite-type phosphates, the two distinct PO_4 tetrahedra are slightly distorted as indicated by the P-O distances between 1.522(2) and 1.552(2) $\text{\AA}$, leading to an mean values of 1.541 $\text{\AA}$ for P(1) and 1.537 $\text{\AA}$ for P(2), close to that calculated by Baur for the anhydrous monophosphates [34].

The A(1)' and A(1)'' sites, located in the large tunnels of the alluaudite structure are partially occupied by Li^+ and Mn^{2+} ions, respectively (Fig. 3b). These sites which reside in the tunnel at $(\frac{1}{2}, 0, z)$ share one face; therefore, they cannot be occupied simultaneously due to their short separation of 1.265 $\text{\AA}$. Their oxygen environments were determined using the procedure

of Donnay and Allman [35] with the ionic radii of Shannon [36]. Accordingly, the environment of A(1)' consists of four oxygen atoms with A(1)'-O distances ranging from 1.85(3) to 2.11(4) Å close to those observed for the A(1)' site in the alluaudite phosphates $\text{Li}_{0.5}\text{Na}_{0.5}\text{MnFe}_2(\text{PO}_4)_3$ and $\text{Li}_{0.75}\text{Na}_{0.25}\text{MnFe}_2(\text{PO}_4)_3$ (from 1.81(5) to 2.10(1) Å). The environment of Mn^{2+} ions within the A(1)'' site consists of five O atoms with A(1)''-O distances ranging from 2.216(5) to 2.371(5) Å. This environment of A(1)'' agree with that reported in $\text{K}_{0.53}\text{Mn}_{2.37}\text{Fe}_{1.24}(\text{PO}_4)_3$ in which Mn-O distances range from 2.253(4) to 2.400(4) Å.

3.2. Mössbauer study

The Mössbauer spectrum (Fig. 4) exhibits two resonance absorption lines with large line widths. An initial refinement using Lorentzian profile lines indicated a single paramagnetic doublet assigned to a unique non symmetry equivalent iron site in accordance with the crystallographic study. The derived isomer shift and quadrupolar splitting are typical of Fe^{3+} ions in a distorted octahedral field [37]. Even so, the obtained linewidth at half maximum was excessively large ($\Gamma = 0.340(2) \text{ mm.s}^{-1}$) and this result was taken as an indication of the presence of a quadrupolar splitting distribution which may be associated with a significant disorder resulting from the statistical distribution of Mn^{2+} and Fe^{3+} in the M(2) site. Moreover, as previously mentioned, these sites are strongly distorted (Table III and Fig.3a) and they share also an oxygen with the A(1)' and A(1)'' sites which can be occupied either by a Li^+ and a Mn^{2+} . Accordingly, a second fit of the spectrum on the basis of a distribution of quadrupolar splitting was undertaken using a fixed linewidth of 0.20 mm.s^{-1} . The isomer shift $\delta = 0.425 \text{ mm.s}^{-1}$ is close to those 0.431 and 0.433 mm.s^{-1} reported for octahedral Fe^{3+} ions in $\text{Na}_2\text{Ca}_{0.5}\text{Fe}_2(\text{PO}_4)_3$ and $\text{Na}_{1.25}\text{Mg}_{1.10}\text{Fe}_{1.90}(\text{PO}_4)_3$, respectively [22, 23]. The mean value of the quadrupolar splitting $\langle \Delta^* \rangle = 0.62 (2) \text{ mm.s}^{-1}$ indicates that the Fe^{3+} site is strongly distorted in agreement with the deformation of the M(2)O₆ octahedron determined by the structural refinement (Fig. 3a). The

quadrupolar splitting values are widely distributed ($0.20 < \Delta < 1.00$ mm/s) confirming the strong disorder in the M(2) environment mentioned above.

3.3. ^7Li NMR study

The ^7Li MAS NMR spectrum (Fig. 5a) exhibits only one isotropic resonance located at +79 ppm. From the large shift observed, one can conclude that the Fermi contact interaction predominates: i.e, the shift is mainly due the presence of electronic spin density on the Li nucleus, typically observed for paramagnetic compounds [38-39]. However, one could have expected to observe several distinct Li signals or a distribution of signals, since the A'(1) lithium site can be surrounded differently by Fe^{3+} and Mn^{2+} paramagnetic ions distributed over the M(1) and M(2) sites (Figure 5b for Li paramagnetic environment). However, these two ions exhibit the same electronic spin state ($t_{2g}^3 e_g^2$), and the occupation of M(1) and M(2) sites by Fe^{3+} or Mn^{2+} can lead to a similar spin transfer on adjacent Li nucleus thus leading to similar shifts. The Mn^{2+} ions in A(1)'' sites could have led to additional different spin transfer its neighboring Li, but since the A(1)' and A(1)'' sites are too close to allow occupancy of adjacent sites, the Li ions in A(1)' sites have no neighboring Mn^{2+} in A(1)'' (Fig. 3b). The hypothesis of the observation of a single Li signal due to rapid exchange at the NMR timescale between the different Li sites was also considered but not further considered since the global lineshape (extension of the spinning side bands) remains large.

3.4. Electrochemical properties

The electrochemical properties of the $\text{Li}_{0.75}\text{Mn}^{\text{II}}_{1.50}\text{Fe}^{\text{III}}_{1.75}(\text{PO}_4)_3$ phase were studied as positive electrode in lithium batteries using a slow C/50 rate, similar to the protocol used in Ref. [6]. The corresponding galvanostatic cycling curve is shown in Fig. 6. Starting with a charge, a very

small amount of Li^+ ions can be removed from the lattice, therefore associated to the oxidation of the Mn^{2+} ions at rather high voltage. The 4.5 V limit voltage is rapidly reached due to a strong polarization of the cell. During the following discharge, lithium is reintercalated up to the composition $\text{Li}_{1.15}$. Therefore Mn^{3+} are reduced back to Mn^{2+} and moreover some Fe^{3+} ions are reduced to Fe^{2+} . As a conclusion, a very limited amount of Li^+ ions can be reversibility deintercalated/intercalated between 1.5 and 4.5 V versus Li^+/Li , involving the two $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couples, what corresponds to a capacity as low as around 30 mAh/g. Similar low capacities were obtained for the most Li-rich compounds in the $\text{Li}_x\text{Na}_{(1-x)}\text{MnFe}_2(\text{PO}_4)_3$ series [6].

The very high polarization observed shows that the electronic and/or ionic transfers are difficult in this structure which contains unconnected chains either for electron and ionic transfers. Moreover, within the M(2)-M(1) chains, the alternation of Mn and Fe hinders a good hopping phenomenon due to the large difference in their redox couple. Concerning the Li^+ ionic diffusion, it may be difficult as Li ions are present only in the tunnel 1 (A(1)' site) isolated from each other and a significant amount of Mn^{2+} ions (0.13) in the A(1)'' also in tunnel 1 probably hinder the diffusion (Fig. 3b). This explains why the reversible capacity is so small and the polarization so large. In the case of LiFePO_4 the presence of few percent of iron in the tunnels (few percent of antisite defect) limits strongly the electrochemical performances [40]. The average voltage around ~ 3.2 V that is lower than the one observed for the olivine LiFePO_4 (~ 3.5 V [3]) for a same main active redox couple $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ and the polarization observed is really strong due to bad electronic and ionic conductivities and will prevent the material to be further used as positive electrode on Li-ion batteries.

4. Conclusion

$\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3$ has been prepared and exhibits an alluaudite structure consisted by chains of edge-sharing $M(2)_2\text{O}_{10}$ [$M(2) = 0.25 \text{ Mn} + 1.75 \text{ Fe}$] and MnO_6 octahedra that run along the $[1\ 0\ \bar{1}]$ direction. Such chains are connected by means of the PO_4 tetrahedra and the resulting 3D framework delimits two sets of hexagonal tunnels, the first at $(0, 0, z)$ is empty and the second $(\frac{1}{2}, 0, z)$ is partially occupied by the Li^+ and Mn^{2+} ions. Mössbauer spectroscopy gave accurate information about the distribution of iron and its local environment. The presence, in this phase, of large tunnels partially occupied by Li^+ ions, shows that it is of interest to know whether it can be a candidate as a positive-electrode material for lithium batteries. Electrochemical cycling tests using $\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3$ as positive electrode in Li batteries were performed: the strong polarization due to poor electronic and ionic conductivities will prevent the application of the material in Li-ion batteries.

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Table I. Crystal data and structure refinement parameters for $\text{Li}_{3/4}\text{Mn}_{3/2}\text{Fe}_{7/4}(\text{PO}_4)_3$
 $(\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3)$

Crystal data	
Formula unit	$\text{Li}_{3/4}\text{Mn}_{3/2}\text{Fe}_{7/4}(\text{PO}_4)_3$ ($\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3$)
Crystal system	Monoclinic
Space Group	$C 2/c$
$a / \text{\AA}$	12.002(5)
$b / \text{\AA}$	12.509(9)
$c / \text{\AA}$	6.404(7)
$\beta / ^\circ$	115.07(4)
$V / \text{\AA}^3$	870.9(12)
Z	4
$D_{\text{cal}} / \text{g.cm}^{-3}$	3.587
Intensity measurements	
Crystal dimensions/mm	$0.07 \times 0.07 \times 0.14$
Apparatus	CAD4 (Enraf- Nonius)
Wavelength	$\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$
Monochromator	Graphite
μ / mm^{-1}	5.631
Scan mode	$\omega/2\theta$
Scan speed	variable
$2\theta_{\text{max}} / ^\circ$	60
Background measuring time	$t_{\text{max}}/2$
Unique reflections, R_{int}	1269, 0.031
Retained reflections [$F_o^2 > 4 \sigma(F_o^2)$]	1180
Indices	$-16 \leq h \leq 15, -1 \leq k \leq 17, -1 \leq l \leq 8$
F(000)	905
Structure solution and refinement	
Intensities correction	Lorentz- polarization
Resolution method	Direct
Absorption correction	Ψ -scan
$T_{\text{max/min}}$	0.67, 0.53
Agreement factors	$R_1 = 0.026, wR_2 = 0.068, S = 1.127$ $[F_o^2 > 4 \sigma(F_o^2)]$
Number of parameters	102
Extinction parameter	0.0065(5)
$(\Delta\rho)_{\text{max, min}} / \text{e. \AA}^{-3}$	0.602, -1.065
Weighting scheme	$W = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 4.121P]$ where $P = [\max(F_o^2, 0) + 2Fc^2]/3$

Table II. Atomic coordinates and equivalent isotropic displacement parameters in Å² (ESDs in parentheses).

Atom	Site	Wyckoff	Occupation	x/a	y/b	z/c	$U_{\text{(eq)}}^a$
Li	A(1)'	8f	3/8	0.510(4)	0.003(2)	0.303(5)	0.05 (1)
Mn(1)	A(1)''	8f	1/8	0.5239(4)	-0.0016(3)	0.4631(8)	0.021(1)
Mn	M(1)	4e	1	0	0.2638(1)	¼	0.010(1)
(Mn, Fe)	M(2)	8f	1/8Mn + 7/8Fe	0.2190(1)	0.1521(1)	0.1304(1)	0.007(1)
P(1)	P	4e	1	0	0.2886(1)	¾	0.006(1)
O(11)	O	8f	1	0.0470(2)	0.2177(2)	0.9667(3)	0.009(1)
O(12)	O	8f	1	0.0982(2)	0.3648(2)	0.7380(3)	0.013(1)
P(2)	P	8f	1	0.2404(1)	-0.1080(1)	0.1328(1)	0.006(1)
O(21)	O	8f	1	0.1830(2)	0.0016(2)	0.1209(4)	0.016(1)
O(22)	O	8f	1	0.3773(2)	-0.0992(2)	0.1935(4)	0.014(1)
O(23)	O	8f	1	0.1715(2)	-0.1648(2)	-0.1025(3)	0.011(1)
O(24)	O	8f	1	0.2239(2)	-0.1785(2)	0.3172(3)	0.010(1)

^a $U_{\text{(eq)}}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected interatomic distances (Å) for $\text{Li}_{3/4}\text{Mn}_{3/2}\text{Fe}_{7/4}(\text{PO}_4)_3$
 $(\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3)$.

M(1)-O(22) × 2	2.188(2)	P(1)-O(11) × 2	1.539(2)
M(1)-O(11) × 2	2.193(3)	P(1)-O(12) × 2	1.543(2)
M(1)-O(23) × 2	2.240(2)	<P(1)-O>	1.541(2)
<M(1)-O>	2.207(3)		
M(2)-O(21)	1.927(3)	P(2)-O(21)	1.522(2)
M(2)-O(12)	2.000(2)	P(2)-O(22)	1.524(2)
M(2)-O(23)	2.026(3)	P(2)-O(23)	1.550(2)
M(2)-O(11)	2.049(2)	P(2)-O(24)	1.552(2)
M(2)-O(24)	2.057(3)	<P(2)-O>	1.537(2)
M(2)-O(24)'	2.209(2)		
<M(2)-O>	2.045(3)		
A(1)''-O(22)	1.85(3)	A(1)''-O(22)	2.216(5)
A(1)''-O(22)'	1.92(4)	A(1)''-O(22)'	2.235(5)
A(1)''-O(12)	2.05(3)	A(1)''-O(12)	2.266(5)
A(1)''-O(12)'	2.11(4)	A(1)''-O(12)'	2.315(5)
		A(1)''-O(22)''	2.371(5)

Figure 1: (a)

view of the structure: projected along the $[0\ 0\ 1]$ direction.

b) Chain formed by the $\text{M}(1)\text{O}_6$ and $\text{M}(2)\text{O}_6$ octahedra.

Perspective

Figure 2: Observed (red) and calculated (black) powder X-ray diagrams for $\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3$ and their difference curve (blue line).

a)

b)

Figure 3: a) The M(1) and M(2) site environments versus Oxygens (in red) with the M(1)-O and M(2)-O distances given in Å. b) Perspective view of the tunnel 1 where are localised the Li^+ ions.

Figure 4: The room temperature ^{57}Fe Mössbauer spectrum for $Li_{0.75}Mn_{1.50}Fe_{1.75}(PO_4)_3$ together with the fitting results.

Figure 5: a) ^7Li MAS NMR spectrum ($\nu_r = 30$ KHz) of the $\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3$ recorded at 38 MHz with a Hahn Echo sequence. * = Spinning Side Bands. b) Li environment versus paramagnetic Fe^{3+} and Mn^{2+} ions located in the M(1) and/or M(2) sites.

Figure 6: Electrochemical cycling curve of $\text{Li}_{0.75}\text{Mn}_{1.50}\text{Fe}_{1.75}(\text{PO}_4)_3$ prepared by solid state reaction used as positive electrode in a Li cell (C/50 rate at room temperature).