$Li_{0.75}Mn_{1.50}Fe_{1.75}(PO_4)_3$: First alluaudite-type iron phosphate containing only Li^+ as alkaline ions

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ABSTRACT

A new iron phosphate $Li_{0.75}Mn_{1.50}Fe_{1.75}(PO_4)_3$ 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 $A(2)A(2)'A(1)A(1)'A(1)''M(1)M(2)_2(PO_4)_3$ general formula with a = 12.002(9) Å, b = 12.509(9) Å, c = 6.404(7) Å, β = 115.07(7)° in the monoclinic $C2/c$ space group. The 3D framework consists of infinite chains of edge-sharing $M(2)_2O_{10}$ dimers and $M(1)O_6$ 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 $Li_{0.75}Mn^{II}_{1.50}Fe^{III}_{1.75}(PO_4)_3$ 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 mA h 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 framwork. Some phosphates phases were investigated as $Li_xNa_{2-x}FeMn_2(PO_4)_3$ [4] $NaMnFe_2(PO_4)_3$ [5], $Li_xNa_{(1-x)}MnFe_2(PO_4)_3$ [6], $Li_{0.47}Na_{0.2}FePO_4$ [7], $Na_2Fe_{1.96}V_{0.96}(PO_4)_3$ [8] and $Na_{1.702}Fe_3(PO_4)_3$ [9]. Recently the group of Yamada showed very high operating voltages for $Na_{2+2x}Fe_{2-x}(SO_4)_3$ 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: $Na_{2.67}Mn_{1.67}(MoO_4)_3$ 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 $Li_xNa_{(1-x)}MnFe_2(PO_4)_3$ 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 $Li_{0.47}Na_{0.2}FePO_4$ 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
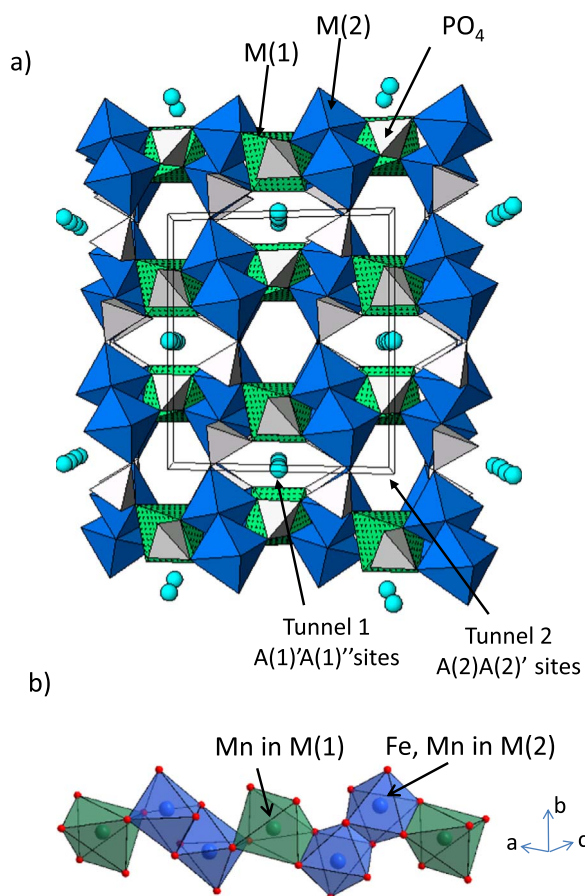
Fig. 1. (a) Perspective view of the structure: projected along the [0 0 1] direction. b) Chain formed by the M(1)O$_6$ and M(2)O$_6$ octahedra.

than 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 Fig. 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$_x$Na$_{(1-x)}$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, ^{7}Li 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$_2$Mo$_2$O$_7$. A starting mixture of LiNO$_3$, MnO, Fe(NO$_3$)$_3$·9H$_2$O, (NH$_4$)$_2$HPO$_4$ and MoO$_3$ corresponding to a molar ratio of LiMnFe$_2$(PO$_4$)$_3$: Li$_2$Mo$_2$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 1 h at 1173 K and subsequently cooled slowly down to room temperature at 10 °C 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 × 0.07 × 0.16 mm was chosen for the structure determination. Data were collected with an Enraf-Nonius CAD4 diffractometer using graphite monochromated MoK$_\alpha$ radiation (λ = 0.7107 Å). 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° ≤ θ ≤ 14.74°. Among a total of 1269 unique reflections collected using the (ω-2θ) scan mode (2θ$_{max}$ = 29.96°), 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$_{min,max}$: 0.57, 0.72).

A pure powder sample with a composition close to the Li$_{0.75}$Mn$_{1.50}$Fe$_{1.75}$(PO$_4$)$_3$ single crystals was synthesized by the conventional solid state reaction starting from a stoichiometric mixture of LiNO$_3$, MnO, Fe(NO$_3$)$_3$·9H$_2$O and (NH$_4$)$_2$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° ≤ 2θ ≤ 80° on a PANalytical diffractometer using CuK$_\alpha$ radiation (λ = 1.5406 Å). This pattern was refined by the Full profile matching, using the Fullprof program [30]. The refined parameters a = 12.004(1) Å, b = 12.484(1) Å, c = 6.389(1) Å and β = 115.00(1)° are in a good agreement with those obtained from single crystal X-ray data. The ICP measurements lead to the following composition: Li$_{0.8(1)}$Mn$_{1.4(1)}$Fe$_{1.8(1)}$(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 2–5 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 α-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
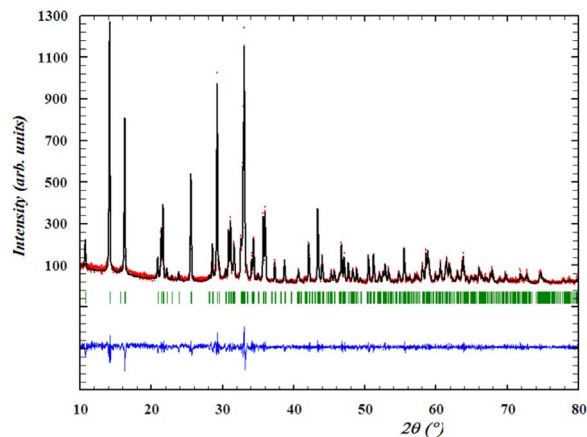

Fig. 2. Observed (red) and calculated (black) powder X-ray diagrams for Li$_{0.75}$Mn$_{1.50}$Fe$_{1.75}$(PO$_4$)$_3$ and their difference curve (blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).