



HAL
open science

A new set of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \times y\text{H}_2\text{O}$ ($0 \leq y \leq 1$) layered phases obtained by topotactic reactions

Khiem Trad, Alain Wattiaux, Mongi Ben Amara, Claude Delmas, Dany Carlier

► To cite this version:

Khiem Trad, Alain Wattiaux, Mongi Ben Amara, Claude Delmas, Dany Carlier. A new set of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \times y\text{H}_2\text{O}$ ($0 \leq y \leq 1$) layered phases obtained by topotactic reactions. *Journal of Solid State Chemistry*, 2018, 262, pp.112-120. 10.1016/j.jssc.2018.03.016 . hal-01760743

HAL Id: hal-01760743

<https://hal.science/hal-01760743>

Submitted on 6 Apr 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**A new set of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot y\text{H}_2\text{O}$ ($0 \leq y \leq 1$) layered phases
obtained by topotactic reactions.**

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

^a CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB UMR 5026, F-33600 Pessac, France

^b UR : Matériaux Inorganiques, Faculté des Sciences, Université de Monastir, avenue de
l'environnement, 5019, Monastir, Tunisia

Abstract

$\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ powder was synthesized by Na^+/K^+ exchange reaction from $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ in aqueous medium. The replacement of the sodium cations by the potassium larger ones and water molecules causes a structural distortion leading to P2/n monoclinic $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$. This new layered phase was characterized by XRD, Mössbauer spectroscopy and magnetic measurements. The study of its thermal stability reveals that other new layered $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot y\text{H}_2\text{O}$ with ($0 \leq y \leq 1$) phases can be stabilized up to 600°C and finally at higher temperature a new $\text{K}_3\text{Fe}_3(\text{PO}_4)_4$ polymorph with a different structural type is irreversibly formed.

Introduction:

Iron phosphate materials with alkali ions exhibit a rich structural chemistry due to the ability of iron to adopt different oxidation states (+2/+3) as well as different oxygen coordinations (octahedron, square pyramid, tetrahedron). Their structures based on complex frameworks built of FeO_n and PO_4 polyhedra sharing corners and/or edges, which provide an interstitial space partially occupied by alkali cations. Those materials have been the subject of intense research as heterogeneous catalysts [1], corrosion inhibitors [2] and more recently positive electrode materials for lithium-ion batteries [3, 4]. In the past few years, we were interested in a layered sodium iron phosphate phase, $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ used as positive electrode material in sodium and lithium batteries [5-6]. The $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ phase was prepared as powder by solid state reaction and characterized by XRD, Mössbauer and NMR spectroscopies and tested as positive electrode material [5-6].

In order to prepare new compounds, ion-exchange technique is well established [7-10]. In this study Na^+/Li^+ and Na^+/K^+ ion-exchanges were carried out. Only the Na^+/K^+ ion exchange procedure was successful and lead to a $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ phase homeotypic to the pristine $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$, that crystallizes in a monoclinic cell. The structure of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ is also close to those $\text{Na}_3\text{Cr}_3(\text{PO}_4)_4$, $\text{K}_3\text{Fe}_3(\text{AsO}_4)_4$ and $\text{K}_3\text{Cr}_3(\text{AsO}_4)_4$ [11-12]. This phase was prepared as single crystals by Lii et al. by hydrothermal synthesis [13]. They used an orthorhombic space group for the structural refinement and report that the formation of pure $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ crystals was rather difficult because of the non-reproducible high-temperature/high-pressure hydrothermal synthesis [13].

In the present paper, we report in a first part, the structural study by XRD and Mössbauer spectroscopy of the monoclinic $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ phase obtained by ion-exchange from $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ together with the magnetic properties of the two phases. In a second part, we

report the study of the thermal stability of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ that reveals the formation of new phases: layered $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot y\text{H}_2\text{O}$ with ($0 \leq y \leq 1$) and a new dehydrated $\text{K}_3\text{Fe}_3(\text{PO}_4)_4$ phase.

Experimental:

$\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ powder was synthesized by a potassium ion exchange reaction from $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$. The $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ powder sample has been synthesized through a solid state reaction as described in Ref. [5]. A mixture of stoichiometric quantities of Na_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)\text{H}_2\text{PO}_4$ were thermal-treated under oxygen flow successively 6 hours at 400 °C and 6 hours at 600 °C and annealed three days at 750°C with intermediate grinding between each thermal treatment. In order to perform the ion exchange reaction, 500 mg of $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ powder was immersed in a concentrated aqueous solution of 5M KCl ($K_{\text{solution}}/Na_{\text{solid}} > 40$). The resulting mixture was heated at 110°C with continuous stirring. The ion exchange process was followed every 24 hours by *ex-situ* X ray diffraction. The progress of ion exchange was also clearly evidenced by the colour change of the reaction medium from greenish yellow to light brown. After 72h a new pure phase was obtained. The sample was then isolated by vacuum filtration followed by rinsing several times with distilled water and acetone and dried in an oven overnight at 80°C. The resulting product was stable in air for several weeks under normal conditions of temperature and hygrometry.

The phase composition was carefully controlled by quantitative analysis to determine the K/P, Na/P and Fe/P ratios using an ICP-OES spectrometer (Varian 720-ES Optical Emission Spectrometer) after complete dissolution of the powder into a hydrochloric acid solution. The water content of the samples has been investigated by ThermoGravimetric Analysis (TGA) experiments using a Setaram 92 set up, by heating the sample under argon flow at 5°C/min between room temperature and 800°C with a stage of 2 hours at 110°C to get rid of the adsorbed water.

Phase identification of the exchanged product was performed by the X-ray powder diffraction method. The pattern was recorded in the $[8 - 80]^\circ$ (2θ) angular range using an 0.0167° (2θ) step and a constant counting time of 40 s. The lattice thermal expansion and the phase transition with rising temperature were studied by *in situ* X-ray diffraction measurements. These data were performed with a PANalytical X'pert Pro diffractometer (Co $K\alpha$ radiation, and iron filter, antiscatter slit of $\frac{1}{2}^\circ$ and divergence slit of 1° on the incident beam path) equipped with an Anton Paar device. The sample was put on an alumina sample-holder and was enclosed in an air atmosphere and heated up to 800°C . Before each measurement, the sample was heated to the defined temperature using a $5^\circ\text{C}/\text{min}$ rate and was kept at that temperature for 10 min for thermal stabilization. Diffraction patterns were collected every 50°C until 150°C (2h /diagram), then every 25°C until 400°C and finally every 50°C again until 800°C . A final XRD pattern was recorded at 25°C , after cooling down the sample back to the room temperature. Full pattern matching and Rietveld refinements were performed using the Fullprof software [14].

Mössbauer measurements were performed at room temperature in transmission geometry with a constant acceleration spectrometer using ^{57}Co source in a Rh matrix. The velocity was calibrated by using pure iron metal as standard material at room temperature. All isomer shifts reported in this work refer to the natural $\alpha\text{-Fe}$ at 293 K.

Magnetic measurements were performed in the temperature range 2 – 300 K, using a Quantum Design MPMS-5S SQUID magnetometer and a 1 T magnetic field.

Results and discussion:

1) Ion exchange reaction from $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$

Na⁺/Li⁺ ion exchange:

As we previously showed, Na₃Fe₃(PO₄)₄ can undergo the electrochemical insertion of lithium ions in the framework [6]. We were especially interested in performing the Na⁺/Li⁺ ion exchange reaction in order to get a new layered lithium iron phosphate that could have been further studied as positive electrode in lithium batteries. However, none of the tested conditions (molten salt (LiNO₃), aqueous solution of LiCl and at different temperature) was successful. In Table I, we collected some of the different ionic exchange conditions tested and the resulting products. In molten salt medium, the XRD patterns of the reaction products taken after different treatment times at 350°C revealed that after 1h30 the initial Na₃Fe₃(PO₄)₄ compound began to decompose and was totally decomposed after 12 hours into Li₃PO₄ and monoclinic Li₃Fe₂(PO₄)₃. Note that the formation of the monoclinic form of Li₃Fe₂(PO₄)₃ was unexpected at 350 °C since it is usually obtained by solid state reaction at higher temperature : 930°C [15]. The molten salt medium allows then a new synthesis reaction, and was recently used in order to prepare new phosphate materials [16].

In order to avoid the compound decomposition we also tested other Na⁺/Li⁺ ion-exchange conditions with moderate treatment temperatures. Note that even after 72 hours, Na₃Fe₃(PO₄)₄ did not react in an aqueous solution of LiCl (5 M). Nevertheless, after a week it decomposes into LiFePO₄.OH. Aqueous acidic medium was also tested, but leads to the decomposition of the phase into FePO₄.2H₂O and ion-exchange reaction in alcohol medium did not lead to better results (Table I).

Na⁺/K⁺ ion exchange:

We were more successful in the case of the Na⁺/K⁺ ion-exchange from Na₃Fe₃(PO₄)₄ that was performed in an aqueous solution of KCl (5M) ($K_{\text{solution}}/Na_{\text{solide}} > 40$) at 110°C during

72 hours. For longer treatment time (1 week), however the new potassium iron phosphate phase transforms to $\text{KFe}_2(\text{OH})(\text{PO}_4)_2(\text{H}_2\text{O})_2$.

Figure 1 shows a comparison of the X-ray diffraction (XRD) patterns of potassium phase and of the starting material $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$. After a 72h ion-exchange reaction, no trace of the precursor is observed. Moreover, the similarity between the X-rays diagrams indicates that the layered framework is kept during the exchange reaction. ICP measurements revealed that the ion-exchange procedure was completed to form $\text{K}_3\text{Fe}_3(\text{PO}_4)_4$ with no traces of sodium remaining in respect to the ICP sensitivity. Nevertheless, the concentration of all these elements was smaller than the expected one, suggesting the possible water molecule intercalation during the reaction in aqueous solution. In a first step, the hygroscopicity of the initial $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ was tested. However, after immersing this phase overnight in water and dry at 100°C , no structural evolution was observed by XRD and no weight loss was observed by TGA. On the opposite, in the case of the potassium phase resulting from the ion-exchange, the TGA shows a weight loss from room temperature to 800°C , which corresponds to the evolution of one water molecule per formula unit (Figure 2). The TGA curve will be discussed in more details in the following. The combination of ICP and TGA analysis leads to $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ formula for the exchanged compound.

The XRD pattern of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ was analysed using the Le Bail method [17]: the unit cell parameters and the profile parameters of a pseudo-Voigt function were refined. From the previous work reported by Lii et al. on a $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ single crystal [13], we first tried to refined our pattern with the orthorhombic cell (*Pnna* space group) they proposed. However, several reflections weren't indexed in this space group. Consequently, we looked for another one that could match our diagram using the Treor program [18]. This leads to a monoclinic elementary cell and systematic diffraction line absences were consistent with the monoclinic *P2/n* space group with a small deviation of the β angle from 90° (note that *P2/n* is a subgroup

of C2/c adopted by $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$). All the diffraction peaks of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ obtained by ion-exchange could therefore be indexed in this space group. As we already evidenced anisotropic strain and size effects leading to line broadening of some of the diffraction peaks in $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ [5], we also further used the Thompson-Cox-Hastings (T.C.H) profile function to refine the XRD pattern of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$. The V and W parameters, representative of the instrumental broadening, were fixed to the values obtained for the LaB_6 standard. In addition, it was necessary to consider two anisotropic models: (i) a general model described by P.W. Stephens to quantify the anisotropic strains [19] and (ii) a model of platelets to describe the anisotropic size effect. For the former model, 9 S_{hkil} independent parameters (S_{400} , S_{040} , ...) and the mixing factor L_σ were required to describe the model in a monoclinic system. For the latter model, the direction perpendicular to the platelets was fixed to be [100] and an additional SZ parameter was refined. Line broadening can be attributed to the stacking disorder and fragmentation or tilting of the crystallites on ion exchange. The Rietveld refinement of the XRD pattern of the starting material $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ showed line broadening of some diffraction lines associated to anisotropic size effect mainly along the a axis (stacking direction of the layers) and strain effects, mainly along the b axis [5]. In $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$, the potassium ions and water molecule present in the interlayer space enhance the strains along the b direction ($S_{040} = 0.23\%$, $S_{220} = 0.38\%$, $S_{022} = 0.6\%$). Figure 3 shows the resulting Le Bail refinement of the XRD of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ pattern in these conditions.

The Le Bail refinement led to rather good reliability factors ($R_{\text{wp}} = 13.8\%$, $R_p = 1.9\%$) indicating a good correlation between the cell model and the experimental data. As expected from the ion-exchange of Na^+ ions by larger K^+ ones and the water intercalation, the cell parameters significantly increased in $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ ($a = 20.8719(1) \text{ \AA}$, $b = 6.5293(1) \text{ \AA}$, $c = 10.7274(1) \text{ \AA}$ et $\beta = 90.232(1)^\circ$) compared to $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ ($a = 19.6494(3) \text{ \AA}$, $b = 6.3924(1) \text{ \AA}$, $c = 10.5969(2) \text{ \AA}$ et $\beta = 91.776(1)^\circ$) (Table II). Due to the large number of

parameters to be refined and the large amount of strains, the Rietveld refinement of the experimental pattern could not be further realized. However, one expects a structure very close to that reported by Lii et al.[13], with a small lattice distortion ($\beta= 90.23^\circ$ instead of 90°). For the structure representation in Figure 4, we used the Lii et al. model shown in comparison to $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$. The $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ phase clearly shows strong similarities with the layered $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$: the layers are constituted of corner-sharing FeO_6 octahedra which are further connected by phosphate tetrahedra through corner and edge sharing. The H_2O molecules are located nearby the K^+ ions, which are in the interslab space; i.e, K(1). There are two different fully occupied crystallographic sites for Fe atoms (4d and 8f) with octahedral coordination, two distinct P atoms (8f) with tetrahedral coordination, two distinct K atoms (K(1) is in a 4c site and K(2) is six coordinated in a 8e site), eight O atoms (8f sites).

The particles size and morphology were examined with scanning electron microscopy (SEM). Figure 5 shows respectively SEM images of $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ (Fig. 5a) and $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ (Fig. 5b). After the ion exchange reaction, the aggregates keep their overall plate-like shape. Due to the layer structure one can assume that the plate face correspond to the (100) plane. The average crystallite diameter and thickness are slightly reduced during the exchange reaction. Nevertheless, cracks appear inside the particles. In both cases, however, the calculated coherence lengths perpendicular to the basal plane (60 nm for $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ and 70 nm for $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$) are smaller than the platelets thickness observed by SEM. This corroborates the presence of structural defects inside the observed particles, after exchanging the sodium ions by potassium ones, leading to smaller coherence domains. From the S_{hkl} values deduced from the XRD refinement the constraints are mainly observed in the b direction, and increased in $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ compared to $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$. Even if the precise origin of these

constraints is not understood, one could have expected their increase using ion-exchange procedure.

Mössbauer spectroscopy:

Mössbauer measurements on $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ were performed on a powder sample at room temperature in comparison to those of the $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ phase [5]. Adjustment of the calculated and experimental spectra was done using a combination of Lorentzian quadrupole doublets. As shown in Figure 6, two doublets were required to fit the experimental spectrum. The characteristic parameters deduced from this refinement: the isomer shift (δ), the quadrupole splitting (Δ) and the full width at half maximum (Γ), are given in Table III. These parameters obtained for $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ are similar to those reported for $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ [5]. The presence of two slightly different isomer shifts of ~ 0.42 mm/s confirm the presence of 2 different sites for the trivalent iron ions, Fe(1) and Fe(2), in an oxygen octahedral environment (Figure 6). The ratio of the surface of the two Mössbauer peaks equal to $\frac{1}{2}$ allows assigning them to the two iron sites present in the structure. The 1.401 and 0.683 mm/s quadrupole splitting's observed for the iron sites in $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ are larger than the 1.153 and 0.315 mm/s values observed in $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ thus indicating that the two iron sites in the potassium compound are more distorted than in the sodium one (Table III).

Magnetic susceptibility:

The magnetic properties of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ powders were measured between 5 and 300 K with an applied field fixed to 10 kOe. Figure 7 shows the evolution of the molar reciprocal magnetic susceptibility χ^{-1} versus temperature of the two compounds. The curves are very similar and show a paramagnetic to antiferromagnetic transition at $T_N \approx 29$ K for $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ and $T_N \approx 27.7$ K for $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$. Above 150 K the curves follow closely the Curie–Weiss law. The Curie constant C was calculated from the slope of the linear variation of χ^{-1} vs. T in the temperature range [160–300] K (Table IV). From the relation $C = (N\mu_{\text{eff}}^2)/(2k_B)$, we obtained the effective magnetic moment μ_{eff} per iron atom (Table IV). The resulting values are close to the $5.91\mu_B/\text{Fe}$ value expected for a high-spin iron (III) compound. The negative value of the paramagnetic Curie temperature (θ_p) indicates the occurrence of dominating antiferromagnetic interactions.

2) Thermal stability of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$

The thermogravimetric analysis (TGA) of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ from 110°C to 800 °C (Fig. 2) shows that the dehydration occurs in two steps corresponding approximately to the loss of $\sim 1/4$ and $3/4$ of the water content. It shows three contributions: at 200°C, 540°C and around 800°C. The first step indicates the possible formation of a new phase at 200°C, that would correspond to a less hydrated $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot 0.75\text{H}_2\text{O}$ polymorph. Above 540 °C, the dehydration is completed.

In situ thermal XRD study

In order to follow the crystal structure evolution upon heating, *in-situ* X-ray diffraction measurements were performed (Figure 8). As seen from the patterns evolution versus temperature (Figure 8a), the dehydration of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ occurs without strong structural modifications up to 600°C indicating that the lattice skeleton is maintained. All the XRD patterns can be indexed in the monoclinic system. The P2/n space group is maintained up to 275°C . In the 300°C - 600°C range the XRD patterns can be indexed in the C2/c space group. Above 600°C , there is a strong structural reorganisation; the patterns are indexed using the C2mb space group.

In the 25°C - 600°C temperature range, the (200) line ($2\theta_{\text{Cu}} \approx 9.6^\circ$) (Figure 8b), indicative of the a cell parameter evolution, shifts gradually slightly towards lower angles from room temperature to 275°C and then shift back toward higher angles together with a line broadening. Other diffraction lines behave similarly to (200) with weak shifts. Therefore within this general trend, it was surprising to observe a strong gradual shift for the (211) line ($2\theta_{\text{Cu}} \approx 20.8^\circ$) (Figure 8b) from room temperature to 275°C and the complete disappearance of the line for higher temperature. This diffraction line was properly indexed at room temperature using the P2/n space group, but could not be indexed at higher temperature whereas all other peaks were still described using the P2/n space group. The rapid displacement of one diffraction line while the other ones are almost fixed indicates the existence of an incommensurate structure for the $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot y\text{H}_2\text{O}$ phase between 25°C to 275°C with ($1 > y > 0.75$). The structure is well ordered at room temperature and the departure of a fraction of water molecules during heating implies a reorganization of both, the K^+ ions and the remaining water molecules in the interslab space leading to an incommensurate structure. Note that the water molecules belong to the K^+ coordination sphere in $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$. The partial loss of H_2O generates then very different K^+ environments. The use of the P2/n space group for the $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot y\text{H}_2\text{O}$ ($1 > y > 0.75$) phases is therefore an approximation here. Above 300°C , a new $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot 0.75\text{H}_2\text{O}$

phase appears that does exhibit larger line broadening. No significant changes are then observed up to 600°C. At 650°C, new diffraction lines appear indicating a phase transition. At 750°C, the new $K_3Fe_3(PO_4)_4$ fully dehydrated phase is pure and its XRD pattern can be indexed with a orthorhombic cell (*C2mb space group*).

***Ex situ* XRD study**

In order to better characterize the new $K_3Fe_3(PO_4)_4 \cdot yH_2O$ phases, *ex situ* XRD patterns were collected after cooling back to room temperature samples treated at 350°C, 600°C and 750°C for 4 hours. From our TGA analysis the corresponding stoichiometry's are $K_3Fe_3(PO_4)_4 \cdot 0.75H_2O$ (monoclinic *C2/c*), $K_3Fe_3(PO_4)_4$ (monoclinic *C2/c*) and $K_3Fe_3(PO_4)_4$ (orthorhombic *C2mb*) respectively. The resulting phases are very sensitive to moisture : after a few hours in contact with air, the $K_3Fe_3(PO_4)_4 \cdot H_2O$ phase is recovered. Special airtight sample holders were therefore used for the XRD patterns acquisition.

a) Layered $K_3Fe_3(PO_4)_4 \cdot 0.75H_2O$ and $K_3Fe_3(PO_4)_4$ monoclinic phases

The XRD patterns of the two phases obtained at 350°C and 600°C, are compared in Figure 9 with the $K_3Fe_3(PO_4)_4 \cdot H_2O$ one. They can be indexed using a monoclinic cell (*C2/c* space group). The refined cell parameters are reported in Table II together with the homeotypic phases $Na_3Fe_3(PO_4)_4$ and $K_3Fe_3(PO_4)_4 \cdot H_2O$ for comparison. The peaks profile was refined using, as before, a Thompson-Cox-Hastings function in order to consider size and constraints effects. The constraints values slightly increase compared to those of the initial $K_3Fe_3(PO_4)_4 \cdot H_2O$ phase.

Since $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot 0.75\text{H}_2\text{O}$ and $\text{K}_3\text{Fe}_3(\text{PO}_4)_4$ phases obtained respectively at 350°C and 600°C crystallize in the $C2/c$ space group, similarly to $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$, the Rietveld refinement was carried out from the atomic coordinates previously established for this material [5] replacing Na by K in the model. In the following only the structure of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot 0.75\text{H}_2\text{O}$ will be discussed. The one of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4$ is really similar and structural parameters are given in supporting information. The oxygen and hydrogen atoms of the water molecule for the $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot 0.75\text{H}_2\text{O}$ were initially ignored. After this first step of the Rietveld refinement, Fourier difference maps were calculated using the GFourier software in order to localize the Oxygen of the H_2O molecule. However, its position could not be determined satisfactorily and neutron diffraction experiments will be required to localize precisely the H_2O molecule. Figure 10 shows the observed, calculated and difference X-ray profiles of the powder diffraction pattern of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot 0.75\text{H}_2\text{O}$. Atomic coordinates are given in Table V. This compound exhibits, as its isotype sodium iron phosphate, a layered structure as shown in Figure 4.

b) High-temperature orthorhombic $\text{K}_3\text{Fe}_3(\text{PO}_4)_4$ phase

The new high temperature dehydrated $\text{K}_3\text{Fe}_3(\text{PO}_4)_4$ phase obtained after the 750°C heat treatment of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ is stable in ambient conditions : it does not rehydrate contrarily to the previous phases. Its room temperature XRD diagram can be indexed with an orthorhombic cell ($C2mb$ space group) with the lattice parameters: $a = 9.301(1) \text{ \AA}$, $b = 32.122(1) \text{ \AA}$ and $c = 13.872(1)$ (Figure 11). From the strong difference between its X-rays diagram with those of $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ and $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot y\text{H}_2\text{O}$, we conclude that the iron-phosphate framework in this new phase completely changed. A similar $\text{K}_3\text{Fe}_3(\text{PO}_4)_4$ phase

obtained as single crystal was reported in B. Lajmi's thesis without its structural determination [20]. The full structural characterization of this phase is unfortunately not completed.

Conclusion:

In our study, we could evidence the formation of a set of new phases $K_3Fe_3(PO_4)_{4,y}H_2O$ synthesized by Na^+/K^+ exchange reaction from $Na_3Fe_3(PO_4)_4$ in aqueous medium followed or not by a thermal treatment. The ion exchange causes a distortion of the structure by the replacement of the sodium cations by the potassium larger ones and water molecules. Thus $K_3Fe_3(PO_4)_{4,y}H_2O$ crystallizes in the P2/n monoclinic space group. This new layered phase was characterized by XRD and ^{57}Fe Mössbauer spectroscopy that allow to compare the structures. The impact of the K^+/Na^+ ion exchange on the structures and on the magnetic properties are reported. The study of the thermal stability of $K_3Fe_3(PO_4)_{4,y}H_2O$ reveals that other new layered monoclinic $K_3Fe_3(PO_4)_{4,y}H_2O$ with $(0 \leq y \leq 1)$ phases can be stabilized between room temperature and $600^\circ C$ and finally another dehydrated orthorhombic $K_3Fe_3(PO_4)_4$ phase is obtained at $750^\circ C$.

Acknowledgements:

The authors wish to thank Cathy DENAGE, Philippe DAGAULT, Laetitia ETIENNE and Jérémy HUMEZ for their technical assistance.

References:

- [1] R. Tahir, K. Banert, S. Sebti, Natural and synthetic phosphates: New and clean heterogeneous catalysts for the synthesis of 5-arylhydantoins, *Applied Catalysis A: General*, 298 (2006) 261 – 264.
- [2] M. Edwards, L. Hidmi, D. Gladwell, Phosphate inhibition of soluble copper corrosion by-product release, *Corrosion Science*, 44, 5 (2002) 1057 – 1071.
- [3] A.K. Padhi, K-S Nanjundaswamy, J.B. Goodenough, Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries, *J Electrochem Soc* 144 (1997) 1188–1194.
- [4] C. Masquelier, L. Croguennec, Polyanionic (Phosphates, Silicates, Sulfates) Frameworks as Electrode Materials for Rechargeable Li (or Na) Batteries, *Chem. Rev.* 113 (8) (2013) 6552–6591
- [5] K. Trad, D. Carlier, L. Croguennec, A. Wattiaux, B.a Lajmi, M. Ben Amara, C. Delmas, A Layered Iron(III) Phosphate Phase, $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$: Synthesis, Structure, and Electrochemical Properties as Positive Electrode in Sodium Batteries, *J. Phys. Chem. C*, 114 (2010) 10034–10044.
- [6] K. Trad, D. Carlier, A. Wattiaux, M. Ben Amara, C. Delmas, Study of a Layered Iron(III) Phosphate Phase $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ Used as Positive Electrode in Lithium Batteries, *J. Electrochem. Soc.*, 157 (2010) A947.
- [7] C. Delmas, J-J Braconnier, P. Hagemuller, A new variety of LiCoO_2 with an unusual oxygen packing obtained by exchange reaction, *Mater. Res. Bull.* 17 (1982) 117.
- [8] R. Armstrong, A. Roberston, R. Gitzendanner, P. Bruce, The Layered Intercalation Compounds $\text{Li}(\text{Mn}_{1-y}\text{Co}_y)\text{O}_2$: Positive Electrode Materials for Lithium–Ion Batteries, *Journal of solid state chemistry*, 145 (1999) 549-556.
- [9] D. Carlier, I. Saadoune, L. Croguennec, M. Ménétrier, E. Suard, C. Delmas, On the metastable O_2 -type LiCoO_2 , *Solid State Ionics*, 144 (2001) 263-276.

- [10] C. Masquelier, C. Wurm, J. Rodríguez-Carvajal, J. Gaubicher, L. Nazar, A Powder Neutron Diffraction Investigation of the Two Rhombohedral NASICON Analogues: γ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$, *Chem. Mater.*, 12 (2) (2000) 525–532.
- [11] F. D'Yvoire, M. Pintardscrepel, E. Bretey, *Comptes Rendus Hebdomadaires Des Seances De L Academie Des Sciences Serie C*, 290(10) (1980) 185–188.
- [12] B. Bouzemi Friaa, H. Boughzala, T. Jouini, Tripotassium trichromium (III) tetraarsenate $\text{K}_3\text{Cr}_3(\text{AsO}_4)_4$: synthesis, structural study, IR spectroscopy characterization and ionic behavior, *J. Solid State Chem.* 173(2) (2003) 273–279.
- [13] K. H. Lii, $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$: an iron(III) phosphate with a layer structure, *European Journal of Solid State and Inorganic Chemistry*, 32(9) (1995) 917–926.
- [14] T. Roisnel, J. Rodriguez-Carvajal, WinPLOTR: A Windows Tool for Powder Diffraction Pattern Analysis *Materials Science Forum*, 378-381 (2001) 118-123.
- [15] C. Masquelier, A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, New Cathode Materials for Rechargeable Lithium Batteries: The 3-D Framework Structures $\text{Li}_3\text{Fe}_2(\text{XO}_4)_3$ (X=P, As), *Journal of Solid State Chemistry* 135 (1998) 228.
- [16] N. Recham, J-N. Chotard, J-C. Jumas, L. Laffont, M. Armand, J.M. Tarascon, Ionothermal Synthesis of Li-Based Fluorophosphates Electrodes, *Chem. Mater.*, 22 (2010) 1142-1148.
- [17] A. Le Bail, H. Duroy, J. Fouquet, Ab initio structure determination of LiSbWO_6 by X-ray powder diffraction, *Mater Res. Bull.*, 23 (1988) 447-452.
- [18] P.E. Werner, L. Eriksson and M. Westdahl, TREOR, a semi-exhaustive trial-and-error powder indexing program for all symmetries, *J Appl Crystallogr* **18** (1985) 367.
- [19] P.W. Stephens, Phenomenological model of anisotropic peak broadening in powder diffraction, *J. Appl. Crystallogr*, 32 (1999) 281-289.
- [20] B. Lajmi, PhD thesis, The crystal chemistry of iron (III) monophosphates with mono and divalent metallic cations, Monastir University (Tunisia), 2005.

Tables captions:

Table I: Some of the exchange conditions used to try to obtain new materials from $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$: LiCl aqueous solutions (at different temperatures and pH values), LiCl solution in ethanol and LiNO_3 molten salt...

Table II: Cell parameters of the different $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot y\text{H}_2\text{O}$ phases presented in this paper compared to those of $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$.

Table III: Fitted Mössbauer parameters of the $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ spectra recorded at room temperature.

Table IV: The magnetic parameters of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4$ and $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$: the Curie constant (C), the Weiss temperature (θ), the Néel temperature (T_N), the experimental effective magnetic moment obtained from the Curie constant ($\mu_{\text{eff exp.}}$) and the theoretical effective magnetic moment ($\mu_{\text{eff theo.}}$).

Table V: Refined structural parameters using the Rietveld method with the Thompson-Cox-Hastings function from the XRD pattern of the $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot 0.75\text{H}_2\text{O}$ phase obtained at 350°C .

Figures captions:

Figure 1: X-ray diffraction patterns of $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ and $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ after Na^+/K^+ ions exchange in aqueous solution.

Figure 2: Thermogravimetric thermal analysis (TGA) of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ performed under argon flow at $5^\circ\text{C}/\text{min}$.

Figure 3: Comparison between the experimental (\bullet) X-ray diffraction pattern of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ ($P2/n$) and the calculated (-) one using the Le Bail method. The difference plot ($I_{\text{obs.}} - I_{\text{calc.}}$) is also given, as well as an enlargement of a selected angular range is given to evaluate the quality of the refinement.

Figure 4: Representation of the structures of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ (a) from Lii et al. [13] and $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ (b) [5].

Figure 5: SEM micrographs of $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ (a) and $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ (b).

Figure 6: Experimental Mössbauer spectra of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ recorded at room temperature and calculated Lorentzian quadrupole doublets associated to Fe(1) and Fe(2).

Figure 7: A plot of the reciprocal susceptibility versus temperature for $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ with an applied field 10 KOe.

Figure 8: *In-situ* XRD patterns recorded while heating $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ from room temperature to 800°C . a) global view and (b) zoom on specific 2θ ranges and temperature domain.

Figure 9: *Ex situ* room temperature XRD patterns of compounds obtained from $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ after heat treatment performed at 350°C and 600°C compared with the one of the parent phase $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$.

Figure 10: Comparison between the experimental (*) X-ray diffraction pattern of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot 0.75\text{H}_2\text{O}$ (*C2/c*) obtained at 350°C and the calculated (-) one using the Rietveld method. The difference plot (Iobs. – Icalc.) is also given, as well as an enlargement of a selected angular range is given to evaluate the quality of the refinement.

Figure 11: Comparison between the experimental (*) X-ray diffraction pattern of $\text{K}_3\text{Fe}_3(\text{PO}_4)_4$ (*C2mb*) obtained at 750°C and the calculated (-) one using the Le Bail method. The difference plot (Iobs. – Icalc.) is also given, as well as an enlargement of a selected angular range.

Table I:

Exchange medium	Temperature	Time reaction	Results
Distilled water	100°C	72h	$\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$
Molten salt LiNO_3	350°C	1h30	$\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$
Molten salt LiNO_3	350°C	12h	Li_3PO_4 $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$
LiCl (5M) aqueous solution Li/Na=40	Room temperature	72h	$\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$
LiCl (5M) aqueous solution Li/Na= 40	100°C	72h	$\text{LiFePO}_4\text{-OH}$
LiCl (5M) aqueous pH=4 Li/Na=40	100°C	72h	$\text{FePO}_4\text{-}2\text{H}_2\text{O}$
LiCl (2M) methanol solution Li/Na=40	60°C	72h	$\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$
LiCl (5M) butanol solution Li/Na=40	110°C	72h	$\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$ Li_3PO_4

Table II:

	Space group	a (Å)	b(Å)	c(Å)	β (°)	V(Å ³)
Na ₃ Fe ₃ (PO ₄) ₄ from Ref. [5]	C2/c	19.6494(3)	6.3924(1)	10.5969(2)	91.776(1)	1330
K ₃ Fe ₃ (PO ₄) ₄ ·H ₂ O from Ref. [13]	Pnna	10.0717(1)	20.823(4)	6.5296(9)	90	1457
K ₃ Fe ₃ (PO ₄) ₄ ·H ₂ O	P2/n	20.857(1)	6.529(1)	10.727(1)	90.15(1)	1460
K ₃ Fe ₃ (PO ₄) ₄ ·0.75H ₂ O (350°C heat treatment)	C2/c	20.865(1)	6.530(1)	10.732(1)	90.44(1)	1462
K ₃ Fe ₃ (PO ₄) ₄ (600°C heat treatment)	C2/c	20.906(1)	6.535(1)	10.731(1)	90.94(1)	1467
K ₃ Fe ₃ (PO ₄) ₄ (750°C heat treatment)	C2mb	9.300(1)	32.122(1)	13.872(3)	90	4144

Table III:

	Site	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	%	Site
$\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$	Fe(1)	0.421(3)	1.401(3)	0.270(2)	35	Fe^{3+} [Oh]
	Fe(2)	0.426(2)	0.683(2)	0.290(1)	65	Fe^{3+} [Oh]
$\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$	Fe(1)	0.409(5)	1.153(5)	0.294(4)	36	Fe^{3+} [Oh]
	Fe(2)	0.413(3)	0.315(3)	0.336(3)	64	Fe^{3+} [Oh]

Table IV:

	C (emu.K.mol ⁻¹) 1)	θ_p (K)	T_N (K)	$\mu_{\text{eff exp.}}$ (μ_B)	$\mu_{\text{eff theo.}}$ (μ_B)
$\text{K}_3\text{Fe}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$	12.6	-191	29.0	5.79	5.91
$\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$	12.0	-183	27.7	5.51	5.91

Table V : Refined structural parameters using the Rietveld method with the Thompson-Cox-Hastings function from the XRD pattern of the $K_3Fe_3(PO_4)_4 \cdot 0.75H_2O$ phase obtained at 350°C.

$K_3Fe_3(PO_4)_4 \cdot 0.75H_2O$ (with $y < 1$)
C2/c

Space group:

$a = 20.8649(3) \text{ \AA}$; $b = 6.5304(3) \text{ \AA}$; $c = 10.7323(3) \text{ \AA}$; $\beta = 90.444(6)^\circ$

Atom	Site	Wyckoff position			Occupancy
Fe(1)	4d	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	1
Fe(2)	8f	0.1631(1)	0.4907(7)	0.7486(4)	1
P(1)	8f	0.2030(2)	0.0130(13)	0.2417(8)	1
O(11)	8f	0.1688(6)	0.8451(17)	0.2756(11)	1
O(12)	8f	0.2522(7)	0.0507(19)	0.3609(12)	1
O(13)	8f	0.1656(7)	0.2164(16)	0.2245(13)	1
O(14)	8f	0.2510(7)	0.9748(21)	0.1557(12)	1
P(2)	8f	0.9018(2)	0.3464(8)	-0.0001(8)	1
O(21)	8f	0.9087(7)	0.4919(24)	0.9019(13)	1
O(22)	8f	0.8911(6)	0.4906(19)	0.1301(13)	1
O(23)	8f	0.9543(5)	0.2302(14)	0.0283(13)	1
O(24)	8f	0.8515(5)	0.2089(14)	0.0110(15)	1
K(1)	4e	0	0.3401(10)	$\frac{1}{4}$	1
K(2)	8f	0.0902(2)	0.1465(6)	0.9823(6)	1

Conditions of the run

Temperature	293 K
Angular range	$5^\circ \leq 2\theta \leq 120^\circ$
Step scan increment (2θ)	0.0167°
Sample displacement (2θ)	$0.005(1)^\circ$
Number of reflections	675

Profile parameters of the Thompson-Cox-Hastings function

Instrumental parameters *: $V = -0.0009$ and $W = 0.0017$

Anisotropic size broadening described using the lsizeModel 1 (*i.e.* a broadening of the (h00)-type reflections): $SZ = 1.33(1)$

Anisotropic strain parameters: $S_{(040)} = 0.27(1)$, $S_{(022)} = 0.56(2)$, $S_{(004)} = 0.04(1)$; $L_\sigma = 0.21(1)$

Conventional Rietveld R-factors :

$R_{wp} = 14.6 \%$; $R_B = 8.2 \%$; $Scor = 3.4$

(*) Determined using LaB_6 as standard