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Partial exchange of the Li^+, Na^+ and K^+ alkaline cations in the $HNi(PO_4)\cdot H_2O$ layered compound

Jaione Escobal[a], José Mesa[a,*], José Pizarro[b], Begoña Bazan[b], María Arriortua[b], Teófilo Rojo[a]

[a]*Dpto de Química Inorgánica, Facultad de Ciencia y Tecnología, Apdo. 644, E-48080 Bilbao, Spain*
[b]*Dpto. de Mineralogía y Petrología,Facultad de Ciencia y Tecnología, Apdo. 644, E-48080 Bilbao, Spain*

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Abstract

The exchange of the Li^+ **(1)**, Na^+ **(2)** and K^+ **(3)** alkaline cations in the layered $HNi(PO_4)\cdot H_2O$ was carried out starting from a methanolic solution containing the $Li(OH)\cdot H_2O$ hydroxide for **(1)** and the $M(OH)$ ($M =$ Na and K) hydroxides together with the $(C_6H_{13}NH_2)_{0.75}HNiPO_4\cdot H_2O$ phases for **(2)** and **(3)**. The compounds are stable until, approximately, 280 °C for **(1)** and 400 °C for phases **(2)** and **(3)**, respectively. The IR spectra show the bands belonging to the water molecule and the $(PO_4)^{3-}$ oxoanion. The diffuse reflectance spectra indicate the existence of Ni(II), d^8, cations in slightly distorted octahedral geometry. The calculated Dq and Racah (B and C) parameters have a mean value of $Dq = 765$, $B = 905$ and $C = 3895\,cm^{-1}$, respectively, in accordance with the values obtained habitually for this octahedral Ni(II) cation. The study of the exchange process performed by X-ray powder diffraction indicates that the exchange of the Li^+ cation in the lamellar $HNi(PO_4)\cdot H_2O$ phase is the minor rapid reaction, whereas the exchange of the Na^+ and K^+ cations needs the presence of the intermediate $(C_6H_{13}NH_2)_{0.75}HNiPO_4\cdot H_2O$ intercalate in order to obtain the required product with the sodium and potassium ions. The Scanning electronic microscopy (SEM) images show a mean size of particle of 5 μm. The Li^+ exchanged compound exhibits small ionic conductivity ($\Omega\,cm^{-1}$ is in the 10^{-8}–10^{-9} range) probably restrained by the methanol solvent. Magnetic measurements carried out from 5 K to room temperature indicate antiferromagnetic coupling as the major interaction in the three phases. Notwithstanding the Li and K phases show a weak ferromagnetism at low temperatures.

Keywords: Phosphates; Exchange reactions; UV-visible spectroscopy; Scanning electronic microscopy; Ionic conductivity; Magnetism

1. Introduction

From the known phosphate compounds, only a limited number form two-dimensional layered structures. The low dimensionality and the intercalation properties of some of these layered phosphates make them attractive and exciting for scientific materials. Since the layered host lattice is deformable along the third dimension, a variety of guest molecules and ions of different shapes and sizes can be accommodated in the interlayer space. They are of considerable interest because of potential applications as ion-exchangers, ionic conductors, etc. An example of this interest is the extensive study of the intercalation behaviors of the layered vanadyl phosphates or α-zirconium phosphates [1,2]. In the last years, a considerable effort has been carried out about the synthesis of 3*d* transition metals (Ni^{2+}, Fe^{3+}, Co^{2+}, Mn^{2+}, etc.) double hydroxides. These compound exhibit several potential applications, especially as cathode for electrochemical batteries [3].

In this work the direct exchange of the Li^+ cation in the $HNi(PO_4)\cdot H_2O$ phase is presented. On the other hand, to induce the formation of new composite materials, the intercalation of alkylamines into layered phases has now become a common technique in the first step of attainment of pillaring compounds [4]. This reaction increases the spacing between the inorganic sheets by formation of an amine bilayer o monolayer that could then be replaced by other species. This method has been used in order to obtain the Na^+ and K^+ exchanged in the $HNi(PO_4)\cdot H_2O$ phase, due to the major size of these two alkaline cations in comparison with that of the Li^+ one.

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*Corresponding author. Fax: +00 34 946013500.
E-mail address: joseluis.mesa@ehu.es (J. Mesa).

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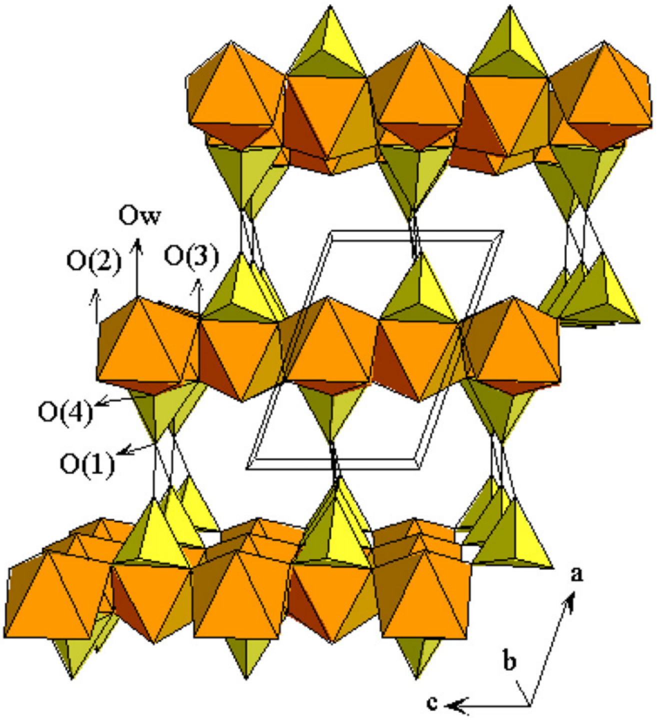

Fig. 1. Polyhedral representation of the crystal structure of HNi(PO$_4$)$\cdot$H$_2$O.

HNi(PO$_4$)$\cdot$H$_2$O was obtained by heating at 170 °C the (NH$_4$)Ni(PO$_4$)$\cdot$H$_2$O dittmarite compound, in atmospheric conditions (humidity of 80% in the syntheses room) [5]. The crystal structure of this phase consists of (100) sheets of NiO$_6$ corner-sharing octahedra cross-linked by (HPO$_4$) groups. These layers are linked by a zig–zag system of hydrogen bonds along the |010| direction, involving the (OH) group of the (HPO$_4$) tetrahedra arranged toward the interlayer space (Fig. 1).

We describe the synthetic procedure used in the attainment of the alkaline, Li$^+$, Na$^+$ and K$^+$ exchanged cations in the layered HNi(PO$_4$)$\cdot$H$_2$O phase. The study of the process has been performed using X-ray powder diffraction techniques. Scanning electronic microscopy (SEM) images of the resulting composites materials are presented together with the spectroscopic and magnetic behavior of these new materials.

2. Synthesis and characterization

2.1. Exchange of Li$^+$ into HNi(PO$_4$)$\cdot$H$_2$O

The exchange of the Li$^+$ cation in the HNi(PO4) phase, previously prepared by the method described by Fraissad and Etienne [6], was carried out from a methanol-solution of Li(OH)$\cdot$H$_2$O **(1)** in which the HNi(PO$_4$) **(2)** compound was spread, with a ratio **(1)**/**(2)** of 2/1. In order to avoid the evaporation of the methanol solvent this reaction mixture, contained on a vessel Pyrex, was isolated of the exterior using an appropriate parafilm. The mixture was maintained with continuous agitation during 7 days, after which it was filtered out, in order to avoid competitive equilibriums. This mechanical operation was repeated several times to obtain the intercalated product after 4 months.

Attempts performed in order to shortening the reaction time by using a more energetic reflux procedure did not give good results, obtaining the same product but with a notable minor crystalline.

The data of the inductively coupled plasma atomic absorption (ICP-AES) and (C, N, H) elemental analysis, allowed us to propose the following empirical chemical formula. Found (%): Li, 3.3; Ni, 30.7; P, 16.2%; C, 2.3; H, 1.8. Li$_{0.9}$NiPC$_{0.4}$H$_{3.7}$O$_{5.4}$, requires: Li, 3.4; Ni, 31.0, P, 16.7, C, 2.5; H, 1.9.

Taking into account the thermogravimetric data that reveal the existence of 0.4 mol of CH$_3$OH and one water molecule per unit formula of compound, the following molecular formula was proposed for this phase, Li$_{0.9}$Ni(PO$_4$)$_{0.9}$(HPO$_4$)$_{0.1}\cdot$H$_2$O$\cdot$0.4(CH$_3$OH).

2.2. Exchange of Na$^+$ and K$^+$ into the (C$_6$H$_{13}$NH$_2$)$_{0.75}\cdot$HNi(PO$_4$)$\cdot$H$_2$O

The greater size of the Na$^+$ and K$^+$ cations in comparison with that of the Li$^+$ one, suggested the use of the layered HNi(PO$_4$)$\cdot$H$_2$O phase previously intercalated with *n*-hexylamine, in order to increase the separation between the layers of Ni(II) phosphate monohydrate and, so, to facilitate the exchange of these alkaline cations.

The *n*-hexylamine intercalated was prepared placing *n*-hexylamine liquid in a Pyrex desecrator, in which the pulverized HNi(PO$_4$)$\cdot$H$_2$O on a Petri capsule is also placed. The desecrator was maintained hermetically closed, in order to create a saturated atmosphere composed by *n*-hexylamine steam. After 12 days of reaction the (C$_6$H$_{13}$NH$_2$)$_{0.75}$HNiPO$_4\cdot$H$_2$O compound was obtained, whose chemical formula was corroborated by C,H,N-elemental analysis.

The exchange of the Na$^+$ and K$^+$ cations into the (C$_6$H$_{13}$NH$_2$)$_{0.75}$HNiPO$_4\cdot$H$_2$O phase was carried out from a methanolic NaOH or KOH solution, on which the *n*-hexylamine intercalate was spread. The molar ratio hydroxide/phosphate was 2/1. This system was maintained isolated with continuous agitation during 7 days, after which the resulting product was filtered out. This procedure was repeated four times and finally the resulting product was isolated by filtration and washed at room temperature with acetone, the total time of reaction being 24 days.

A similar analytical and thermogravimetric procedure to that used in the case of the lithium exchange allowed obtaining the chemical formula of these two phases. Found: Na, 9.4; Ni, 26.1; P, 14.6; C, 3.5; H, 2.1. Li$_{0.9}$Ni(PO$_4$)$_{0.9}$(HPO$_4$)$_{0.1}\cdot$H$_2$O$\cdot$0.6(CH$_3$OH) requires: Na, 9.6; Ni, 27.0; P, 14.8; C, 3.7; H, 2.3. Found: K, 16.7; Ni, 27.6; P, 15.0; C, 0.5; H, 1.1. K$_{0.9}$Ni(PO$_4$)$_{0.9}$

$(HPO_4)_{0.1} \cdot H_2O \cdot 0.1(CH_3OH)$ requires: K, 16.9; Ni, 28.0; P, 15.5; C, 0.6; H, 1.2.

These results indicate that the amount of the methanol molecules incorporated to these phases cannot be controlled, because this compound acts as solvent of the reagents in these reactions. On the other hand, the attempts performed in order to incorporate the Li^+ cation in the $(C_6H_{13}NH_2)_{0.75} \cdot HNi(PO_4) \cdot H_2O$ phase gave a very small crystalline lithium exchanged compound.

Finally, to note that the exchanged forms of the $HNi(PO_4) \cdot H_2O$ phase have not any relation with the $LiNi(PO_4)$ and $KNi(PO_4)$ compounds which exhibit a compact three-dimensional crystal structure [7].

3. Results and discussion

3.1. Thermogravimetric analysis

The thermogravimetric curves for the three phases were obtained in 30–800 °C range at 5 °C/min and using N_2-atmosphere. The results are shown in Fig. 2. The thermograms of the Li and Na phases are very similar and slightly different from that of the K compound. The thermogram of the Li and Na phases show two initial steps. The first one from room temperature to, approximately, 150 °C that can be attributed to the evaporation of the solvent occluded in the compound. The experimental mass loss is approximately 7.5% for methanol in the lithium phase, being the theoretical loss of 6.7. In the case of the sodium compound the experimental mass loss concerning to the elimination of the methanol molecules is 9.5%, being the theoretical loss of 9.0%. The second step is extended from 150 °C up to 400 °C and corresponds to the loss of the water molecules. The experimental mass losses are 9.0% and 9.5% for the Li and Na phases, respectively, being the theoretical mass losses of 9.4% and 8.8% for every phase. In the thermogram of the K compound three steps can be distinguished. The first one, from room temperature and 200 °C being the loss mass of 1.6% (theoretical 1.5%) that can be attributed to the elimination of the methanol adsorbed by the phase. The second one, is extended up to 280 °C, corresponds to a loss of 9% (theoretical 8.6%) in mass and is associated with the elimination of the water molecule. The third step starts at, approximately, 280 °C, for the Li phase and at, approximately, 400 °C for the Na and K compounds. This can be attributed to the decomposition of an amount of $(HPO_4)^{2-}$ anion in the form of $(PO_4)^{3-}$, similarly to that observed in the thermal decomposition of the nickel(II)-dittmarite [8]. The inorganic residues at 800 °C, analyzed by X-ray diffraction powder, are formed by $Li_2Ni_3(P_2O_7)$ [$P2_1/c$, $a = 7.189(1)$, $b = 7.744(1)$, $c = 9.331(1)$ Å, $\beta = 110.3(1)°$] [9a] and $LiNi(PO_4)$ [$Pnma$, $a = 10.03(1)$, $b = 5.854(1)$ and $c = 4.681(1)$ Å] [9b] for the lithium exchanged phase. In the inorganic residue of the exchanged sodium compound can be observed the presence of the peaks corresponding to the $Na_4Ni_9(PO_4)_6$ [Cm, $a = 10.55(1)$, $b = 13.98(1)$, $c = 6.39(1)$ Å and $\beta = 104.8(1)°$] [9c], the $NaNi_4(PO_4)_3$ [$Amam$, $a = 9.892(1)$, $b = 14.84(1)$ and $c = 6.357(1)$ Å] [9d] and finally the $Na_4Ni_3(PO_4)_2(P_2O_7)$ phase [$Pna2_1$, $a = 18.01(1)$, $b = 10.41(1)$ and $c = 6.496(1)$ Å] [9e]. In the case of the potassium exchanged compound the inorganic residue contains the $K_2Ni_4(PO_4)_2(P_2O_7)$ [$C2/c$, $a = 10.30(1)$), $b = 13.67(1)$, $c = 18.153(1)$ Å and $\beta = 102.9(1)°$] [9f] and $K_2Ni(P_2O_7)$ phases [$P2_1$, $a = 9.230(1)$, $b = 17.54(1)$, $c = 8.319(1)$ Å and $\beta = 91.4(1)°$] [9g].

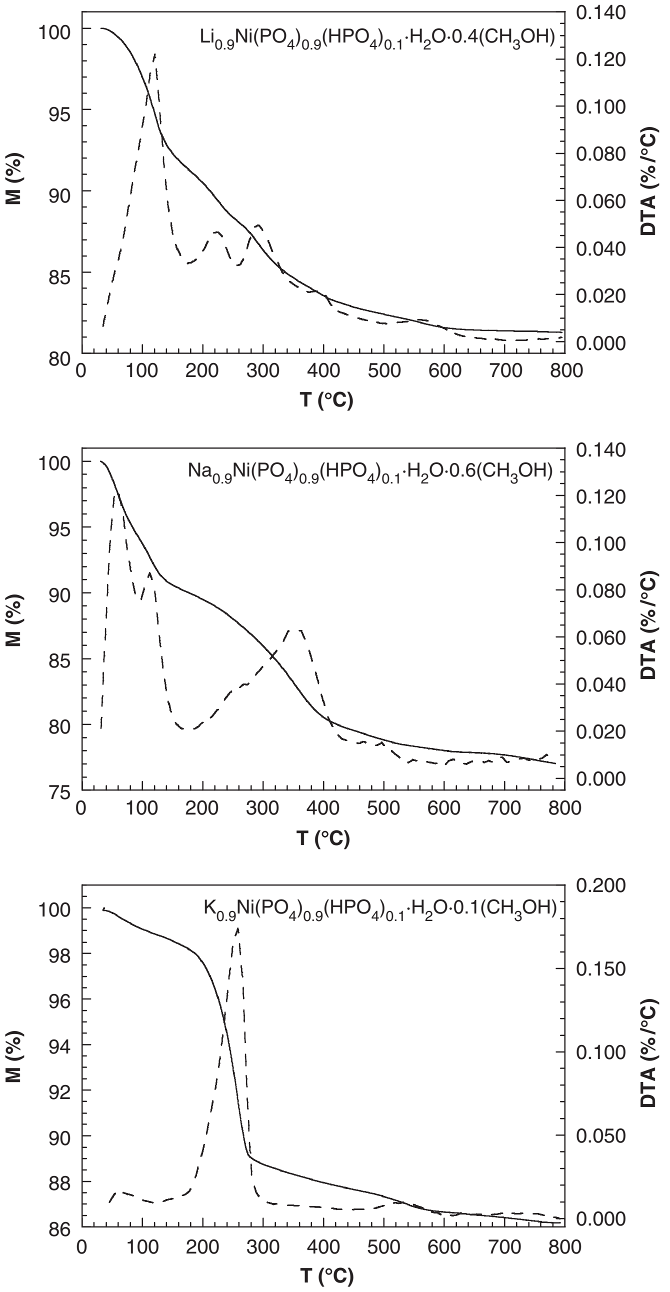

Fig. 2. Thermogravimetric curves of the Li^+, Na^+ and K^+ partially exchanged compounds.

The thermal results indicate that the elimination of the methanol and water molecules of the alkaline exchanged forms give rise to inorganic residues different from those of $MNi(PO_4)$ phases with $M =$ Li and K [7].

3.2. IR and UV–visible spectroscopies

All the phases exhibit bands in the 3500–3060 cm^{-1} range, which are assigned to the stretching vibration of the water molecules, $\nu_{st}(OH)$, in good agreement with the existence of these molecules coordinated to the Ni(II) cation and the presence of an amount of the methanol solvent. In the 1650–1610 cm^{-1} range the band belonging to the deformation mode of the water molecule, δ(O–H–O), are observed, corroborating the existence of the water molecules in these phases. The bands in the 1150–920 cm^{-1} are due to the asymmetric stretching vibration of the $(PO_4)^{3-}$ anions, $\upsilon_{as}(PO_4)$. The splitting observed in this vibrational mode is due to the distortion exhibited by the tetrahedral $(PO_4)^{3-}$ groups. The symmetric stretching vibrations, $\nu_s(PO_4)$, appear in the 690–625 cm^{-1} range. The bands corresponding to the asymmetric deformation of the $(PO_4)^{3-}$ anions are located in the 595–540 cm^{-1} range. These bands are in the range habitually found for the phosphate compounds [10].

The diffuse reflectance spectra of these compounds exhibit the essential characteristic of octahedral coordinated Ni(II) compounds. Three absorption bands ascribed to the spin-allowed transitions $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ are observed at the following frequencies: 7325, 12820, 23585 cm^{-1} for Li phase; 7850, 12905, 23810 cm^{-1} for Na compound and 7810, 12905, 23805 cm^{-1} for K compound. The spin forbidden transitions $^3A_{2g} \rightarrow {}^1E_g(F)$ and $^1T_{2g}$ can be observed at, 14390, 21320 cm^{-1} for Li; 14410, 21400 cm^{-1} for Na and 14390, 21300 cm^{-1} for K. The Dq and Racah (B and C) parameters were calculated by fitting the experimental frequencies to an energy level diagram for octahedral d^8 system [11]. The values obtained are $Dq = 735$, $B = 930$, $C = 3825$ cm^{-1} being $C/B = 4.1$ for Li; 785, 890, 3945 cm^{-1} with $C/B = 4.4$ for Na and 780, 895, 3920 cm^{-1} being $C/B = 4.4$ for K. These results are in the range habitually found for slightly distorted octahedral coordinated Ni(II) compounds [12].

3.3. Study of the exchange process by X-ray powder diffraction

A study of the different steps in the process of the exchange of the Li$^+$, Na$^+$ and K$^+$ into the layered HNi(PO$_4$) has been performed using X-ray powder diffraction data. The results are shown in Figs. 3–5.

The exchange of Li$^+$ takes place more rapidly in the first weeks in comparison with the later days. The intensity of the diffraction peaks shows a notable decreasing with the progress in the intercalation procedure. The first diffraction maximum (100) is displaced towards minor values of 2θ with the advance of the intercalation experiment. So, the intercalation of Li$^+$ in the $HNi(PO_4) \cdot H_2O$ phase originates an increase in the separation of the layers of this phosphate, in good agreement with the major size of the Li$^+$ in comparison with that of the H$^+$. The values of the reticular space, d(Å), corresponding to the (1 0 0) plane in

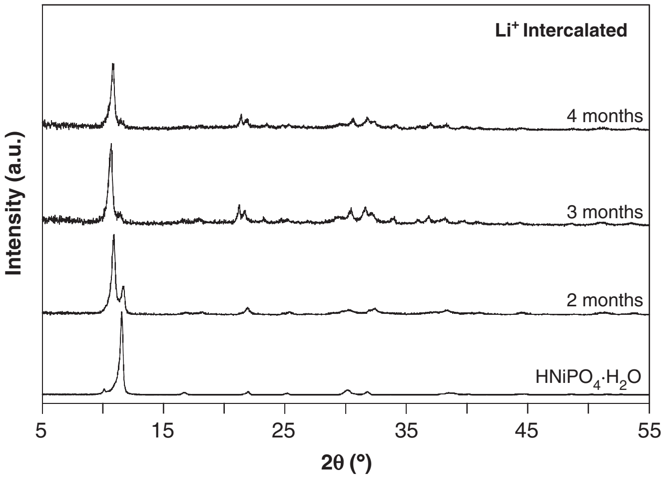

Fig. 3. X-ray powder diffraction pattern of the exchange procedure of Li$^+$ into the $HNi(PO_4) \cdot H_2O$ phase.

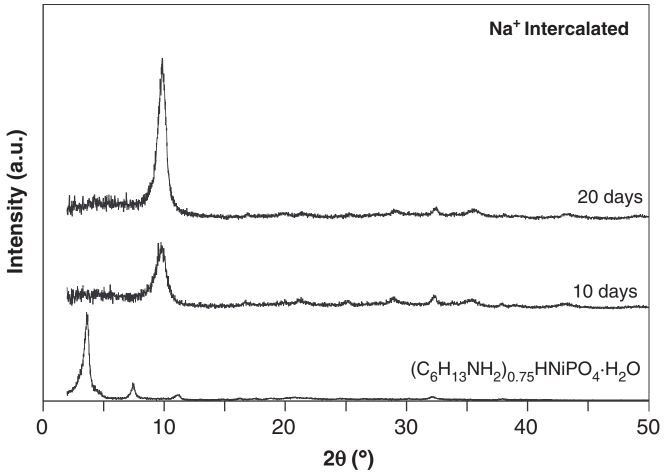

Fig. 4. X-ray powder diffraction pattern of the exchange procedure of Na$^+$ into the $HNi(PO_4) \cdot H_2O$ phase.

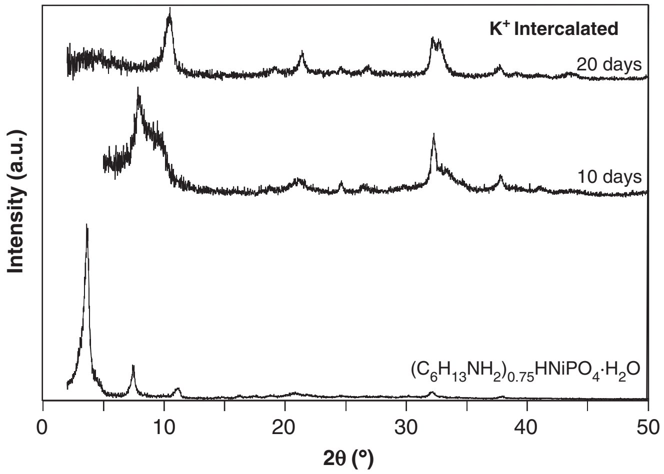

Fig. 5. X-ray powder diffraction pattern of the exchange procedure of K$^+$ into the $HNi(PO_4) \cdot H_2O$ phase.

the intercalated product is $d_{100} = 8.12$ Å, whereas than that in $HNi(PO_4)\cdot H_2O$ is $d_{100} = 7.66$ Å.

The exchange of Na^+ and K^+ is more rapid than that of the Li^+. This fact is originated because the intercalation procedure takes place into the $(C_6H_{13}NH_2)_{0.75}HNiPO_4\cdot H_2O$ compound with a major separation between the layers than that in $HNi(PO_4)\cdot H_2O$. In both cases, the Na^+ and K^+ intercalation reactions, the values of the d_{100} spacing are displaced towards minor values in comparison with that of the n-hexylamine intercalate, because the alkaline cation has a minor volume than that of the double layer of n-hexylamine present in $(C_6H_{13}NH_2)_{0.75}HNiPO_4\cdot H_2O$ [5], $d_{100(\text{n-hexylamine})} = 23.76$, $d_{100(Na^+)} = 8.99$ and $d_{100(K^+)} = 8.63$ Å.

Taking into account the distance between the layers in $HNiPO_4\cdot H_2O$ the d_{100} spacing must increase with increasing size of the alkaline cation. The ionic radii for Li^+, Na^+ and K^+ are 0.68, 0.97 and 1.33 Å, respectively. However, the results do not show this sequence, this way, $d_{(100(Li^+))} = 8.12$, $d_{(100(Na^+))} = 8.99$ and $d_{(100(K^+))} = 8.63$. These results could be explained if the methanol amount contained in the potassium exchanged phase is considered, 0.1 mol, smaller than that contained in the other two exchanged compounds, 0.4 mol for lithium and 0.6 mol for sodium phase. These results indicate that the incorporation of the methanol molecules plays a more important role in the final value of the interlayer space of these phases, than that of the ionic radius of the alkaline cations.

3.4. Scanning electronic microscopy

The SEM images of the three intercalates are shown in Figs. 6–8. In all cases the samples are formed by very thin micro-crystals, with a size of approximately 5 μm. The morphology of the crystals is lamellar in good agreement with the crystallographic data. In the case of de Li^+ intercalate the micro-crystals are more round, probably due to an effect of the time that was necessary to perform the intercalation reaction (4 months).

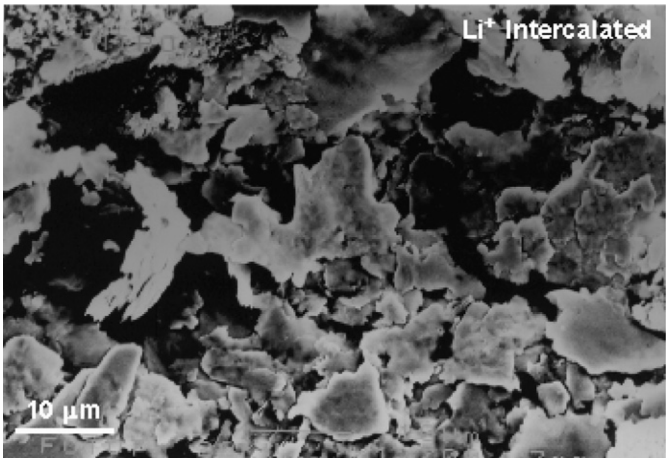

Fig. 6. SEM image of the morphology of the crystals for the Li^+ exchanged phase.

Fig. 7. SEM image of the morphology of the crystals for the Li^+ exchanged phase.

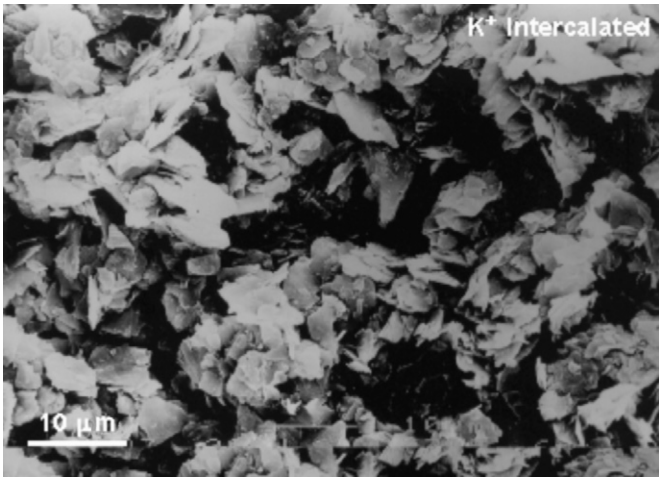

Fig. 8. SEM image of the morphology of the crystals for the Li^+ exchanged phase.

3.5. Ionic conductivity

The Bauerle method of the complexes impedances for obtaining the ionic conductivity under direct current was used [13]. The fit of the data using the Arrhenius expression, $\sigma = Ae^{(-\Delta E\sigma/RT)}$ allowed to obtain the value of the activation energy, $\Delta E = 0.085$ eV for the lithium phase. This value corresponds with a small ionic conductivity with a resistance in the 10^{-8}–$10^{-9}\,\Omega\,cm^{-1}$ range. It is important to note that the ionic conductivity of the Li-phase is strongly affected by the amount of methanol incorporated between the layers, which preclude obtaining a greater value of the conductivity, because the mobility of this small Li^+ cation is restrained by the methanol molecules. So, it is possible to conclude that the lithium compound behaves as an aslant. Consequently, measurements for the Na^+ and K^+ partially exchanged compounds were not performed.

3.6. Magnetic behavior

Magnetic measurements were performed on powdered samples in the 4.5–300 K range, under magnetic fields of 1000 and 100 G. The thermal evolution of the magnetic susceptibility, χ_m, and the $\chi_m T$ product are shown in Fig. 9. In the three phases the values of χ_m increases with decreasing temperature. The χ_m vs. T curve of the Li^+ and Na^+ intercalates does not show maximum, however, in the case of the K^+ intercalate a maximum can be observed at, approximately, 7.7 K.

The $(\chi_m)^{-1}$ vs. T curve for the Na^+ exchanged form can be fitted to the Curie–Weiss law for temperatures above 15 K. The values of the Curie constant and Weiss-temperature are 1.29 cm^3 K/mol and –37.8 K, respectively. The values of Curie constant is near to the value of 1.20 cm^{3}K/mol expected for a Ni(II) cation with $g = 2.2$. The $\chi_m T$ vs. T curve decreases continuously from 1.2 cm^{3}K/mol at room temperature up to 0.2 cm^3 K/mol at 4.2 K. This continuous decreasing and the negative value of the Weiss-temperature indicate the existence of antiferromagnetic couplings in this phase.

The Li^+ and K^+ exchanged phases show a different evolution of the $\chi_m T$ vs. T curve in comparison with that of the Na^+ one. In both, lithium and potassium compounds, the $\chi_m T$ vs. T curves decrease continuously from room temperature, showing a relative minimum at, approximately 26 K, after which the curves show a maximum at approximately 12.8 and 16.6 K, for the Li^+ and K^+ compounds, respectively. Below these temperatures, the $\chi_m T$ vs. T curves decrease up to 4.5 K. The global evolution of the $\chi_m T$ vs. T curves for these phases indicate a predominantly antiferromagnetic behavior, however the increase observed in the thermal evolution of these curves suggest the existence of a ferromagnetic contribution, manifested at temperatures greater than those of the final antiferromagnetic ordering.

In order to confirm the existence of a ferromagnetic component in the magnetic behavior of these two phases, susceptibility measurements at 100 G were performed (see

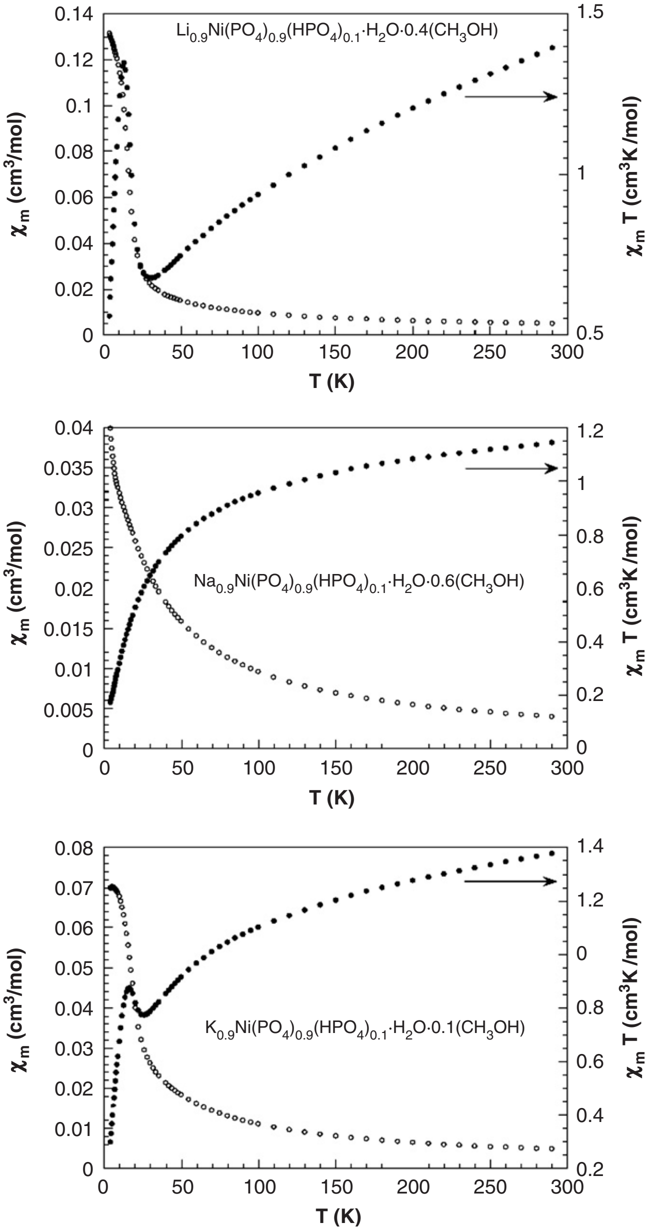

Fig. 9. Thermal evolution of the χ_m and $\chi_m T$ curves for the Li^+, Na^+ and K^+ exchanged compounds.

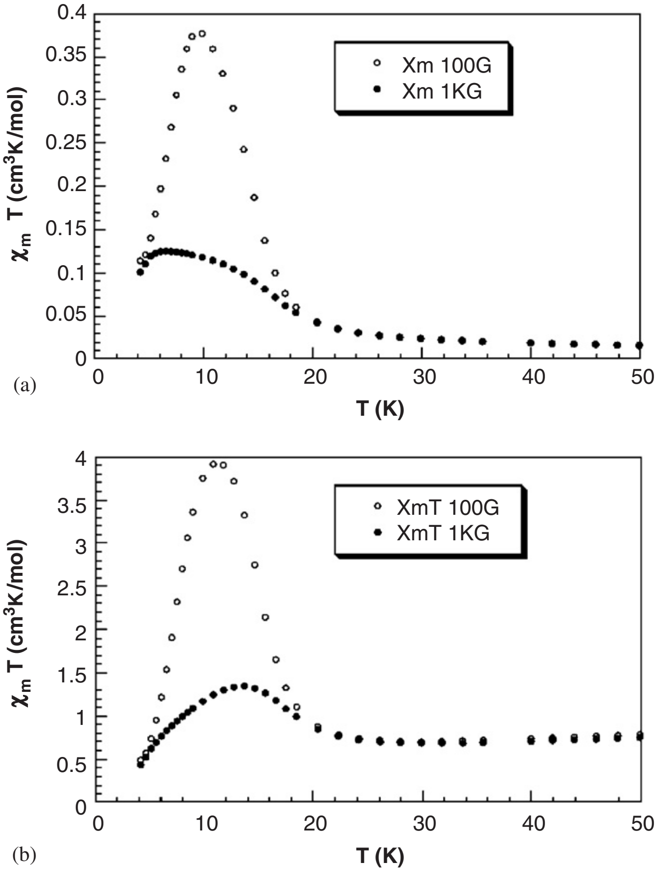

Fig. 10. Thermal evolution of the χ_m and $\chi_m T$ curves at 1000 and 100 G for Li^+ phase.

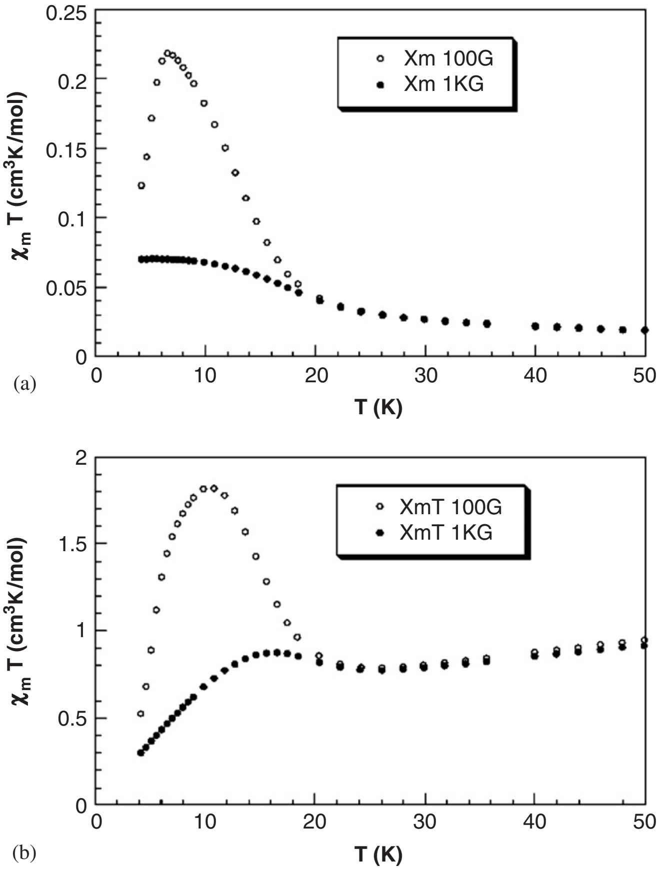

Fig. 11. Thermal evolution of the (a) χ_m and (b) $\chi_m T$ curves at 1000 and 100 G for K^+ phase.

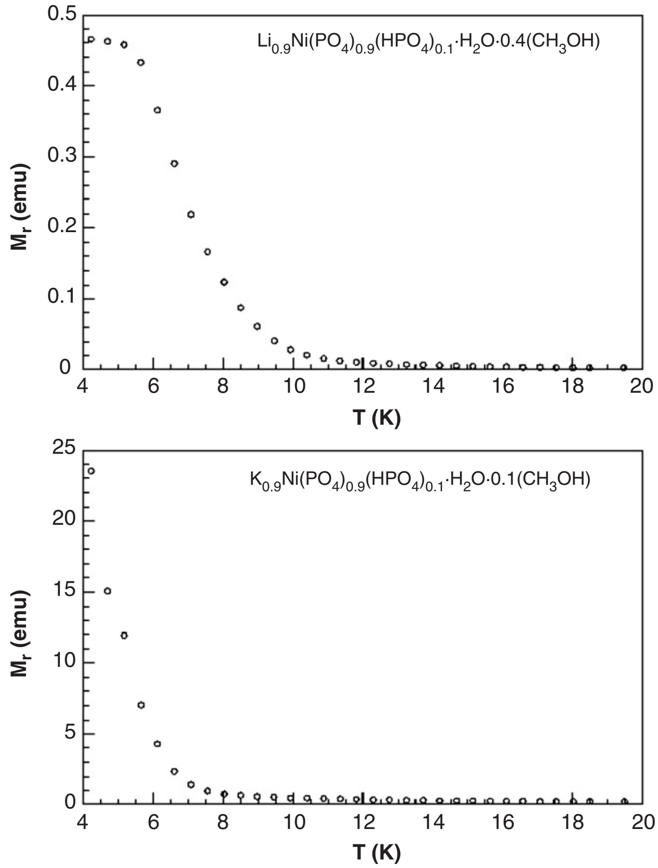

Fig. 12. Remnant magnetization measured at 100 G for Li^+ and K^+ compounds.

Figs. 10 and 11). In both cases a dependence of the susceptibility with the magnetic field applied can be observed. On the other hand, for both, lithium and potassium intercalates, a decreasing of the remnant magnetization, measured at 100 G, is observed (Fig. 12). The results confirm the existence of ferromagnetic couplings established at greater temperatures than those of the final antiferromagnetic behavior. The Neel temperatures estimated from the remnant magnetization vs. T curves are, approximately, 10 and 8 K, for lithium and potassium compounds, respectively.

4. Concluding remarks

Three new partially exchanged composite compounds, Li^+, Na^+ and K^+ in $HNi(PO_4) \cdot H_2O$, have been synthesized in methanolic solution. The limit of thermal stability is minor for the Li^+-intercalated and maximum for the Na^+ and K^+-compounds. The interlayer space of these intercalated phases follows the order $d_{(100(Li^+))} = 8.12$, $d_{(100(Na^+))} = 8.99$ and $d_{(100(K^+))} = 8.63$. The order of magnitude in the interlayer space does not follow the expected value taking into account the relative size of the alkaline ions. Nevertheless, the results can be understood if the amount of methanol solvent that exists in these composite materials is considered. From the ionic conductivity point of view these materials behave as aslant. Magnetic behavior indicates antiferromagnetic couplings as the major interactions. However, a weak phenomenon of ferromagnetism is present in the lithium and sodium phases.

Acknowledgments

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