Available online at www.sciencedirect.com
ScienceDirect
Journal of Solid State Chemistry 179 (2006) 3768–3775
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

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*

Received 10 May 2006; received in revised form 31 July 2006; accepted 12 August 2006
Available online 23 August 2006

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 $C = 3895\,\text{cm}^{-1}$, 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 ($\Omega\,\text{cm}^{-1}$ 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.

---

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

0022-4596/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2006.08.019

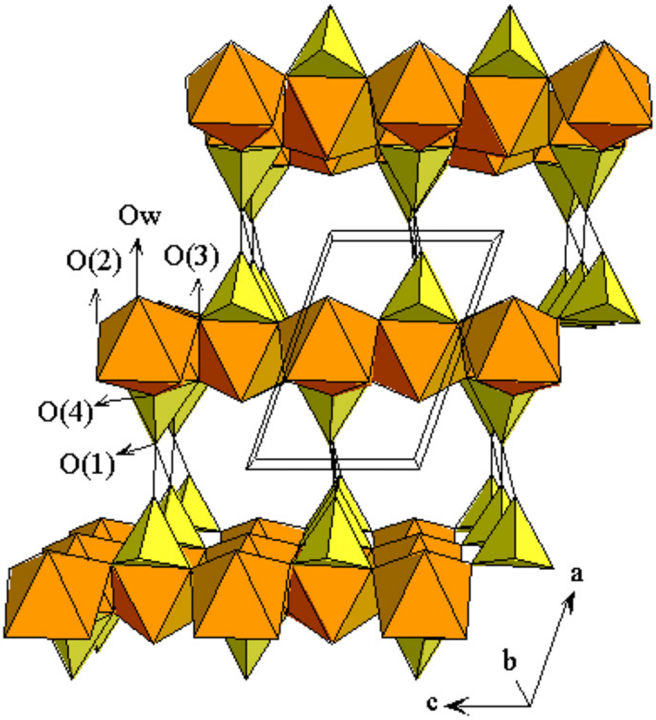

Fig. 1. Polyhedral representation of the crystal structure of $HNi(PO_4) \cdot H_2O$.

$HNi(PO_4) \cdot H_2O$ was obtained by heating at 170 °C the $(NH_4)Ni(PO_4) \cdot H_2O$ 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 $HNi(PO_4) \cdot H_2O$ 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 $HNi(PO_4) \cdot H_2O$

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 $Li(OH) \cdot H_2O$ **(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_3OH and one water molecule per unit formula of compound, the following molecular formula was proposed for this phase, $Li_{0.9}Ni(PO_4)_{0.9}(HPO_4)_{0.1} \cdot H_2O \cdot 0.4(CH_3OH)$.

2.2. Exchange of Na^+ and K^+ into the $(C_6H_{13}NH_2)_{0.75} \cdot HNi(PO_4) \cdot H_2O$

The greater size of the Na^+ and K^+ cations in comparison with that of the Li^+ one, suggested the use of the layered $HNi(PO_4) \cdot H_2O$ 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 $HNi(PO_4) \cdot H_2O$ 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 $(C_6H_{13}NH_2)_{0.75}HNiPO_4 \cdot H_2O$ compound was obtained, whose chemical formula was corroborated by C,H,N-elemental analysis.

The exchange of the Na^+ and K^+ cations into the $(C_6H_{13}NH_2)_{0.75}HNiPO_4 \cdot H_2O$ 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. $Li_{0.9}Ni(PO_4)_{0.9}(HPO_4)_{0.1} \cdot H_2O \cdot 0.6(CH_3OH)$ 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. $K_{0.9}Ni(PO_4)_{0.9}$