Synthesis and Characterization of α-Titanium Phosphate/Propylamine Intercalation Compounds Containing Transition-Metal Ions

Belén F. Alfonso*, Camino Tribajo, Miguel A. Salvadó, Pilar Pertierúa, Santiago García-Grandá, Jesús Rodríguez-Fernández, Jesús A. Blanco, and José R. García

Received November 30th, 2004; accepted March 15th, 2005.

Abstract. Polycrystalline intercalated TiM2H2−nPO4·yCnH2n−1NH2·H2O compounds with transition metal (TM) ions (Mn+ = Co2+, Ni2+, Fe3+ or Cr3+) have been prepared by means of an indirect route and characterised using X-ray diffraction, scanning electron microscopy, chemical and thermal analysis, X-ray absorption and magnetic measurements. These novel pillared layered materials, which were obtained from the monoclinic (P2/c space group) α-Ti(HPO4)2·H2O phase, lose their crystallinity after intercalation. However all the TM ions are octahedrally surrounded by 6 oxygen atoms, although the X-ray absorption spectra evidence a clear dependence on the temperature. Surprisingly, all the materials behave as paramagnetic down to 1.5 K, but they exhibit different colours, what means that they are optically active (Co2+: violet; Ni2+: pale green; Fe3+: yellow; Cr3+: dark green).

Keywords: α-Titanium phosphate; Layered compounds; Intercalation; Ion exchange; Transition metals; Magnetic properties

1 Introduction

Over the last decade, the field of functional molecular materials has experienced a large progress since the discovery of a great variety of emergent solid state properties, such as conductivity, superconductivity, non linear optics, and magnetic order [1]. Crystal engineering, through different synthesis routes, is searching for new physical—chemical phenomena and potent novel applications where two of the above mentioned properties could be combined. In particular, the magnetic behaviour depends strictly on the crystal building in which 3d cations are located. Likewise, ligand type, nature of binding ions, total charge, polarity of peripheral groups are important factors in the network construction. The search for new synthetic routes for achieving new materials is of current interest in modern inorganic chemistry [2].

In the last time many compounds have been synthesized in which magnetic interactions between transition metal ions are essentially confined to one or two dimensions [3]. For example the layer perovskites M2M′X4, which adopt structures based on the K2NiF4 type lattice, have proved a rich source for the magnetic system model [4]. All compounds of this series have relatively high symmetry, and the exchange interaction, responsible for establishing of the magnetic order, is mediated by monoatomic anions. Other compounds based on hybrid organic/inorganic crystals have been studied in which the exchange is provided by complex ions [5]. In this context, the layered metal phosphates have been poorly explored [6] until now.

As a part of an ongoing research program undertaken by our group to synthesize novel layered materials, different 3d cations (Co2+, Ni2+, Fe3+ or Cr3+) were inserted between the layers of metal phosphates.

The first crystalline metal(IV) phosphate, Zr(HPO4)2·H2O, was obtained by reflux in H3PO4 of a zirconium phosphonate gel [7]. This crystalline layered phase [8] can also be synthesized by hydrothermal methods [9] and by direct precipitation with [10] or without [11] prior formation of zirconium(IV) fluorocomplexes. Later, independent works of several laboratories [12] succeed in synthesizing an interesting family of these materials: M(HPO4)2·H2O (M = Ti, Zr, Hf, Sn, Pb).

The α-titanium phosphate, α-Ti(HPO4)2·H2O, is a layer compound with a flexible layer structure that, although it has ion-exchange properties, presents low affinity towards transition-metal ions. The synthesis of ion-exchange phases with elements of the first short period is possible by means of an indirect route [13]. In a first stage, by reaction between the acid inorganic solid (α-titanium phosphate) and the vapour of an organic base (e.g., n-alkylamine), an intercalation compound (in this case, Ti(HPO4)2·2C2H2n+1NH2·H2O) is obtained. In a second step, the intercalation compound reacts with an aqueous solution of the desired metal salt, and the substitution of interlayer organic cation by the inorganic metal cation takes place [14].
In this paper, the synthesis and characterization of both TiM$^\text{II}$H$_2$−2x(PO$_4$)$_2$·yC$_3$H$_7$NH$_2$·wH$_2$O (M$^\text{II}$ = Co, Ni) and TiM$^\text{III}$H$_2$−3x(PO$_4$)$_2$·yC$_3$H$_7$NH$_2$·wH$_2$O (M$^\text{III}$ = Fe, Cr) materials is reported.

2 Experimental Section

2.1 Synthesis

The α-Ti(HPO$_4$)$_2$·H$_2$O (α-TiP) was obtained following the Alberti method [15] using 10 M H$_3$PO$_4$ and reflux for 48 hours. The starting titanium phosphate gel was prepared by precipitation of a TiCl$_4$/HCl aqueous solution with dilute H$_3$PO$_4$ [16]. The crystalline solid was washed with distilled water until pH = 3.5. Intercalation compounds with n-propylamine, represented by Eq. (1), were obtained by placing for six days the α-TiP in an atmosphere saturated with n-propylamine vapour at room temperature [17]. The samples were dried in air at 50 °C. The intercalation process leads to the formation of a compound (α-TiP/PrA) in which the amine reaches the all active centers of the material. The basal spacing of this material is 16.9 Å (7.6 Å for α-TiP), with a ion-exchange theoretical capacity of 5.32 meq/g (7.75 meq/g for α-TiP).

α-Ti(HPO$_4$)$_2$·H$_2$O+2 C$_3$H$_7$NH$_2$→Ti(HPO$_4$)$_2$·2C$_3$H$_7$NH$_2$·H$_2$O (1)

The α-TiP/PrA material, obtained previously, was equilibrated with MC$_n$ aqueous solutions [n-valent metal cation = cobalt(II), nickel(II), iron(III), chromium(III)] containing different amounts of the transition-metal (N = 1, 2, 3, 4, 5, 6, 8) at a concentration of 10 meq M$^{n+}$/g of solid). The mixture stayed in a bath at 25.0 ± 1 °C with continuous agitation during 48 hours. The solids, Ti$_x$M$_n$H$_{2n}$-α(PO$_4$)$_2$·y C$_3$H$_7$NH$_2$·wH$_2$O (M$_n$TiP), were separated by centrifugation, washed with distilled water, and dried in air at room temperature.

Table 1 Values of x, y, and w in the compounds:

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>y</th>
<th>w</th>
<th>Sample</th>
<th>x</th>
<th>y</th>
<th>w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_x$TiP</td>
<td>0.29</td>
<td>0.84</td>
<td>3.0</td>
<td>Ni$_x$TiP</td>
<td>0.26</td>
<td>0.83</td>
<td>3.6</td>
</tr>
<tr>
<td>Co$_x$TiP</td>
<td>0.51</td>
<td>0.61</td>
<td>4.3</td>
<td>Ni$_x$TiP</td>
<td>0.49</td>
<td>0.65</td>
<td>5.1</td>
</tr>
<tr>
<td>Co$_x$TiP</td>
<td>0.86</td>
<td>0.58</td>
<td>5.1</td>
<td>Ni$_x$TiP</td>
<td>0.78</td>
<td>0.41</td>
<td>7.1</td>
</tr>
<tr>
<td>Co$_x$TiP</td>
<td>0.90</td>
<td>0.35</td>
<td>5.7</td>
<td>Ni$_x$TiP</td>
<td>0.98</td>
<td>0.23</td>
<td>6.7</td>
</tr>
<tr>
<td>Co$_x$TiP</td>
<td>0.98</td>
<td>0.09</td>
<td>6.6</td>
<td>Ni$_x$TiP</td>
<td>0.98</td>
<td>0.05</td>
<td>6.8</td>
</tr>
<tr>
<td>Co$_x$TiP</td>
<td>1.00</td>
<td>0.11</td>
<td>6.3</td>
<td>Ni$_x$TiP</td>
<td>0.97</td>
<td>0.07</td>
<td>6.7</td>
</tr>
<tr>
<td>Co$_x$TiP</td>
<td>0.98</td>
<td>0.07</td>
<td>6.4</td>
<td>Ni$_x$TiP</td>
<td>0.97</td>
<td>0.05</td>
<td>7.2</td>
</tr>
<tr>
<td>Co$_x$TiP</td>
<td>0.98</td>
<td>0.09</td>
<td>6.5</td>
<td>Ni$_x$TiP</td>
<td>0.98</td>
<td>0.07</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Table 2 Values of x, y, and w in the compounds:

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>y</th>
<th>w</th>
<th>Sample</th>
<th>x</th>
<th>y</th>
<th>w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_x$TiP</td>
<td>0.11</td>
<td>1.11</td>
<td>3.3</td>
<td>Cr$_x$TiP</td>
<td>0.12</td>
<td>1.06</td>
<td>3.8</td>
</tr>
<tr>
<td>Fe$_x$TiP</td>
<td>0.19</td>
<td>1.02</td>
<td>3.7</td>
<td>Cr$_x$TiP</td>
<td>0.22</td>
<td>0.96</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe$_x$TiP</td>
<td>0.31</td>
<td>0.81</td>
<td>4.7</td>
<td>Cr$_x$TiP</td>
<td>0.34</td>
<td>0.78</td>
<td>7.5</td>
</tr>
<tr>
<td>Fe$_x$TiP</td>
<td>0.33</td>
<td>0.52</td>
<td>5.5</td>
<td>Cr$_x$TiP</td>
<td>0.43</td>
<td>0.49</td>
<td>8.9</td>
</tr>
<tr>
<td>Fe$_x$TiP</td>
<td>0.47</td>
<td>0.17</td>
<td>7.8</td>
<td>Cr$_x$TiP</td>
<td>0.51</td>
<td>0.19</td>
<td>13.2</td>
</tr>
<tr>
<td>Fe$_x$TiP</td>
<td>0.49</td>
<td>0.12</td>
<td>7.2</td>
<td>Cr$_x$TiP</td>
<td>0.55</td>
<td>0.16</td>
<td>12.2</td>
</tr>
<tr>
<td>Fe$_x$TiP</td>
<td>0.61</td>
<td>0.06</td>
<td>7.4</td>
<td>Cr$_x$TiP</td>
<td>0.57</td>
<td>0.12</td>
<td>13.1</td>
</tr>
<tr>
<td>Fe$_x$TiP</td>
<td>0.63</td>
<td>0.01</td>
<td>7.7</td>
<td>Cr$_x$TiP</td>
<td>0.58</td>
<td>0.10</td>
<td>11.2</td>
</tr>
</tbody>
</table>

The formula data of the synthesized pillared materials, M$_n$TiP, are presented in Table 1 for the di-valent transition metal ions and Table 2 for tri-valent transition metal ions.

2.2 Analytical procedures

The phosphorus and titanium content in the solids was determined by using a SpectraSpec DCP-AES spectrometer after dissolving a weighed amount in HF aqueous solution. The content in carbon and nitrogen in the solids were made with a micro-analyzer Perkin Elmer 2400B. The thermal analysis of solids was performed on a Mettler model TA4000-TG50 (rate of heating 10 °C min$^{-1}$, nitrogen atmosphere with a flux volume of 5 ml min$^{-1}$). The pH of the solutions after the equilibration with the exchanger was measured using a Corning 340 pH meter. Initial and final concentrations of transition-ions in solution were measured using a Perkin Elmer lambda-20 spectrometer. The same equipment allowed the determination of the released phosphate groups, as a phosphorovanadomolybdate heteropolycomplex [18]. The affinity of the material for the transition-ions was expressed through the conversion values, which were obtained according to the formula in Eq. (2).

$$C(\%) = \frac{\text{meq (M}^{n+}/\text{g (α-TiP/PrA))}}{5.32 \text{meq (H}^+)/\text{g (α-TiP/PrA)}} \times 100$$

The powder X-ray diffraction pattern of the solids was performed using a Philips model PW 1729/1720 with CuKα radiation. The FT-IR data were obtained on a spectrophotometer Perkin Elmer 577, using the KBr pellet technique. The scanning electronic microscopy (SEM) images were obtained on a JEOL 6100, operating to 20 kV.

The X-ray absorption coefficients encompassing the Co, Ni, Fe and Cr absorption edges were collected using the BM29 beamline at the ESRF (Grenoble, France). It was not very difficult to grind the...
powders to a suitable particle size in order to use the Extended X-ray absorption fine-structure (EXAFS) transmission mode. EXAFS data were collected from the milled powders and thin foils of Co, Ni, Fe and Cr. Following established EXAFS analysis procedures, a line was fit to the preabsorption edge region and the area under this line and its extrapolation were removed from the spectrum using the VIPER software [19].

Magnetic susceptibility measurements (dc) were performed under an applied magnetic field of 2 kOe over the temperature range 1.8 \( \leq T (K) \leq 300 \) K using a Quantum Design PPMS of the Laboratorio de Fisica de la Materia Condensada (Universidad de Cantabria, Spain).

3 Results and Discussion

In all cases, the contact of the solid with MCl\(_n\) (M\(^{n+}\) = Co\(^{2+}\), Ni\(^{2+}\), Fe\(^{3+}\), Cr\(^{3+}\)) aqueous solutions produces materials in which the transition-metal content in solid phase increases as it undergoes his initial concentration in liquid phase, while that both the solution equilibrium pH and the solid phase propylamine concentration decreases (Figs. 1a, 1b, and 1c). The \( \alpha \)-TiP/PrA has higher affinity towards the di-valent cations than towards the tri-valents, and cobalt- and nickel-phases easily reach values near to the ion-exchange theoretical capacity. The degradation of the material (Fig. 1d) is independent to the metal-ion type, and it is a function of the equilibrium pH, being practically negligible in the conditions of synthesis appropriate for the transition-metal phases of greater conversion.

The elementary analysis of solids indicates that the amount of amine in the material decreases with the increase in the amount of retained metal-ion (Fig. 2). The process is visualized by IR (as an example, Figure 3 shows the IR spectra of some iron phases), where the disappearance of the propylamine characteristic bands (between 1629 cm\(^{-1}\) and 1396 cm\(^{-1}\)) can be observed. The quantification of propylamine concentration in solid phase, and its comparison with the transition-metal concentration (Fig. 4) indicates that, in strict sense, the reaction cannot be considered like a process of ion-exchange between both propylyamonium and transition-metal cations. Independently of this fact, the amount of residual amine is very small in the metal-saturated phases.

The SEM images, which allow us to monitor how the morphology of the sample evolves during the above com-
Intercalation Compounds Containing Transition-Metal Ions

Figure 5 SEM images: (a) \(\alpha\)-TiP; (b) \(\alpha\)-TiP/PrA and (c) Fe\textsubscript{10}TiP.

The combination of XRD and SEM shows that the \(\alpha\)-TiP is constituted by pseudohexagonal plates of average dimensions 5000 x 5000 x 1850 Å\(^3\) [20]. The application of these techniques to the both \(\alpha\)-TiP/PrA and M\textsubscript{N}TiP compounds indicates that although their morphology is quite similar, measurable differences are observed. In relation to starting material \(\alpha\)-TiP, the plates width remains quite constant, whereas the average area of the face of the plate decreases slightly.

Figure 6. Powder X-ray diffraction patterns: (a) \(\alpha\)-TiP/PrA; (b) Fe\textsubscript{1}TiP; (c) Fe\textsubscript{2}TiP; (d) Fe\textsubscript{8}TiP; (e) Fe\textsubscript{10}TiP.

Figure 7 Interlayer planar distance \(d_{002}\) of the materials M\textsubscript{N}TiP as a function of the TM (\(\bullet\) Co\textsuperscript{2+}, \(\square\) Ni\textsuperscript{2+}, \(\bigcirc\) Fe\textsuperscript{3+}, \(\bullet\) Cr\textsuperscript{3+}) conversion (see Eq. (2) in the text) in the basal spacing. Note that the distance \(d_{002}\) has change after the treatment with propylamine.

The powder X-ray diffraction pattern of the different samples after accomplishing the different steps on the synthesis route are show in Figure 6. It can be seen that the clearest pattern that originated after the intercalation of the 3d cations is the loss of long range order in these materials, and the increases of the \(d_{002}\) interplanar distance (see Fig. 7) with the propylamine. After the intercalation process this distance \(d_{002}\) decreases with the TM conversion, becoming amorphous for the higher amount of TM within the interlayer spacing. Moreover, the effect is more accused in the tri-valent ions than in the di-valents ones (Fig. 7).

Figure 8 compiles the thermal analysis data of three representative samples of the Cr\textsubscript{N}TiP family. The thermogravimetric curves shows that the thermal decomposition of new materials takes place in two well-differentiated temperature zones. In the first stage, at temperatures lower than 200 °C, the weakly bonded water is desorbed. The weight loss at higher temperatures is due, sequentially, to the both strongly linked interlayer species (crystallization water and
propylamine) and hydrogenphosphate group condensation. These processes are manifested as shoulders in the DTG-curve (see asterisks in the Fig. 8a). When the ion-substitution degree increases, the concentration of both organic and hydroxyl groups decrease in the interlayer space. In Fig. 8d it can be observed the relative importance of the weight loss due to these groups with respect to that it takes place at a lower temperature.

Figure 9a contains the normalized Ni-edge EXAFS spectra for the Ni_{10}TiP compound as a representative example. It is worth noting that all the X-ray-absorption spectra are quite similar for the different 3d cations, showing an important dependence on the temperature. Thus, the data can be compared in terms of phase and amplitude of the EXAFS oscillations to determine similarities or differences between the samples studied and also to provide information as to the signal-to-noise characteristics of the experiment. The Fourier-transformed EXAFS data for Ni_{10}TiP is presented in Fig. 9b. All the data resemble closely each other, the relative amplitude and radial distance of Fourier peaks appearing over the range 1 to 7 Å.

From the intensity of the first peak we conclude that each Ni atom in this Ni_{10}TiP compound is octahedral and is surrounded by 6 oxygen atoms, the Ni-O distance being 2.06 Å. This EXAFS X-ray results are consistent with the X-ray diffraction data. The former are completely explained by picturing the α-titanium phosphate after the intercalation of the 3d cations: each Ni atom has a definite number of nearest neighbours at a definite distance, but not unit of structure repeats itself identically at regular internals in three dimensions, and the materials are not crystalline after...
Intercalation Compounds Containing Transition-Metal Ions

Figure 10 Temperature dependence of the reciprocal magnetic susceptibility for the M10TiP (■ Co²⁺, □ Ni²⁺, ○ Fe³⁺, ● Cr³⁺), The upper part contains information on the experimental and theoretical paramagnetic moments $\mu_{\text{eff}}$ and the paramagnetic Curie temperature $\theta_P$ (see text).

Figure 11 Photography of the samples: (a) Co₁₀TiP; (b) Ni₁₀TiP; (c) Fe₁₀TiP and (d) Cr₁₀TiP.

the intercalation process. For the analysis only first nearest-neighbours have been taken into account. Although we have made several different attempts for describing the rest of Fourier peaks no satisfactory models were found considering second and/or third nearest neighbors. Further experiments using small angle X-ray or neutron scattering could help us in explaining more in detail the microstructure of these materials.

The X-ray absorptions, XANES and EXAFS, corresponding to lines K of respective ions (Co²⁺, Ni²⁺, Fe³⁺, Cr³⁺) were measured at room temperature with the purpose to study the local order around the metal transition ions for some selected samples (fraction of the interleave: 0.1, 0.2, 0.3, 1.0), as well as the evolution in temperature (150, 450 and 600 °C) for compositions 0.1 and 1.0. The local environments have been revealed independent of the composition of the material but it varies markedly with the heat treatment.

The measurements of the magnetic susceptibility, $\chi$, as a function of the temperature were performed in the intercalated phases of the $\alpha$-TiP/PrA samples with the richest Co²⁺, Ni²⁺, Fe³⁺ and Cr³⁺ ion concentrations. For these compositions no magnetic order was detected in the range of temperatures measured from 300 K to 1.8 K. In all the cases, the magnetic susceptibility is characterized by exhibiting a Curie-Weiss law, see Eq. (3), where $C$ is the Curie constant for the 3d ions and $\theta_P$ is the paramagnetic Curie temperature.

$\chi = \frac{C}{T - \theta_P}$ (3)

$C = N_A \frac{[L(L+1)+4S(S+1)] \mu_B^2}{3k_B}$ (4)

From the analysis of the mentioned laws we have been able to extract the information on the total spin angular momentum and the magnetic Curie temperature (see table in Fig. 10). The former is in quite good agreement with that obtained from the Hund’s rules assuming that the total orbital angular momentum is zero. This phenomenon is known as the quenching of the total angular momentum, owing to the existence of a crystalline electric field (CEF) created by the local environment around the 3d cations. This CEF is also responsible for the different colors that present the MₙTiP materials studied, (see the photo in Fig. 11). Up to now we have been able to synthesize only polycrystalline samples of these materials. This feature limits further more precise optical measurements for determining the CEF state and splitting of the 3d ions in the octahedral symmetry that we have deduced from our EXAFS data.

In conclusion, we have shown that our experimental procedure enabled the preparation of new $\alpha$-titanium phosphate/propylamine intercalation compounds containing metal ions such Co²⁺, Ni²⁺, Fe³⁺ or Cr³⁺ that exhibit optical properties, although these materials do not present a long range crystalline order. Further efforts are needed for crystallising new materials where both optical and magnetic properties could be combined.

Acknowledgment. This work was supported by MEC (Spain), Research Projects Nos. MAT2002-04178-C04 and MAT2003-02940. We thank both Dr. Stuart Ansell (ESRF) for his help during the EXAFS experiments and the ESRF for the provision of the synchrotron beam time.

References


