Synthesis, Vibrational Spectroscopy and Non-Isothermal Kinetic Decomposition of Fe(H2PO4)2·2H2O

ABSTRACT

Fe(H2PO4)2·2H2O nanoparticle was synthesized by a simple and cost-effective method using iron metal and phosphoric acid as starting chemicals. The thermal transformation products from the synthesized Fe(H2PO4)2·2H2O according to the thermal treatment at 150 and 400 °C were found to be FeH2P2O7 and Fe2P4O12, respectively. The activation energies of decomposition reaction of Fe(H2PO4)2·2H2O were calculated through the isoconversional methods of Ozawa and Kissinger-Akahira-Sunose (KAS), and the possible conversion functions have been estimated through Coats-Redfern method. The synthesized Fe(H2PO4)2·2H2O and its thermal transformation products were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), and FTIR spectroscopy. Room temperature magnetization results showed a ferromagnetic behavior of the Fe(H2PO4)2·2H2O and its thermal transformation products, having the hysteresis loops in the range of -10000 Oe < H < +10000 Oe with the strong specific magnetization values in the range of 32.25–96.28 emu/g at 10 kOe.

Key Words: Fe(H2PO4)2·2H2O, Synthesis, Non-isothermal Kinetics, Ferromagnetic behavior
**Introduction**

The acid inorganic salts, such as hydrogen phosphate, arsenates, sulphates, etc. are known to possess optical, electrical and magnetic properties of practical importance, which are determined by the presence of very strong hydrogen bonds in their crystal lattices (Koleva & Mehandjiev, 2006). The development of electric devices increases the need for new materials, especially in storage and electric energy production areas. Moreover, the recent use of transition metal phosphates like LiFePO₄ as a positive electrode for Li ion batteries generates a great interest for this class of material (Huang et al., 2001), (Masquelier et al., 1998), (Padhi et al., 1997), (Masquelier et al., 2000), (Delacourt et al., 2004). Several transition metal phosphates were screened as electrode material such as Nasicon type phases Li₃Fe₂(PO₄)₃ (Masquelier et al., 1998) or dimetalphosphate LiFePO₄ (Padhi et al., 1997). Among the acid phosphates the well-known compounds of the isostructural M(H₂PO₄)₂·2H₂O (M=Mn, Co, Ni) series have been subject of numerous investigations because of interesting ferro- and antiferroelectric phase transitions, which occur at different temperatures (they crystallize in monoclinic space group P2₁/n with Z = 2) (Koleva & Mehandjiev, 2006). Very few studies on the synthesis and crystal structure of Fe(H₂PO₄)₂·2H₂O have been previously reported. Bagieu-Beucher et al. (1976) and Koleva & Efferberger (2007) reported crystal structure of the synthesized Fe(H₂PO₄)₂·2H₂O from phosphoric acid and ferrous carbonate or native iron at low temperature with long time period. These synthesis methods were performed in an argon atmosphere (99.999 wt%) in order to prevent the oxidation of Fe²⁺. However, there are no data in the literature about magnetic properties of the dihydrogen phosphate of Fe(H₂PO₄)₂·2H₂O. Recently, nanocrystalline magnetic materials have been receiving more and more attention due to their novel materials properties, which are significantly different from those of their bulk counterparts (Masquelier et al., 1998). For practical applications, it is of particular importance to study the ferromagnetic properties in nanocrystalline materials as they will be potentially useful for ferrofluids, magnetic recording and biomedical applications.

In the present study, we report for the first time the synthesis and magnetic properties of nanocrystalline Fe(H₂PO₄)₂·2H₂O by a simple chemical method using iron metal and phosphoric acid at 40 °C with short time consuming (15 min). Thermal stability of Fe(H₂PO₄)₂·2H₂O was investigated by thermogravimetric-differential thermal analysis (TG-DTA). The kinetics analysis of the non-isothermal results for Fe(H₂PO₄)₂·2H₂O decomposition steps were carried out using the isoconversional methods of Ozawa (1965) and Kissinger-Akahira-Sunose (KAS) (1957) and the possible conversion functions had been estimated through the comparative methods (Coats & Redfern, 1964). The synthesized Fe(H₂PO₄)₂·2H₂O and its thermal transformation nanocrystalline products were characterized by XRD, FT-IR, SEM and VSM techniques.

**Experimental**

The Fe(H₂PO₄)₂·2H₂O compound was prepared by adding 2 mL of 70 % H₃PO₄ to 0.5585 g of Fe (c) (99.99 %, Fluka). The resulting solution was heated on a hot plate at 40 °C with continuous stirring until H₂(g) was completely evolved (15 min). The...
nearly dry sample was obtained and then 10 mL of acetone was added to allow highly crystalline product to be developed. The prepared solid was filtered by suction pump, washed with acetone and dried in air. The iron content of Fe(H₂PO₄)₂•2H₂O compound was determined by dissolving in 0.0126 M hydrochloric acid using atomic absorption spectrophotometry (AAS, Perkin Elmer, Analyst 100).

Thermal analysis measurements (thermo-gravimetry, TG; differential thermogravimetry, DTG; and differential thermal analysis, DTA) were carried out by a Pyris Diamond Perkin Elmer apparatus by increasing temperature from 50 to 400 °C with calcined α-Al₂O₃ powder as the standard reference. The experiments were performed in static air, at heating rates of 5, 10, 15, and 20 K min⁻¹. The sample mass was kept 6.0-10.0 mg into alumina crucible without pressing.

The structure and crystalline size of the prepared sample and its thermal transformation products were studied by XRD using a D8 Advanced powder diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu Kα radiation (λ = 0.1546 nm). The Scherrer method was used to evaluate the crystalline size (Cullity, 1977). The morphology of the selected resulting samples were examined with Scanning Electron Microscopy (SEM) using LEO SEM VP1450 after gold coating.

The room temperature FTIR spectra were recorded in the range of 4000-370 cm⁻¹ with 8 scans on a Perkin-Elmer Spectrum GX FT-IR/FT-Raman spectrometer with the resolution of 4 cm⁻¹ using KBr pellets (spectroscopy grade, Merck).

The magnetic properties of the prepared sample and its thermal transformation products were examined at 293 K using a vibrating sample magnetometer (VSM 7403, Lake Shore, USA).

**Results and discussion**

**Thermal analysis**

In order to confirm the exact amount of water of hydration and also study the thermal stability of the prepared Fe(H₂PO₄)₂•2H₂O sample, thermogravimetric analysis (TG-DTG-DTA) were performed. The TG-DTG-DTA curves of Fe(H₂PO₄)₂•2H₂O are shown in Fig. 1. The TG curve shows the weight loss between 30 and 500 °C, which involving the dehydration of the coordinated water molecules (2 mol H₂O) and an intramolecular dehydration of the protonated phosphate groups (2 mol H₂O). A large number of intermediate compounds, such as acid polyphosphate Fe(H₂PO₄)₂, acid condensed phosphate FeH₂P₂O₇ and mixtures of intermediate of both have been registered. The eliminations of water were observed in three areas: 80-150, 150-300 and 300-450 °C. The corresponding observed weight losses are 15.89, 4.47 and 3.92 % by mass, which correspond to 2.54, 0.72 and 0.63 mol of water. Total mass loss is 24.28 % (3.89 mol H₂O) and iron cyclophosphate Fe₅P₄O₁₂ is found to be the final product of the thermal decomposition at T > 400 °C. Three endothermic effects over the temperature region are shown in the DTA curve, namely at 118, 173, and 215 °C. Thermal transformations of Fe(H₂PO₄)₂•2H₂O relate to the elimination of water of crystallization as shown below:
Subsequently, it has been shown that the water of crystallization cannot be usually removed without the destruction of anion, because the second and third steps of the scheme given above are often overlapped (Samuskevich & Lukyyanchenko, 1998). This result is also in agreement with those reported in literatures (Samuskevich & Lukyyanchenko, 1999), (Samuskevich et al., 1997). In order to gain the complete dehydration of Fe(H$_2$PO$_4$)$_2$ · 2H$_2$O, the sample was heated in the furnace at 150 and 400 °C for 2 h and the decomposition products were obtained to be FeH$_2$P$_2$O$_7$, and Fe$_2$P$_4$O$_{12}$, respectively.

The specificity of the thermal decomposition was characterized by identification of the bonds to be selectively activated due to energy absorption at vibrational level. These bonds were assigned by comparing of the calculated wavenumbers with the observed wavenumbers in the FT-IR spectra. This breaking of the bond is assimilated with a Morse oscillators (Vlaev et al., 2004) coupled non-linear (Vlase et al. 2003) with the harmonic oscillators of the thermic field. Following, a theoretical treatment developed by Vlase et al. (2003), the relation between the maximum temperature peak $T_p$ (DTA) at maximum heating rate (20 K min$^{-1}$) for the decomposition step is 395.15 K. The calculated harmonic energy ($\omega_{calc}$) values of the decomposition step were 1656, 3036 and 3312 cm$^{-1}$, which correspond to 6, 11 and 12 quanta numbers, respectively. These wavenumbers are closely to the water vibration of water of crystallization reported in the literatures (Colthup et al., 1964) and exhibited a very good agreement with the observed wavenumbers from FT-IR spectra for the bonds suggested being broken. This result confirms thermal decomposition step correspond to the elimination of water of crystallization.

The specific activation is possible also due to more than one quanta, or by a higher harmonic: $\omega_{sp} = q\omega_{calc}$, $q \in N$, where $\omega_{sp}$ is the assigned spectroscopic number for the bond supposed to break. In order to corroborate the calculated data with the spectroscopic ones, we drew up the FT-IR spectra of the studied compound. According to the above mentioned equation, the $T_p$ (DTA) at maximum heating rate (20 K min$^{-1}$) for the decomposition step is 395.15 K. The calculated harmonic energy ($\omega_{calc}$) values of the decomposition step were 1656, 3036 and 3312 cm$^{-1}$, which correspond to 6, 11 and 12 quanta numbers, respectively. These wavenumbers are closely to the water vibration of water of crystallization reported in the literatures (Colthup et al., 1964) and exhibited a very good agreement with the observed wavenumbers from FT-IR spectra for the bonds suggested being broken. This result confirms thermal decomposition step correspond to the elimination of water of crystallization.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
$\alpha$ & Temperature / K & $\beta = 5$ & $\beta = 10$ & $\beta = 15$ & $\beta = 20$ \\
\hline
0.2 & 376.29 & 381.51 & 384.77 & 386.31 \\
0.3 & 377.71 & 383.89 & 387.11 & 389.38 \\
0.4 & 379.32 & 385.10 & 388.85 & 390.90 \\
0.5 & 380.97 & 386.74 & 390.61 & 392.46 \\
0.6 & 382.11 & 388.49 & 392.51 & 395.00 \\
0.7 & 384.16 & 390.47 & 394.60 & 396.87 \\
0.8 & 387.04 & 393.85 & 397.75 & 399.95 \\
\hline
\end{tabular}
\caption{$\alpha$ – data at different heating rates, $\beta$ (K min$^{-1}$), for dehydration of Fe(H$_2$PO$_4$)$_2$·2H$_2$O.}
\end{table}
kinetics studies

calculation of the activation energy

dehydration of crystalline hydrates is a solid-state process of the type (vyazovkin, 2000), (zhang et al., 2005), (gao et al., 1993): a(solid) -> b (solid) + c (gas). the kinetics of such reactions is described by various equations taking into account the special features of their mechanisms. as one of the non-isothermal multiple-scan methods for kinetics studies, isoconversional method is also called a model-free method because no kinetic model was set before the calculation of activation energy. ozawa (1965) and kas (1957) methods are two representative ones of model-free, which are convenient to calculate the activation energy. in a stage of the decomposition of fe(h₂po₄)₂·2h₂o, ozawa and kas equations were used to determine the activation energy. the equations used for €\alpha$ calculation are:

ozawa equation:

\[
\log \beta = \log \left( \frac{AE_\alpha}{R g(\alpha)} \right) - 2.315 - 0.456 \left( \frac{E_\alpha}{RT} \right)
\]  

kass equation:

\[
\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AE_\alpha}{R g(\alpha)} \right) - \frac{E_\alpha}{RT}
\]

where a (the pre-exponential factor) and e (the activation energy) are the arrhenius parameters; t is temperature (k) ; \(\alpha\) is the extent of conversion and r is the gas constant (8.314 j mol⁻¹ k⁻¹). the arrhenius parameters, together with the reaction model, are sometimes called the kinetic triplet. \(g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}\) is the integral form of the \(f(\alpha)\), which is the reaction model that depends on the reaction mechanism.

according to isoconversional method, the basic data of \(\alpha\) and t collected from the tg curves of the second dehydration of fe(h₂po₄)₂·2h₂o at various heating rates (fig. 1a) are illustrated in table 1. according to the above mentioned equations, the plots of log \(\beta\) versus 1000/\(t\) (ozawa) and ln \(\beta/T^2\) versus 1000/\(t\) (kas) corresponding to different \(\alpha\) can be obtained by a linear regression of least-square method, respectively. the ozawa and kas analysis results of four tg measurements at below 200 °c are presented in fig. 2 a and b, respectively. the activation energies \(e_\alpha\) can be calculated from the slopes of the straight lines with better linear correlation coefficient (\(r^2 > 0.99\). the slopes change depending on \(\alpha\) for the dehydration reaction of fe(h₂po₄)₂·2h₂o. the activation energies are calculated at four different heating rates via the ozawa and kas methods in the \(\alpha\) range of 0.2 to 0.8.
and are shown in Table 2. The activation energy values calculated by the KAS method are close to those obtained by Ozawa method, so the results are credible. The little change of the activation energies on $\alpha$, lead to the conclusion that the dehydration reaction of Fe(H$_2$PO$_4$)$_2$$\cdot$2H$_2$O could be a single kinetic mechanism.

The water in crystalline hydrate may be considered either as water of crystallization (crystal water) or as coordinated water. The water eliminated at 150 °C and below can be considered as water of crystallization, whereas water eliminated at 200 °C and above indicates its co-ordination by the metal atom (Gao et al., 1993), (Gabal et al., 2003). Water molecules eliminated at intermediate temperatures can be coordinately linked water as well as coordinated water. The dehydration temperatures obtained in this work suggest that the water in Fe(H$_2$PO$_4$)$_2$$\cdot$2H$_2$O can be considered as water of crystallization (Fig. 1). However, the strengths of binding between water molecules in the crystal lattice are different and, consequently, results in different dehydration temperatures and kinetic parameters. The activation energy for the release of crystal water lie in the range of 50–130 kJ mol$^{-1}$, while the value for coordinately bounded one are higher than this range (Gabal et al., 2003). The calculated activation energies from Ozawa and KAS methods for the dehydration reaction (Table 2) suggest that the water molecules are coordinately linked water as well as crystal one. This result is not consistent with the dehydration temperature obtained from DTA–TG experiments, which may be due to the overlapped of the decomposition steps.

Estimation of the conversion function and the pre-exponential factor

For one-step reaction, the estimation of kinetic parameters can be turned into a multiple linear regression problem through the Coats-Redfern equation (1964).

Coats-Redfern equation:
\[
\ln \left( \frac{g(\alpha)}{T^2} \right) = \ln \left( \frac{AE_\alpha}{R g(\alpha)} \right) - \frac{E_\alpha}{RT}
\]  

Hence, $\ln \left( \frac{g(\alpha)}{T^2} \right)$ calculated for the different $\alpha$ values at the single $\beta$ value on $1/T$ must give rise to a single master straight line, so the activation energy and the pre-exponential factor can be calculated from the slope and intercept through ordinary least-square estimation. The activation energy, pre-exponential factor and the correlation coefficient can be calculated from the equation of the Coats-Redfern combined with 20 conversion functions (Zhang et al., 2005), (Gabal et al., 2003). The most probable mechanism for the dehydration step was determined following the commonly employed method. The values of $E$ obtained by three methods as Ozawa, KAS and the Coats-Redfern must not only be approximately equal, but must also correspond to a higher linear correlation coefficient ($r^2 >0.99$). The optimized values from the Coats-Redfern method are the data of activation energy and $\ln A$, which were calculated with the best equation. From the above analysis, we can draw a conclusion that the obtained possible conversion function is $F_\alpha$ model for the dehydration of Fe(H$_2$PO$_4$)$_2$$\cdot$2H$_2$O, and the corresponding function is $f(\alpha) = (1-\alpha)^{1/2}$ and $g(\alpha) = 2[(1-\alpha)^{1/2}]$. The corresponding kinetic parameters of Coats-Redfern are $E_\alpha = 101.68 \pm 8.05$ kJmol$^{-1}$, $\ln A = 15.38 \pm 3.49$ s$^{-1}$ and $n = 3/2$ ($R^2 = 0.99408$).
Figure 2 Ozawa (a) and KAS (b) analysis of thermal decomposition step of Fe(H₂PO₄)₃·2H₂O

Table 2 Activation energies (E₀) vs. correlation coefficient (r²) calculated by Ozawa and KAS methods for the dehydration of Fe(H₂PO₄)₃·2H₂O.

<table>
<thead>
<tr>
<th>α</th>
<th>Ozawa method</th>
<th>KAS method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E₀ / kJ mol⁻¹</td>
<td>r²</td>
</tr>
<tr>
<td>0.2</td>
<td>155.49</td>
<td>0.9983</td>
</tr>
<tr>
<td>0.3</td>
<td>137.57</td>
<td>0.9992</td>
</tr>
<tr>
<td>0.4</td>
<td>138.47</td>
<td>0.9994</td>
</tr>
<tr>
<td>0.5</td>
<td>139.69</td>
<td>0.9987</td>
</tr>
<tr>
<td>0.6</td>
<td>127.43</td>
<td>0.9998</td>
</tr>
<tr>
<td>0.7</td>
<td>129.70</td>
<td>0.9994</td>
</tr>
<tr>
<td>0.8</td>
<td>129.58</td>
<td>0.9987</td>
</tr>
<tr>
<td></td>
<td>Average: 136.85 ± 13</td>
<td>0.9977</td>
</tr>
</tbody>
</table>

Figure 3 XRD patterns of Fe(H₂PO₄)₃·2H₂O (a), Fe(H₂PO₄)₃·2H₂O calcined at 150 (b) and 400 (c) °C.

Figure 4 FTIR spectra of Fe(H₂PO₄)₃·2H₂O (a), Fe(H₂PO₄)₃·2H₂O calcined at 150 (b) and 400 (c) °C.
X-ray power diffraction

The XRD patterns of Fe(H₂PO₄)₂ • 2H₂O and the Fe(H₂PO₄)₂ • 2H₂O calcined at 150 and 400 °C are shown in Fig. 3. All detectable peaks of the Fe(H₂PO₄)₂ • 2H₂O and the calcined Fe(H₂PO₄)₂ • 2H₂O at 150 and 400 °C are indexed as Fe(H₂PO₄)₂ • 2H₂O, FeH₂P₂O₇ and Fe₂P₂O₁₄ structures, which are identified using the standard data of PDF # 751444, PDF # 200517 and PDF # 782285, respectively. These results indicated that the three crystal structures are in monoclinic system with space group P2₁/n (Z = 2) for Fe(H₂PO₄)₂ • 2H₂O and C2/c (Z = 4) for Fe₂P₂O₁₄ (PDF # 200517 for FeH₂P₂O₇ has no data available). The average crystallite sizes and lattice parameters of Fe(H₂PO₄)₂ • 2H₂O, FeH₂P₂O₇ and Fe₂P₂O₁₄ were calculated from X-ray spectra and are tabulated in Table 3. The lattice parameters of Fe(H₂PO₄)₂ • 2H₂O and Fe₂P₂O₁₄ are comparable to those of the standard data of PDF # 751444 and PDF # 782285, respectively.

FT-IR spectroscopy

The FT-IR spectra of the Fe(H₂PO₄)₂ • 2H₂O and Fe(H₂PO₄)₂ • 2H₂O calcined at 150 and 400 °C are shown in Fig. 4. The IR spectrum of Fe(H₂PO₄)₂ • 2H₂O is very similar to those M(H₂PO₄)₂ • 2H₂O (M=Mn, Co, Ni) observed by Koleva and Mehandjiev (2006), which are assigned relating to the fundamental vibrating units, H₂PO₄⁻ and H₂O. The strong bands in the region of 1150–950 cm⁻¹ are attributed to the P–O stretching vibrations. The bending OPO vibrations appear in the region of 450–600 cm⁻¹. The couple bands at 1250 and 796 cm⁻¹ are assigned to the in-plane and out-of-plane bending modes of P–O–H, respectively. The band around 900 cm⁻¹ could be due either to the γOH vibrations.
Table 3  Average crystallite sizes and lattice parameters of Fe(H₂PO₄)₂•2H₂O and its transformation products calculated from XRD data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>a  (Å)</th>
<th>b  (Å)</th>
<th>c  (Å)</th>
<th>β  (°)</th>
<th>Average Crystallite sizes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(H₂PO₄)₂•2H₂O</td>
<td>DIF. PDF - This work</td>
<td>7.25(1)</td>
<td>10.10(0)</td>
<td>5.32(0)</td>
<td>95.71(0)</td>
<td>28±4</td>
</tr>
<tr>
<td>FeH₂P₂O₇</td>
<td>PDF# 200517</td>
<td>11.94</td>
<td>8.37</td>
<td>9.93</td>
<td>118.74</td>
<td>-</td>
</tr>
<tr>
<td>(Fe(H₂PO₄)₂•2H₂O</td>
<td>calcined 150 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>27 ± 6</td>
</tr>
<tr>
<td>Fe₃P₂O₁₂</td>
<td>PDF#782285</td>
<td>-0.86</td>
<td>-0.43</td>
<td>-0.63</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>(Fe(H₂PO₄)₂•2H₂O</td>
<td>calcined 400 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>29±6</td>
</tr>
</tbody>
</table>

or to the P–O stretching vibration. The weak band at about 635 cm⁻¹ is due to the water libration. In the O–H stretching mode region the multiple bands, which are characteristic for the acid salts (Xu et al., 1998), (Chapman, 1968) appear as ABC trio bands at about 3130–3180 cm⁻¹ (A band), 2380–2440 cm⁻¹ (B band) and 1680–1860 cm⁻¹ (C band). The νₕₒₒ stretching modes of HOH in Fe(H₂PO₄)₂•2H₂O appear at 3140 cm⁻¹ (Vₕ) and 3320 cm⁻¹ (Vₖ). The doublet bands at 1630 and 1567 cm⁻¹ contribute both to the C band and to water bending mode.

The FTIR spectrum of the calcined Fe(H₂PO₄)₂•2H₂O at 150 °C (Fig.3b) is similar to that of FeH₂P₂O₇ (Harcharras et al., 2003), (Harcharras et al., 2003). The infrared spectrum can be interpreted on the basis of characteristic vibrations of PO₂ group, P–OH bond and POP bridge. The P–O stretching modes of the [PO₄]₄⁻ ion are known to appear in the 1250–975 cm⁻¹ region (Steger et al., 1968). The symmetric PO₂ stretching vibrations (Vₕₒₒ PO₂) for the FeH₂P₂O₇ sample are observed in the range of 1000-1100 cm⁻¹, while the asymmetric stretching vibrations (Vₕₒₒ PO₂) are located at 1100 and 1200 cm⁻¹. The asymmetric (Vₕₒₒ POP) and symmetric stretch (Vₖₒₒ POP) bridge vibrations for this sample are observed in 900-1000 and 400-700 cm⁻¹ regions, respectively. The PO₃ deformation, rocking modes, the POP deformations, the torsional and external modes are found in the 400–230 cm⁻¹ region.

The FTIR spectrum of the calcined Mn(H₂PO₄)₂•2H₂O at 400 °C (Fig.3c) is similar to that of Fe₃P₂O₁₂ (Ramakrishnan et al., 1985). The vibrational modes of P₂O₁₂⁴⁻ ion are assigned according to the literatures (Ramakrishnan et al., 1985), Corbridge & Lowe, (1954), (Rajkumar et al., 1985). One of the most noteworthy features of this spectrum is the presence of strong bands in the ranges of 1350-1220, 1150-1100, 1080-950, and 780-400 cm⁻¹. These bands can be assigned to Vₕₒₒ OPO, Vₕₒₒ OPO, Vₕₒₒ POP, and Vₖₒₒ POP vibrations, respectively. The observation of a strong Vₕₒₒ PO band is known to be the most striking feature of cyclotetraphosphate spectra, along with the presence of the Vₕₒₒ OPO¹ band.
it was shown that the crystal structure is monoclinic (space group C2/c) with a cyclic structure of the \([P_2O_5]^4\) anion. This has been confirmed by the FTIR measurement

**Scanning electron microscopy**

The morphologies of Fe(H_2PO_4)_2•2H_2O and Fe(H_2PO_4)_2•2H_2O calcined at 150 and 400 °C are shown in Fig. 5. The morphologies of Fe(H_2PO_4)_2•2H_2O and Fe(H_2PO_4)_2•2H_2O calcined at 150 and 400 °C show coalescence in aggregates of irregularly shaped crystals of different sizes. The corresponding SEM micrographs of the mentioned compounds appear to be highly agglomerated caused primarily by the process of dissolution in precipitation and thermal decomposition reactions.

**The magnetic properties**

The specific magnetization curves of Fe(H_2PO_4)_2•2H_2O and Fe(H_2PO_4)_2•2H_2O calcined at 150 and 400 °C obtained from room temperature VSM measurements are shown in Fig. 6. This curve is typical for a strong magnetic material and indicates clear hysteresis ferromagnetism in the field range of ±10 000 Oe, which this range the specific magnetization increases with increasing field and strong in the field range investigated (± 10 kOe). Specific saturated magnetization (M_s) values of 96.28, 32.25 and 37.78 emu/g were observed for Fe(H_2PO_4)_2•2H_2O and Fe(H_2PO_4)_2•2H_2O calcined at 150 and 400 °C, respectively. It is worth noting that the higher value of 96.28 emu/g obtained in Fe(H_2PO_4)_2•2H_2O sample was compared with the Ms of bulk Fe_3O_4 (92 emu/g) (Soumhi et al., 2001), (Huil-li et al., 2007), and to the reported the magnetic properties of nanoparticles are usually smaller than those of the corresponding bulk materials. Gupta and Gupta (2005) reported the Ms value of Fe_3O_4 nanoparticles are in the range of 30–50 emu/g. The coercive forces (Hc) obtained on the increasing and decreasing filed sides (blanket) were 488.76 ± 488.76, 503.07 ± 503.07 and 501.76 ± 501.76 Oe for Fe(H_2PO_4)_2•2H_2O and the Fe(H_2PO_4)_2•2H_2O calcined at 150 and 400 °C, respectively. Ferromagnetic properties of Fe(H_2PO_4)_2•2H_2O and the Fe(H_2PO_4)_2•2H_2O calcined at 150 and 400 °C were reported for the first time.

**Conclusion**

Fe(H_2PO_4)_2•2H_2O powder was successfully synthesized by a simple method using Fe metal and phosphoric acid at 40 °C with short time consuming (15 min.). Kinetic analysis from non-isothermal TG applying model-fitting method results a single value of E on the different θ which can be assigned to a simple reaction. The activation energy calculated for the decomposition of Fe(H_2PO_4)_2•2H_2O by different methods and techniques were found to be consistent. This indicates that the activation energy of decomposition is independent on process and the nature of non-isothermal methods as well as TGA. The kinetic model that better described the reaction of dehydration of Fe(H_2PO_4)_2•2H_2O was the F_d model as simple n-order reaction. The corresponding function is \( f(\alpha) = (1-\alpha)^{1/2} \) and \( g(\alpha) = \frac{2[(1-\alpha)^{1/2}-1]}{1+2(1-\alpha)^{1/2}} \). The structures, morphology and magnetic properties of synthesized powder and its transformation products were investigated. The presented synthesis method is simple, cost-effective and environmental friendly and can be used to prepare other interesting materials.
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