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Thermoanalytical investigation of iron phosphate obtained by spontaneous precipitation from aqueous solutions

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Abstract

Iron(III) phosphate has been precipitated under supersaturation conditions from equimolecular aqueous solutions of 0.025 M $Fe(NO_3)_3{\cdot}9H_2O$ and K_2HPO_4, at pH = 2.00 and at ambient temperature. The precipitate has been characterised by TG/DTG/DTA and DSC techniques, chemical analysis, IR-spectroscopy and X-ray powder diffraction. A yellowish-white amorphous solid of formula $Fe_2(HPO_4)_3{\cdot}xH_2O$ has been obtained. Alternatively, a pinkish-white amorphous precipitate of formula $FePO_4{\cdot}2H_2O$ is obtained under the same conditions from $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ using hydrogen peroxide as the oxidising agent. Although the IR spectra and the thermal behaviour of both compounds are quite different, they crystallise as $FePO_4$ when annealed at 650 °C in air. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: $FePO_4$; Thermal analysis; Amorphous compounds; IR-spectroscopy; X-ray powder diffraction

1. Introduction

$LiFePO_4$ has recently been in focus as a viable cathode material in secondary lithium batteries [1,2], owing to its good electrochemical performances. In addition is iron environmentally friendly and cheap. Because of difficulties of lithium to be extracted/reinserted reversibly through the diminished surface area of the $LiFePO_4/FePO_4$ interface [2] only an utilisation of 70% is reached after a few electrochemical cycles. It has been claimed by [3] that a "new synthetic route" to obtain $LiFePO_4$ allows a 95–100% utilisation and good cyclability. Similarly, it has recently been proposed a synthesis of ε-$VOPO_4$ that allows production of chemically lithiated Li_xVOPO_4, which displays good electrochemical performances compared to the structurally similar α-$LiVOPO_4$ synthesised via high-temperature solid state route [4].

Wet chemical methods, such as hydrothermal, template and precipitation methods, provide intimate mixing of the component elements in the solution allowing finer particles to be produced by rapid homogeneous nucleation. Powders obtained by the generally used "high-temperature" methods are generally coarse.

Although the chemistry of iron phosphates is well-known, the preparation methods needed to obtain well-defined chemical microstructure depend on the conditions of synthesis. Iron(III) phosphate is usually synthesised by precipitation by adding a solution of disodium phosphate to a solution of an iron(III) salt [5]. However, complexes chemical reactions, such as the formation of phosphato complexes, do occur in aqueous solutions, and the reaction mechanism depends on the starting concentration of iron and phosphate and the solution pH [6]. Iron phosphate

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is a well-known catalyst for oxidative dehydrogenation reaction [7]. It has been prepared by aqueous solutions of acidic ferric nitrate and diammonium hydrogen phosphate at pH about 7.5 and ambient temperature [8]. Several authors have studied the formation of iron phosphate by precipitation from aqueous solutions since this is an excellent and cost-effective method for remotion of phosphate in wastewaters [9,10]. The iron phosphate has been also studied as ferroelectric material [11,12].

In the present paper, we report on the synthesis of $FePO_4$ materials by spontaneous precipitation from aqueous solutions. The obtained precipitates have been characterised by thermoanalytical techniques, chemical analysis, infrared spectroscopy and X-ray diffraction.

2. Experimental

2.1. Instrumentation

A TG/DTA apparatus SDT 2960 (TA Instruments, Dorking, England) was used. Samples between 5 and 10 mg were heated over the temperature range from ambient to 800 °C at a heating rate of 5 °C min^{-1} in air atmosphere at 100 ml min^{-1} flow rate. The α-Al_2O_3 was used as reference material. Samples were run in open platinum pans. The MDSC 2920 (TA Instruments) was used for the DSC experiments. Samples were analysed in aluminium pans with lids, in an atmosphere of dry nitrogen flowing at 120 ml min^{-1}. Samples were equilibrated at −20 °C for 5 min and then ramped at 10 °C min^{-1} to 400 °C.

pH was measured with a SA520 pH-meter (Orion, Beverly, MA, USA), using a C2005-8 red rod combined pH electrode (Radiometer, Copenhagen, Denmark). For standardisation standard buffer solutions from Aldrich were used.

Elemental composition of the precipitates (Fe, P) was determined by flame and graphite atomic absorption spectrometry (Varian 220 FS, Victoria, Melgrave, Australia). The amount of iron(II) in the samples was determined by automated potentiometric titration.

The infrared spectra (IR) in the region 4000–400 cm^{-1} were recorded on a Perkin-Elmer spectrometer (Norwalk, CT, USA). The compounds were pulverised and diluted with KBr powder.

The precipitates and the calcined products (in air at 400 and 650 °C for 24 h) were characterised by X-ray powder diffraction analysis (Philips PW 3710 diffractometer) using Cu Kα radiation.

2.2. Reagents and standard solutions

De-ionised water (18 MΩ cm) produced by a Milli-Q water production system (Millipore, Bedford, MA) was used to prepare all solutions. $Fe(NO_3)_3 \cdot 9H_2O$ (Fluka, p.a.), $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and K_2HPO_4 (Carlo Erba, RPE) crystalline solids were dissolved in de-ionised water to prepare iron and phosphate stock solutions. The stock solutions were standardised by atomic absorption spectrometry. Stock standard solutions of iron and phosphorus (Aldrich) at 1000 ppm were used for the preparation of the working standard solutions for the iron and phosphorus AAS determination. All acids used were of analytical reagent grade. Hydrogen peroxide 30% weight (reagent grade, Ashland Chemical Italiana) and ammonium hydroxide 32% weight (electronic grade, Rudi Pont) were used.

2.3. Preparation

A solution of 0.025 M $Fe(NO_3)_3 \cdot 9H_2O$ (having an initial pH of 1.8–1.9) was added at ambient temperature to a constantly stirred equimolecular solution of K_2HPO_4, previously acidified with nitric acid at $pH = 2.00$, in a 1:1 volume proportion. A yellowish-white precipitate started to form immediately and the addition rates were maintained constant in order to keep the pH at 2.00 by dropwise addition of concentrated ammonium hydroxide solution.

An amount of 3 ml of concentrated hydrogen peroxide solution was added to a solution of 0.025 M $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ under vigorously stirring. Then this solution was added at ambient temperature to an equimolecular solution of K_2HPO_4, previously acidified with nitric acid at $pH = 2.00$, in a 1:1 volume proportion, under constantly stirring. A pinkish-white precipitate started to form immediately and the addition rates were maintained constant in order to keep the pH at 2.00 by dropwise addition of concentrated ammonium hydroxide solution.

The precipitates were kept for 7 days in contact with the mother liquor without stirring. The solution pH was daily monitored and adjusted to $pH = 2.00$. Aliquots of the supernatant were periodically withdrawn; filtered through membrane filter (0.8 μm) and the filtrates were analysed for the total iron and phosphorus content. Then, the precipitates were collected on membrane filter (0.8 μm), washed several times with de-ionised water and dried in air in a dry-room ($RH < 0.2\%$) for several days, unlike otherwise stated. Prior to characterisation the powder samples were crushed in an agate mortar.

3. Results and discussion

Yellowish-white solid iron phosphate is obtained under supersaturation conditions that allows spontaneous precipitation from iron(III) and dipotassium phosphate aqueous solutions at $pH = 2.00$ and ambient temperature. The insoluble precipitate has been identified as being completely amorphous by X-ray powder diffraction. The chemical analysis of the precipitate gives 28 wt.% Fe_{total} and 19 wt.% P_{total}, suggesting the molar ratio $Fe_{total}:P_{total} = 2:3$. This indicates that the precipitate is $Fe_2(HPO_4)_3 \cdot xH_2O$. These results are in good agreement with those obtained by [9], where an acidic iron phosphate has been grown on a porous polymer by precipitation from a $Fe(NO_3)_3 \cdot 9H_2O$–K_2HPO_4–H_2O solution.

A pinkish-white solid is obtained under supersaturation conditions sufficient for spontaneous precipitation from iron(II) and dipotassium phosphate aqueous solutions at $pH = 2.00$ and ambient temperature when hydrogen peroxide is used as oxidising agent. The insoluble precipitate has been identified as completely amorphous by X-ray powder diffraction. The chemical analysis suggests a molar ratio $Fe_{total}:P_{total} = 1:1$, indicating the general formula $FePO_4 \cdot xH_2O$. The oxidation of Fe^{2+} to Fe^{3+} with

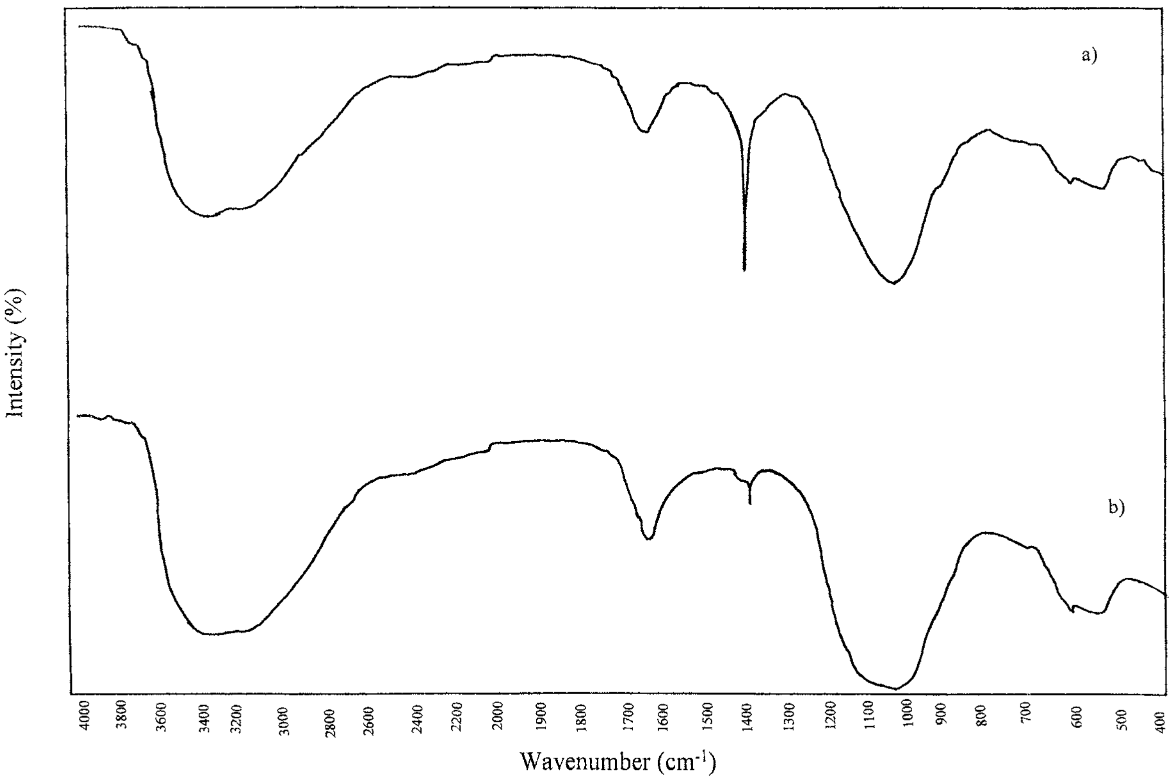

Fig. 1. IR spectra of the compounds obtained by precipitation from equimolecular solutions of: (a) $Fe(NO_3)_3 \cdot 9H_2O$ and K_2HPO_4 and (b) $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and K_2HPO_4 using hydrogen peroxide as oxidising agent, at $pH = 2.00$ and at ambient temperature.

Table 1
Concentration of iron and phosphate in the mother liquor and the solution pH values as a function of days of storage

Time (days)	[Fe] (10^{-4} M)	[P] (10^{-4} M)	pH
(a) Equimolecular solution of 0.025 M $Fe(NO_3)_3{\cdot}9H_2O$ and K_2HPO_4 at pH = 2.00 and ambient temperature			
3	15.0	9.8	1.99
4	12.9	9.8	1.94
5	12.0	9.7	2.00
6	11.1	9.6	2.00
7	10.9	9.5	1.99
(b) Equimolecular solution of 0.025 M $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ and K_2HPO_4, using hydrogen peroxide as oxidising agent, at pH = 2.00 and ambient temperature			
3	2.2	3.0	1.99
4	1.7	2.0	1.95
5	1.6	1.9	2.00
6	1.6	1.8	2.00
7	1.5	1.8	2.01

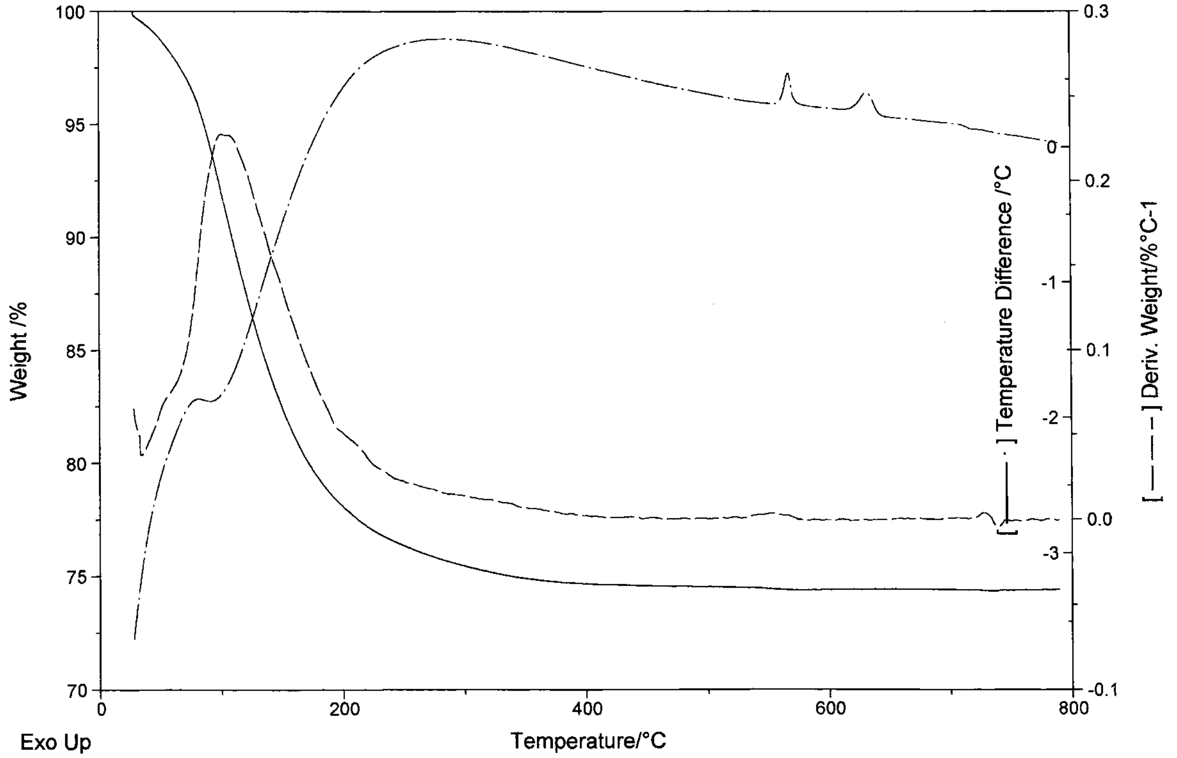

Fig. 2. TG/DTG/DTA curves of the compound obtained by precipitation from equimolecular solutions of $Fe(NO_3)_3{\cdot}9H_2O$ and K_2HPO_4 at pH = 2.00 and at ambient temperature. Heating rate of 5 °C min^{-1} in flowing air.

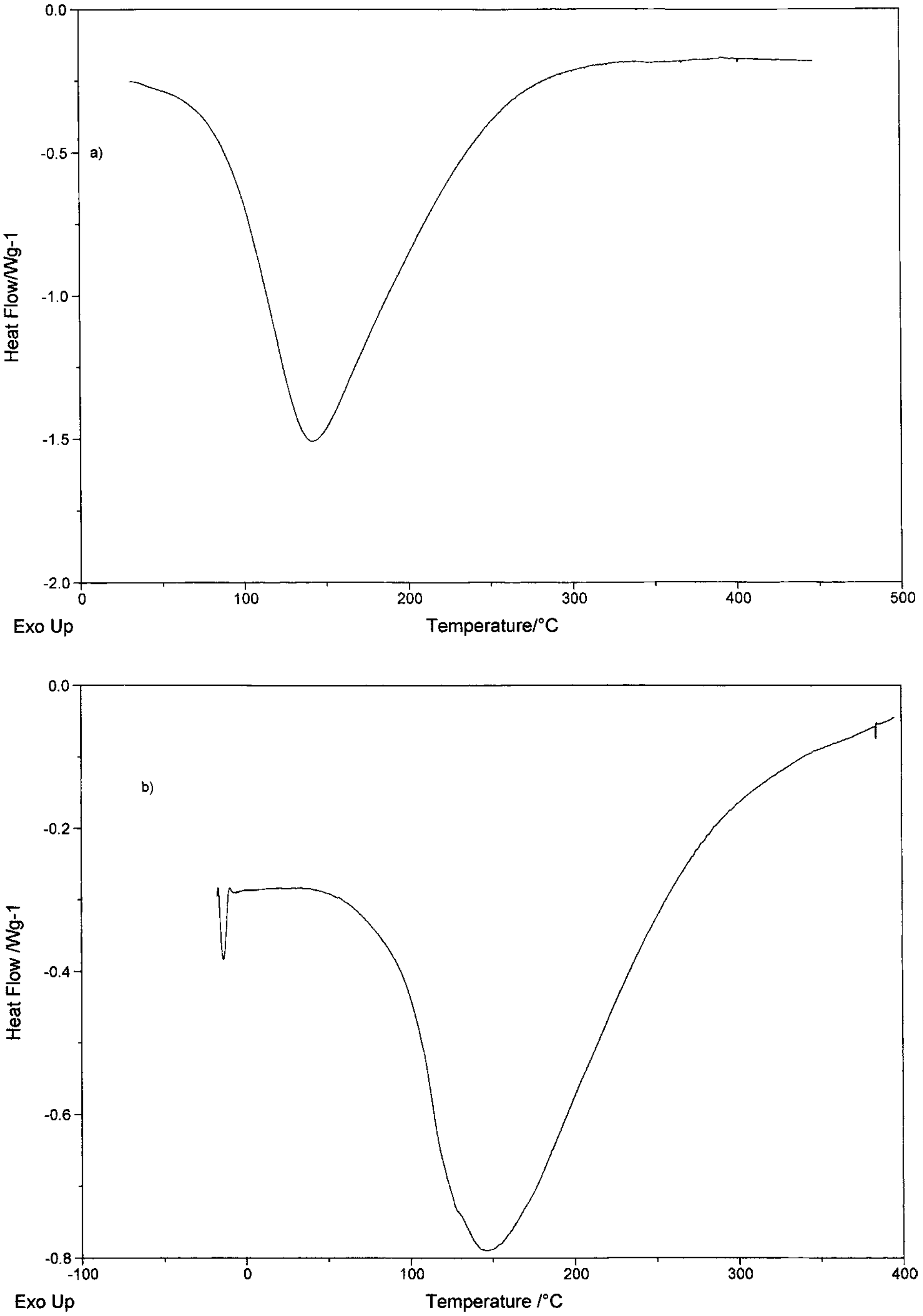

Fig. 3. DSC signals of the compounds obtained by precipitation from equimolecular solutions of: (a) $Fe(NO_3)_3 \cdot 9H_2O$ and K_2HPO_4 and (b) $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and K_2HPO_4 using hydrogen peroxide as oxidising agent, at pH = 2.00 and at ambient temperature. Heating rate of 10 °C min^{-1} in flowing N_2.

hydrogen peroxide is complete. Fe^{2+} compounds are not observed in the final product.

The onset of the precipitation resulted in a drop in the solution pH according to the following equation:

$$Fe^{3+}(l) + H_2PO_4^-(l) + 2H_2O(l) \rightarrow FePO_4 \cdot 2H_2O(s) + 2H^+(l) \quad (1)$$

The concentrations of iron and phosphate in the mother liquor and the solution pH values reported as a function of the number of days of storage (Table 1). As it can be seen the slow decrease of the pH in the solution indicates that the precipitation process has not completely stopped after the 4th day, irrespective of the starting solutions.

Fig. 1 shows the infrared spectra of the two phosphate compounds. The overall characteristics are similar to that reported in [13,10]. Just like the model compound $FePO_4{\cdot}2H_2O$, the spectra have strong and very wide band with maximum at 3400 cm^{-1}. Then, different to the model compound they have a medium intensity band at 1630 cm^{-1} and a strong and very narrow band at 1380 cm^{-1} for the yellowish-white solid (Fig. 1(a)), whereas a very small and narrow peak at the same wavenumber is showed for the pinkish-white solid (Fig. 1(b)). Then, again in accordance with what is observed for the model compound, they have a strong and wide band at 1030 cm^{-1}, and a medium band with maximum at 530 cm^{-1} overlapping with a small, sharp peak at 600 cm^{-1}. The absorption bands at 1630 cm^{-1} is attributed to the water bending vibrations, whereas the absorption bands at 1380 cm^{-1} is due to the bending vibration of O–H···O bond as occurs analogously in KH_2PO_4 [14].

The TG/DTG/DTA curves of the yellowish-white precipitate are shown in Fig. 2. A weight loss of 26% is seen in the TG curve over the temperature region 50–400 °C. A corresponding peak is observed in the DTG curve. Endothermic effects over the temperature region are shown in the DTA curve at 120 °C and in the DSC curve at 142 °C (Fig. 3(a)). It has been reported that the dehydration of some hydrate metal

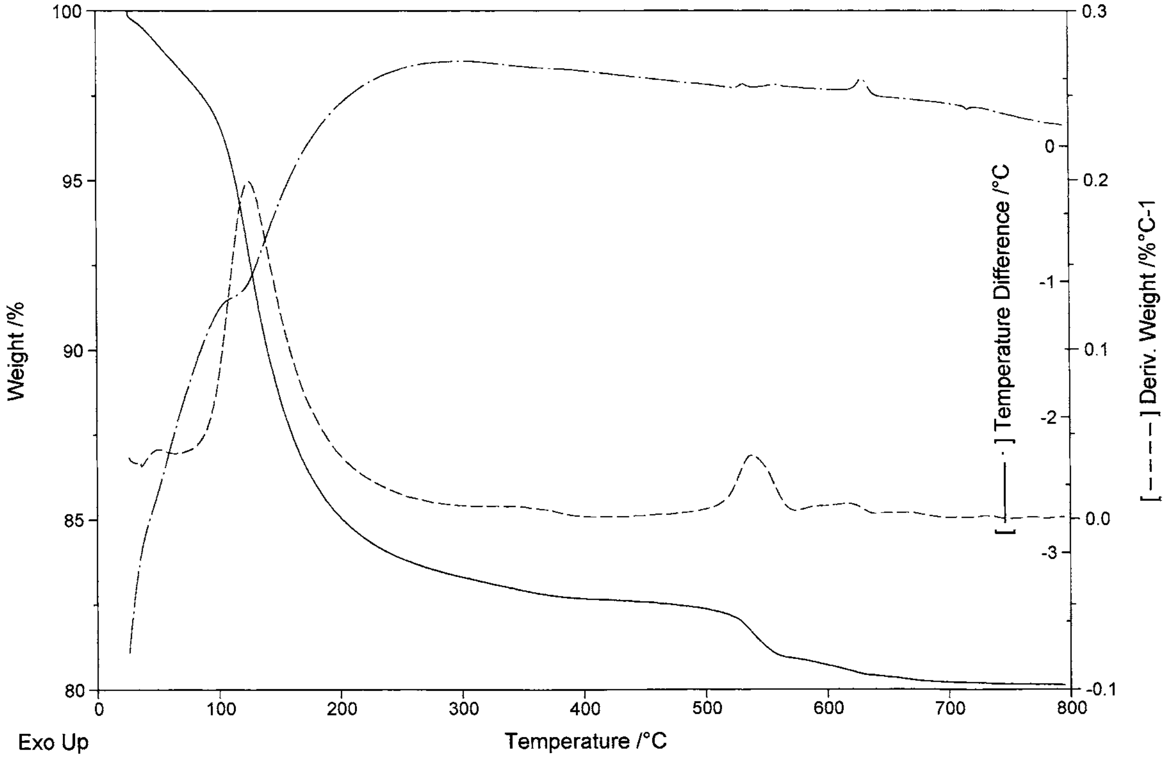

Fig. 4. TG/DTG/DTA curves of the compound obtained by precipitation from equimolecular solutions of $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ and K_2HPO_4 at pH = 2.00 and at ambient temperature, using hydrogen peroxide as oxidising agent. Heating rate of 5 °C min^{-1} in flowing air.

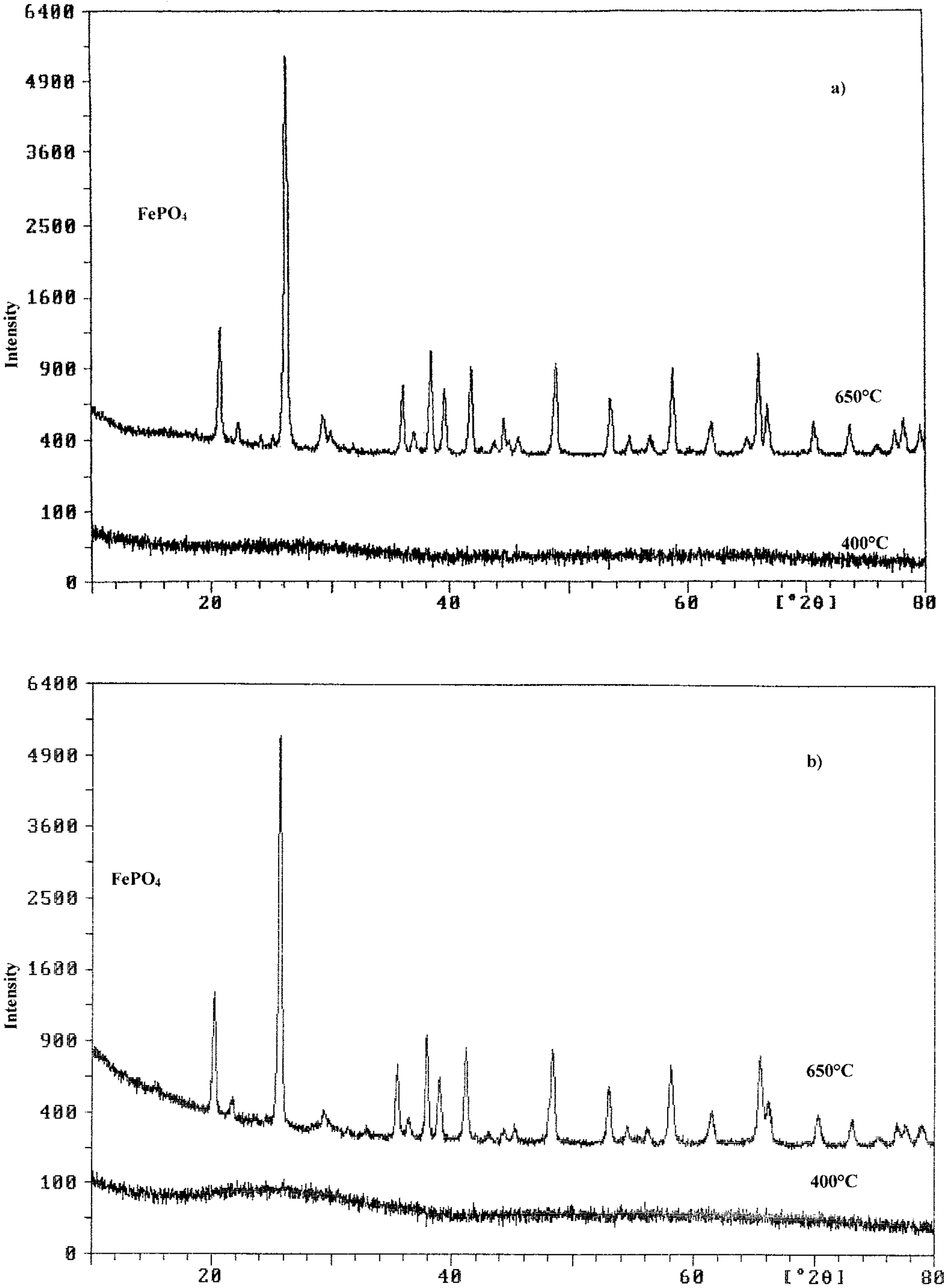

Fig. 5. X-ray powder diffraction patterns of compounds obtained by precipitation from equimolecular solutions of: (a) $Fe(NO_3)_3 \cdot 9H_2O$ and K_2HPO_4 and (b) $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and K_2HPO_4 using hydrogen peroxide as oxidising agent, at pH = 2.00 and at ambient temperature, and calcined at different temperatures in air.

phosphate proceeds by both anion disproportion and condensation, yielding amorphous and acid products [15]. At higher-temperature two exothermic effects are displayed in the DTA curve, namely, at 571 and 630 °C, which are not accompanied by appreciable weight loss in the TG curve (Fig. 2). These effects likely indicate two-step structural transformation of the FePO framework [16]. Finally, a weak endothermic effect occurs at 717 °C without appreciable weight loss. This effect is ascribed to the $\alpha \rightarrow \beta$ transition as reported for quartz-like materials of type MXO_4 (M = B, Al, GA, Fe, Mn and X = P, As) [11].

The TG/DTG/DTA curves of the pinkish-white precipitate are displayed in Fig. 4. Over the temperature range from ambient to 400 °C there is a weight loss in the TG curve with a peak at 150 °C in the derivative curve. An endothermic effect is shown in the corresponding DTA curve at 120 °C. The mass loss of 17% corresponds to the presence of two molecules of water per mole of compound. The DSC signal shows an endothermic effect at 150 °C in the temperature range between −20 and 400 °C with a shoulder at 200 °C (Fig. 3(b)). The melting endotherm between −20 and 0 °C corresponds to water which had recrystallised during the DSC treatment; it seems natural to suppose that this water is physically adsorbed on the solid. At higher-temperature a weight loss of 2.6% between 500 and 700 °C is observed in the TG curve. The weight loss may be associated to decomposition at 490 °C of the coprecipitated ferric or ammonium sulphate. The presence of sulphate was confirmed by precipitation as barium sulphate from the acidic dissolved solution. Three exothermic peaks, namely at 532, 558 and 630 °C, are displayed in the DTA curve. Finally, a weak endothermic effect occurs at 716 °C without appreciable weight loss is observed, which is attributed to the $\alpha \rightarrow \beta$ transition as abovementioned for the yellowish-white precipitate.

Fig. 5(a) and (b) show the X-ray diffraction patterns of the amorphous precipitates calcined at different temperatures in air. Upon heating at 400 °C, the residue products still remain amorphous. On further heating at 650 °C, the X-ray diffraction patterns of the final products show a series of diffraction peaks, indicating that a transformation from amorphous to a crystalline phase of the precipitates occurs at higher-temperature. All reflections are attributed to the anhydrous $FePO_4$, which has a trigonal structure [17]. These results are in good agreement with the results reported by [8], where the $FePO_4$ transforms from amorphous to a crystalline phase at about 600 °C.

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