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Hydrothermal synthesis of iron(III) phosphates in the presence of urea

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Iron(III) phosphates have been synthesized directly under mild hydrothermal conditions. The reaction of $FeCl_3$, H_3PO_4 and $(NH_2)_2CO$ aqueous solutions at 180 °C leads to the formation of four individual compounds: $FePO_4{\cdot}2H_2O$, $Fe(NH_4)(HPO_4)_2$, $Fe_2(NH_4)(OH)(PO_4)_2{\cdot}2H_2O$ and $Fe(NH_3)_2PO_4$. The reaction product depends on the Fe : P : C molar ratio in the reaction mixture. The effect of urea on the reaction route is discussed.

Introduction

Traditional methods of preparation of crystalline inorganic compounds at high temperatures, such as condensation growth,[1] chemical vapor transport growth,[2] vapor–liquid–solid growth,[3] flux growth[4] and solution alloy growth,[5] have been used successfully for a long time and have usually given excellent results. However, the situation is rapidly changing now. An increasing interest is being shown in synthetic methods that could be carried out at low or moderate temperatures (150–350 °C) and can produce metastable compounds exhibiting unusual and valuable properties. Among such methods, hydrothermal syntheses are regarded as the most promising.[6] In the majority of the hydrothermal reactions water is used as a solvent and they are carried out at below critical temperature and under autogenous pressure. Under such conditions the solubility of the reactants increases significantly, which enables them to react in a specific way, with the formation of compounds that differ from the thermodynamically stable phases formed under traditional solid state reactions. This technique has been used successfully for the synthesis of zeolites,[7,8] phosphates,[9–14] arsenates[15,16] and some metal oxides.[17–19] Recently, by exploiting the presence of cationic organic templates in hydrothermal preparations of d-block metal phosphates, a large variety of metastable phases with layered and open frameworks have been synthesized. It was found that the type of compound formed depends upon the exquisitely sensitive relationship between the charge, shape and volume of the cationic template and the nature of the void formed in the anionic framework. Complex hydrogen bonding between protonated amine templates and framework oxygen atoms has been shown to be a particularly influential factor in determining which material will crystallize under given conditions. A relatively large number of framework atoms are required to encapsulate completely the bulky organic templates, and a certain correlation therefore exists between the complexity of the framework formed and the size of the template.

Iron(III) phosphates exist as minerals and have a rich crystal chemistry. These minerals are often basic and/or hydrated phosphates and belong to the most perplexing substances in the mineral kingdom.[20] Synthetic iron(III) phosphates are of particular interest by virtue of application in the selective oxidation of methanol, as well as for the diversity of their structural chemistry and magnetic properties. Several new compounds in the iron(III) phosphate family have been synthesized recently by the hydrothermal method.[21–29]

In this paper we present our results on the direct synthesis of iron(III) phosphates under mild hydrothermal conditions by the reaction of $FeCl_3(aq)$ and $H_3PO_4(aq)$ in the presence of urea. It was shown earlier on the example of metal oxides[30] and trivalent metal phosphates[31–34] syntheses that a slow hydrolytic decomposition of urea in the reaction mixture at elevated temperature, catalysed by the presence of acids, enables homogeneous precipitation of products. Such materials can not be obtained by using other alkali metal hydroxides, whereas the kinetics of urea hydrolysis determines the nature of the solid phase obtained.

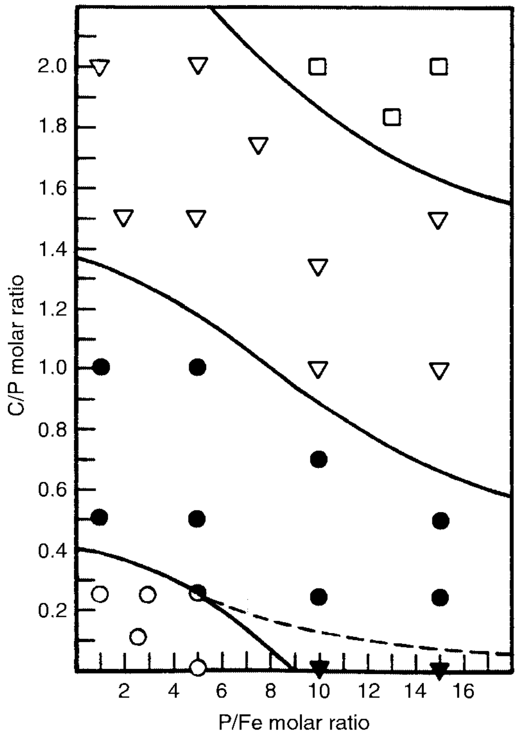

Fig. 1 Phase diagram for the formation of iron(III) phosphates by reaction of $FeCl_3(aq)$ and $H_3PO_4(aq)$ in the presence of urea: $FePO_4{\cdot}2H_2O$ (○), $Fe(NH_4)(HPO_4)_2$ (●), $Fe_2(NH_4)(OH)(PO_4)_2{\cdot}2H_2O$ (▽), $Fe(NH_3)_2PO_4$ (□) and no precipitation (▼).

Results and discussion

By studying the hydrothermal reactions in the system $FeCl_3$–H_3PO_4–$(NH_2)_2CO$–H_2O, the formation of several different iron(III) phosphate products was found depending both on the molar ratio of iron- and phosphorus-containing reagents in the reaction mixture and on the acidity of the solution. Regulation of the acidity of the reaction system was achieved by adding different amounts of urea, which decomposes gradually with release of $NH_3(aq)$. Fig. 1 shows the ranges of concentration

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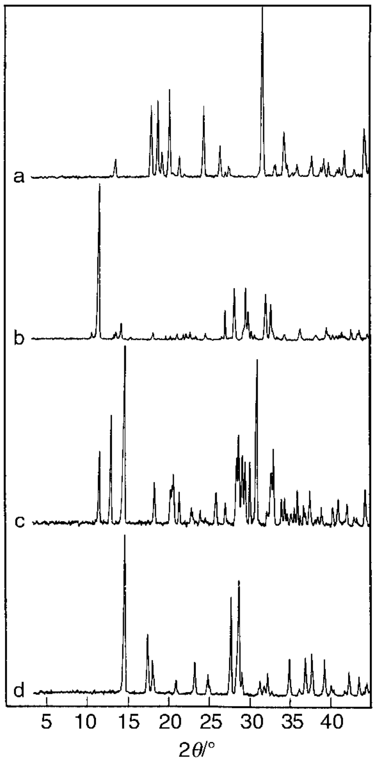

Fig. 2 Powder XRD patterns for: (a) $FePO_4 \cdot 2H_2O$, (b) $Fe(NH_4)(HPO_4)_2$, (c) $Fe_2(NH_4)(OH)(PO_4)_2 \cdot 2H_2O$, and (d) $Fe(NH_3)_2PO_4$.

used for the preparation of individual crystalline phases. In the absence of urea and when the P : Fe molar ratio is higher than 10 : 1, no precipitation of solid products was observed. At lower P : Fe molar ratios (<10 : 1) the formation of $FePO_4 \cdot 2H_2O$ as the sole product takes place.

The addition of urea to the reaction system favors the synthesis of the new compounds. The compound $FePO_4 \cdot 2H_2O$ as a pure phase is formed when the molar ratio C : P < 0.4 : 1 and P : Fe < 7 : 1 (pH 1.0 to 1.5). The XRD powder pattern of this compound is shown in Fig. 2a. The positions and intensities of its X-ray diffraction peaks correspond well to those of the $FePO_4 \cdot 2H_2O$[35] of metastrengite structure.[36] Elemental analysis supports this composition (Table 1). The IR spectra (Fig. 3a) confirm the absence of N-containing groups. Thermal treatment of this material shows that the release of the crystal water takes place in one step at *ca.* 200 °C (Fig. 4a). Fig. 5a shows that the material has irregular prismatic particles.

The compound $Fe(NH_4)(HPO_4)_2$ is formed at higher C : P molar ratios in the reaction system (Fig. 1). The XRD powder pattern of this compound (Fig. 2b) corresponds to that of the compound prepared by suspension of freshly precipitated colloidal iron(III) phosphate in a $NH_4H_2PO_4$(aq) solutions in the range (0.5 to 3 mol dm^{-3}) in a sealed container and aged at temperatures of 27 to 145 °C at pH 2.0 to 3.5.[37] The analytical data (Table 1) are consistent with this composition. The presence of protonated ammonium groups manifests itself as strong bands at 3248 (ν NH_4^+) and 1430 cm^{-1} (δ NH_4^+) in the IR spectrum (Fig. 3b). The P–OH groups give rise to a shallow absorption at 2566 cm^{-1} (ν OH) and in a shift of the ν PO_4 band from its usual position at 1021 to 1067 cm^{-1}. The TG curve (Fig. 4b) shows that the thermal decomposition of this compound takes place in two steps. The first stage (*ca.* 350 °C) is related to the loss of ammonia, whereas in the second step (*ca.* 600 °C) the condensation of the hydrogenphosphate groups takes place. The SEM micrograph (Fig. 5b) shows small plates of *ca.* 1 µm width.

Spheniscidite, $Fe_2(NH_4)(OH)(PO_4)_2 \cdot 2H_2O$, is known as a mineral isotypic with leucophosphite, $Fe_2K(OH)(PO_4)_2 \cdot 2H_2O$.[38,39] Spheniscidite was synthesized recently hydrothermally[21] in the presence of 1,3-diaminopropane. In our preparation, this iron(III) hydroxophosphate is formed at relatively high pH (9–11) of the reaction system, when large amounts of urea were added (Fig. 1c). Elemental analysis (Table 1) and XRD powder data (Fig. 2c) confirm the assigned formula $Fe_2(NH_4)(OH)(PO_4)_2 \cdot 2H_2O$. The presence of ammonium ions in the solid introduces strong bands at 3024 (δ NH_4^+) and 1430 cm^{-1} (δ NH_4^+) in the IR spectrum, as well as signals for OH groups at 3483 cm^{-1} (Fig. 3c). The TG and DTG curves (Fig. 4c) show that decomposition takes place in three to

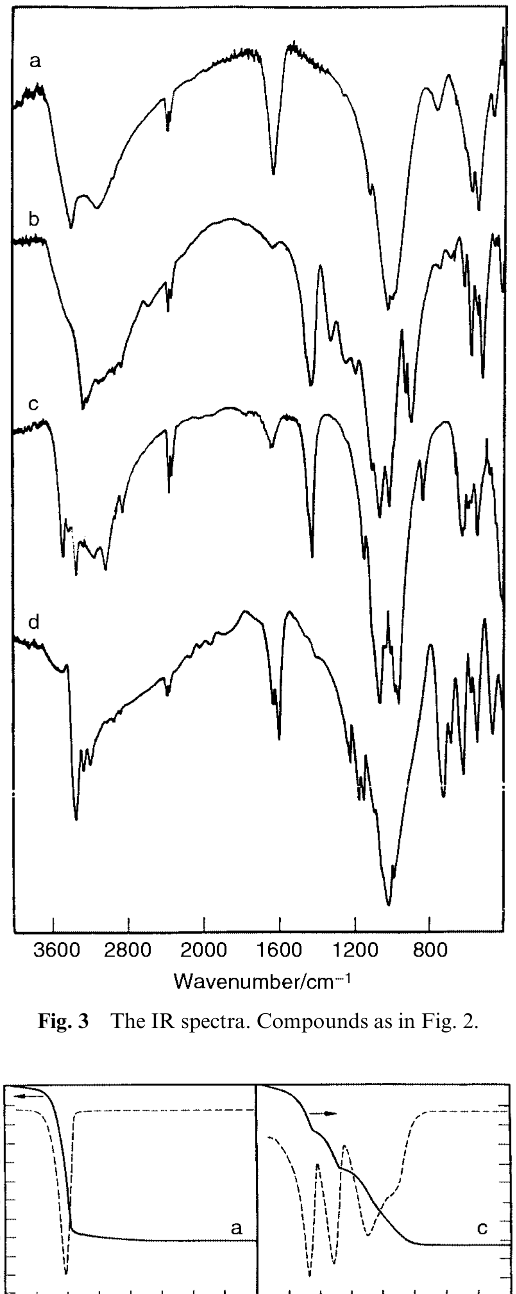

Fig. 3 The IR spectra. Compounds as in Fig. 2.

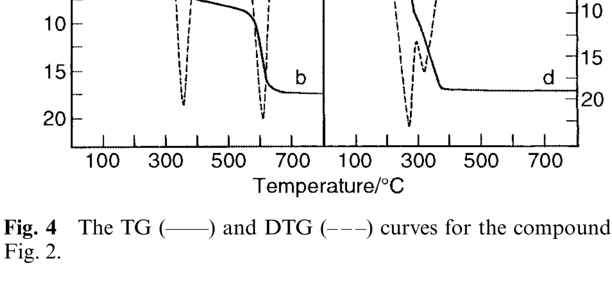

Fig. 4 The TG (——) and DTG (– – –) curves for the compounds in Fig. 2.

Table 1 Analytical data and weight loss (w.l.) at 800 °C for the compounds synthesized

	$FePO_4·2H_2O$		$Fe(NH_4)(HPO_4)_2$		$Fe_2(NH_4)(OH)(PO_4)·2H_2O$		$Fe(NH_3)_2PO_4$	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
%Fe	29.7	29.91	21.4	21.02	29.5	29.99	30.2	30.23
%P	16.3	16.59	23.1	23.32	17.2	16.63	16.8	16.77
%N	—	—	5.2	5.26	3.6	3.75	15.2	15.14
%w.l.	20.5	19.26	17.36	16.55	20.7	19.04	19.0	18.39

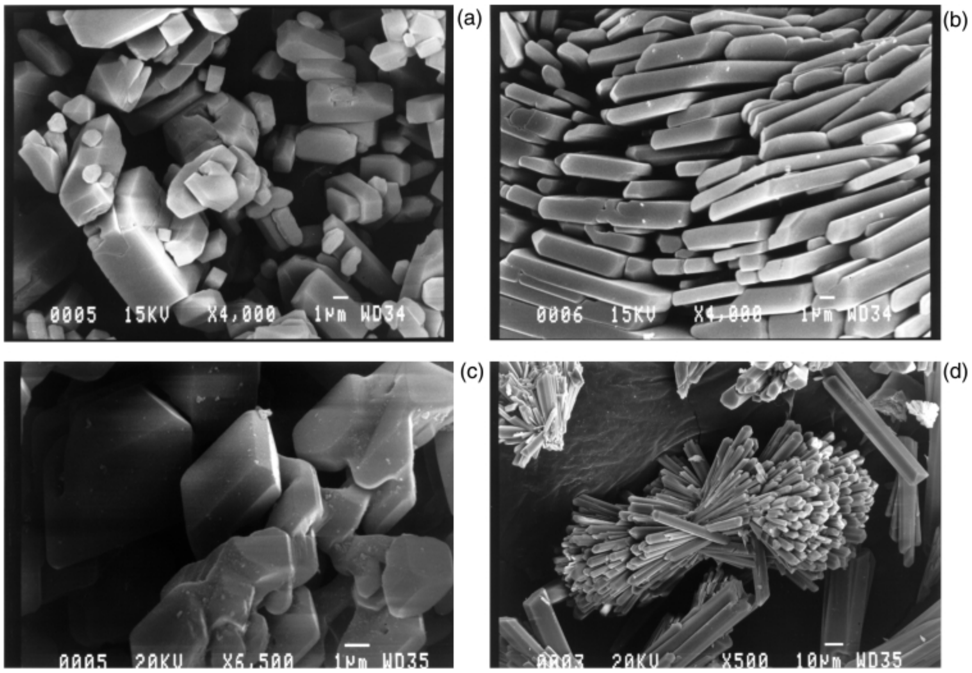

Fig. 5 The SEM images for the compounds in Fig. 2.

four steps. The first (*ca.* 170 °C) corresponds to the loss of two water molecules, the second (*ca.* 250 °C) to loss of ammonia. At higher temperatures, water is lost due to the condensation of hydroxyl and hydrogenphosphate groups. Fig. 5c shows the SEM image for this compound.

When the molar ratios in the reaction system are $C:P < 1.7:1$ and $P:Fe > 10:1$ (pH > 10), $Fe(NH_3)_2PO_4$ is formed (Figs. 1d and 2d, Table 1). The IR spectrum of this solid (Fig. 3d) indicates the presence of ammonia molecules, bands at 3341, 3253 (free ν NH_3) and 1591 cm^{-1} (δ NH_3 asym). The structural analysis confirms this point.[40] The structure consists of a three-dimensional network of octahedral FeO_4N_2 and tetrahedral PO_4 groups linked by vertex sharing. Two crystallographically independent ammonia molecules are linked to iron. The structure encloses one principal channel running parallel to the *a* axis, into which the hydrogen atoms of the ammonia molecules project. In agreement with the structural data, the SEM image (Fig. 5d) indicates that the compound has a fibrous morphology. The TG and DTG curves are presented in Fig. 4d. It is seen that the novel iron(III) phosphate is a thermally stable compound, because it does not lose mass until *ca.* 250 °C. The mass loss occurs in two steps. The desorption of the first ammonia molecule takes place at *ca.* 270 °C, whereas the second molecule is released at *ca.* 340 °C.

Conclusion

A new route for the hydrothermal synthesis of iron(III) phosphates is described. The compounds produced are very sensitive to the presence of urea in the reaction system and to its concentration. Without urea and at low urea concentration only $FePO_4·2H_2O$ is formed. With increase of the urea concentration the formation of the iron(III) hydrogenphosphate, $Fe(NH_4)(HPO_4)_2$, takes place. Further increase in urea concentration, resulting in progressive neutralization of H_3PO_4 and pH increase in the reaction media, provides favorable conditions for the formation of another iron(III) hydroxophosphate, $Fe_2(NH_4)(OH)(PO_4)_2·2H_2O$. When the amount of urea added is very high, the ammonia molecules present in the reaction media act as template agents and a new compound, $Fe(NH_3)_2PO_4$, is formed. The structures of all phases obtained have a three-dimensional network with iron octahedrally co-ordinated by oxygen atoms (FeO_6) or oxygen and nitrogen atoms (FeO_4N_2).

Experimental

Synthesis

In all cases an aqueous solution of $FeCl_3$ (1 mol dm^{-3}) was used as an initial source of iron, and 85% H_3PO_4 was used as a source of phosphorus. The synthetic procedure included first the preparation of H_3PO_4–$(NH_2)_2CO$ solutions with C:P molar ratio varying from 0.25 to 2:1, and then mixing $FeCl_3$(aq) and phosphorus containing solutions in a desired molar ratio (P:Fe = 0.5–15:1) in a 250 cm^3 Teflon lined stainless steel vessel. The total volume of a reaction mixture was 40 cm^3. The reaction vessel was sealed and heated at 180 °C for 6 days. The solid product was filtered off, thoroughly washed with an excess of deionized water and dried in air.

Analytical procedures

The diffractometer used was a Philips model PW 1729/1720 ($\lambda = 1.5418$ Å). Thermal analysis was performed on a Mettler TA 4000 (TG 50 model, nitrogen atmosphere, heating rate 10 °C min^{-1}). The infrared spectra were recorded with a Perkin-Elmer 1000 FT-IR spectrophotometer. Microanalytical data (C, H and N) were obtained with a Perkin-Elmer Model 2400B elemental analyzer. The phosphorus and iron contents of the solids were determined with a SpectraSpectrometer DCP-AEC after dissolving a weighed amount of sample in HF(aq). Micrographs were recorded with a JEOL JSM-6100 electron microscope operating at 20 kV.

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