



Crystals of New Ferric Acid Phosphate, $\text{Fe}_3\text{H}_3(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$, Performed by Inorganic Sol-Gel Process

A. ELYAHYAOU^{*}, S. BOUHLASSA^{*} and I. MAATALLAH

Laboratoire de Radiochimie, Faculté des Sciences, Université Mohammed V, B.P. 1014, Rabat, Morocco

(Received: 25 September 2001; in final form: 2 May 2002)

Key words: phosphate, phosphoric acid, iron (III), inorganic sol-gel process

Abstract

Crystals of $\text{Fe}_3\text{H}_3(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$ are obtained at room temperature and 50 °C from phosphate gel prepared by evaporation of H_3PO_4 and FeX_3 ($\text{X} = \text{NO}_3^-$, Cl^-). Optimal experimental conditions of crystal formation are defined. X-ray powder diffraction, IR absorption spectroscopy and TGA analysis are undertaken to investigate the effect of starting solution compositions on the nature and the growth of crystals. Formulation of synthesised phosphate is proposed on the basis of the composition comparison with the iron phosphate compounds formerly studied. A relation between OH group, phosphorus (or phosphate) and iron contents of the examined phosphates is found. The unit cell parameters are obtained from powder X-ray diffraction data. It is hexagonal with unit cell dimensions $a = 9.114(7)$ Å, $c = 16.715(3)$ Å and $V = 1202.62$ Å³. The BET surface area of this phosphate is measured and a value of 5.0 m²/g is obtained.

Introduction

In recent years, a method of synthesising metal phosphate xerogels directly from concentrated phosphoric solutions was investigated [1–4]. This method is not a real sol-gel process. It has the advantage of preparing phosphate materials in more convenient processing conditions. The process can be performed at room temperature by evaporation of phosphoric acid solutions of metallic cation. The principal area of focus has been the preparation of optical materials [5–7].

The iron phosphates have been mainly studied as catalysts [8–10] and used in several applications, for example agriculture, ceramic and glasses [11–16]. The common forms discussed in the literature were precipitated from alkaline iron phosphate mixtures, or obtained by the solid state reaction route.

In the current study we report the preparation of a new ferric acid phosphate using the above-mentioned inorganic process.

Experimental

Instrumentation and analysis

Chemical products are of reagent grade and are used without further purification.

X-ray powder

X-ray powder diffraction experiments were carried out at room temperature using a Siemens D 5000 diffractometer monitored with copper K_α radiation ($\lambda = 1.5418$ Å).

Thermal gravimetric analysis (TGA)

The powdered samples were investigated by TGA with a monitored Seteram apparatus, using platinum crucibles and aluminium oxide as reference material. A heating rate of 5 °C per minute was used.

IR absorption spectroscopy analysis

Infrared absorption spectra in the range 4000–400 cm⁻¹ were obtained using the KBr pellet technique by a Perkin Elmer 577 IR spectrometer.

Chemical analysis

Synthesised crystals were carefully washed with ethanol and then wiped with the filter papers to eliminate the possibility of gel adhesion prior to determination of iron and phosphorus contents.

BET measurement

The BET surface area of the samples growing from 1M H_3PO_4 with $R = 2$ and 3 were obtained from nitrogen adsorption-desorption at -196 °C with a Micromeritics apparatus. Prior to the measurements, all samples were outgazed under vacuum at 110 °C for tow hours.

Synthesis

The ferric phosphate xerogels were synthesised using the inorganic process which was carried out by evaporating Fe^{3+} - H_3PO_4 solutions at room temperature or at 50 °C. The initial solutions were made at room temperature by mixing ferric chloride (or nitrate) and phosphoric acid solutions. The concentration ($\text{C}_{\text{H}_3\text{PO}_4}$) of investigated H_3PO_4 medium

* Authors for correspondence.

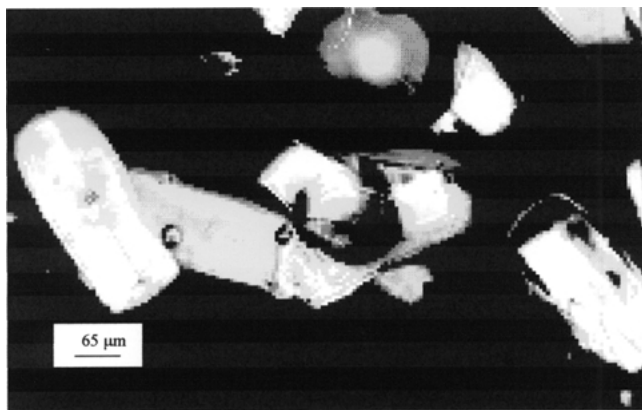


Photo 1. Crystals of iron (III) phosphate taken by microscope in polarised light.

range from 1 to 4M and the molar ratio of H_3PO_4 to Fe ($R = \text{C}_{\text{H}_3\text{PO}_4}/\text{C}_{\text{Fe}}$) range from 1 to 3.

To define optimal conditions where crystal formation occurs, and to examine the effect of the anion associated with iron (III), a series of investigations were undertaken at room temperature and 50°C in several systems $\text{H}_3\text{PO}_4\text{-FeX}_3$ ($\text{X} = \text{Cl}^-, \text{NO}_3^-$). It has been shown that the nature of the drying process products depends on the R value. For $1 \leq R \leq 3$ and $R > 3$ gel and precipitate are obtained, respectively. For R ranging between 1 and 2, gels are transparent. However, the opacity of these transparent gels increased when the drying process was carried out at room temperature (or 50°C) for longer periods. This phenomenon is most probably due to the crystal formation. The result of the optical microscopy analysis shown in Photo 1 corroborates this hypothesis. It was found that crystals having a maximal size of $325\ \mu\text{m}$ were obtained specially in the case $\text{C}_{\text{H}_3\text{PO}_4} = 1\ \text{M}$ and $R = 2$. On the other hand, it has been noted that, for R ranging between 2 and 3, crystals were obtained at room temperature and at 50°C for an aging period of a week and 3 days respectively.

It is concluded that the temperature and the nature of the anions associated with iron(III) have no effect on the crystal formation process in the explored conditions.

Experimental results

To identify the synthesised compounds, and to specify the dependence of their nature on the initial concentrations of both Fe(III) and H_3PO_4 , several crystals were analysed by X-ray diffraction, thermal gravimetric analysis, infrared absorption spectroscopy and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) techniques.

X-ray diffraction analysis

Effect of Fe(III) concentration

Figures 1 and 2 depict the X-ray spectra corresponding to several phosphate compounds made in H_3PO_4 1M with $1 \leq R \leq 3$; from both of which it appears that the obtained products are amorphous for $R < 2$ and well crystallised for $R \geq 2$. Moreover, the spectra are similar but their peak

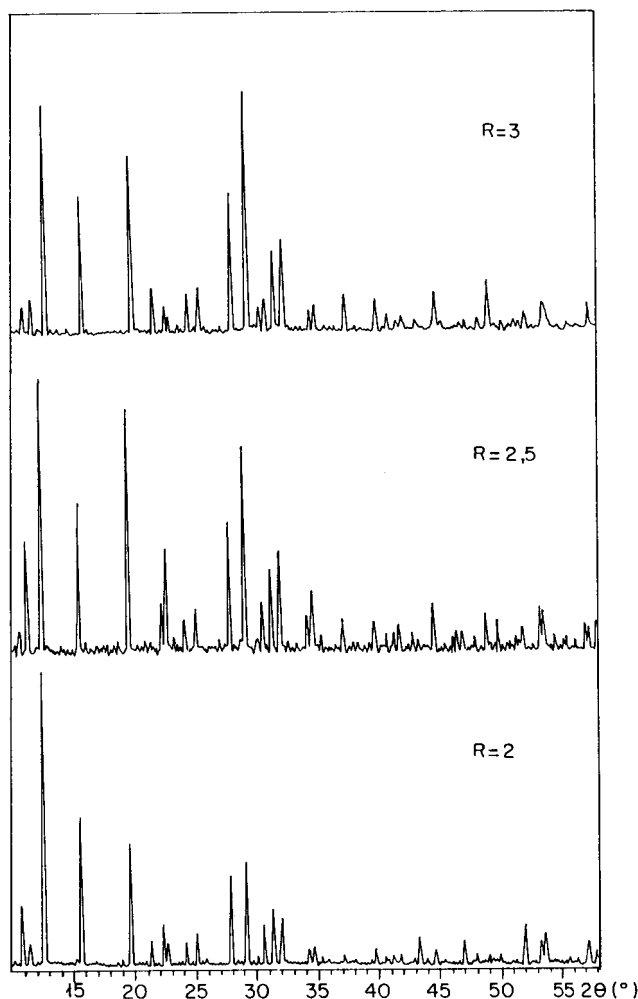


Figure 1. Diffractograms of xerogels obtained in $\text{C}_{\text{H}_3\text{PO}_4} = 1\ \text{M}$ with $2 \leq R \leq 3$.

intensities are different (Figure 1). These results clearly reveal the effect of Fe(III) concentration on the crystallisation process.

Effect of phosphate concentration

Figure 3 represents the XRD patterns of compounds prepared under the following experimental conditions: $R = 2$, $2 \leq \text{C}_{\text{H}_3\text{PO}_4} \leq 4\ \text{M}$. It should be pointed out that (i) the pattern of this figure and those of Figure 3 are similar and (ii) the H_3PO_4 and Fe(III) concentration effects are similar.

The results of chemical analysis of phosphorus and iron atomic ratios, performed on crystals made in 1 M H_3PO_4 with $R = 2, 2.5$ and 3 are 1.33, 1.8 and 2.5, respectively. As can be observed, there is an appreciable deviation between the composition of the starting solution and that found in the resulting crystals.

IR absorption spectroscopy analysis

To interpret results of the IR absorption spectroscopy, we refer to the range of vibration of phosphate and hydrogen-phosphate groups, given in Tables 2 and 3 respectively [1].

The IR spectra of crystals made in 1M H_3PO_4 solutions with $R = 2$ and 3 are reported in Figure 4. Figure 5 exhib-

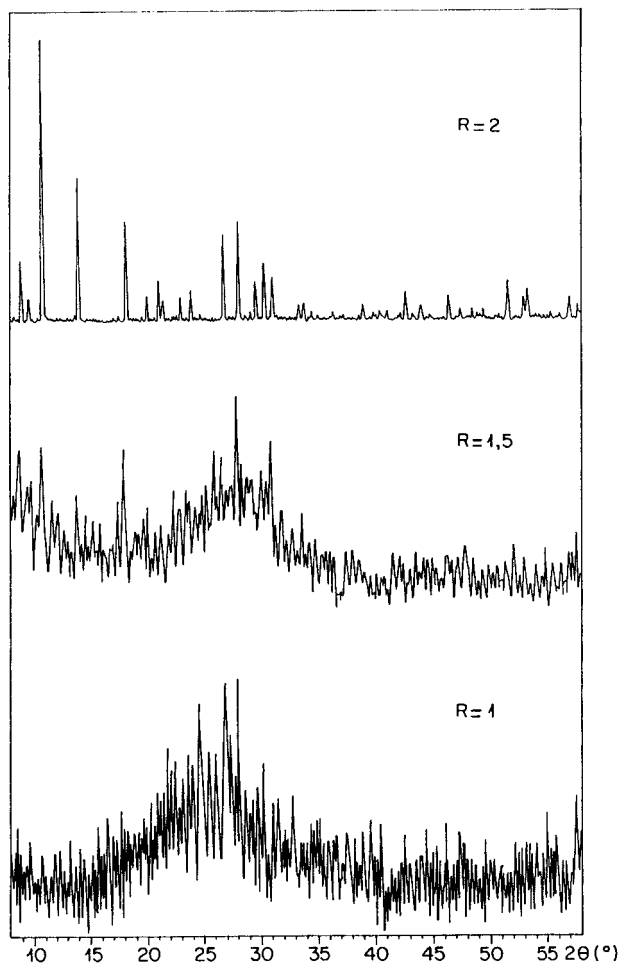


Figure 2. Diffractograms of xerogels obtained in $\text{CH}_3\text{PO}_4 = 1 \text{ M}$ with $1 \leq R \leq 2$.

its the IR spectra of crystals obtained from phosphoric acid media with $R = 2$ and $2 \leq \text{C}_{\text{H}_3\text{PO}_4} \leq 4 \text{ M}$. In all spectra the same bands are obtained, but their intensities vary with R and $\text{C}_{\text{H}_3\text{PO}_4}$. Assignment of all frequencies is proposed in Table 4. These results are in good agreement with X-ray diffraction analysis; there seems to be a correlation between the synthesised phosphates and the starting solutions. The IR analysis supports the presence of hydrogenphosphate ions in the compounds.

Thermal gravimetric analysis (TGA)

To identify the numbers of water molecules, the loss weight of crystals synthesised in $1 \text{ M H}_3\text{PO}_4$ with $R = 2$ was investigated by thermal gravimetric analysis. The TGA thermogram shown in Figure 6 exhibits four endothermic peaks: two peaks at 130 and 260 °C related to dehydration process, peaks at 350 °C and 500 °C assigned to the phase transformations.

According to the experimental data, the synthesised phosphate can be formulated (temporally) as $\text{Fe}_3\text{H}_{3+x}(\text{PO}_4)_4(\text{OH})_x \cdot (6-x)\text{H}_2\text{O}$. The indexing of the X-ray pattern of this compound is performed by means of the program TREOR90 from the first 20 lines [17]. A hexagonal solution is found with the figures of merit $M_{20} =$

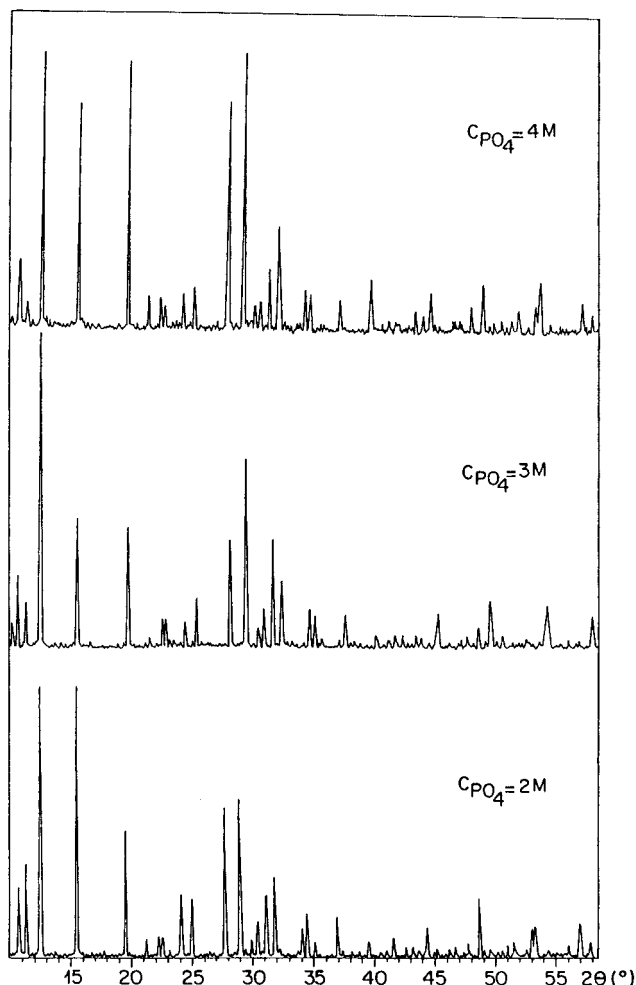


Figure 3. Diffractograms of xerogels obtained in $\text{CH}_3\text{PO}_4 = 2, 3$ and 4 M with $R = 2$.

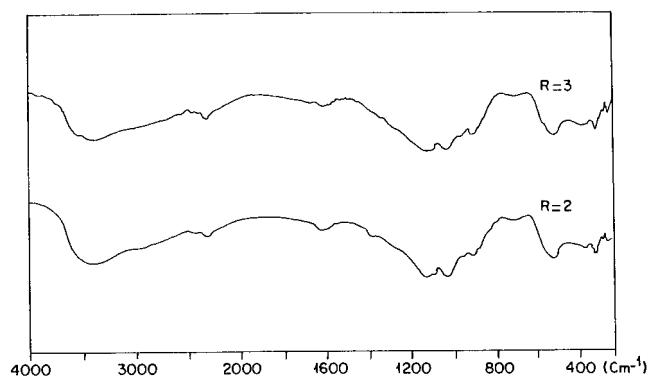


Figure 4. IR spectra of xerogels obtained in $\text{CH}_3\text{PO}_4 = 1 \text{ M}$ with $R = 2$ and 3 .

$20 F_{20} = 21(0.024954, 37)$. After a least-squares refinement using the ADFAP program, the unit cell dimensions are $a = 9.114(7) \text{ \AA}$, $c = 16.715(3) \text{ \AA}$ and $V = 1202.62 \text{ \AA}^3$ [18]. The powder pattern is fully indexed (Table 1). The measured density (2.16 g/cm^3) reveals the presence of $Z = 2$ formulae per unit. These parameters are comparable to those preliminary obtained on the same material with the four-circle diffractometer data.

Table 1. X-ray powder diffraction data of xerogel obtained in 1 M H_3PO_4 with $R = 2$

h k l	d_{obs}	d_{cal}	$2\theta_{\text{obs}}$ (deg)	$2\theta_{\text{cal}}$ (deg)
0 0 2	8.316	8.3576	10.62	10.58
1 0 0	7.866	7.8936	11.23	11.20
1 0 1	7.086	7.1377	12.47	12.39
1 0 2	5.719	5.7386	15.47	15.43
1 1 0	4.549	4.5573	19.49	19.46
0 0 4	4.178	4.1788	21.24	21.24
1 1 2	3.996	4.0011	22.21	22.20
2 0 0	3.941	3.9468	22.53	22.51
1 0 4	3.692	3.6932	24.07	24.08
2 0 2	3.566	3.5877	24.94	24.93
2 0 3	3.216	3.2206	27.71	27.68
1 1 4	3.083	3.0800	28.93	28.98
2 1 0	2.982	2.9835	29.93	29.93
2 1 1	2.937	2.9370	30.40	30.41
2 0 4	2.869	2.8693	31.14	31.15
2 1 2	2.809	2.8098	31.82	31.82
2 1 3	2.630	2.6301	34.05	34.06
3 0 1	2.601	2.5991	34.44	34.48
2 1 4	2.433	2.4281	36.90	36.99
2 2 0	2.280	2.2786	39.48	39.52
3 1 0	2.197	2.1892	41.03	41.20
3 1 1	2.170	2.1707	41.48	41.57
2 2 3	2.094	2.1091	43.14	42.84

Table 2. Vibration domains of PO_4 ions

Frequencies (cm^{-1})	Assignments
1020–1080	ν_3 Vibration
940–970	ν_1 Vibration
500–560	ν_4 Vibration
360–420	ν_2 Vibration

It must be noted, however, that this cell is similar to that of the $(\text{NH}_4)\text{H}_8\text{Fe}_3(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$ compound, which crystallises with the hexagonal system and space group $\text{P}31\text{c}$ [19].

Specific surface area

The results of the obtained BET surface area show that the crystals made at $R = 2$ and 3 have specific surface areas of

Table 3. Vibration domains of hydrogenphosphate ions

Frequencies (cm^{-1})	Assignments
3000–2525	(P)–OH Vibration
2400–2000	(P)–OH Deformation
1400–1200	P–O(H) Vibration
1030–820	P–O(H) Vibration
540–450	P–O(H) Deformation

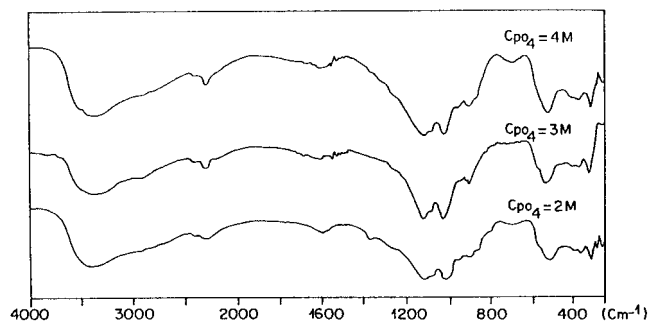


Figure 5. IR spectra of xerogels obtained in $\text{CH}_3\text{PO}_4 = 2, 3$ and 4 M with $R = 2$.

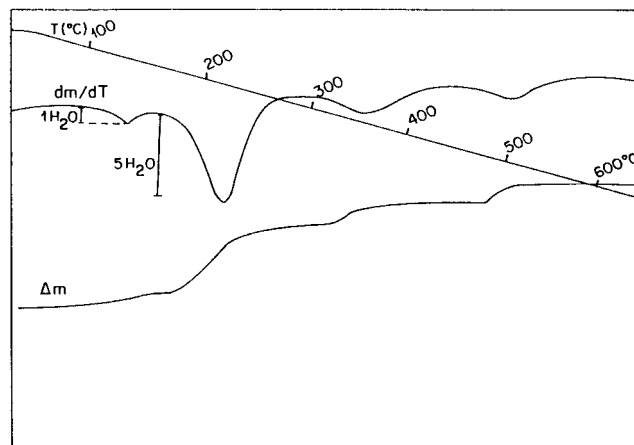


Figure 6. Thermogram of crystal obtained in CH_3PO_4 with $R = 2$.

$5.0 \text{ m}^2/\text{g}$ and $6.0 \text{ m}^2/\text{g}$ respectively. These values are relatively high whilst bibliographic data are in the range 0.4 – $6.4 \text{ m}^2/\text{g}$ [8]. For the amorphous product synthesised under the present conditions, the surface area is $1.7 \text{ m}^2/\text{g}$.

Discussion

On the basis of the available experimental data, we cannot propose a defined formulation of our new compound, because it does not allow us to distinguish between iron phosphates having a different number of water molecule contents, for example $\text{Fe}_3\text{H}_3(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}_3\text{H}_{3+x}(\text{PO}_4)_4(\text{OH})_x \cdot (6-x)\text{H}_2\text{O}$. So, to distinguish between these entities, bibliographic investigations are undertaken. A relationship between OH, Fe and PO_4 contents in many well defined iron phosphates (Table 5) is then established. Figure 7 shows the variation of the molar ratio OH/Fe (m/x) as a function of molar ratio Fe/PO_4 (x/z). A linear dependence is observed when x/z is higher than unity.

From these results, the OH contents of iron phosphates, $\text{Fe}_x\text{H}_y(\text{PO}_4)_z(\text{OH})_m \cdot n\text{H}_2\text{O}$ is: $m = 0$ when $x/z \leq 1$ and $m \neq 0$ when $x/z > 1$. In this case, this parameter is given by the equation: $m = 0.82x^2/z - 0.37x$.

Taking into account these results, our compound would not contain a hydroxyl group, since it is characterised by a molar ratio x/z equal to $3/4$. It can, consequently, be formulated as $\text{Fe}_3\text{H}_3(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$.

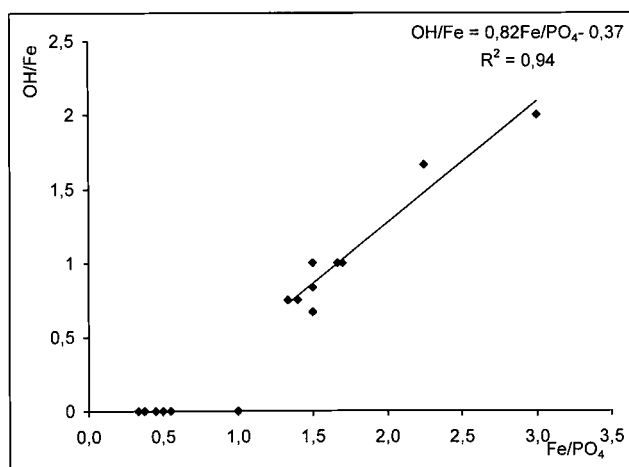
Table 4. IR frequencies of crystals obtained at ambient temperature in 1–4 M H₃PO₄ with 2 ≤ R ≤ 3

Frequencies (cm ⁻¹)				Assignments
R = 2		R = 3		
C _{PO₄} = 1 M	C _{PO₄} = 3 M	C _{PO₄} = 4 M	C _{PO₄} = 1 M	
3420	3400	3400	3420	Symmetric and asymmetric stretching of water molecules
2340	2300	2300	2340	Deformation of (P)–O(H)
1630	1630	1630	1630	Deformation of water molecules
1140	1140	1140	1140	Asymmetric vibration of PO ₄ ³⁻ ions
1020	1010	1010	1010	Symmetric stretching of PO ₄ ³⁻ ions
910	920	920	910	Vibration of (P)–O(H)
530	540	540	530	Asymmetric deformation of PO ₄ ³⁻ ions

Table 5. Atomic ratio OH:Fe, H:Fe and Fe:PO₄ in various bibliographic iron phosphate compounds

Compounds	OH:Fe	H:Fe	Fe:PO ₄	Ref.
FeH ₃ P ₂ O ₈ ·H ₂ O	0:1	3:1	1:2	20
Fe(H ₂ PO ₄) ₃	0:1	0:1	1:3	21
FePO ₄ ·2H ₂ O	0:1	0:1	1:1	22
Fe ₃ (H ₃ O)H ₁₄ (PO ₄) ₈ ·4H ₂ O	0:3	15:3	3:8	23
Fe ₃ H ₉ (PO ₄) ₆ ·6H ₂ O	0:3	9:3	3:6	24
Fe ₃ H ₁₅ (PO ₄) ₈ ·4H ₂ O	0:3	15:3	3:8	24
Fe ₃ (PO ₄) ₂ (OH) ₂	2:3	0:3	3:2	25
Fe ₃ (PO ₄) ₂ (OH) ₃	3:3	0:3	3:2	26
Fe ₄ (PO ₄) ₃ (OH) ₃ ·5H ₂ O	3:4	0:4	4:3	27
Fe ₄ (PO ₄) ₃ (OH) ₃ ·12H ₂ O	3:4	0:4	4:3	28
Fe ₅ (PO ₄) ₃ (OH) ₅ ·2H ₂ O	5:5	0:5	5:3	29
Fe ₅ (PO ₄) ₃ (OH) ₅	5:5	6:1	5:3	29
Fe ₆ (PO ₄) ₄ (OH) ₅ ·4H ₂ O	5:6	0:6	6:4	30
Fe ₃ (PO ₄)(OH) ₆ ·3H ₂ O	6:3	0:3	3:1	31
Fe ₉ (PO ₄) ₄ (OH) ₁₅	15:9	0:9	9:4	29
Fe ₃ H ₃ (PO ₄) ₄ ·6H ₂ O	?:3	3:3	3:4	*

*This work.

Figure 7. Evolution of the atomic ratio OH:Fe versus Fe:PO₄, in various bibliographic iron phosphate compounds.

The obtained experimental results show that crystallisation occurs in explored phosphoric media when the total concentration ratio of phosphate to ferric ions ranges between 2 and 3. These phosphate compounds are isotype to the Fe₃H₃(PO₄)₄·6H₂O crystal as revealed by X-ray diffraction analysis and corroborated by IR spectroscopy. In addition, these phosphates prepared by the present inorganic-like sol-gel process have a relativity higher surface area compared to those prepared by other techniques, such as precipitation and annealing methods. Indeed, surface areas of iron compounds prepared by precipitation are between 0.7 and 2.8 m²/g for Fe₂P₂O₇ and by annealing are 0.4 m²/g for Fe₇(PO₄)₆. However, our data are comparable to those obtained by the dry evaporation route for instance 6.4 m²/g for FePO₄ [8]. By the way, the technique used in this work has the advantage of being performed at lower temperature.

Conclusion

A new iron acid phosphate, with the chemical formula Fe₃H₃(PO₄)₄·6H₂O, is synthesised using a wet chemical process. Details concerning synthesis conditions are described. It is found that the H₃PO₄ concentration as well as the atomic ratio PO₄/Fe are decisive parameters for the nature of the synthesis products. Well-crystallised phosphates, with different compositions, are obtained in the examined solutions if PO₄/Fe ranges between 1 and 3. The Fe₃H₃(PO₄)₄·6H₂O compound is obtained in 1 M phosphoric acid solution with PO₄/Fe = 2.

The products are characterised by X-ray diffraction, infrared spectroscopy, chemical and thermal gravimetric analysis.

On the other hand, the non-hydroxylation of the synthesised phosphate Fe₃H₃(PO₄)₄·6H₂O, is proposed on the basis of investigations on bibliographic data, from which a relationship between OH/Fe and PO₄ contents is established. The unit cell is obtained from X-ray powder diffraction. It is hexagonal with the cell parameters $a = 9.114(7)$ Å, $c = 16.715(3)$ Å and $V = 1202.62$ Å³. The surface area of this compound is measured by the BET technique. A relatively high value of 5.0 m²/g is obtained.

Acknowledgement

We are indebted to Dr. A. Benabad and L. El-Amari for helpful discussions about indexing X-ray diffraction data.

References

- V. Brandel, G. Iroulart, E. Simoni, M. Genet, and J.P. Audière: *New J. Chem.* **14**, 113 (1990). [
- V. Brandel, G. Iroulart, E. Simoni, and M. Genet: *New J. Chem.* **15**, 247 (1991).
- L. Lou, J. Mugner, M. Bahtat, V. Brandel, and M. Genet: SPIE sol-gel opticsII, SPIE, San Diego, CA, **1758**, 83 (1992).
- L. Lou, E. Simoni, V. Brandel, and M. Genet: *Thin Solid Films* **73**, 238 (1994).
- H. Huang, S. Dunn Bruce, and I. Zink Jeffrey: *J. Am. Chem. Soc.* **122**, 3739 (2000).
- W. Cheng, E. Baudrin, S. Dunn Bruce, and I. Zink Jeffrey: *J. Mater. Chem.* **11**, 92 (2001).
- H. Michael Huang, M. Hermes Soyez, S. Dunn Bruce, and I. Zink Jeffrey: *Chem. Mater.* **12**, 231 (2000).
- J.M.M. Millet: *Thèse d'état*, Université Claude Bernard, Lyon I, France, (1990).
- L. Hilberg, L.R. Hulther, and E. Gramatkovski: *Am. J. Chem. Nut* **50**, 125 (1989).
- B. Rebenstrof, T. Lindblad, and L.T. Anderson: *J. Catalysis* **128**, 293 (1991).
- R. Glemza, V.O. Parent, and W.A. Welsh: *Catalysis Today* **14**, 175 (1992).
- M. Ijjaalli, B. Malaman, C. Gleitzer, J.K. Warner, Hriljac, and J.A. Che: *Am. Solid State Chem.* **86**, 159 (1990).
- B. Ech-chahed, F. Jenndt, B. Malaman, and C. Gleitzer: *J. Solid State. Chem.* **74**, 47 (1988).
- Q. Hibben, E. Lu, Y. Haruvy, and S.E. Webber: *Chem. Mater.* **6**, 76 (1994).
- B. Rebenstrof and T. Lindblad: *J. Catalysis* **128**, 303 (1991).
- D. Coster and J. Friprat: *J. Chem. Mater.* **5**, 1204 (1993).
- P.E. Werner, L. Erikson, and M. Wesdahl: *J. Appl. Crystallogr.* **18**, 367 (1985).
- C.C. Plam, J. Choynet, and B. Raveau: *Bull. Acad. Roy. Belg. Cl. Sc.* **61**, 473 (1973).
- P.B. Moore and Araki: *Am. Min.* **64**, 578 (1979).
- A. Frazier: *Ind. Eng. Chem. Res.* **28**, 225 (1989).
- F. D'Yvoire: *Bull. Soc. Chim. France, Dec.* 2277 (1961).
- Aldrige et al.: *J. Appl. Chem.* **13**, 17 (1963) (A.S.T.M. card 2-250)
- K. Warstard and W. Frazier: *Powder Diffraction* **2**, 187 (1987).
- Tennessee valley authority: *Crystallogr. Prop. of Fertilizer Cmpds., Bull. y- 217*, II (1991).
- D. Rouzies and J.M.M. Millet: *Hyperfine Interactions* **77**, 11 (1993).
- P.B. Moore: *Nature* **251**, 305 (1974).
- J. Melgarejo, S. Gali, and C. Ayora: *Neues Jahrb. Min. Monatsh.* 446 (1988).
- W.A. Gordon: *Am. Min.* **35**, 132 (1950).
- P.B. Moore: *Am. Min.* **55**, 135, (1970).
- D.J. Fisher: *Bertr. Min. petr.* **5**, 204 (1956).
- Smith and Deganello, University of Chicago, Illinois, USA, (1971) (A.S.T.M. card 24-527).