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Effects of temperature and phosphoric acid addition on the solubility of iron phosphate dihydrate in aqueous solutions☆



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ABSTRACT

As important controlling factors for the synthesis of iron phosphate materials by liquid-phase precipitation, the solubilities of iron phosphate dihydrate were systematically measured at H_3PO_4 concentrations from 1.13 wt% to 10.7 wt%, temperature from 298.15 to 363.15 K, and atmosphere pressure in this work. The solubility was found to increase 5 orders of magnitude or more with increasing the concentration of phosphoric acid, and decrease 1 to 2 orders of magnitude with increasing the equilibrium temperature. The phosphoric acid addition and temperature were found to affect the solubility of iron phosphate dihydrate by the formation or dissociation of coordination species, which could further accelerate the phase transformation from the amorphous iron phosphate dihydrate to orthorhombic iron phosphate dehydrate by dissolution–recrystallization mechanism. The high dependences of the solubility of iron phosphate materials on H_3PO_4 concentration and temperature were also well predicted by calibration equations, which are meaningful for quantitatively understanding the precipitation process and sequential crystalline structure transformation and pursuing a rational strategy for synthesizing specific iron phosphate materials.

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1. Introduction

Interest in iron phosphate compounds has always been intensive due to their impressive performance and wide application in the fields of battery [1–2], catalysis [3–5], wastewater purification [6,7], ferroelectrics [8], and *etc.* [9]. It has been well recognized that the manipulation of the structure and size of iron phosphate materials is of great importance for achieving various and competitive functions [10–12]. For examples, as cathode materials for lithium/sodium ion batteries, iron phosphates with amorphous or orthorhombic heterosite structure were found to exhibit much better electrochemical performance due to the existence of plenty of migration routes for carrier ions [13–15]. Although α -Quartz iron phosphate is inert in electrochemical activity, it shows high performance to catalyze the gas-phase selective oxidation of benzene to phenol [16], in which the tetrahedral-coordinated Fe is the active center. As for enhancing the electrochemical performance or the catalytic activity, a choice is to facilitate both electron and carrier ions migration or expose more active sites by reducing the size of iron phosphate materials mentioned above.

The synthesis of iron phosphate compounds commonly starts from versatile precipitation reactions between dissolved iron (III) and

phosphate ions in aqueous solution [17–23]. The reaction conditions, especially in terms of temperature and pH, directly determine the reactants participating in the fast precipitation process. In following, the growth process of the as-prepared precipitates affords products with diversity in size, morphology and crystalline structure [6,24]. The solubilities of iron phosphate materials are important controlling factors throughout the conversion process. Chang and Jackson firstly determined the solubility of strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) in water at room temperature after 8 to 21 days equilibrium experiments [25]. Assuming that $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ dissociates into Fe^{3+} , H_2PO_4^- and OH^- , the calculated solubility product (K_{sp}) of strengite was between $10^{-33.5}$ and 10^{-35} . According to the heat capacities at temperatures between 8 and 310 K and the heat of formation at 298 K, Egan *et al.* obtained similar value ($10^{-34.56}$) by thermodynamic calculation [26]. The measurements on strengite solubility in dilute H_3PO_4 by Nriagu *et al.* [27] also confirmed the scale of K_{sp} ($10^{-34.88}$). Besides, Dean assumed that the amorphous iron phosphate ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) dissociates into Fe^{3+} , PO_4^{3-} and H_2O in water, and reported K_{sp} of 9.92×10^{-29} at 298 K [28].

However, there exist complex dissociations and complexations in the aqueous solution of iron phosphate materials, and the calculation of solubility from K_{sp} is difficult. On the other hand, considering versatile iron phosphate materials and broad pH/temperature window for synthesis, the measurements on their solubilities are still scarce. In this work, we selected amorphous iron phosphate dihydrate (the direct product of precipitation) as solute, phosphoric acid as a pH regulator with foreign ions free, and systematically investigate the effects of

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temperature and phosphoric acid addition on the solubility of iron phosphate dihydrate in aqueous solutions. The concentration of phosphoric acid and temperature varied from 1.13 wt% to 10.7 wt% and 298.15 to 363.15 K, respectively. The quantitative variation laws as well as fundamental data of solubilities were of great importance for understanding and designing iron phosphate materials synthesis processes.

2. Experimental Section

2.1. Chemicals

The iron (III) phosphate dihydrate ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) was purchased from the Sigma-Aldrich. The orthophosphoric acid (H_3PO_4 , aq. soln.) was purchased from Alfa Aesar. The hydrochloric acid (HCl, 36 wt%–38 wt%) was purchased from Beijing Chemical Works. All of the reagents were used as received without further purification. Ultrapure deionized water (18.2 M Ω) was used throughout the experiments for solution preparation and vessel cleaning.

2.2. Solution preparation

All the vessels used throughout the experiments were thoroughly cleansed. They were firstly washed by 1 mol·L⁻¹ HCl solution under sonication for 2 h to remove any possible impurities. Then the vessels were thoroughly rinsed by ultrapure deionized water and further sonicated for another 1 h. The water cleaning procedure was repeated for three times. Finally, they were dried at 105 °C in air overnight.

The H_3PO_4 solutions with various concentrations were prepared by diluting purchased 85% H_3PO_4 solution and stored in volumetric flasks. The exact concentrations of H_3PO_4 , determined by an inductively coupled plasma-optical emission spectrometer, were listed in Table 1, in which the pH value and density measured at room temperature were also provided.

2.3. Equilibrium procedure

A typical equilibrium procedure was described as follows. Firstly, 50 ml of phosphoric acid solution was transferred to conical flask added with sufficient amount of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ powders in advance. And then, the conical flask was sealed and placed in a thermostatic oven (DHG-9035A, HONGHUA) at temperature above 308.15 K, or in a thermostatic bath equipped with a refrigeration system (LSHZ-300, HAOCHEG) at temperature below 308.15 K. The temperature uncertainty for equilibrium was ± 0.1 K. According to Chang's results [25], the equilibrium time was set as long as 30 days to approach the liquid–solid equilibrium, after which the supernatant was carefully drawn out by a single-use syringe. The syringe nozzle was equipped with a 0.22 μm filter head to remove any possible solid and get clear liquid samples for solubility measurement. The residual solid was isolated by suction filtration, washed by water, and dried at 105 °C in air overnight for crystalline structure characterization.

2.4. Analysis and characterization

The iron and phosphorus contents in liquid samples were analyzed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, iCAP6300, ThermoFisher) or an inductively coupled plasma-mass

spectrometer (ICP-MS, iCAPQ, ThermoFisher). The limit of detection of ICP-OES for iron is 10^{-8} g·g⁻¹. The power of the plasma was 1150 W. Peristaltic pump rotation speed was 100 r·min⁻¹. The limit of detection of ICP-MS for iron is 10^{-12} g·g⁻¹. The power of the plasma was 1548 W. Argon gas in high-purity (99.9999%) was used as the carrier gas with flow rate 0.952 L·min⁻¹. Each sample was measured for three times or more, and the average value was reported. Some selected samples were also characterized by UV–vis spectrometer (UV-2450, Shimadzu Corporation) with 5 nm slit width. The solid phase was characterized by X-ray diffraction (XRD, D8-Advance, 40 kV, 40 mA) using Cu K α radiation at a 5° min⁻¹ scanning rate.

3. Results and Discussion

3.1. Solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in deionized water

The solubility data of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in deionized water (18.2 M Ω) at temperatures from 298.15 to 363.15 K and atmosphere pressure are presented in Table 2. Herein, we assume that $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ dissociates to Fe^{3+} and PO_4^{3-} , and the solubility product (K_{sp}) of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ is expressed as Eq. (1).

$$K_{\text{sp}} = [\text{Fe}^{3+}] \times [\text{PO}_4^{3-}] \times [\text{H}_2\text{O}]^2 \quad (1)$$

Table 2
Solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in deionized water at 298.15 to 363.15 K and atmospheric pressure[ⓐ]

T/K	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ solubility $\times 10^6$ /g·kg ⁻¹	Appearance of residues	T/K	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ solubility $\times 10^6$ /g·kg ⁻¹	Appearance of residues
298.15	1.48 ± 0.05	Light yellow	323.15	1.20 ± 0.02	Light yellow
303.15	1.45 ± 0.04	Light yellow	333.15	1.04 ± 0.02	Light yellow
308.15	1.40 ± 0.03	Light yellow	343.15	0.72 ± 0.02	Light yellow
313.15	1.37 ± 0.03	Light yellow	353.15	0.58 ± 0.01	Light yellow
318.15	1.27 ± 0.02	Light yellow	363.15	0.11 ± 0.004	Light yellow

[ⓐ] The standard uncertainty of the temperature is 0.1 K; standard uncertainty of the pressure is 0.005 MPa; the relative standard uncertainty for concentration of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ is below 0.05.

In the aqueous solution, Fe^{3+} could be hydrolyzed to $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$; phosphoric acid has a three-step dissociation process generating various phosphate anions [29]. When using deionized water as solvent, the content of phosphorus equals to that of iron in solution; the interaction between iron species and phosphate species could be neglected because the concentration of OH^- is much higher than that of phosphate species. As the contents of phosphorous and iron in solution being measured, the concentrations of Fe^{3+} and PO_4^{3-} can be calculated according to the hydrolysis constant of Fe^{3+} and the dissociation constant of phosphoric acid previously reported [30,31] directly. In this work, the K_{sp} of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ at 298.15 K was calculated as 5.39×10^{-29} , close to Dean's report (9.92×10^{-29}) [28]. It indicates the reliability of our solubility measurements. From Table 2, it could be found that the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ monotonously decreases with the temperature increasing. The solubility at 343.15 K is only half of that at 298.15 K.

Table 1
The composition, pH value and density of various solvents

Entry	1	2	3	4	5	6	7	8	9	10
H_3PO_4 concentration/wt%	0.00	1.13	2.24	3.33	4.33	5.51	6.57	7.62	8.63	10.7
pH	7.02	1.35	1.13	0.98	0.90	0.82	0.75	0.69	0.64	0.52
ρ /g·ml ⁻¹	1.015	1.022	1.027	1.034	1.038	1.042	1.050	1.055	1.065	1.072

3.2. Solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in various H_3PO_4 solutions

The dissolution behavior of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in H_3PO_4 solutions is complex due to the formation of various complex ions at acidic environment. The composition of complex ion is significantly dependent on the amount of H_3PO_4 acid. Considering the interactions between one iron ion and one phosphate ion only, Stumm *et al.* indicated that FeHPO_4^+ was of majority when the concentration of H^+ was below $2 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, otherwise $\text{FeH}_2\text{PO}_4^{2+}$ was the main species [32]. While, when the concentration of H_3PO_4 was largely excessive over that of iron ions, multi-ligands complex may become dominant, such as $\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$, $\text{FeH}_3(\text{PO}_4)_2$, $\text{FeH}_5(\text{PO}_4)_2^{2+}$, $\text{Fe}(\text{H}_2\text{PO}_4)_3$, and $\text{FeH}_7(\text{PO}_4)_3^+$ [33]. The $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ crystals with varied morphologies and structures were usually synthesized under such conditions, but until now, little thermodynamic knowledge is available about these complexes, and there is no report on the solubility data of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ at high H_3PO_4 concentration ($\geq 0.1 \text{ mol} \cdot \text{L}^{-1}$). Herein, we measured the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in H_3PO_4 solutions with its concentration from 1.13 wt% to 10.7 wt% and temperatures from 298.15 to 363.15 K. All the results are listed in Table 3.

As seen, the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in 1.13 wt% H_3PO_4 is $0.490 \text{ g} \cdot \text{kg}^{-1}$ at 298.15 K, even more than three hundred thousand times of that in deionized water ($1.48 \times 10^{-6} \text{ g} \cdot \text{kg}^{-1}$). The jump of solubility with H_3PO_4 addition implies that some complex interactions between Fe^{3+} and phosphate ions become significant to convert Fe^{3+} to soluble coordination species, and boost the dissolving of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. In detail, H_2PO_4^- is of the main anionic species in the solution containing 1.13 wt% H_3PO_4 , so the iron in the soluble $(\text{FeH}_2\text{PO}_4)^{2-}$ can be much more than that as Fe^{3+} and results in abnormal growth of solubility. When the H_3PO_4 concentration increases from 1.13 wt% to 10.7 wt%, the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ increases further, but the trend becomes smooth. Fig. 1 shows the phenomena intuitively, in which the variance of the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ could reach one to two orders of magnitude. We attempt to calibrate the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (y) with the H_3PO_4 concentration (x) by equation $y = A \cdot x^b$. Table 4 lists the calibration results. At every temperature except for 298.15 K, the correlation coefficients are over 0.95, indicating that the calibration results agree with the measurements well. The exponent b determines the sensitivity of the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ on the H_3PO_4 concentration. As the temperature is 308.15 K or higher, b almost keeps in the range from 2.4 to

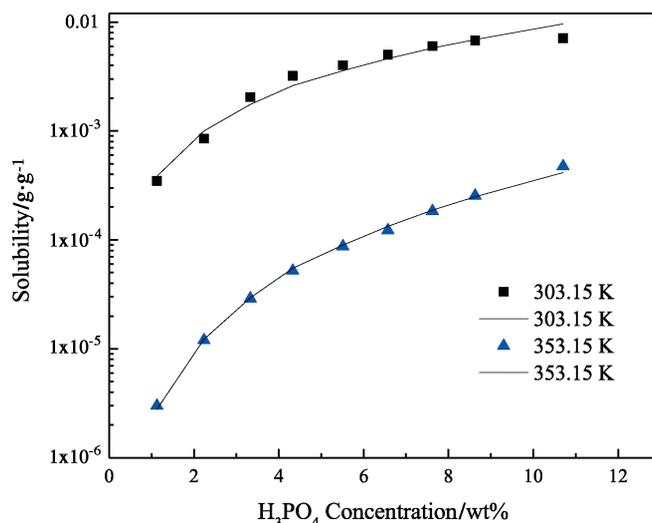


Fig. 1. The dependence of solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ on the concentration of H_3PO_4 at atmospheric pressure. The dots and lines correspond to the experimental data and calculated results, respectively.

Table 4

Parameters for calibrating the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ with H_3PO_4 concentration

T	A	b	r ²	T	A	b	r ²
298.15	0.0325	0.612	0.721	323.15	0.353	2.68	0.998
303.15	0.0827	1.05	0.958	333.15	0.377	2.76	0.996
308.15	1.57	2.43	0.952	343.15	0.129	2.42	0.983
313.15	7.07	3.39	0.994	353.15	0.189	2.68	0.997
318.15	0.589	2.74	0.981	363.15	0.206	2.76	0.991

2.8. In other words, doubling the H_3PO_4 concentration could increase the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ by 5 to 7 times. As for the effect of temperature on the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, the case of using H_3PO_4 solution as solvent is similar with that of using deionization water as solvent, *i.e.*, the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ decreases with the increasing of

Table 3

Solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in various concentrations of H_3PO_4 solutions at 298.15 to 363.15 K and atmospheric pressure[Ⓛ]

H_3PO_4 concentration /g $\text{H}_3\text{PO}_4 \cdot (100 \text{ g H}_2\text{O})^{-1}$	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ solubility /g $\cdot \text{kg}^{-1}$					Appearance of residues
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	
1.13	0.490 ± 0.006	0.346 ± 0.004	0.022 ± 0.000	0.015 ± 0.000	0.008 ± 0.000	White
2.24	1.268 ± 0.011	0.851 ± 0.007	0.126 ± 0.001	0.050 ± 0.001	0.025 ± 0.000	White
3.33	5.658 ± 0.082	2.038 ± 0.021	0.282 ± 0.002	0.182 ± 0.002	0.105 ± 0.001	White
4.33	6.170 ± 0.095	3.196 ± 0.030	0.503 ± 0.004	0.341 ± 0.002	0.189 ± 0.002	White
5.51	6.403 ± 0.103	4.006 ± 0.043	0.808 ± 0.006	0.417 ± 0.004	0.229 ± 0.002	White
6.57	6.523 ± 0.105	5.012 ± 0.060	1.570 ± 0.013	0.589 ± 0.004	0.307 ± 0.002	White
7.62	6.666 ± 0.097	5.973 ± 0.052	3.960 ± 0.041	1.097 ± 0.007	0.561 ± 0.004	White
8.63	6.879 ± 0.101	6.760 ± 0.058	4.546 ± 0.034	1.750 ± 0.019	0.928 ± 0.004	White
10.7	7.398 ± 0.114	7.102 ± 0.086	6.566 ± 0.058	3.617 ± 0.034	1.956 ± 0.029	White
	323.15 K	333.15 K	343.15 K	353.15 K	363.15 K	
1.13	0.006 ± 0.000	0.005 ± 0.000	0.004 ± 0.000	0.003 ± 0.000	0.003 ± 0.000	White
2.24	0.021 ± 0.000	0.016 ± 0.000	0.013 ± 0.000	0.012 ± 0.000	0.011 ± 0.000	White
3.33	0.051 ± 0.001	0.036 ± 0.000	0.031 ± 0.000	0.029 ± 0.000	0.025 ± 0.000	White
4.33	0.103 ± 0.001	0.075 ± 0.001	0.054 ± 0.001	0.052 ± 0.001	0.050 ± 0.001	White
5.51	0.153 ± 0.002	0.123 ± 0.001	0.090 ± 0.002	0.087 ± 0.001	0.081 ± 0.001	White
6.57	0.252 ± 0.002	0.187 ± 0.002	0.159 ± 0.002	0.122 ± 0.001	0.119 ± 0.001	White
7.62	0.370 ± 0.004	0.300 ± 0.004	0.267 ± 0.002	0.184 ± 0.002	0.164 ± 0.001	White
8.63	0.626 ± 0.004	0.473 ± 0.007	0.398 ± 0.004	0.254 ± 0.002	0.215 ± 0.002	White
10.7	1.335 ± 0.006	0.946 ± 0.013	0.789 ± 0.004	0.474 ± 0.007	0.443 ± 0.006	White

[Ⓛ] The standard uncertainty of the temperature is $u(T) = 0.1 \text{ K}$; standard uncertainty of the pressure is $u(p) = 0.005 \text{ MPa}$; the relative standard uncertainty for concentration of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ is below $u(r) = 0.02$.

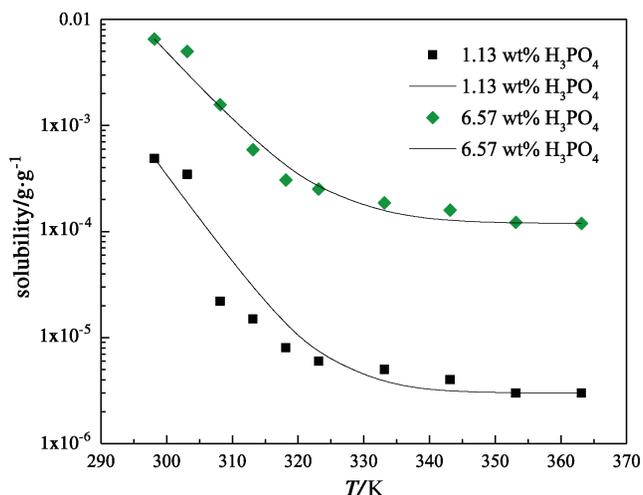


Fig. 2. The dependence of solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ on temperature at atmospheric pressure. The dots and lines correspond to the experimental data and calculated results, respectively.

temperature. Fig. 2 shows two typical curves reflecting the effect of temperature. The solubility seems to approach a constant value with the increasing of temperature, so we attempt to exploit equation $y = y_0 + A \cdot e^{-x/t}$ to calibrate the solubility (y) with temperature (x). Table 5 lists the calibration results. The correlation coefficients can reach 0.90 to 0.95. With the increasing of H_3PO_4 concentration, y_0 almost increases monotonously as expected, and t increases in general. The increasing of t implies that the sensitivity on temperature decreases. Considering the effects of temperature and H_3PO_4 concentration comprehensively, high temperature and low H_3PO_4 concentration are appropriate to enlarge the relative variance of solubility with temperature or H_3PO_4 concentration adulation. Otherwise, low temperature and high H_3PO_4 concentration should be selected to shrink the relative variance of solubility. The two groups of calibrating equations, with the H_3PO_4 concentration and temperature as independent variables, respectively, could be used to predict the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in H_3PO_4 solutions with concentration from 1.13 wt% to 10.7 wt% at temperatures from 298.15 K to 363.15 K.

3.3. The identification of the solid phase

It should be noticed that the solid residues have different appearances in Tables 1 and 2. In Table 1, the residues obtained in deionized water were light yellow, the same with the original amorphous $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. In Table 2, all the residues obtained in H_3PO_4 solutions turn to be white without exception. We used X-ray diffraction technique to check whether crystalline phase transition takes place in powder samples, Fig. 3 presents XRD patterns for two typical samples. One corresponds to the light yellow powders obtained in water at 353.15 K. The other corresponds to the white powders obtained in 5.51 wt% H_3PO_4 solution at 353.15 K. As seen, there is no diffraction peak detected for the light yellow powders, indicating the amorphous

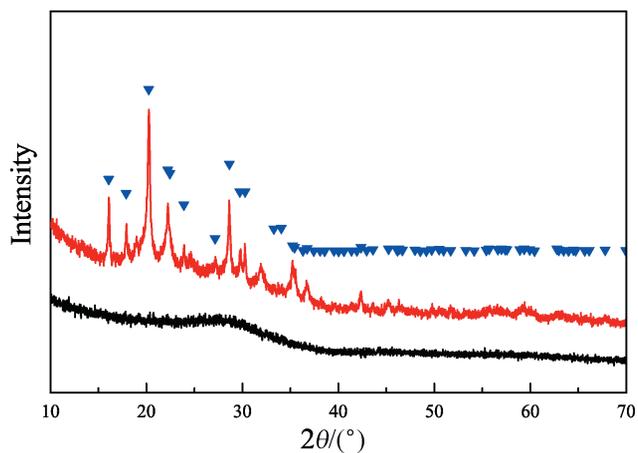


Fig. 3. XRD spectra of solid residues in water (bottom) and in 5.51 wt% H_3PO_4 solution (top) at 353.15 K.

feature of residual $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, the same with the original. Differently, after long residence in H_3PO_4 solutions, the white powders obtained in 5.51 wt% H_3PO_4 addition at 353.15 K show sharp diffraction peaks in good agreement with orthorhombic $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ standard data of PDF no. 33-0667. The results evidence that the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in H_3PO_4 solutions experiences the dissolution of amorphous $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and followed recrystallization of orthorhombic $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. Compared with the amorphous $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, the orthorhombic $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ is more stable in thermodynamics in aqueous solution. Since the transformation from amorphous $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ to orthorhombic $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ abides a dissolution–recrystallization mechanism, the solubility of amorphous $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ may determine the rate of the whole process. In water, the extremely low solubility of amorphous $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ leads that the transformation seems to be blocked during 30 days of experiment. *Vice versa*, the addition of H_3PO_4 makes the transformation process accelerates much and becomes remarkable.

3.4. Understanding iron phosphate materials preparation based on the solubility data

The soluble iron and phosphorus, determined by solubility in thermodynamics, is of iron source and phosphorus source for iron phosphate materials preparation. So, the information on the solubility and dissolving process of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ can help to understand and design the preparation of various iron phosphate materials. In detail, for amorphous iron phosphate materials, the long residence of as prepared products in H_3PO_4 solution should be avoided to inhibit the crystalline phase transition, and high temperature is suitable to decrease the size of products by decreasing the solubility as well as increasing the supersaturation. For the preparation of iron phosphate crystalline materials by dissolution–recrystallization mechanism, high temperature and high H_3PO_4 concentration are appropriate conditions, since high H_3PO_4 concentration can improve the dissolution of precursors and high temperature can decrease the solubility of final products and increase the yield. When using $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ as the controlled iron or phosphorous

Table 5
Parameters for calibrating the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ with temperature

Parameter	H_3PO_4 concentration/wt%								
	1.13	2.24	3.33	4.33	5.51	6.57	7.62	8.63	10.7
y_0	3.0×10^{-6}	1.1×10^{-5}	2.5×10^{-5}	5.0×10^{-5}	8.1×10^{-5}	1.2×10^{-4}	1.6×10^{-4}	2.2×10^{-4}	2.0×10^{-4}
A	4.6×10^{21}	1.3×10^{21}	9.3×10^{18}	4.8×10^{18}	6.6×10^{18}	5.3×10^{17}	5.6×10^{16}	3.1×10^{14}	1.1×10^{12}
t	5.19	5.39	6.10	6.21	6.16	6.50	6.94	7.89	9.28
r^2	0.902	0.934	0.990	0.975	0.958	0.938	0.957	0.965	0.912

sources, high H_3PO_4 concentration and low temperature could accelerate the providing of iron or phosphorous, while low H_3PO_4 concentration and high temperature have the opposite effect.

4. Conclusions

The solubilities of iron phosphate dihydrate in deionized water and phosphoric acid solutions at high mass concentrations from 1.13% to 10.7% were systematically measured at temperature from 298.15 to 363.15 K and atmosphere pressure. The solubility was found to increase 5 orders of magnitude or more with increasing the concentration of phosphoric acid, and decrease 1 to 2 orders of magnitude with increasing the equilibrium temperature. The phosphoric acid addition and temperature were found to affect the solubility of iron phosphate dihydrate by the formation or dissociation of coordination species, which could further accelerate the phase transformation from the amorphous iron phosphate dihydrate to orthorhombic iron phosphate dehydrate by dissolution–recrystallization mechanism. The high dependences of the solubility of iron phosphate materials on H_3PO_4 concentration and temperature could be well predicted by calibration equations and effectively exploited to regulate the precipitation, crystallization and growth processes between iron (III) and phosphate ions in aqueous solutions for synthesizing iron phosphate materials with diversified crystalline structure and morphology.

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