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The crystal structure of $Fe^{2+}Fe_2^{3+}(PO_3OH)_4(H_2O)_4$: a new synthetic compound of mineralogic interest

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Abstract

The new synthetic compound $Fe^{2+}Fe_2^{3+}(PO_3OH)_4(H_2O)_4$ is monoclinic, space group $P2_1/n$, $a = 5.152(1)$, $b = 16.629(2)$, $c = 8.749(1)$ Å, $\beta = 90.84(1)°$, $Z = 2$, $D = 2.7(1)$ g/cm³. The crystal structure was determined by direct methods and refined by the least-squares method to an R value of 0.049 for 1313 observed reflections. The structure consists of Fe^{2+} ions in special positions and Fe^{3+} ions in general positions, both octahedrally coordinated by water, and $(PO_3OH)^{2-}$ ligands which share vertices to the octahedra. Average bond distances are Fe^{2+}-O = 2.15, Fe^{3+}-O = 1.98 and P-O = 1.54 Å.

Introduction

In the S(10) synthesis, described in the following section, the presence of radial groups of yellow transparent acicular crystals was observed during a study to define favorable hydrothermal conditions for the growth of lipscombite and barbosalite crystals, two dimorphous phosphates of ideal composition $Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2$, previously synthesized by Gheith (1953). Due to the small quantity of crystals obtained, the chemical composition was inferred through the gravimetric determination of its water content, and by the information obtained from Mössbauer spectroscopy of the valence states and the relative composition of the iron ions.

Synthesis and characterization

The yellow crystals were synthesized hydrothermally. Vivianite $[Fe_3^{2+}(PO_4)_2(H_2O)_8]$ and ferrous carbonate $[FeCO_3]$ in the ratio of 3:1 were reacted at 220°C for one week with 3 to 4 parts of ferric acid phosphate and one ml of water for each 0.5 g of compound present. In order to minimize contamination, the charge was isolated from vessel walls in a quartz capsule with a teflon cover. The ferric phosphate was prepared by reacting up to 13 g of Fe_2O_3 in 60 ml of boiling orthophosphoric acid (85% concentration). The white precipitate was used in the synthesis without washing out the excess acid. The ferrous phosphate (vivianite), was synthesized by the Evans method (Mattievich and Danon, 1977), and the ferrous carbonate was precipitated from a ferrous sulphate solution by sodium bicarbonate.

The room temperature Mössbauer spectrum (Fig. 1, Table 1) of the resulting crystals shows Fe^{3+} and Fe^{2+} in the proportion 2.2:1. The deviation from a 2:1 ratio was due to vacancies (of Fe^{2+}) statistically distributed in the crystal.

Microscopic observation in an inert atmosphere shows that at about 200°C, the crystals lose their transparency, becoming opaque and black. This is not a sudden process, but propagates slowly from the hottest point. At higher temperatures the crystals become blue.

Gravimetric analysis (Fig. 2) showed water loss at two different temperatures. Table 2 gives the pyrolytic results in an inert atmosphere, as compared with calculated values, assuming an ideal stoichiometric composition $Fe^{2+}Fe_2^{3+}(PO_3OH)_4(H_2O)_4$. The fact that the measured loss of water does not correspond to the calculated values (4.2 instead of 4.0 and 1.6 instead of 2.0) suggests that the stoichiometry is not ideal as suggested by the Mössbauer data.

Experimental

Weissenberg and precession photographs showed monoclinic symmetry with systematic absences $h0l$, $h + l \neq 2n$ and $0k0$, $k \neq 2n$, consistent with the space group $P2_1/n$.

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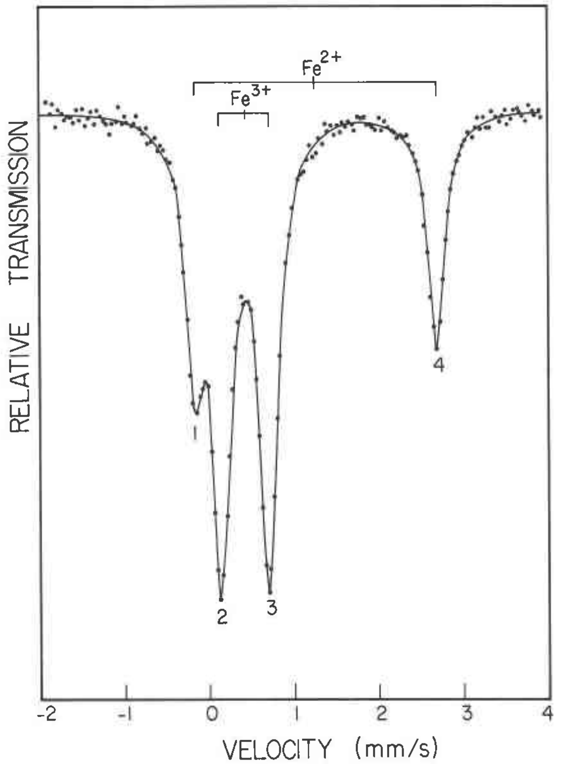

Fig. 1. Mössbauer spectrum of the S(10) powder sample at room temperature (velocity relative to metallic iron).

A crystal 0.25 × 0.12 × 0.08 mm was mounted on a CAD-4 Enraf-Nonius diffractometer. Cell dimensions and the orientation matrix for data collection were calculated by least-squares refinement from 25 centered reflections using Mo$K\alpha$ radiation (λ = 0.71033 Å) with graphite monochromator. Diffraction intensities for reflections having θ in the range 1–30° were measured by the θ–2θ scan technique, using a variable scan speed between 5.0 and 10.0° min^{-1} determined by a fast prescan of 10.0° min^{-1}. Of the 2390 measured reflections, 1313 had $I \geq 3\,\sigma(I)$, with $\sigma(I)$ estimated from counting statistics. The intensities of two standard reflections were essentially constant over the duration of the experiment. The intensities were corrected for the Lorentz-polarization factor but not for absorption (μ = 32.38 cm^{-1}) and for extinction. The atomic scattering factors and the dispersion correction factors were taken from *International Tables for X-ray Crystallography, Vol. IV* (1974).

Structure determination and refinement

The structure was determined by direct methods using the program MULTAN-80 (Main et al., 1980) with 268 reflections with E > 1.59. An E-map based on the solution of the highest absolute figure of merit (1.2864) and the lowest residual index (9.25) showed the iron, phosphorus and the three of the oxygen positions. The remaining seven oxygen atoms were located by successive difference-Fourier calculations.

Anisotropic refinement was carried out with minimization of $\sum w(|F_o| - |F_c|)^2$ with $w = 1.064[\sigma^2(F_o) + 0.00076F_o^2]^{-1}$, where $\sigma(F_o)$ is the *esd* for the observed amplitude based on counting statistics. The hydrogen atoms were found by difference Fourier synthesis and the same temperature factor was assigned as that of the atom to which they are attached. Neither the hydrogen positions nor their temperature factors were refined.

Table 1. Mössbauer parameters of $Fe^{2+}Fe_2^{3+}(PO_3OH)_4(H_2O)_4$, S(10) synthesis, measured at 295 K

	I. S. (mm/s)	Q. S. (mm/s)	Doublets relative intensity
Fe^{2+}	1.24	2.87	0.91
Fe^{3+}	0.42	0.58	2.00

I. S. relative to metalic iron at 295ºK

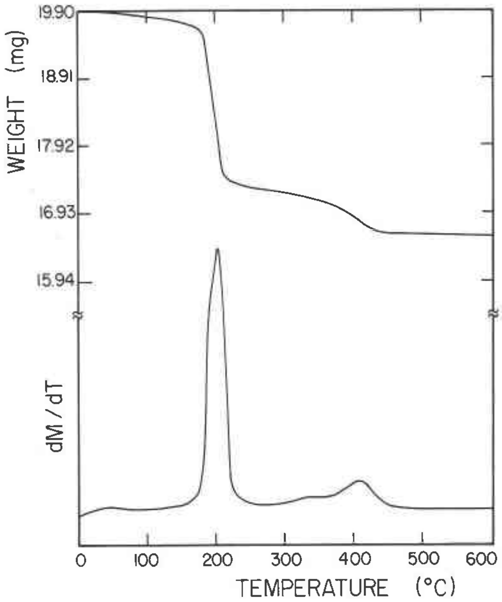

Fig. 2. Thermogravimetric analysis of the S(24) sample. dM/dT = mass variation/temperature variation.

Table 2. Comparison of the calculated and observed pyrolysis. Experimental data refer to sample S(10) heated in an inert atmosphere

	Experimental (mg)	Calculated (mg)	Number of sublimated water molecules
Starting mass	31.8		
1st mass loss	3.9	3.7	4.2 H_2O
2nd mass loss	1.4	1.8	1.6 H_2O
Total	5.3	5.5	5.8 H_2O

Proposed pyrolitic reaction

1st at 230 °C : $Fe^{2+}Fe_2^{3+}(PO_3OH)_4(H_2O)_4 \rightarrow Fe^{2+}Fe_2^{3+}(PO_3OH)_4 + 4\ H_2O \uparrow$

2nd at 450 °C : $Fe^{2+}Fe_2^{3+}(PO_3OH)_4 \rightarrow Fe^{2+}Fe_2^{3+}(P_2O_7)_2 + 2\ H_2O \uparrow$

Table 5. Atomic coordinates and equivalent isotropic temperature factors for $Fe^{2+}Fe_2^{3+}(PO_3OH)_4(H_2O)_4$

Atom	x/a	y/b	z/c	B_{iso}(Å^2)
Fe(1)=Fe^{2+}	0.5000	0.5000	0.5000	1.01(4)
Fe(2)=Fe^{3+}	0.2539(2)	0.2029(1)	0.3683(1)	0.75(2)
P(1)	0.7454(3)	0.3060(1)	0.4938(2)	0.59(4)
P(2)	0.7645(3)	0.0794(1)	0.3054(2)	0.81(4)
O(1)	0.4768(9)	0.2988(3)	0.4210(6)	1.0(1)
O(2)	0.764(1)	0.2648(3)	0.6493(6)	1.3(1)
O(3)	0.7872(9)	0.4008(3)	0.5156(6)	0.9(1)
O(4)	0.9579(9)	0.2772(3)	0.3872(6)	1.0(1)
O(5)	1.0410(9)	0.1061(3)	0.3417(6)	1.3(1)
O(6)	0.563(1)	0.1381(3)	0.3559(7)	1.6(2)
O(7)	0.7337(9)	0.0573(3)	0.1362(6)	1.3(1)
O(8)	0.709(1)	-0.0006(4)	0.3986(8)	2.6(2)
OW(1)	0.310(1)	0.4432(3)	0.3059(7)	1.9(2)
OW(2)	0.237(1)	0.1769(4)	0.6010(6)	1.6(2)
H1W(1)	0.3641	0.3933	0.3536	1.9
H2W(1)	0.1271	0.4381	0.2923	1.9
H1W(2)	0.0612	0.2001	0.6442	1.6
H2W(2)	0.3762	0.1948	0.6852	1.6
H(1)	0.8738	0.4089	0.6177	0.9
H(2)	0.6415	0.0019	0.4965	2.6

* *The hydrogen parameters were not refined.*

Table 6. Interatomic distances (Å) and angles (°) for $Fe^{2+}Fe_2^{3+}(PO_3OH)_4(H_2O)_4$

Fe(1) octahedron			Fe(2) octahedron		
Fe(1)	- O(3)	2.219(5)	Fe(2)	- O(1)	2.018(5)
	- O(7)^{i}	2.061(5)		- O(4)^{iv}	1.972(5)
	- OW(1)	2.162(6)		- O(5)^{iv}	1.960(5)
average		2.147		- O(6)	1.928(5)
				- O(2)^{v}	1.932(5)
				- OW(2)	2.097(5)
			average		1.984
O(3)	- O(7)^{i}	2.613(5)	O(6)	- O(1)	2.766(5)
	- O(7)^{ii}	2.925(5)		- O(2)^{v}	2.857(5)
	- OW(1)^{iii}	3.079(5)		- O(5)iv	2.749(5)
OW(1)^{iii}	- O(7)^{ii}	2.919(5)		- OW(2)	2.823(5)
average		2.884	O(4)^{iv}	- O(1)	2.711(5)
				- O(2)^{v}	2.725(5)
				- O(5)^{iv}	2.905(5)
				- OW(2)	2.842(5)
			O(1)	- O(2)^{v}	2.814(5)
				- OW(2)	2.861(5)
			O(5)^{iv}	- O(2)^{v}	2.971(5)
				- OW(2)	2.736(5)
			average		2.813
P(1) tetrahedron			P(2) tetrahedron		
P(1)	- O(1)	1.515(5)	P(2)	- O(5)	1.520(5)
	- O(2)	1.524(5)		- O(6)	1.498(5)
	- O(3)	1.601(5)		- O(7)	1.533(6)
	- O(4)	1.523(5)		- O(8)	1.583(6)
average		1.541	average		1.534
O(1)	- O(2)	2.527(5)	O(5)	- O(6)	2.519(5)
	- O(3)	2.461(5)		- O(7)	2.515(5)
	- O(4)	2.524(5)		- O(8)	2.518(5)
O(2)	- O(3)	2.546(5)	O(6)	- O(7)	2.517(5)
	- O(4)	2.518(5)		- O(8)	2.451(5)
O(3)	- O(4)	2.505(5)	O(7)	- O(8)	2.492(5)
average		2.514	average		2.502
Fe(1) octahedron			Fe(2) octahedron		
OW(1)	- O(3)	90.7(2)	O(4)^{iv}	- O(1)	85.6(2)
OW(1)	- O(7)^{i}	87.4(3)	O(5)^{v}	- O(4)^{iv}	95.3(2)
O(3)	- O(7)^{i}	86.1(3)	O(2)^{v}	- O(1)	89.0(2)
average		88.1	O(6)	- O(5)^{iv}	90.0(2)
			OW(2)	- O(1)	88.3(2)
			OW(2)	- O(4)	90.1(2)
			OW(2)	- O(5)^{iv}	85.1(2)
			OW(2)	- O(6)	89.2(2)
			average		89.1
P(1) tetrahedron			P(2) tetrahedron		
O(2)	- O(1)	112.6(3)	O(6)	- O(5)	113.3(3)
O(3)	- O(1)	104.3(3)	O(7)	- O(5)	110.9(3)
O(3)	- O(2)	109.1(3)	O(7)	- O(6)	112.3(3)
O(4)	- O(1)	112.4(3)	O(8)	- O(5)	108.4(3)
O(4)	- O(2)	111.5(3)	O(8)	- O(6)	105.4(3)
O(4)	- O(3)	106.6(3)	O(8)	- O(7)	106.2(3)
average		109.4	average		109.4

The indices refer to the following symmetry operations: i = -1/2 + x, 1/2 - y, 1/2 + z; ii = 3/2 - x, 1/2 + y, 1/2 - z; iii = 1 - x, 1 - y, 1 - z; iv = -1 + x, y, z; v = -1/2 + x, 1/2 - y, -1/2 + z.

The refinement converged to an R of 0.049 and R_w of 0.057 omitting unobserved reflections, and an R of 0.10 for all reflections. The calculations were done on a VAX computer with the SHELX-76 system of programs (Sheldrick, 1976). The projection shown in Figure 3 was calculated with the program ORTEP (Johnson, 1965) incorporated in the Enraf-Nonius Structure Determination Package.

The calculated and observed structure factors are listed in Table 3. The anisotropic thermal parameters for the non-hydrogen atoms are given in Table 4.[1] The atomic coordinates and equivalent isotropic temperature factors are given in Table 5. The interatomic distances and angles are given in Table 6.

Description of the structure

The Fe^{2+}-oxygen octahedron is formed by the *trans*-coordination of two water OW(1) ligands and by four oxygen atoms of the P-oxygen tetrahedra. The Fe^{3+} ion is coordinated to one water OW(2) ligand and to five oxygen atoms of the P-oxygen tetrahedra. As can be seen in Figure 3, only heteropolyhedral vertex linkages are formed.

The two tetrahedra are approximately regular, with their geometry being in fair agreement with published values for iron phosphates (Moore and Araki, 1976; Moore et al., 1974). The mean Fe^{2+}-O and Fe^{3+}-O distances agree with the values in the above cited papers and also with the sums of effective ionic radii (Shannon, 1976). There are some distances greater than the average value, such as Fe^{2+}-O(3), Fe^{2+}-OW(1), Fe^{3+}-OW(2), P(1)-O(3) and P(2)-O(8). Those values lead to disagreements with the electrostatic valence calculations of cations relative to anions, as shown in Table 7 (Pauling, 1960, p. 548), giving a clear indication of the acceptor or donor character of the respective hydrogen bond involved. The calculation of the bond strength sums around Fe^{2+} and Fe^{3+} gives 1.94 and 3.01 v.u., respectively (Brown and Shannon, 1973).

All the hydrogen atoms in the structure participate in hydrogen bonding. The bond distances are given in Table 6 and are shown in Figure 3. The water OW(1) forms a strong hydrogen bond (2.736 Å) with O(1) and a weak bond with O(3)^{ii} (3.36 Å), similar to those in hureaulite (2.70 and 3.50 Å; Moore and Araki, 1973) and

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[1] To obtain a copy of Tables 3 and 4, order Document AM-86-294 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006. Please remit $5.00 in advance for the microfiche.

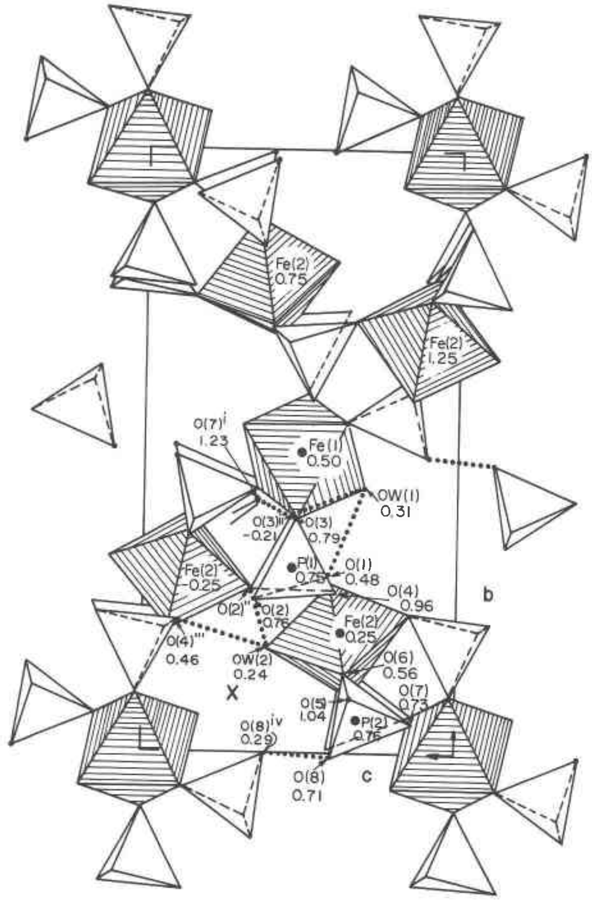

Fig. 3. Polyhedral projection of the $Fe^{2+}Fe_2^{3+}(PO_3OH)_4(H_2O)_4$ structure along the **a** axis; the heights are given as fractional coordinates in x. The hydrogen bond contacts are indicated by dotted lines. The symmetry operations are the same as in Table 6 and the atom labels refer to Table 5.

$Fe_3^{2+}(PO_4)_2H_2O$ (2.72 and 3.43 Å; Moore and Araki, 1975). The structure shows an unusual hydrogen bond between O(8) [=$(OH)^-$] and O(8)^{iv}, generated by the symmetry operation iv = 1 − x, −y, 1 − z, around the symmetry center at ½, 0, ½ (and also 0, ½, 0). It is worth mentioning that of all the hydrogen atoms located on the difference Fourier maps, the H(2) atom involved in this bond was the one that showed the best discrimination against the background. See Table 8 for hydrogen bonds.

Table 7. Electrostatic valence balances (Σ^-) of cations about anions

		Σ
O(1)	P(1)+Fe(2)	1,75
O(2)	P(1)+Fe(2)	1,75
O(3) = OH^-	P(1)+Fe(1)+H	2,42
O(4)	P(1)+Fe(2)	1,75
O(5)	P(2)+Fe(2)	1,75
O(6)	P(2)+Fe(2)	1,75
O(7)	P(2)+Fe(1)	1,58
O(8) = OH^-	P(2)+H	2,08
OW(1) = H_2O	Fe(1)+2H	2,00
OW(2) = H_2O	Fe(2)+2H	2,17

Table 8. Hydrogen bonds (Å)

D	A	D-A	D-H *	H-A	< D-H-A (°)*
O(3) -H(1).....	O(7)^i	2.614(6)	1.005	1.942(4)	121.7
O(8) -H(2).....	O(8)^{iv}	2.808(6)	0.928	2.037(5)	139.5
OW(1)-H1W(1)...	O(1)	2.736(7)	0.968	1.772(5)	173.3
OW(1)-H2W(1)...	O(3)^{ii}	3.36(1)	0.957	2.713(4)	125.6
OW(2)-H1W(2)...	O(2)^{ii}	2.882(7)	1.060	1.874(5)	157.3
OW(2)-H2W(2)...	O(4)^{iii}	2.843(7)	1.064	1.872(5)	149.8

* *Not refined*
Symmetry operations: i = 1/2+x, 1/2−y, 1/2+z; ii = −1+x, y, z; iii = −1/2+x, 1/2−y, 1/2+z; iv = 1−x, −y, 1−z.

An interesting characteristic of the structure is the presence of an empty region, forming a true channel along [100]. This channel, marked with an X in Figure 3, is defined to a large extent by water molecules and the O(8) hydrogen bond of the acid phosphate. It has some resemblance to the "acid pocket" observed by Moore and Araki (1973) in the hureaulite structure.

Discussion

Mössbauer measurements on three different synthesized samples of this phosphate showed the Fe^{3+}/Fe^{2+} ratio to vary from 2.20 to 2.56. The thermogravimetric measurement on the S(24) sample shows Fe^{3+}/Fe^{2+} = 2.56, and corresponds to the rupture of bonds between H_2O and the Fe ions at about 200°C (Fig. 2). Assuming the ideal stoichiometric composition, the mass change corresponds to a loss of 4.3 H_2O, instead of the expected 4.0 H_2O. The second mass variation between 300°C and 400°C is less well-defined, but corresponds to only 1.2 H_2O, instead of the ideal 2.0 H_2O.

The S(24) sample shows an X-ray powder diffraction pattern indistinguishable from that of the S(10) sample, suggesting that both are the same phase. Consequently, the cause of the differences in the Fe^{3+}/Fe^{2+} ratios and the amount of H_2O in these samples must be attributed to Fe^{2+} vacancies statistically distributed throughout the crystal. This suggests that the yellow phosphate may belong to a continuous series of compounds of variable composition, the limits of which are not yet well defined. This may also account for the fact that the temperature factor of Fe^{2+} is higher than the temperature factor of Fe^{3+} (Table 5).

The two-step loss of water in the thermogravimetric analysis (Fig. 2) is additional evidence for the crystallographically determined composition, as there are two different sites for the water molecules. Indeed, besides the 4.3 H_2O observed in the first step, the dM/dT variation shows two activation energies, corresponding to two kinds of water: one bonded to Fe^{2+} and the other bonded to Fe^{3+}. At higher temperature, the loss of 1.6 and 1.2 water molecules, in the S(10) and S(24) samples can be explained by the reduction of the acid orthophosphates to pyrophosphates.

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