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ORIGINAL PAPER

Hydrothermal Synthesis and Structure of $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$

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Abstract Single crystals of iron and manganese phosphate $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$ was synthesized by hydrothermal method. The compound crystallizes in the $Fe_7(PO_4)_6$ structure type and is isotypic with the solid solution $M_{7-x}M'_x(HPO_4)_4(PO_4)_2$ where M is Fe, Co, Mg, Mn. The compound is triclinic, *P*-1, a = 6.571(5), b = 7.993(3), c = 9.547(2) Å, $\alpha = 103.97(1)°$, $\beta = 109.29(2)°$, $\gamma = 101.57(3)°$. The structure is based on a three-dimensional framework of distorted edge-sharing MO_6 and MO_5 polyhedra, forming infinite chains, which are interlinked by corner-sharing with PO_4 tetrahedra. The formula unit is centrosymmetric, with all atoms in general positions except for one Fe atom, which has site symmetry -1.

Keywords Hydrothermal synthesis · Iron phosphate · Manganese phosphate

Introduction

A large number of metal phosphates have been synthesized and characterized in recent years. These materials are of great interest to both the industrial and academic sector, since they may find a variety of applications. Iron phosphate was well known to be effective for the oxidative dehydrogenation of isobutyric acid to methacrylic acid [1]. Recently it was found that iron phosphate will show a unique catalytic performance for obtaining pyruvic acid from lactic acid [2, 3] and glyoxylic acid from glycolic acid [4, 5]. The metal phosphate structures, generally, comprise a vertex linkage between the M–O polyhedra and the PO_4 tetrahedra, forming chain, layer, and three-dimensional structures. Hydrothermal techniques can be used as an adequate synthetic method to obtain minerals or complex phosphate with transition metals. Our material is one of isostructural series $M_{7-x}M'_x(XPO_3OH)_4(XO_4)_2$ compounds (M, M′ = first row transition metals, X = P, As, V), as the solid solution $Co_{4.32}\,Mn_{2.68}(PO_3(OH))_4(PO_4)_2$ [6], the compound $Co_7(PO_3(OH))_4(PO_4)_2$ [7] and the magnesium arsenate $Mg_7(AsO_3(OH))_4(AsO_4)_2$ [8]. The synthesis of an iron-manganese phosphate $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$ is reported in this work along with its structural study.

Experimental

The title compound was prepared from reaction mixtures of H_3PO_4 (4 mmol) with FeO (5 mmol) and MnO (5 mmol) in approximately 10 mL of water. The starting mixture was transferred and sealed onto a 23-mL-capacity PTFE-lined stainless steel Parr autoclave under autogenous pressure, filled to approximately 25% volume capacity, and all reactants were stirred briefly before heating. The reaction mixture was heated at 200 °C for 3 days, followed by slow cooling to room temperature, to obtain needle-shaped crystals. The resulting products were filtered off, washed with deionized water, and dried in air. This phase is characterized by electron-microprobe with a CAMECA SX-50 instrument (University of Louvain-la-Neuve, Belgium), under an accelerating voltage of 15 kV and a prob current of 20 nA. The standards used were the Kabira

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graftonite (Fe, Mn, P), The content of Fe, Mn and P is 46.421% FeO, 4.083% MnO, 44.539% P_2O_5 and 3.769% H_2O.

A needle single-crystal of $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$ with dimensions given in the crystal data table, was selected under a polarizing microscope. Diffraction data were collected at room temperature on an automated diffractometer using graphite-monochromated Mo Kα radiation. Details of crystal data, intensity collection, and some features of the structure refinement are reported in Table 1. Corrections for Lorentz and polarization effects were done and also for absorption with the empirical ψ scan method [9]. The structures were solved by Patterson methods with SHELXS97 [10] in the *P*-1 space group, which allowed to obtain the positions of Fe,Mn and phosphorus atoms. The refinement of the crystal structure was performed by full matrix least-squares based on F^2, using SHELXL97 program [10], obtaining the oxygen atoms. When refining, the occupancy of the two crystallographic sites Fe(2) and Fe(3) exhibited a significant deviation from the full occupancy, indicating a substitution with Mn atom. Finally, the refinement lead to 90 and 10% occupancies respectively for Fe and Mn atoms. Final R-factors are given in Table 1, together with the maximum and minimum peaks in the final Fourier differences synthesis and the goodness of fit. Anisotropic displacement parameters were assigned to all nonhydrogen atoms. The positions of all H atoms were located from a difference electron-density map and were then refined with an O–H bond-length restraint of 0.95(5) Å and with U_{iso}(H) fixed at a value of 0.05 Å^2. The final atomic positional parameters of $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$ are listed in Table 2. The bond distances and angles of $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$ are given in Tables 3 and 4. The structure drawing was made using DIAMOND.

Table 1 Crystal data and structure refinement for $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$

Formula	$Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$
Formula weight (g mol^{-1})	964.18
Crystal system	Triclinic
Space group	*P*-1
a (Å)	6.571(5)
b (Å)	7.993(3)
c (Å)	9.547(2)
α (°)	103.97(1)
β (°)	109.29(2)
γ (°)	101.57(3)
Volume (Å^3)	437.2(7)
Z	1
ρ_{calc} (Mg m^{-3})	3.662
F(000)	468
Collection data	
Temperature (K)	293(2)
μ (mm^{-1})	6.257
Radiation, λ(Mo Kα) (Å)	0.71073
Crystal size mm	0.30 × 0.08 × 0.05
Range θ (°)	2.40–26.96
Interval *h*, *k*, *l*	$0 \le h \le 8$, $-10 \le k \le 9$, $-12 \le l \le 11$
No. of measured reflections	2071
No. of independent reflections	1902
R(int)	0.0159
Refinement	
Data/restraints/parameters	1902/6/172
R factors [$I > 2\sigma(I)$]	R1 = 0.0368
	wR2 = 0.0969
R factors [all data]	R1 = 0.0420
	wR2 = 0.1008
Max. and Min. of electronic Residual density (e Å^{-3})	0.943, −1.350
G. O. F	1.060

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$

	sof	x/a	y/b	z/c	U(eq)
Fe(1)	0.500	0.5000	0.5000	0.5000	0.010(1)
Fe(2)	0.894(1)	0.1119(1)	0.0443(1)	0.3880(1)	0.009(1)
Mn(2)	0.106(3)	0.1119(1)	0.0443(1)	0.3880(1)	0.009(1)
Fe(3)	0.791(1)	0.4499(1)	0.7855(1)	0.9851(1)	0.011(1)
Mn(3)	0.209(1)	0.4499(1)	0.7855(1)	0.9851(1)	0.011(1)
Fe(4)	1	0.2233(1)	0.6869(1)	1.2194(1)	0.011(1)
P(1)	1	0.4157(2)	0.9198(1)	0.6730(1)	0.008(1)
P(2)	1	0.9140(2)	0.7305(1)	0.8734(1)	0.010(1)
P(3)	1	0.2722(2)	0.3561(1)	0.7224(1)	0.008(1)
O(1)	1	0.7694(5)	0.5508(4)	0.7394(3)	0.013(1)
O(2)	1	0.2740(5)	0.3138(4)	0.5560(3)	0.012(1)
O(3)	1	0.2012(5)	0.9625(4)	0.5863(3)	0.011(1)
O(4)	1	0.4808(4)	0.3296(4)	0.8370(3)	0.012(1)
O(5)	1	0.2904(5)	0.5631(4)	0.7735(3)	0.013(1)
O(6)	1	0.6259(4)	1.0403(4)	0.6664(3)	0.011(1)
O(7)	1	0.0542(4)	0.2540(4)	0.7288(3)	0.012(1)
O(8)	1	0.3921(5)	0.7179(4)	0.5963(3)	0.014(1)
O(9)	1	0.7728(5)	0.7899(5)	0.9716(4)	0.021(1)
O(10)	1	1.1214(5)	0.7067(4)	0.9917(3)	0.014(1)
O(11)	1	0.9795(5)	0.8810(4)	0.8107(4)	0.018(1)
O(12)	1	0.4453(5)	0.9547(4)	0.8455(3)	0.013(1)

U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor

Table 3 Selected bond lengths in $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$

Bond	Distance (Å)	Bond	Distance (Å)
Fe1–O8	2.130(3)	Fe4–O1^{v}	2.038(3)
Fe1–O8^{i}	2.130(3)	Fe4–O6^{vi}	2.049(3)
Fe1–O2	2.175(3)	Fe4–O10^{vii}	2.108(3)
Fe1–O2^{i}	2.175(3)	Fe4–O7^{viii}	2.150(3)
Fe1–O1	2.261(3)	Fe4–O4^{v}	2.201(3)
Fe1–O1^{i}	2.261(3)		
Fe2–O11^{i}	2.062(3)	P1–O3	1.532(3)
Fe2–O3^{ii}	2.092(3)	P1–O12	1.540(3)
Fe2–O6^{i}	2.141(3)	P1–O6	1.547(3)
Fe2–O3^{iii}	2.143(3)	P1–O8	1.554(3)
Fe2–O2	2.152(3)	P2–O11	1.517(3)
Fe2–O7^{iv}	2.234(3)	P2–O10	1.537(3)
Fe3–O4^{v}	2.086(3)	P2–O1	1.538(3)
Fe3–O5	2.112(3)	P2–O9	1.582(3)
Fe3–O12	2.114(3)	P3–O7	1.528(3)
Fe3–O12^{vi}	2.114(3)	P3–O4	1.536(3)
Fe3–O10^{vii}	2.150(3)	P3–O2	1.546(3)
Fe3–O9	2.162(3)	P3–O5	1.576(3)

Symmetry codes: (i) –x + 1, −y + 1, −z + 1; (ii) x, y − 1, z; (iii) −x, −y + 1, −z + 1; (iv) −x, −y, −z + 1; (v) −x + 1, −y + 1, −z + 2; (vi) −x + 1, −y + 2, −z + 2; (vii) x − 1, y, z; (viii) −x, −y + 1, −z + 2

Discussion and Conclusion

The compound $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$ has a complex three-dimensional structures in which the cation metal centers are bridged by PO_4^{3-} and HPO_4^{2-} groups as seen in the hureaulite structure [11–13].

The M(1) atom is placed in the center of the unit cell with a crystallographic occupancy factor of 1/2 as found in the hureaulite structure. The M(1), M(2), M(3) atoms have octahedral coordination. The M(4) atom has fivefold coordination with a distorted trigonal bipyramidal environment of oxygen, as was also found by Moore and Araki [14] and Calvo [15] in the cases of $Fe_3(H_2O)(PO_4)_2$. The structure represented in Fig. 1 is formed by M(2), M(3), M(4) polyhedra sharing edges in infinite chains along the direction [0 −2 0]. The sequence of metal atoms in the chain follows the scheme M(3)–M(3)′–M(4)–M(2)′–M(2)–M(4)′ where the primes refer to the polyhedra generated by the inversion symmetry operation, without specifying the translation, as shown in Fig. 2.

The M(1) octahedron shares corners with four oxygen atoms [O(2) of M(2), O(2)′ of M(2)′, O(1) of M(4) and O(1)′ of M(4)′] and two oxygen atoms [O(8) of P(1) and O(8)′ of P(1)′]. This fact is the most striking feature of the structures: The M(1) octahedron connects four infinite chains of zigzag, shared edged polyhedra. Each of the PO_4 tetrahedra shares the four corners with metal polyhedra.

Table 4 Selected bond angles in $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$

Moiety	Angle(°)	Moiety	Angle(°)
O8–Fe1–O8^{i}	180.0(1)	O12–Fe3–O9	82.9(1)
O8–Fe1–O2	90.7(1)	O12^{vi}–Fe3–O9	97.8(1)
O8^{i}–Fe1–O2	89.2(2)	O10^{vii}–Fe3–O9	164.7(1)
O8–Fe1–O2^{i}	89.2(2)	O1^{v}–Fe4–O6^{vi}	139.3(1)
O8^{i}–Fe1–O2^{i}	90.7(1)	O1^{v}–Fe4–O10^{vii}	122.9(1)
O2–Fe1–O2^{i}	180.0	O6^{vi}–Fe4–O10^{vii}	94.9(2)
O8–Fe1–O1	90.7(1)	O1^{v}–Fe4–O7^{viii}	104.3(1)
O8^{i}–Fe1–O1	89.2(2)	O6^{vi}–Fe4–O7^{viii}	82.5(1)
O2–Fe1–O1	87.4(2)	O10^{vii}–Fe4–O7^{viii}	97.9(2)
O2^{i}–Fe1–O1	92.5(1)	O1^{v}–Fe4–O4^{v}	84.9(1)
O8–Fe1–O1^{i}	89.2(2)	O6^{vi}–Fe4–O4^{v}	89.7(1)
O8^{i}–Fe1–O1^{i}	90.7(1)	O10^{vii}–Fe4–O4^{v}	77.6(1)
O2–Fe1–O1^{i}	92.5(1)	O7^{viii}–Fe4–O4^{v}	170.7(1)
O2^{i}–Fe1–O1^{i}	87.4(2)	O3–P1–O12	108.2(1)
O1–Fe1–O1^{i}	180.0	O3–P1–O6	110.8(2)
O11^{i}–Fe2–O3^{ii}	178.7(1)	O12–P1–O6	109.8(1)
O11^{i}–Fe2–O6^{i}	90.0(1)	O3–P1–O8	110.1(1)
O3^{ii}–Fe2–O6^{i}	89.6(2)	O12–P1–O8	109.3(2)
O11^{i}–Fe2–O3^{iii}	94.2(1)	O6–P1–O8	108.7(1)
O3^{ii}–Fe2–O3^{iii}	85.7(1)	O11–P2–O10	112.1(2)
O6^{i}–Fe2–O3^{iii}	161.7(1)	O11–P2–O1	111.6(2)
O11^{i}–Fe2–O2	96.8(1)	O10–P2–O1	111.0(1)
O3^{ii}–Fe2–O2	84.5(1)	O11–P2–O9	107.6(2)
O6^{i}–Fe2–O2	105.8(1)	O10–P2–O9	104.9(1)
O3^{iii}–Fe2–O2	91.5(1)	O1–P2–O9	109.2(2)
O11^{i}–Fe2–O7^{iv}	98.1(1)	O7–P3–O4	111.3(1)
O3^{ii}–Fe2–O7^{iv}	80.7(1)	O7–P3–O2	114.8(2)
O6^{i}–Fe2–O7^{iv}	78.5(1)	O4–P3–O2	110.5(1)
O3^{iii}–Fe2–O7^{iv}	83.2(1)	O7–P3–O5	106.8(1)
O2–Fe2–O7^{iv}	164.5(1)	O4–P3–O5	108.7(2)
O4^{v}–Fe3–O5	104.9(1)	O2–P3–O5	104.1(1)
O4^{v}–Fe3–O12	166.4(1)	P2–O1–Fe4^{v}	119.1(2)
O5–Fe3–O12	87.4(1)	P2–O1–Fe1	129.6(2)
O4^{v}–Fe3–O12^{vi}	90.43(1)	P3–O2–Fe2	120.4(2)
O5–Fe3–O12^{vi}	163.1(1)	P3–O2–Fe1	121.7(2)
O12–Fe3–O12^{vi}	78.2(1)	P1–O3–Fe2^{ix}	130.6(2)
O4^{v}–Fe3–O10^{vii}	79.2(1)	P1–O3–Fe2^{iii}	135.1(2)
O5–Fe3–O10^{vii}	81.7(1)	P3–O4–Fe3^{v}	137.1(1)
O12–Fe3–O10^{vii}	108.7(1)	P3–O4–Fe4^{v}	121.6(2)
O12^{vi}–Fe3–O10^{vii}	94.5(1)	P3–O5–Fe3	136.1(1)
O4^{v}–Fe3–O9	91.43(1)	P1–O6–Fe4^{vi}	127.0(1)
O5–Fe3–O9	89.1(1)	P1–O6–Fe2^{i}	127.1(1)

Symmetry codes: (i) −x + 1, −y + 1, −z + 1; (ii) x, y − 1, z; (iii) −x, −y + 1, −z + 1; (iv) −x, −y, −z + 1; (v) −x + 1, −y + 1, −z + 2; (vi) −x + 1, −y + 2, −z + 2; (vii) x − 1, y, z; (viii) −x, −y + 1, −z + 2; (ix) x, y + 1, z; (x) x + 1, y, z

The average octahedral M^{2+}–O and tetrahedral P–O distances are within the values of other well-refined structures. The M–O distances have intermediate values between

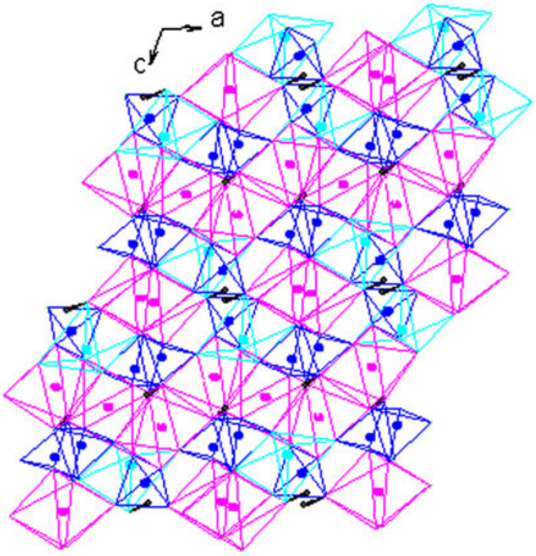

Fig. 1 Polyhedral representation of the crystal structure of $Fe_{6.36}Mn_{0.64}(PO_3(OH))_4(PO_4)_2$

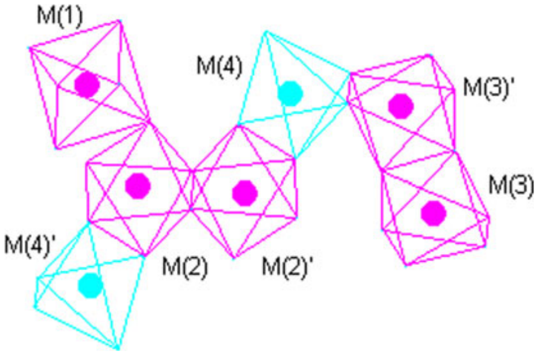

Fig. 2 Schematic representation of the edge-sharing polyhedral chain of metal atoms. The primes designate the polyhedra generated by the inversion symmetry operation, without specifying the translations

2.062(3) and 2.261(3) Å, compatibles with the occupation of metal valences in these sites. Interatomic angles reveal distortions of the octahedra, varying from $O(12)^{vi}$–Fe(3)–O(12) = 78.16° to O(1)–Fe(1)–$O(1)^{i}$ = 180° where i = −x + 1, −y + 1, −z + 1 and vi = −x + 1, −y + 2, −z + 2. The P–O hydrogen phosphate bond distance range is 1.516–1.581 Å and the average P–O phosphate tetrahedral distance has a mean value of 1.546 Å. The O–P–O bonds range from 104.1° to 114.9°. Strong hydrogen bonds between the OH groups of the HPO_4 tetrahedra and the O atoms, help to consolidate the crystal structure. One OH group is involved in a very short hydrogen bond with a distance of (O10–H2···O9) = 2.472(3) Å. The shortest distance between metal atoms is along the chains, with M(2)–$M(2)^{iv}$ = 3.104 Å, iv = −x, −y, −z + 1. The topology of metal–metal interaction network in the structure, leads to a possible frustrated spin–spin coupling and glassy magnetic behaviour.

Further details of the crystal structure investigations(s) may be obtained in writing from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number(s) CSD-380294.

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