Fe$_2^{II}$(PO$_4$)(OH), a synthetic analogue of wolfeite

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This paper reports the hydrothermal synthesis and crystal structure refinement of diiron(II) phosphate hydroxide, Fe$_2^{II}$(PO$_4$)(OH), obtained at 1063 K and 2.5 GPa. This phosphate is the synthetic analogue of the mineral wolfeite, and has a crystal structure topologically identical to those of minerals of the triplite–triploidite group. The complex framework contains edge- and corner-sharing FeO$_4$(OH) and FeO$_4$(OH)$_2$ polyhedra, linked *via* corner-sharing to the PO$_4$ tetrahedra (average P—O distances are between 1.537 and 1.544 Å). Four five-coordinated Fe sites are at the centers of distorted trigonal bipyramids (average Fe—O distances are between 2.070 and 2.105 Å), whereas the coordination environments of the remaining Fe sites are distorted octahedra (average Fe—O distances are between 2.146 and 2.180 Å). The Fe—O distances are similar to those observed in natural Mg-rich wolfeite, except for two Fe—O bond distances, which are significantly longer in synthetic Fe$_2^{2+}$(PO$_4$)(OH).

Comment

Wolfeite, (Fe,Mn)$_2^{2+}$(PO$_4$)(OH), is a rare phosphate mineral which has been reported in granitic pegmatites (Smeds *et al.*, 1998; Roda *et al.*, 2004) and in metamorphosed phosphatic ironstones (Robinson *et al.*, 1992; Stalder & Rozendaal, 2002). Wolfeite belongs to the triplite–triploidite group of minerals (Strunz & Nickel, 2001; Chopin *et al.*, 2003), which also includes the following phosphates: triplite [(Mn,Fe)$_2^{2+}$(PO$_4$)F; Waldrop, 1969], zwieselite [(Fe,Mn)$_2^{2+}$(PO$_4$)F; Yakubovich *et al.*, 1978], triploidite [(Mn,Fe)$_2^{2+}$(PO$_4$)(OH); Waldrop, 1970], wagnerite [(Mg,Fe^{2+})$_2$(PO$_4$)F; Coda *et al.*, 1967], staněkite [(Mn,Fe^{2+},Mg)Fe^{3+}(PO$_4$)O; Keller *et al.*, 2006] and joosteite [Mn^{2+}(Mn^{3+},Fe^{3+})(PO$_4$)O; Keller *et al.*, 2007].

The crystal structures of these phosphates are topologically identical but, owing to the periodic ordering of the F atoms along the *b* axis, several polytypes have been observed for the F-rich compositions, such as, for example, wagnerite-*Ma2bc* (*P*2$_1$/*a*, *b* ≃ 13 Å), wagnerite-*Ma5bc* (*Ia*, *b* ≃ 32 Å), wagnerite-*Ma7bc* (*P*2$_1$, *b* ≃ 45 Å) and wagnerite-*Ma9bc* (*Ia*, *b* ≃ 57 Å) (Chopin *et al.*, 2003; Ren *et al.*, 2003). The crystal structure of

wolfeite has been solved on a natural Mg-rich sample with composition (Fe$_{1.84}$Mg$_{0.16}$)(PO$_4$)(OH), collected in the Big Fish River area, Yukon Territory, Canada (Kolitsch, 2003). The *b* unit-cell parameter, 13.169 (3) Å, indicates that this sample corresponds to the polytype *Ma2bc*, with space group *P*2$_1$/*a*.

During an extensive investigation of the stability of Na–Fe–Mn-bearing phosphates at high pressure, we performed a hydrothermal experiment at 1063 K and 2.5 GPa, starting from the composition NaFe^{2+}(PO$_4$). This experiment produced small brown isometric crystals, associated with a white powder identified as a maricíte-type compound, NaFe^{2+}(PO$_4$). An electron-microprobe analysis of the brown crystals (see below), coupled with a single-crystal structure determination, indicated that they correspond to the synthetic analogue of wolfeite, Fe$_2^{2+}$(PO$_4$)(OH), which has not been synthesized previously. The crystal structure of this pure end-member is reported here and compared with the structure of natural Mg-rich wolfeite (Kolitsch, 2003).

The crystal structure of Fe$_2^{2+}$(PO$_4$)(OH) has been refined in the monoclinic space group *P*2$_1$/*a*, and shows a complex framework based on edge- and corner-sharing FeO$_4$(OH) and FeO$_4$(OH)$_2$ polyhedra, linked *via* corner-sharing to the PO$_4$ tetrahedra (Figs. 1 and 2). The four PO$_4$ tetrahedra show regular topologies, with average P—O distances of 1.541 (P1), 1.537 (P2), 1.542 (P3) and 1.544 Å (P4). The five-coordinated Fe1, Fe4, Fe6 and Fe8 sites are at the centers of distorted trigonal bipyramids, with average Fe—O distances of 2.102 (Fe1), 2.105 (Fe4), 2.070 (Fe6) and 2.080 Å (Fe8), whereas the coordination environments of the Fe2, Fe3, Fe5 and Fe7 sites are distorted octahedra, with average Fe—O distances of 2.180 (Fe2), 2.178 (Fe3), 2.152 (Fe5) and 2.146 Å (Fe7). These Fe—O distances are similar to those observed in natural Mg-rich wolfeite (Kolitsch, 2003), except for the Fe6—O and Fe7—O bond distances, which are significantly longer in synthetic Fe$_2^{2+}$(PO$_4$)(OH) (Fe6—O = 2.062 and Fe7—O = 2.139 Å in natural Mg-rich wolfeite). This feature can be explained by the smaller effective ionic radius of Mg^{2+} (0.720 Å; Shannon, 1976), which replaces Fe^{2+} (0.780 Å; Shannon, 1976) on the Fe6 (24% Mg) and Fe7 (19% Mg) crystallographic sites of natural wolfeite (Kolitsch, 2003).

Bond-valence sums were calculated for each ion using the parameters of Brown & Altermatt (1985). The P-atom bond-valence sums range from 4.88 to 4.96 valence units (v.u.), and the O-atom bond-valence sums are within the normal acceptable range (1.78–2.01 v.u.). Atoms O17–O20 have bond-valence sums of 1.04–1.20 v.u., thus indicating that they correspond to the four OH groups of the wolfeite structure (Kolitsch, 2003). For the Fe sites, the bond-valence sums are between 1.84 and 2.04 v.u., thus confirming that iron is essentially divalent. The brown color of the crystals is probably a result of the presence of small amounts of Fe^{3+}.

The hydrogen-bonding scheme of Fe$_2^{2+}$(PO$_4$)(OH) (Table 1) is similar to that observed in natural Mg-rich wolfeite (Kolitsch, 2003), with weak hydrogen bonds showing O···O distances between 2.72 and *ca* 3.2 Å. Three of the four OH groups are involved in bifurcated or trifurcated hydrogen

bonds, whereas the bond donated by the O20—H4 group has a single acceptor (Table 1).

Experimental

The title compound was synthesized under hydrothermal conditions. The starting material was prepared by mixing $NaH_2PO_4 \cdot H_2O$, Fe and Fe_2O_3 in the ratio 1:0.33:0.33. The homogenized mixture (about 25 mg) was sealed in a gold tube (outer diameter = 2 mm and length = 15 mm) containing 2 mg of distilled water. The gold capsule was then inserted into a piston-cylinder apparatus of the type described by Boyd & England (1960), using a pressure cell consisting of rock salt and fired pyrophyllite, with a graphite cylinder as resistance furnace. The sample was maintained for 3 d at 1063 K and 2.5 GPa. The synthesized products consisted of a mixture of small brown isometric crystals of wolfeite, associated with a white powder identified as marićite, $NaFe^{2+}(PO_4)$. A chemical analysis of the title compound has been performed. The average of ten point analyses gives P_2O_5 31.32, FeO 64.52, H_2O 3.97 (calculated value), total 99.81 wt%. The chemical composition, calculated on the basis of one P atom, corresponds to $Fe_{2.04}^{2+}(PO_4)(OH)$.

Figure 1
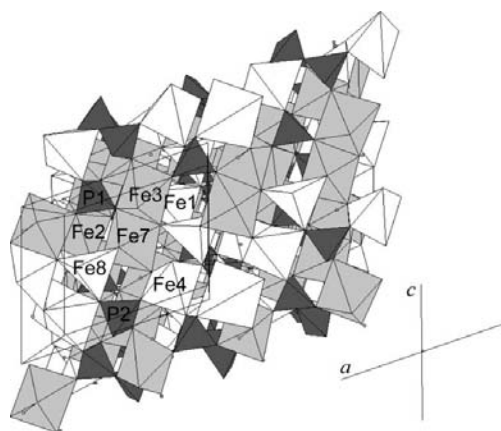A polyhedral representation of the crystal structure of $Fe_2^{2+}(PO_4)(OH)$, projected along [010] (perspective view). The P tetrahedra are dark grey, the $FeO_4(OH)_2$ octahedra are light grey and the $FeO_4(OH)$ trigonal bipyramids are white. The small grey circles represent H atoms.

Figure 2
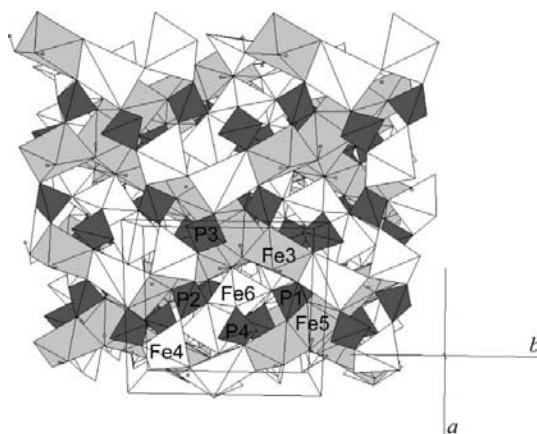The crystal structure of $Fe_2^{2+}(PO_4)(OH)$, projected along [001] (perspective view). For key, see Fig. 1.

Crystal data

$Fe_2(PO_4)(OH)$	$V = 1493.8 (2)$ Å^3
$M_r = 223.67$	$Z = 16$
Monoclinic, $P2_1/a$	Mo $K\alpha$ radiation
$a = 12.265 (1)$ Å	$\mu = 8.09$ mm^{-1}
$b = 13.197 (1)$ Å	$T = 293 (2)$ K
$c = 9.7385 (9)$ Å	$0.09 \times 0.07 \times 0.05$ mm
$\beta = 108.63 (1)°$	

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire2 CCD area detector	Diffraction, 2002) $T_{min} = 0.399$, $T_{max} = 0.476$
Absorption correction: numerical (after shape optimization; *CrysAlis RED*; Oxford	23682 measured reflections 8936 independent reflections 4515 reflections with $I > 2\sigma(I)$ $R_{int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	305 parameters
$wR(F^2) = 0.065$	All H-atom parameters refined
$S = 0.86$	$\Delta\rho_{max} = 0.86$ e Å^{-3}
8936 reflections	$\Delta\rho_{min} = -0.74$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O17—H1$\cdots$O9^i	0.77 (3)	2.20 (4)	2.719 (3)	126 (4)
O17—H1$\cdots$O1^{ii}	0.77 (3)	2.32 (4)	2.777 (3)	119 (4)
O17—H1$\cdots$O10^{ii}	0.77 (3)	2.55 (4)	3.161 (3)	138 (4)
O18—H2$\cdots$O5	0.77 (3)	2.30 (4)	2.839 (2)	128 (3)
O18—H2$\cdots$O4^{iii}	0.77 (3)	2.52 (3)	2.992 (3)	121 (3)
O19—H3$\cdots$O12	0.67 (3)	2.34 (4)	2.803 (3)	127 (4)
O19—H3$\cdots$O4^{iv}	0.67 (3)	2.39 (4)	2.795 (2)	121 (4)
O19—H3$\cdots$O11^{iv}	0.67 (3)	2.54 (4)	3.067 (3)	137 (4)
O20—H4$\cdots$O7	0.87 (3)	2.19 (3)	2.731 (2)	120 (2)

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$.

In early refinement cycles, H atoms were refined freely and isotropically, but atom H3 was localized at only 0.54 Å from O19. The O—H distances were then restrained to 0.82 (5) Å with the DFIX instruction of *SHELXL97* (Sheldrick, 1997). The relatively large isotropic displacement parameter of atom H1 probably corresponds to an artefact. In the final refinement cycle, atomic coordinates identical to those of Kolitsch (2003) were used.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3034). Services for accessing these data are described at the back of the journal.

References

Boyd, F. R. & England, J. L. (1960). *J. Geophys. Res.* **65**, 741–748.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Chopin, C., Armbruster, T. & Leyx, C. (2003). EGS–AGU–EUG Joint Assembly, Abstract book, p. 8323.
Coda, A., Giuseppetti, G. & Tadini, C. (1967). *Atti. Acad. Naz. Lincei R. Cl. Sci. Fis. Mater. Nat.* **43**, 212–224.
Dowty, E. (1993). *ATOMS for Windows*. Version 2.3. Shape Software, Kingsport, Tennessee, USA.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Keller, P., Fontan, F., Velasco Roldan, F. & de Parseval, P. (2007). *Neues Jahrb. Mineral. Abh.* **183**, 197–201.
Keller, P., Lissner, F. & Schleid, T. (2006). *Eur. J. Mineral.* **18**, 113–118.
Kolitsch, U. (2003). *Acta Cryst.* E**59**, i125–i128.
Oxford Diffraction (2002). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.69. Oxford Diffraction, Abingdon, England.
Ren, L., Grew, E. S., Xiong, M. & Ma, Z. (2003). *Can. Mineral.* **41**, 393–411.
Robinson, G. W., Van Velthuizen, J., Ansell, H. G. & Sturman, B. D. (1992). *Miner. Rec.* **23**, 5–47.
Roda, E., Pesquera, A., Fontan, F. & Keller, P. (2004). *Am. Mineral.* **89**, 110–125.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Smeds, S.-A., Uher, P., Černý, P., Wise, M. A., Gustafsson, L. & Penner, P. (1998). *Can. Mineral.* **36**, 377–394.
Stalder, M. & Rozendaal, A. (2002). *Mineral. Mag.* **66**, 915–927.
Strunz, H. & Nickel, E. H. (2001). In *Strunz Mineralogical Tables*. Stuttgart: E. Schweizerbart'sche Verlagsbuchhandlung.
Waldrop, L. (1969). *Z. Kristallogr.* **130**, 1–14.
Waldrop, L. (1970). *Z. Kristallogr.* **131**, 1–20.
Yakubovich, O. V., Simonov, M. A., Matvienko, E. N. & Belov, N. V. (1978). *Sov. Phys. Dokl.* **23**, 11–13.