Refinement of pyrobelonite, PbMn^{II}VO$_4$(OH), a member of the descloizite group

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Pyrobelonite [lead manganese(II) vanadate(V) hydroxide], PbMn^{II}VO$_4$(OH), has been refined in space group *Pnma*. It is isostructural with descloizite, PbZnVO$_4$(OH). Mn^{II}O$_4$(OH)$_2$ octahedra share edges to form infinite chains parallel to the *b* axis. Distorted VO$_4$ tetrahedra share vertices with the octahedra to form a compact framework, in which voids are occupied by [3+4]-coordinated Pb^{2+} cations. All atoms except O3 are on special positions with site symmetry $\bar{1}$ (Mn) or *.m.* (remaining atoms).

Key indicators

Single-crystal X-ray study

T = 293 K

Mean σ(V–O) = 0.004 Å

R factor = 0.018

wR factor = 0.047

Data-to-parameter ratio = 14.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Pyrobelonite, PbMn^{II}VO$_4$(OH), is a member of the descloizite group of lead oxysalt minerals with the general formula PbM(XO_4)(OH), where M = Cu^{2+}, Fe^{2+}, Mn^{2+} or Zn, and X = As^{5+} or V^{5+} (Mandarino, 1999). These minerals are orthorhombic and crystallize in either space group *Pnma* or $P2_12_12_1$; the space group of the Fe^{2+}–As member (gabrielsonite), originally reported as $P2_1ma$ (Moore, 1967), is uncertain (a current single-crystal study by the author suggests $Pna2_1$, but also strongly indicates the presence of twinning – the structure could not be solved so far).
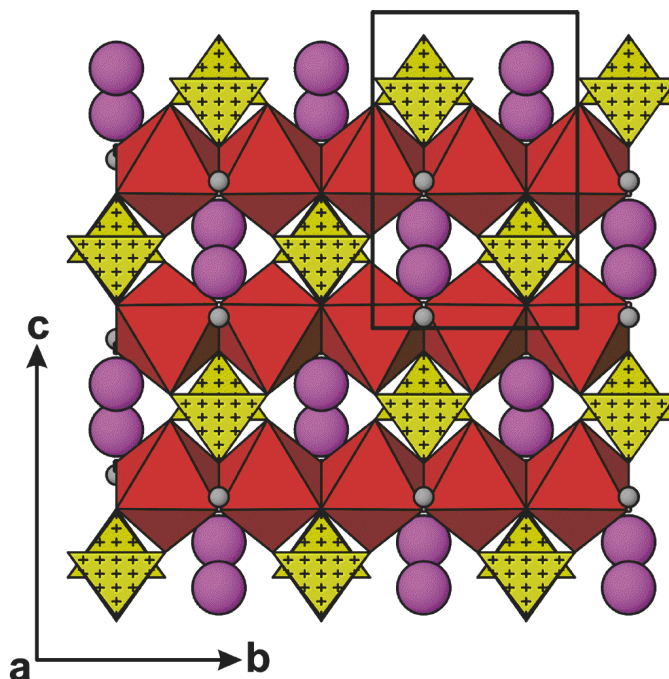

Figure 1
View of the crystal structure of pyrobelonite along [100]. Mn^{II}O$_4$(OH)$_2$ octahedra are red, VO$_4$ tetrahedra are yellow and marked with crosses, Pb atoms are shown as large violet spheres and the H atom is represented by a small grey sphere.
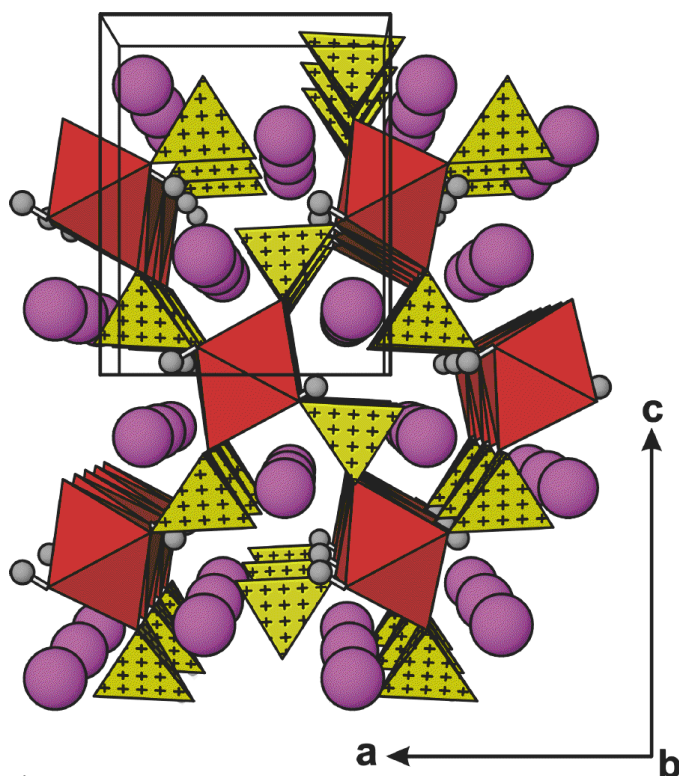
Figure 2
The structure of pyrobelonite in a perspective view along [010], showing the corner-linkage between the $Mn^{II}O_4(OH)_2$ octahedra and the VO_4 tetrahedra. Designations as in Fig. 1.

Figure 3
Anisotropic displacement ellispoids (99% probability level) of the atoms in a selected fragment of the pyrobelonite structure.

The crystal structure of pyrobelonite was originally determined by Donaldson & Barnes (1955) and isotropically refined in space group *Pnma* to a conventional *R* index of 0.09. However, the H atom was not detected and the authors suggested that the correct space group might be *Pn2₁a*. Later, Qurashi & Barnes (1963) argued that pyrobelonite may crystallize in *P2₁2₁2₁*.

Due to a general interest in the crystallography and crystal chemistry of secondary lead minerals, the structure of pyrobelonite was studied again in order to determine the correct space group, the location of the H atom, and to provide high-precision geometrical parameters. The sample studied is from the Iron Monarch iron ore mine, South Australia (Pring *et al.*, 1989, 1999) and consists of dark-red anhedral grains embedded in a matrix. EDS analyses showed major Pb, Mn and V components, and negligible amounts of impurities. The pyrobelonite grains are associated with pale-yellow vanadinite, $Pb_5(VO_4)Cl$.

The present structure refinement demonstrates that pyrobelonite crystallizes in space group *Pnma* and is isostructural with descloizite, $PbZnVO_4(OH)$ (Hawthorne & Faggiani, 1979). Refined single-crystal unit-cell parameters are close to those reported earlier (Barnes & Qurashi, 1952; Donaldson & Barnes, 1955; Moore, 1967; Barnes & Ahmed, 1969; Rodnova, 1993). The calculated density, 5.828 Mg m^{-3}, is in very good agreement with the value reported by Moore (1967), 5.82 Mg m^{-3} (previously measured values were highly inconsistent; see Donaldson & Barnes, 1955).
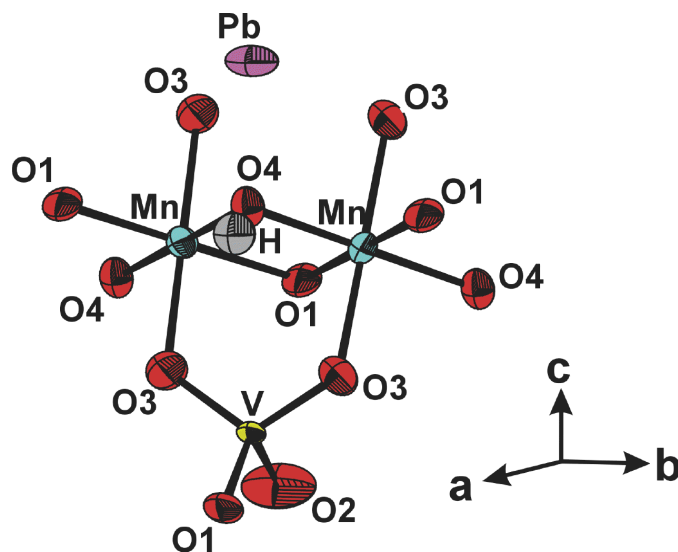
The structure is characterized by $Mn^{II}O_4(OH)_2$ octahedra ($<Mn^{II}–O> = 2.17$ Å) sharing edges to form infinite chains parallel to the *b* axis (Figs. 1–3). Distorted VO_4 tetrahedra share vertices with the octahedra to form a compact framework. V—O bond lengths average 1.73 Å; the previously reported low-precision bond lengths ranged from 1.62 (12) to 1.83 (12) Å (Donaldson & Barnes, 1955). Voids in the framework are occupied by the [3+4]-coordinated Pb^{2+} cation, which has seven O ligands. Two further O atoms are both at a distance of 3.2843 (15) Å. The H atom is bonded to OH4 and is involved in a medium-strong hydrogen bond donated to O2, with an OH4···O2 distance of 2.783 (5) Å. Bond-valence sums for the metal cations, calculated using the parameters of Brese & O'Keeffe (1991), give 1.93 v.u. for Pb, 2.16 v.u. for Mn and 4.93 v.u. for V.

The decorated chain present in pyrobelonite and other descloizite-type minerals is also found, first, in the structure of linarite [$PbCu(SO_4)(OH)_2$]-type minerals (Effenberger, 1987) and, secondly, as a fundamental building block of the sheets in the structure types of tsumcorite, $Pb(Zn,Fe^{3+})_2(AsO_4)_2(OH,H_2O)_2$ (Tillmanns & Gebert, 1973), and bermanite, $Mn^{II}Mn^{III}_2(PO_4)_2(OH)_2·4H_2O$ (Kampf & Moore, 1976). Details on these relationships are discussed by Hawthorne (1994).

Experimental

The title compound is a natural sample (see above).

Crystal data

$PbMnVO_4(OH)$	Mo $K\alpha$ radiation
$M_r = 394.08$	Cell parameters from 898
Orthorhombic, *Pnma*	reflections
$a = 7.646$ (2) Å	$\theta = 3.5–30.0°$
$b = 6.179$ (1) Å	$\mu = 42.11$ mm^{-1}
$c = 9.507$ (2) Å	$T = 293$ (2) K
$V = 449.15$ (17) Å^3	Fragment, dark red
$Z = 4$	$0.08 \times 0.08 \times 0.05$ mm
$D_x = 5.828$ Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	699 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.014$
Absorption correction: numerical	$\theta_{max} = 30.0°$
($maXus$; Mackay *et al.*, 1998)	$h = -10 \rightarrow 10$
$T_{min} = 0.059$, $T_{max} = 0.125$	$k = -8 \rightarrow 8$
1242 measured reflections	$l = -13 \rightarrow 13$
714 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.024P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.018$	$+ 1.300P]$
$wR(F^2) = 0.047$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.15$	$(\Delta/\sigma)_{max} < 0.001$
714 reflections	$\Delta\rho_{max} = 1.26$ e Å^{-3}
49 parameters	$\Delta\rho_{min} = -1.80$ e Å^{-3}
H-atom coordinates refined	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0086 (4)

Table 1
Selected geometric parameters (Å, °).

Pb—OH4	2.354 (4)	Mn—O1^{iv}	2.221 (3)
Pb—O3	2.470 (3)	Mn—O3^{ii}	2.221 (3)
Pb—O1^{i}	2.744 (4)	V—O2	1.656 (4)
Pb—O3^{ii}	2.781 (3)	V—O1	1.747 (4)
Pb—O2^{i}	2.841 (4)	V—O3	1.755 (3)
Mn—OH4^{iii}	2.082 (3)	V—O3^{v}	1.755 (3)
OH4^{iii}—Mn—O1^{iv}	87.92 (10)	OH4^{iii}—Mn—O3^{vii}	88.15 (13)
OH4—Mn—O1^{iv}	92.08 (10)	OH4—Mn—O3^{vii}	91.85 (13)
OH4^{iii}—Mn—O3^{ii}	91.85 (13)	O2—V—O1	104.9 (2)
OH4—Mn—O3^{ii}	88.15 (13)	O2—V—O3	107.12 (11)
O1^{iv}—Mn—O3^{ii}	88.83 (12)	O1—V—O3	111.90 (10)
O1^{vi}—Mn—O3^{ii}	91.17 (12)	O3—V—O3^{v}	113.3 (2)

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (iii) $-x, -y, 1 - z$; (iv) $x, y - 1, z$; (v) $x, \frac{3}{2} - y, z$; (vi) $-x, 1 - y, 1 - z$; (vii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
OH4—H$\cdots$O2^{i}	0.77 (9)	2.02 (9)	2.783 (5)	176 (8)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

The H atom was constrained to have a U_{iso} value of 0.02 Å^2. The refined O—H distance is 0.77 (9) Å. The largest two peaks in the final difference Fourier map are closest to O2 (at 1.66 Å) and OH4 (at 1.10 Å). The next three peaks are closest to the Pb atom.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO and SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL*97.

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