ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Highly frustrated synthetic end member $Mn_2(PO_4)OH$ in the triplite-triploidite family

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Table S1 Synthetic phosphates and arsenates with triploidite- and triplite-type crystal structures*

Chemical formula	*a*, Å	*b*, Å	*c*, Å	β, grad	*V*, Å^3	Reference
Triploidite structural group, space group $P2_1/a$						
$Mn_2(PO_4)OH$, synth. triploidite	12.411(1)	13.323(1)	10.014(1)	108.16(1)	1573.3	This work
$Fe_2(PO_4)OH$, synth. wolfeite	12.265(1)	13.197(1)	9.739(1)	108.63(1)	1493.8	1
$Mg_2(PO_4)F$, synth. wagnerite	11.961(2)	12.731(3)	9.650(1)	108.22(1)	1395.8	2
$Mg_2(PO_4)OH$, synth. hydroxylwagnerite	12.069(4)	12.859(3)	9.656(3)	108.49(3)	1421.2	3
$Cd_2(PO_4)OH$	13.097(3)	14.089(3)	10.566(2)	108.38(3)	1850.2	4
$Zn_2(PO_4)[F_{0.86}(OH)_{0.14}]$	11.972(1)	12.793(1)	9.690(1)	108.26(1)	1409.3	5
$ZnFe(PO_4)OH$	12.154(3)	13.149(6)	9.678(3)	109.00(2)	1462.4	6
$Co_2(PO_4)F$	11.955(4)	12.802(4)	9.712(2)	108.14(2)	1417.0	7
$Mn_2(AsO_4)OH$, synth. sarkinite	12.780(2)	13.613(2)	10.219(2)	108.83(1)	1682.5	8
Triplite structural group, space group $I2/a$						
$Mn_2(PO_4)F$, synth. triplite	12.099(4)	6.510(5)	10.094(2)	106.28(1)	763.2	9
$Fe_2(PO_4)F$, synth. zwieselite	11.999(3)	6.489(1)	9.890(3)	107.72(2)	733.5	10
$Co_2(PO_4)F$	12.018(2)	6.437(1)	9.674(2)	109.17(2)	710.7	11
$Cu_2(PO_4)F$	11.741(3)	6.182(1)	9.962(2)	108.67(2)	685.1	12
$Cd_2(PO_4)F$	12.503(2)	6.693(1)	10.519(1)	106.42(1)	844.3	13
$Fe_2(AsO_4)F$	12.471(1)	6.623(1)	10.045(1)	108.90(1)	784.0	14
$Cd_2(AsO_4)F$	12.737(5)	6.847(1)	10.694(4)	106.00(6)	896.5	15

*Originally reported unit-cells are transformed to $P2_1/a$ and $I2/a$ space-group settings for clear comparison

Table S2 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the $Mn_2(PO_4)OH$. *U*(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

Atom	*x*	*y*	*z*	*U*(eq)
Mn1	0.53593(6)	0.17404(5)	0.89405(5)	0.00927(15)
Mn2	0.45274(6)	0.32274(5)	1.07644(5)	0.00871(15)
Mn3	-0.05631(6)	0.07540(5)	0.58293(5)	0.00852(15)
Mn4	0.03498(6)	0.07151(5)	0.90274(5)	0.00874(15)
Mn5	-0.20481(6)	0.25149(5)	0.80459(5)	0.01021(15)
Mn6	0.19087(6)	0.26892(5)	0.68192(5)	0.00929(15)
Mn7	-0.31283(6)	-0.02130(5)	0.68738(5)	0.00811(15)
Mn8	0.29041(6)	-0.00337(5)	0.80284(5)	0.01058(15)
P1	0.62138(10)	0.42769(8)	0.92499(8)	0.0062(2)
P2	-0.12167(10)	0.17766(8)	1.07798(8)	0.0062(2)
P3	0.11789(10)	0.32649(8)	0.92500(8)	0.0061(2)
P4	0.38508(10)	0.07765(8)	1.07615(8)	0.0061(2)
O1	-0.0248(3)	0.0923(2)	1.0608(2)	0.0096(6)
O2	0.0218(3)	0.2353(2)	0.8835(2)	0.0101(6)
O3	0.2614(3)	0.0469(2)	0.9731(2)	0.0114(6)
O4	0.4701(3)	0.1626(2)	1.0434(2)	0.0103(6)

O5	0.3113(3)	0.1628(2)	0.7944(2)	0.0119(6)
O6	0.5173(3)	0.0121(2)	0.8778(2)	0.0101(6)
O7	0.5192(3)	0.3420(2)	0.9302(2)	0.0104(6)
O8	-0.1877(3)	0.0826(2)	0.8017(2)	0.0119(6)
O9	0.0676(3)	0.0327(2)	0.7447(2)	0.0114(6)
O10	0.3313(3)	0.3844(2)	0.6736(2)	0.0099(6)
O11	-0.2980(3)	0.4040(2)	0.8413(2)	0.0104(6)
O12	0.5724(3)	0.2190(2)	0.7401(2)	0.0100(6)
O13	-0.1896(3)	0.3497(2)	0.6698(2)	0.0089(6)
O14	0.4704(3)	0.4778(2)	1.1152(2)	0.0096(6)
O15	-0.2743(3)	0.0545(2)	0.5442(2)	0.0112(6)
O16	0.7629(3)	0.2029(2)	0.9670(2)	0.0090(6)
O17	0.0329(3	0.0864(2)	0.4509(2)	0.0103(6)
O18	-0.0255(3)	0.2298(2)	0.6195(2)	0.0090(6)
O19	0.2356(2)	0.2980(2)	1.0344(2)	0.0109(6)
O20	0.1807(3)	0.3591(2)	0.8314(2)	0.0101(6)
H1	0.052(5)	-0.0260(7)	0.734(4)	0.034(15)
H2	0.285(3)	0.174(3)	0.848(2)	0.020(13)
H3	0.560(5)	0.2782(6)	0.731(4)	0.033(15)
H4	-0.212(3)	0.077(3)	0.857(2)	0.025(14)

Table S3 Bond valence data for synthetic triploidite, $Mn_2(PO_4)OH$

Atom	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Mn7	Mn8	P1	P2	P3	P4	H1	H2	H3	H4	Σ
O1				0.30 0.30						1.19						0.04	1.83
O2				0.34	0.35						1.25						1.94
O3				0.34				0.24				1.26		0.07			1.91
O4	0.37	0.34										1.22		0.05	0.09		2.07
O5(OH)	0.32					0.45		0.31						0.88			1.96
O6	0.36							0.35				1.24					1.95
O7	0.25	0.40							1.21								1.86
O8(OH)				0.33	0.28		0.44									0.87	1.92
O9(OH)			0.45	0.38				0.35					0.83				2.01
O10						0.42	0.34					1.19			0.02		1.97
O11					0.23			0.34	1.25						0.05		1.87
O12(OH)	0.39	0.45			0.36										0.84		2.04
O13					0.36			0.27		1.23			0.09				1.95
O14		0.41					0.37		1.21								1.99
O15			0.43				0.35		1.23								2.01
O16	0.33				0.30					1.22						0.09	1.94
O17			0.43 0.31								1.26		0.08				2.08
O18			0.42			0.40				1.20							2.02
O19		0.43				0.33					1.23						1.99
O20						0.30	0.40				1.21						1.91
Σ	2.02	2.03	2.04	1.99	1.88	1.90	1.90	1.86	4.90	4.84	4.95	4.91	1.00	1.00	1.00	1.00	

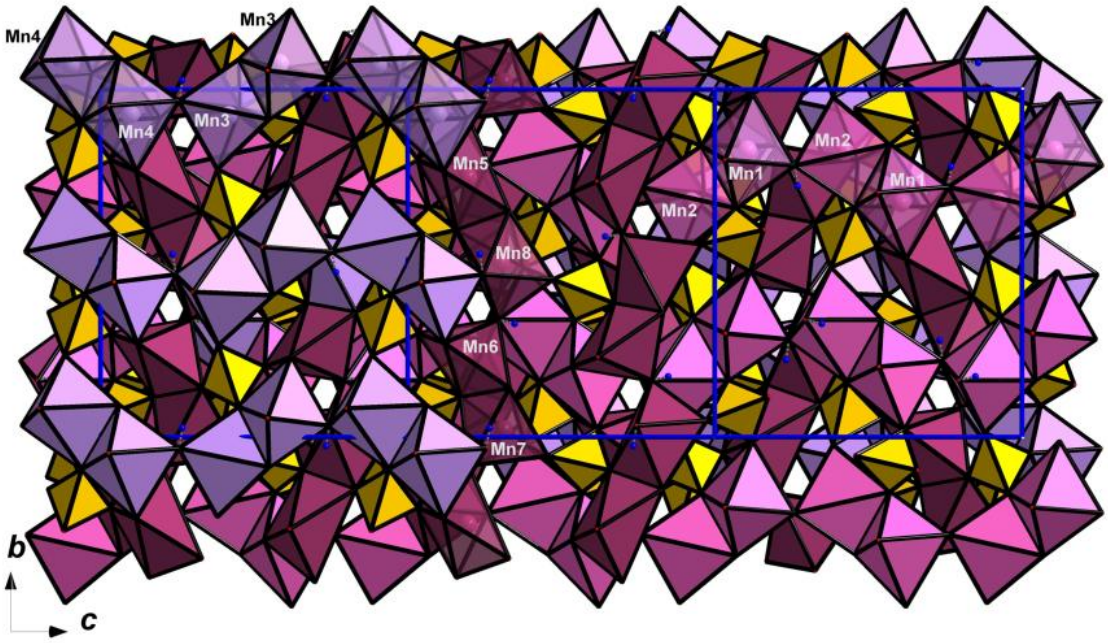

Fig. S1 The $Mn_2(PO_4)OH$ crystal structure in *yz* projection.

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