Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2024

SUPPLEMENTARY INFORMATION

Crystal structure of $KMnPO_4F$ with short and long range order inside the layered magnetic system

Olga V. Yakubovich,[1] Larisa V. Shvanskaya,[1,2] Galina V. Kiriukhina,[1,3] Sergei Simonov,[4] Anatoliy S. Volkov,[5] Olga V. Dimitrova,[1] Vladimir V. Korolev,[1,2] Yevgeniy A. Ovchenkov,[1,2] Alexander N. Vasiliev[1,2]*

[1]Moscow State University, Moscow 119991, Russia
[2]National University of Science and Technology, Moscow 119049, Russia
[3]Institute of Experimental Mineralogy, RAS, Chernogolovka 142432, Russia
[4]Institute of Solid State Physics, RAS, Chernogolovka 142432, Russia
[5]Skolkovo Institute of Science and Technology, Moscow 121205, Russia

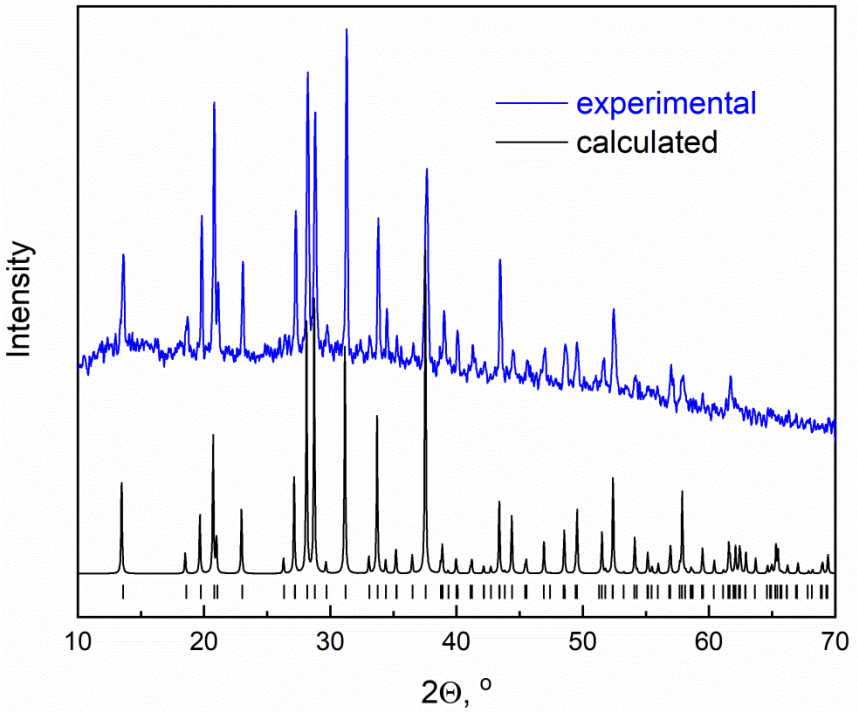

Fig. S1. Experimental and calculated powder XRD pattern of $KMnPO_4F$ (the vertical ticks indicate the Bragg positions).

Table S1. Selected geometric parameters for $KMnPO_4F$ (Å)

Mn1—F1	1.825 (2)	K1—O4^{iii}	2.931 (3)
Mn1—O5	1.887 (3)	K1—O3^{viii}	3.088 (3)
Mn1—O2^{i}	1.919 (3)	K1—O3^{ix}	3.106 (3)
Mn1—O4^{ii}	1.919 (3)	K1—O5^{vii}	3.160 (3)
Mn1—O3^{iii}	2.092 (3)	K1—O4^{i}	3.249 (3)
K1—F1	2.590 (3)	P1—O3	1.529 (3)
K1—F1^{iv}	2.712 (3)	P1—O5	1.534 (3)
K1—O5^{v}	2.760 (3)	P1—O4	1.538 (3)
K1—F1^{vi}	2.839 (3)	P1—O2	1.552 (3)
K1—O2^{vii}	2.879 (3)		

Symmetry code(s): (i) *x*+1/2, -*y*+1/2, -*z*+1; (ii) -*x*+1, *y*+1/2, -*z*+1/2; (iii) *x*-1/2, -*y*+1/2, -*z*+1; (iv) *x*-1/2, -*y*+3/2, -*z*+1; (v) -*x*+3/2, -*y*+1, *z*+1/2; (vi) *x*+1/2, -*y*+3/2, -*z*+1; (vii) -*x*+1/2, -*y*+1, *z*+1/2; (viii) *x*, *y*+1, *z*; (ix) -*x*+1, *y*+1/2, -*z*+3/2.

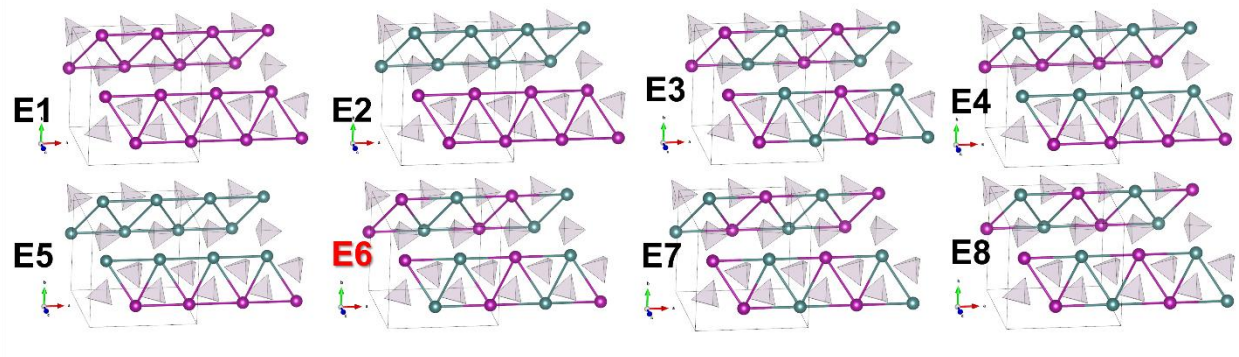

Fig. S2. The spin configurations considered in DFT calculations for $KMnPO_4F$. Green and magenta atoms represent spin up and spin down orientations of Mn^{3+}; PO_4^{3-} groups are shown by grey tetrahedra. The lowest energy configuration 6 is marked in red.

Table S2. Crystal chemical data, synthesis conditions and magnetic properties of phosphates related to the *AM*PO_4F morphotropic series

$BaCu^{2+}PO_4Cl$	*a* 7.885(2) *V* 495.9(2) *b* 8.650(1) ρ 4.44 *c* 7.270(1) *Z* 4	orthorhombic $P2_12_12_1$ (D^4_2) chiral	Cu^{2+} 0.57 *S* = 0.5, $3d^9$	Cu−O3 1.937(4) Cu− O4 2.076(4) O1 1.981(4) Cl 2.773(4) O2 1.981(4) **Cl' 3.259(4)**	Synthesis from flux at 800° C.	Etheredge & Hwu, 1995
$BaFe^{3+}PO_4F_2$	*a* 5.2440(2) *V* 470.52(3) *b* 12.7889(5) ρ *c* 7.1765(2) *Z* 4 β 102.142(2)	monoclinic $P2_1/n$ (C^5_{2h}) centrosym-metric	Fe^{3+} 0.64_5 *S* = 2.5, $3d^5$	Fe1−F2 1.926(4)x2 Fe2−F1 1.992(4)x2 O1 1.950(4)x2 F1 1.964(4)x2 O3 2.003(4)x2 O2 2.023(4)x2	Hydrothermal synthesis at 230° C. A spin−flop transition at 2 K (field at Bsf = 3.1 T), stemming from the antiferromagnetic ordering of chain formed by F sharing octahedra.	Jiang *et al*., 2019
$BaMn^{3+}PO_4F_2$*	*a* 5.1463(9) *V* 461.1 *b* 12.691(2) ρ 4.69 *c* 7.871(1) *Z* 4 β 116.24(3)	monoclinic $P2_1/c$ (C^5_{2h}) centrosym-metric	Mn^{3+} 0.65 *S* = 2, $3d^4$	Mn1−O2 1.870(5)x2 Mn2−F1 1.858(4)x2 O4 2.014(5)x2 O3 1.936(5)x2 F2 2.024(4)x2 F2 2.042(5)x2	Hydrothermal synthesis at 234° C. Antiferromagnetic long-range ordering at 14 K.	Pei *et al*., 2016
$BaMn^{3+}PO_4FCl$ *	*a* 7.221(1) *V* 521.60 *b* 8.535(1) ρ 4.35 *c* 8.870(1) *Z* 4 β 107.41(3)	- " -	Mn^{3+} 0.65 *S* = 2, $3d^4$	Mn−O1 1.881(3) Mn−O3 1.924(3) O2 1.884(3) F 2.108(2) O4 1.916(3) Cl 2.640(1)	Hydrothermal synthesis at 234° C. Antiferromagnetic long-range ordering at 9.8 K.	Pei *et al*., 2016

* Low-temperature X-ray diffraction data.

References

1. K. M. S. Etheredge, S. J. Hwu, *Inorg. Chem.* 1995, **34**, 11, 3123-3125.
2. J. Jiang, S. Lee, B. Zhu, Y. Yu, J. C. Waerenborgh, K.-Y. Choi, & M. Lü, *Inorg. Chem.* 2019, **58**, (1), 133-142.
3. D.-T. Pei, W. Sun, Y.-X. Huang, Z.-M. Sun, Y. Pan, J.-X. Mi, *J.Solid State Chem.,* 2016**, 234**, 29-35.