SUPPLEMENTARY MATERIAL

$KNi_{0.93}Fe^{II}_{0.07}Fe^{III}(PO_4)_2$ - the new type of structure for compounds of composition $M^{I}M^{II}M^{III}(PO_4)_2$

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CN *– Coordination number*

$\boldsymbol{R}_{\mathbf{sd}}$ *– Radius of spherical domain*

***D*(CP)** *– The shift of an atom from the centroid of its coordination polyhedron and coordinates of the centroid*

***D*(VDP)** *– The shift of an atom from the centroid of its Voronoi-Dirichlet polyhedron and coordinates of the centroid*

Atom, Top *– The values of division coefficients used for bonds between central atom and atoms, forming Voronoi-Dirichlet polyhedron, if they differ from 0.5*

***CN*(*m*:*l*:*n*)** *– Total coordination number of the atom, written as n:m:l, where n, m and l are the numbers of 'direct', 'half-direct' and 'indirect' neighbors*

NV *– The number of vertices of Voronoi-Dirichlet polyhedron*

V *– Volume of Voronoi-Dirichlet polyhedron/coordination polyhedron*

S *– Surface area of Voronoi-Dirichlet polyhedron*

$\boldsymbol{C}_{\boldsymbol{pac}}$ *– Packing coefficient*

$\mathbf{C}_{cov}$ *– Covering coefficient*

$\mathbf{G}_{3}$ *– Dimensionless second moment of inertia of Voronoi-Dirichlet polyhedron*

Face distribution *– Combinatorial properties of VDP faces written as the number of vertices (edges) of a face/the number of such faces*

Vertex distribution *– Combinatorial properties of VDP vertices written as the number of edges (faces), that meet in a vertex/the number of such vertices*

Dist *– The distance between central atom and* X_i *atom*

$\boldsymbol{S}_{Seg}$ *– The area of the face*

$\boldsymbol{V}_{Seg}$ *– The volume of a pyramid with the face in a bottom and the central atom in the top*

$\mathbf{S}_{Ang}$ *– The solid angle of the face*

NV *– The number of vertices (edges) of the face*

Phi *– The angle (*X_i*–central atom–VDP centroid)*

Data S1. Voronoi-Dirichlet polyhedra calculation parameters for K1A

########################
$KNi_{0.93}Fe_{1.07}(PO_4)_2$
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Central atom: K1A
R_{sd}: 1.717
D(CP): 0.461 (0.2717 0.1796 0.8073)
D(VDP): 0.142 (0.2095 0.1765 0.8088)
Atom: 2.751 < **r** < 4.426 <**r**>=3.420
Top: 1.814 < **R** < 2.332 <**R**>=2.052
CN = 14:0:5
NV = 34
V = 21.204/89.359
S = 41.614
C_{pac} = 0.514
C_{cov} = 2.504
G_3 = 0.081332669
Face distribution: {3/2 4/4 5/6 6/2 7/3 8/1 9/1}
Vertex distribution: {3/34}

Table S1.

N	***Atom***	***x***	***y***	***z***	***Dist,Å***	***S_{Seg},%***	***V_{Seg},%***	***S_{Ang},%***	***Phi,°***
1	O7	-0.118	0.256	0.555	2.751	12.01	10.81	12.24	90.13
2	O1	-0.226	0.082	0.912	2.839	10.30	9.56	11.17	155.23
3	O2	0.414	0.079	1.087	2.853	11.23	10.48	11.79	98.95
4	O6	0.450	0.336	0.970	2.871	12.58	11.81	12.65	78.07
5	O5	-0.235	0.311	0.803	2.890	8.30	7.84	9.20	129.01
6	O8	-0.083	0.086	0.531	2.923	8.86	8.47	9.46	87.67
7	O7	-0.118	0.244	1.055	3.177	5.29	5.50	5.53	146.81
8	O1	0.774	0.082	0.912	3.209	7.14	7.49	6.93	46.78
9	O3	0.493	0.013	0.670	3.289	6.93	7.45	6.61	51.09
10	O4	-0.056	-0.047	0.776	3.443	4.12	4.64	3.85	109.94
11	O5	0.765	0.311	0.803	3.567	6.28	7.33	4.99	34.04
12	O6	0.450	0.164	0.470	3.752	4.61	5.66	3.65	35.24
13	O7	0.882	0.244	1.055	3.809	0.54	0.68	0.48	56.25
14	O4	0.056	0.453	0.724	4.108	0.29	0.39	0.21	88.20
15	O2	0.586	-0.079	0.913	4.199	0.00	0.00	0.00	74.34
16	O2	0.414	0.421	0.587	4.426	0.35	0.51	0.23	55.07

Data S2. Voronoi-Dirichlet polyhedra calculation parameters for K1B

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$KNi_{0.93}Fe_{1.07}(PO_4)_2$
########################
Central atom: K1B
Rsd: 1.725
D(CP): 0.182 (0.2735 0.1884 0.7909)
D(VDP): 0.031 (0.2510 0.1807 0.7903)
Atom: 2.689 < **r** < 4.141 <**r**>=3.347
Top: 1.718 < **R** < 2.221 <**R**>=2.000
CN = 16:0:3
NV = 34
V = 21.484/92.947
S = 41.709
$\mathbf{C_{pac}}$ = 0.474
$\mathbf{C_{cov}}$ = 2.135
$\mathbf{G_3}$ = 0.080532253
Face distribution: {3/2 4/4 5/4 6/5 7/3 9/1}
Vertex distribution: {3/34}

Table S2.

N	***Atom***	***x***	***y***	***z***	***Dist,Å***	S_{Seg}***,%***	V_{Seg}***,%***	S_{Ang}***,%***	***Phi,°***
1	O7	-0.118	0.256	0.555	2.689	12.07	10.50	12.93	135.63
2	O6	0.450	0.336	0.970	2.844	11.97	11.01	12.32	37.30
3	O8	-0.083	0.086	0.531	2.869	8.67	8.05	9.57	161.83
4	O1	0.774	0.082	0.912	3.005	8.11	7.88	8.58	52.25
5	O2	0.414	0.079	1.087	3.043	9.94	9.78	9.84	60.94
6	O3	0.493	0.013	0.670	3.048	7.78	7.67	8.15	100.21
7	O5	-0.235	0.311	0.803	3.134	7.02	7.12	7.15	106.13
8	O5	0.765	0.311	0.803	3.231	8.01	8.38	7.38	42.44
9	O1	-0.226	0.082	0.912	3.247	8.18	8.59	7.83	115.86
10	O6	0.450	0.164	0.470	3.356	6.98	7.58	6.34	105.69
11	O7	-0.118	0.244	1.055	3.569	3.54	4.09	3.23	83.88
12	O4	-0.056	-0.047	0.776	3.622	3.43	4.02	3.05	125.78
13	O7	0.882	0.244	1.055	3.661	0.81	0.96	0.77	6.64
14	O4	0.056	0.453	0.724	4.067	0.59	0.77	0.45	84.74
15	O2	0.414	0.421	0.587	4.141	1.38	1.84	1.01	79.70