Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

Synthesis, Crystal Structure of $Fe[SeO_4]OH$ and Prediction of Polytypes in the extended $R[MO_4]Z$ Family

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Polytypes generation using superspace approach. Input files for *JANA2006* software

.m40

```
   10    0    0    1    0
 1.000000 0.000000 0.000000 0.000000 0.000000 0.000000      100000
 0.000000 0.000000 0.000000                                 000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      000000
Fe        1  1     0.500000 0.127000-0.250000 0.750000      000  0  0  0
 0.030000 0.000000 0.000000 0.000000 0.000000 0.000000      0101100000
O1        3  1     1.000000 0.125000-0.253000 0.433000      000  0  0  0
 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
O2        3  1     0.500000 0.288000-0.017000 0.250000      100  1  0  0
 0.030000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
τ  0.500000                                                 0
 0.000000 0.000000                                          00
 0.000000                                                   0
O2a       3  1     0.500000 0.288000 0.517000 0.250000      100  1  0  0
 0.030000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
1 - τ  0.500000                                             0
 0.500000 0.000000                                          00
 0.000000                                                   0
O3        3  1     0.500000-0.042000-0.018000 0.250000      100  1  0  0
 0.030000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
τ  0.500000                                                 0
 0.000000 0.000000                                          00
 0.000000                                                   0
O3a       3  1     0.500000-0.042000 0.518000 0.250000      100  1  0  0
 0.030000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
1 - τ  0.500000                                             0
 0.500000 0.000000                                          00
 0.000000                                                   0
Se        2  1     0.500000 0.124000 0.867000 0.250000      100  1  0  0
 0.030000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
τ  0.500000                                                 0
 0.000000 0.000000                                          00
 0.000000                                                   0
Sea       2  1     0.500000 0.124000 0.633000 0.250000      100  1  0  0
 0.030000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
1 - τ  0.500000                                             0
 0.500000 0.000000                                          00
 0.000000                                                   0
O4        3  1     0.500000-0.126000-0.341000 0.750000      100  1  0  0
 0.030000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
τ  0.500000                                                 0
 0.000000 0.000000                                          00
 0.000000                                                   0
O4a       3  1     0.500000-0.126000 0.841000 0.750000      100  1  0  0
 0.030000 0.000000 0.000000 0.000000 0.000000 0.000000      0000000000
1 - τ  0.500000                                             0
 0.500000 0.000000                                          00
 0.000000                                                   0
```

.m50

```
Version Jana2006
title
cell 7.589 7.259 6.562 90 90 90
esdcell 0.03 0.04 0.04 0 0 0
ndim 4 ncomp 1
qi 0 0 0.5          <-- q = γc* = ½ c*
qr 0 0 0
spgroup Pnam(00g)000 62 3
lattice P
symmetry x1 x2 x3 x4
symmetry -x1 -x2 x3+1/2 x4
symmetry -x1+1/2 x2+1/2 -x3 -x4
symmetry x1+1/2 -x2+1/2 -x3+1/2 -x4
symmetry -x1 -x2 -x3 -x4
symmetry x1 x2 -x3+1/2 -x4
symmetry x1+1/2 -x2+1/2 x3 x4
symmetry -x1+1/2 x2+1/2 x3+1/2 x4
unitsnumb 4
atlist Fe S O5 H0
formtab -62
atom Fe atradius 1.26 color 181113000
atom S atradius 1.04 color 255250000
atom O atradius 0.74 color 254003000
atom H atradius 0.46 color 255204204
commen 1 0 -2
commen 0 1 0
commen 1 0 0
tzero 0             <-- t0
lambda 0.71075 radtype 1 lpfactor 1
monangle 6.0823 perfmono 0.5
nalpha 2 kalpha1 0.709317 kalpha2 0.713607 kalphar 0.499
roundmethod 1
end
```

Figure S1. Input files used with the *JANA2006* software[32] to generate Fe[*M*O4]OH (*M* = S, Se) polytypes from the average structure. Variable parameters, γ in the modulation vector **q** = γ***c****, t_0 -cut in the x_4 axis, and occupancy parameter τ, are shown by red arrows. Note that parameter τ equal to Δx_4 is the *JANA2006* software.

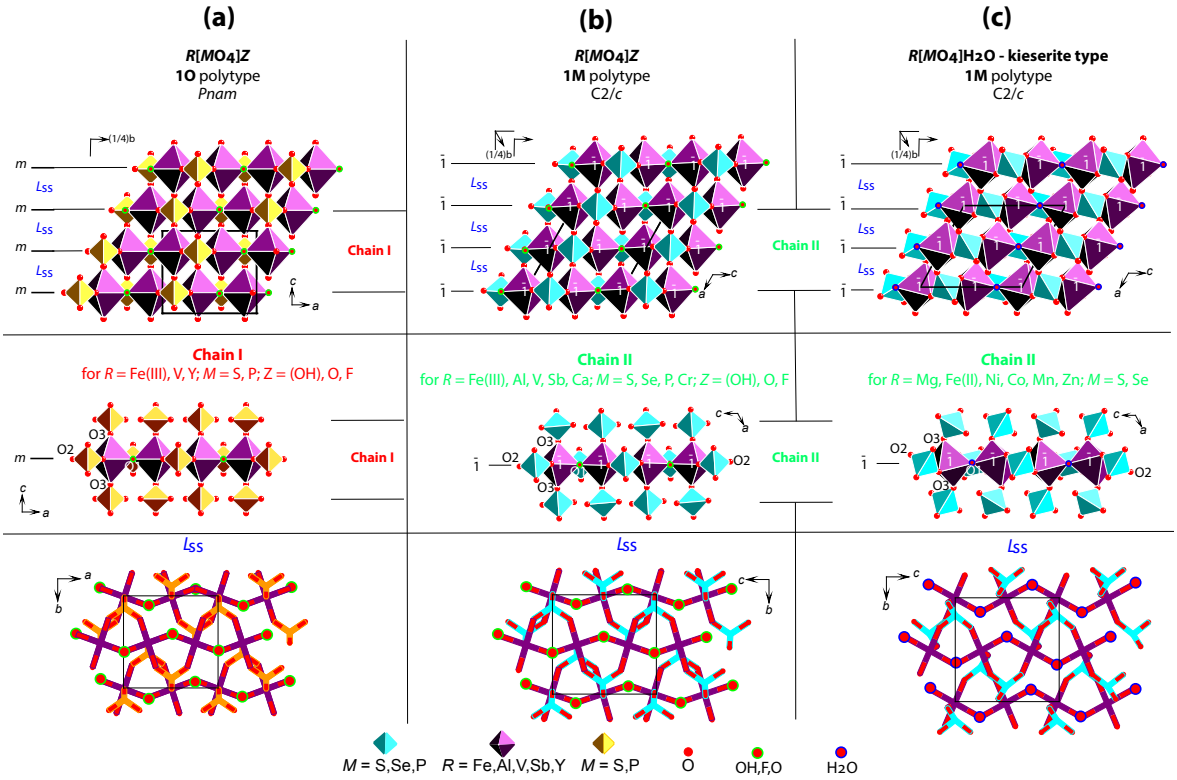

Figure S2. Sketch of structures formed by *L*-layers, similar to Fe[MO_4]OH (*M* = S, Se). Panel **(a)**: β-V[SO_4]O,[16] Y[SO_4]F[25] and V[HPO_4]O[30] structure types with the space group *Pnam* can be attributed to **1O** (*m*,…) polytype. Panel **(b)**: structure types Fe^{III}[SO_4]F,[21,22] $CaCrF_5$ (= Ca[CrF_4]F),[23,24] and Al[SO_4]OH[20] with space group *C*2/*c* can be identified with **1M** ($\bar{1}$,…) polytype. Panel **(c)**: the kieserite structure type with the general formula R^{II}[MO_4]H_2O (*R* = Mg, Fe, Ni, Co, Mn, Zn; M = S, Se, As) can also be assigned to **1M** polytype, since H_2O molecules are at least and deform the structure, but do not change the space group and atomic sites of this polytype. The symmetry elements are sown in terms internationally accepted by IUCr.

Table S1. Experimental atomic parameters for $R[MO_4]Z$ in comparison to the predicted for the **1M** polytype (Space group $C2/c$; $a \approx c \approx 7.5 \pm 0.3$ Å, $b \approx 7.2 \pm 0.2$ Å, $\beta \approx 120.0°$). Wyckoff symbol, coordinates and site symmetry indicated in square brackets for the *R*, *M*, *Z* and O sites.

Compound	Variable positional parameters of atoms				3D structure type	Reference
	R [4a (0 0 0); $\bar{1}$]	*M* [4e (0 y ¼); 2]	*Z* [4e (0 y ¼); 2]	O [8f (x, y, z); 1]		
$R[MO_4]Z$ **Predicted**	*R*	*M* **y = 0.616**	*Z* **y = 0.095**	O1: **0, 0.733, 0.0840** O2: **0.683, 0, 0.842**	**1M** polytype (kieserite-like)	Present work
$Fe(SeO_4)(OH)$	Fe^{III}	Se^{VI} y = 0.613	O_{OH} y = 0.091	O1: 0, 0.736, 0.0645 O2: 0.693, 0.025, 0.8382	**1M** polytype (kieserite-like)	Present work
$Fe(SO_4)(OH)$	Fe^{III}	S^{VI} y = 0.615	O_{OH} y = 0.097	O1: -0.010, 0.736, 0.0817 O2: 0.684, 0.008, 0.8460	$Fe(SO_4)(OH)$ (kieserite-like)	[14]
$Fe(SO_4)H_2O$	Fe^{II}	S^{VI} y = 0.653	O_{H2O} y = 0.144	O1: 0.096, 0.768, 0.156 O2: 0.670, -0.044 0.8985	$Mg(SO_4)H_2O$ (kieserite)	[8]
$Ni(SeO_4)H_2O$	Ni^{II}	Se^{VI} y = 0.662	O_{H2O}: y = 0.127	O1: 0.112, 0.781, 0.150 O2: 0.685, -0.047, 0.922	$Mg(SO_4)H_2O$ (kieserite)	[12, 13]
$Fe(SeO_4)H_2O$ (simulated)	Fe^{II}	Se^{VI} y = 0.665	O_{H2O} y = 0.135	O1: 0.118, 0.777, 0.153 O2: 0.682, -0.047, 0.912	$Mg(SO_4)H_2O$ (kieserite)	[11]
$Al(SO_4)(OH)$	Al^{III}	S^{VI} y = 0.623	O_{OH} y = 0.086	O1: 0.004, 0.743, 0.0800 O2: 0.688, 0.003, 0.8465	$Al(SO_4)(OH)$ (kieserite-like)	[20]
$Fe(SO_4)F$	Fe^{III}	S^{VI} y = 0.603	F y = 0.083	O1: -0.004, 0.734, 0.0840 O2: 0.684, 0.014, 0.8460	$Fe(SO_4)F$ (kieserite-like)	[21,22]
$V(PO_4)F$	V^{IV}	P^{V} y = 0.625	F y = 0.082	O1: -0.006, 0.746, 0.0750 O2: 0.701, -0.002, 0.8460	$Fe(SO_4)F$ (kieserite-like)	[22]
$Sb(PO_4)O$	Sb^{V}	P^{V} y = 0.665	O y = 0.089	O1: 0.088, 0.775, 0.1250 O2: 0.685, -0.056, 0.9010	$CaCrF_5$ (= $Ca(CrF_4)F$ (kieserite-like)	[23,24]

Table S2. Experimental atomic parameters for $R[MO_4]Z$ for the **1O** polytype (Space group *Pnma*; $a \approx 7.5 \pm 0.3$ Å, $b = 0.5a\sqrt{3} \approx 6.5 \pm 0.3$ Å, $c \approx 7.2 \pm 0.2$ Å). Wyckoff symbol, coordinates and site symmetry indicated in square brackets for the *R*, *M*, *Z* and O sites.

Compound	Variable positional parameters of atoms				3D Structure type	Refe-rence
	R [4c (x, ¼, z); *m*.]	*M* [4c (x, ¼, z); *m*.]	*Z* [4c (x, ¼, z); *m*.]	O O1: [8d (x, y, z);1] O3: [4c (x, ¼, z); *m*.] O4: [4c (x, ¼, z); *m*.]		
$V(SO_4)O$ Pauflerite	V^{IV} x=0.335, z=0.267	S^{VI} x=0.123, z=0.868	O x=0.626, z=0.168	O1: 0.375, 0.563, 0.243 O3: x=0.955, z=-0.019 O4: x=0.284, z= -0.010	β-$VO(SO_4)$ (pauflerite)	[16]
$Fe(SO_4)(OH)$	Fe^{III} x=0.375, z=0.25	S^{VI} x=0.125, z=0.866	O_{OH} x=0.625, z=0.155	O1: 0.375, 0.567, 0.25 O3: x=0.959, z=-0.017 O4: x=0.291, z= -0.017	β-$VO(SO_4)$ (pauflerite)	[15]
$Y(SO_4)F$	Y^{III} x=0.445 z=0.152	S^{VI} x=0.093, z=0.814	F x=0.706, z=0.200	O1: 0.439, 0.582, 0.173 O3: x=0.980, z=-0.013 O4: x=0.259, z= -0.118	$Y(SO_4)F$ (pauflerite-like)	[25]
$V(HPO_4)O$	V^{IV} x=0.333, z=0.265	P^{V} x=0.123, z=0.875	O x=0.633, z=0.160	O1: 0.373, 0.560, 0.235 O3: x=0.955, z=-0.001 O4: x=0.291, z= -0.007	β-$VO(SO_4)$ (pauflerite)	[30]