$A(VO_2F)(SeO_3)$ (A = Sr, Ba) and $Ba(MOF_2)(TeO_4)$ (M = Mo, W): First Examples of Akali-earth Selenites/Tellurites with Fluorinated d^0-TM Octahedron

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Supporting Information

Table S1. Selected Bond Distances (Angstroms) for the four title compounds.

$Sr(VO_2F)(SeO_3)$			
Sr(1)-F(1)	2.454(2)	V(1)-O(4)	1.667(3)
Sr(1)-F(1)#1	2.480(2)	V(1)-O(2)#3	1.968(3)
Sr(1)-O(1)#2	2.582(3)	V(1)-O(3)#7	1.969(3)
Sr(1)-O(1)#3	2.587(3)	V(1)-F(1)	2.034(2)
Sr(1)-O(3)	2.594(3)	V(1)-O(4)#4	2.304(3)
Sr(1)-O(4)#4	2.611(3)	Se(1)-O(1)	1.651(3)
Sr(1)-O(2)#5	2.673(3)	Se(1)-O(3)	1.736(3)
Sr(1)-O(5)#6	2.686(3)	Se(1)-O(2)	1.747(3)
V(1)-O(5)	1.618(3)		
$Ba(VO_2F)(SeO_3)$			
Ba(1)-F(1)	2.614(2)	V(1)-O(2)	1.664(3)
Ba(1)-F(1)#1	2.673(2)	V(1)-O(3)	1.976(3)
Ba(1)-O(1)#2	2.738(3)	V(1)-O(5)#5	1.972(3)
Ba(1)-O(1)	2.754(3)	V(1)-F(1)	2.025(2)
Ba(1)-O(5)#3	2.772(3)	V(1)-O(2)#5	2.304(3)
Ba(1)-O(3)#4	2.790(3)	Se(1)-O(1)	1.648(3)
Ba(1)-O(2)#5	2.795(3)	Se(1)-O(5)	1.734(3)
Ba(1)-O(4)#6	2.840(3)	Se(1)-O(3)	1.740(3)
V(1)-O(4)	1.623(3)		
$Ba(MoOF_2)(TeO_4)$			
Mo(1)-O(5)	1.719(5)	Mo(1)-F(2)	2.163(3)
Mo(1)-O(4)	1.727(4)	Te(1)-O(3)	1.889(4)
Mo(1)-O(2)	1.875(4)	Te(1)-O(1)	1.921(4)
Mo(1)-O(3)	2.013(4)	Te(1)-O(1)#1	2.061(4)
Mo(1)-F(1)	2.098(4)	Te(1)-O(2)#2	2.062(4)
$Ba(WOF_2)(TeO_4)$			
W(1)-O(5)	1.752(6)	W(1)-F(2)	2.113(5)
W(1)-O(4)	1.751(6)	Te(1)-O(3)	1.907(6)
W(1)-O(1)	1.876(6)	Te(1)-O(2)	1.919(6)
W(1)-O(3)#1	1.985(6)	Te(1)-O(1)	2.053(6)
W(1)-F(1)	2.076(5)	Te(1)-O(2)#2	2.061(6)

Symmetry transformations used to generate equivalent atoms:

For compound **1**: #1 -x+1/2, y+1/2, z; #2 -x, -y, -z+1; #3 x+1/2, -y+1/2, -z+1; #4 -x+1, -y, -z+1; #5 x,-y+1/2,z+1/2; #6 -x+1,y+1/2,-z+3/2; #7 -x+1/2, y-1/2, z. For compound **2**: #1 -x+3/2, y+1/2, z; #2 -x+3/2, y-1/2, z; #3 x+1/2, -y+1/2, -z+1; #4 x+1/2, y, -z+1/2; #5 -x+1, -y, -z+1; #6 -x+1, y+1/2, -z+1/2. For compound **3**: #1 -x-1, -y+1, -z-1; #2 x, -y+1/2, z-1/2. For compound **4**: #1 x, -y-1/2, z-1/2; #2 -x-1, -y, -z-1.

Table S2. Important Angles (deg) for the four title compounds.

$Sr(VO_2F)(SeO_3)$ (**1**)			
O(1)-Se(1)-O(3)	103.24(13)	O(5)-V(1)-F(1)	95.41(12)
O(1)-Se(1)-O(2)	100.75(13)	O(4)-V(1)-F(1)	158.72(11)
O(3)-Se(1)-O(2)	102.69(13)	O(2)#1-V(1)-F(1)	82.26(10)
O(5)-V(1)-O(4)	105.73(13)	O(3)#3-V(1)-F(1)	80.35(10)
O(5)-V(1)-O(2)#1	99.61(14)	O(5)-V(1)-O(4)#2	171.46(12)
O(4)-V(1)-O(2)#1	96.28(13)	O(4)-V(1)-O(4)#2	82.76(11)
O(5)-V(1)-O(3)#3	100.56(13)	O(2)#1-V(1)-O(4)#2	79.98(11)
O(4)-V(1)-O(3)#3	93.21(12)	O(3)#3-V(1)-O(4)#2	77.74(11)
O(2)#1-V(1)-O(3)#3	154.43(11)	F(1)-V(1)-O(4)#2	76.07(9)
$Ba(VO_2F)(SeO_3)$ (**2**)			
O(1)-Se(1)-O(5)	103.05(15)	O(4)-V(1)-F(1)	94.55(14)
O(1)-Se(1)-O(3)	101.04(14)	O(2)-V(1)-F(1)	160.56(12)
O(5)-Se(1)-O(3)	102.90(14)	O(3)-V(1)-F(1)	82.15(11)
O(4)-V(1)-O(2)	104.86(15)	O(5)#1-V(1)-F(1)	80.30(11)
O(4)-V(1)-O(3)	98.27(14)	O(4)-V(1)-O(2)#1	172.25(14)
O(2)-V(1)-O(3)	95.99(13)	O(2)-V(1)-O(2)#1	82.59(12)
O(4)-V(1)-O(5)#1	102.98(13)	O(3)-V(1)-O(2)#1	78.52(11)
O(2)-V(1)-O(5)#1	93.96(13)	O(5)#1-V(1)-O(2)#1	78.33(10)
O(3)-V(1)-O(5)#1	153.34(12)	F(1)-V(1)-O(2)#1	78.07(10)
$Ba(MoOF_2)(TeO_4)$ (**3**)			
O(3)-Te(1)-O(1)	97.0(2)	O(2)-Mo(1)-O(3)	156.86(18)
O(3)-Te(1)-O(1)#1	91.82(18)	O(5)-Mo(1)-F(1)	161.88(19)
O(1)-Te(1)-O(1)#1	76.5(2)	O(4)-Mo(1)-F(1)	93.7(2)
O(3)-Te(1)-O(2)#2	86.42(18)	O(2)-Mo(1)-F(1)	82.34(17)
O(1)-Te(1)-O(2)#2	79.62(18)	O(3)-Mo(1)-F(1)	79.67(18)
O(1)#1-Te(1)-O(2)#2	155.67(18)	O(5)-Mo(1)-F(2)	89.08(18)
O(5)-Mo(1)-O(4)	104.4(2)	O(4)-Mo(1)-F(2)	166.1(2)
O(5)-Mo(1)-O(2)	96.4(2)	O(2)-Mo(1)-F(2)	83.43(16)
O(4)-Mo(1)-O(2)	98.1(2)	O(3)-Mo(1)-F(2)	77.45(15)
O(5)-Mo(1)-O(3)	96.2(2)	F(1)-Mo(1)-F(2)	72.81(15)
O(4)-Mo(1)-O(3)	97.48(19)		
$Ba(WOF_2)(TeO_4)$ (**4**)			
O(5)-W(1)-O(4)	103.5(3)	O(3)#1-W(1)-F(2)	78.8(2)
O(5)-W(1)-O(1)	97.2(3)	F(1)-W(1)-F(2)	73.3(2)
O(4)-W(1)-O(1)	95.1(3)	O(3)-Te(1)-O(2)	93.8(3)
O(5)-W(1)-O(3)#1	97.4(3)	O(3)-Te(1)-O(1)	86.4(3)
O(4)-W(1)-O(3)#1	96.8(3)	O(2)-Te(1)-O(1)	79.8(2)
O(1)-W(1)-O(3)#1	158.5(2)	O(3)-Te(1)-O(2)#2	91.2(3)
O(5)-W(1)-F(1)	94.1(3)	O(2)-Te(1)-O(2)#2	76.4(3)
O(4)-W(1)-F(1)	162.3(2)	O(1)-Te(1)-O(2)#2	155.9(2)
O(1)-W(1)-F(1)	82.8(2)	O(3)-Te(1)-O(5)#3	169.8(2)

O(3)#1-W(1)-F(1)	80.4(2)	O(2)-Te(1)-O(5)#3	75.9(2)
O(5)-W(1)-F(2)	167.3(3)	O(1)-Te(1)-O(5)#3	92.2(2)
O(4)-W(1)-F(2)	89.0(2)	O(2)#2-Te(1)-O(5)#3	85.9(2)
O(1)-W(1)-F(2)	83.6(2)		

Symmetry transformations used to generate equivalent atoms:

For compound **1**: #1 x+1/2, -y+1/2, -z+1; #2 -x+1, -y, -z+1; #3 -x+1/2, y-1/2, z. For compound **2**: #1 -x+1, -y, -z+1. For compound **3**: #1 -x-1, -y+1, -z-1; #2 x, -y+1/2, z-1/2. For compound **4**: #1 x, -y-1/2, z-1/2; #2 -x-1,-y,-z-1; #3 -x-1, y+1/2, -z-3/2.

Table S3 The state energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of the title compounds.

Compounds	k-points	L-CB	H-VB
$Sr(VO_2F)(SeO_3)$ (**1**)	G (0.000, 0.000, 0.000)	3.073	0
	Z (0.000, 0.000, 0.500)	3.08514	-0.09702
	T (-0.500, 0.000, 0.500)	3.08313	-0.16035
	Y (-0.500, 0.000, 0.000)	3.07029	-0.10658
	S (-0.500, 0.500, 0.000)	3.09084	-0.13886
	X (0.000, 0.500, 0.000)	3.08828	-0.12085
	U (0.000, 0.500, 0.500)	3.09931	-0.16228
	R (-0.500, 0.500, 0.500)	3.09778	-0.14311
$Ba(VO_2F)(SeO_3)$ (**2**)	G (0.000, 0.000, 0.000)	3.10498	0
	Z (0.000, 0.000, 0.500)	3.10644	-0.10159
	T (-0.500, 0.000, 0.500)	3.11237	-0.14268
	Y (-0.500, 0.000, 0.000)	3.10684	-0.08654
	S (-0.500, 0.500, 0.000)	3.13214	-0.1043
	X (0.000, 0.500, 0.000)	3.12692	-0.06054
	U (0.000, 0.500, 0.500)	3.13298	-0.11497
	R (-0.500, 0.500, 0.500)	3.13455	-0.11531
$Ba(MoOF_2)(TeO_4)$ (**3**)	Z (0.000, 0.000, 0.500)	2.75698	-0.24301
	G (0.000, 0.000, 0.000)	2.64406	-0.17483
	Y (0.000, 0.500, 0.000)	2.70762	-0.22726
	A (-0.500, 0.500, 0.000)	2.65014	-0.17646
	B (-0.500, 0.000, 0.000)	2.5737	0
	D (-0.500, 0.000, 0.500)	2.73358	-0.21463
	E (-0.500, 0.500, 0.500)	2.68771	-0.21222
	C (0.000, 0.500, 0.500)	2.76725	-0.26559
$Ba(WOF_2)(TeO_4)$ (**4**)	Z (0.000, 0.000, 0.500)	3.37492	-0.2273
	G (0.000, 0.000, 0.000)	3.29843	-0.16247
	Y (0.000, 0.500, 0.000)	3.38066	-0.20375
	A (-0.500, 0.500, 0.000)	3.32165	-0.14864
	B (-0.500, 0.000, 0.000)	3.23902	0
	D (-0.500, 0.000, 0.500)	3.37873	-0.20979
	E (-0.500, 0.500, 0.500)	3.33768	-0.21114
	C (0.000, 0.500, 0.500)	3.43487	-0.24488

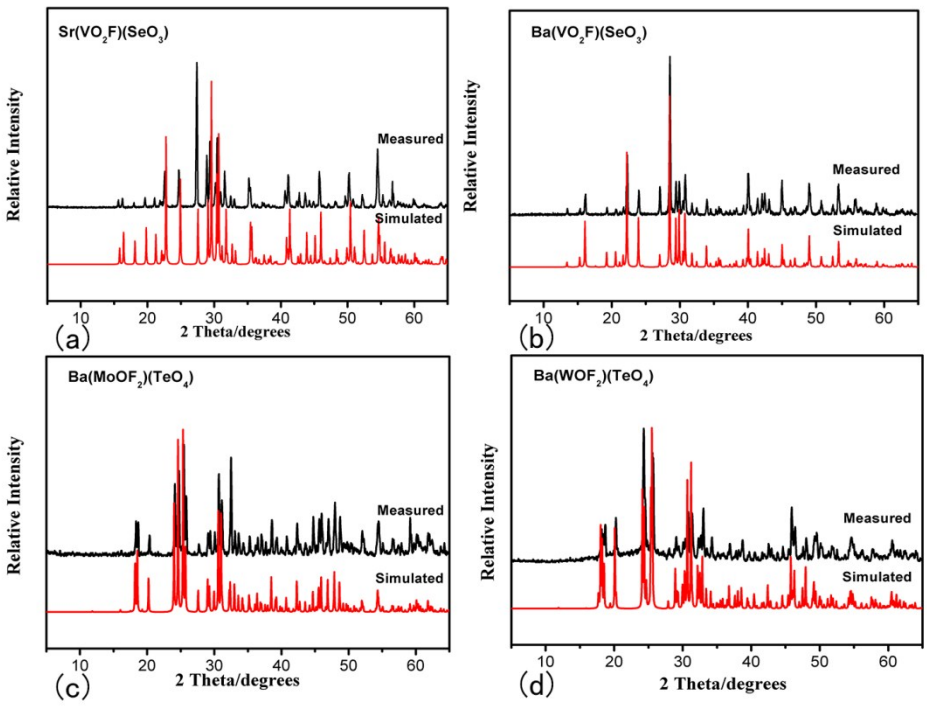

Fig. S1 Simulated and experimental XRD powder patterns of **1** (a), **2** (b), **3** (c) and **4** (d).

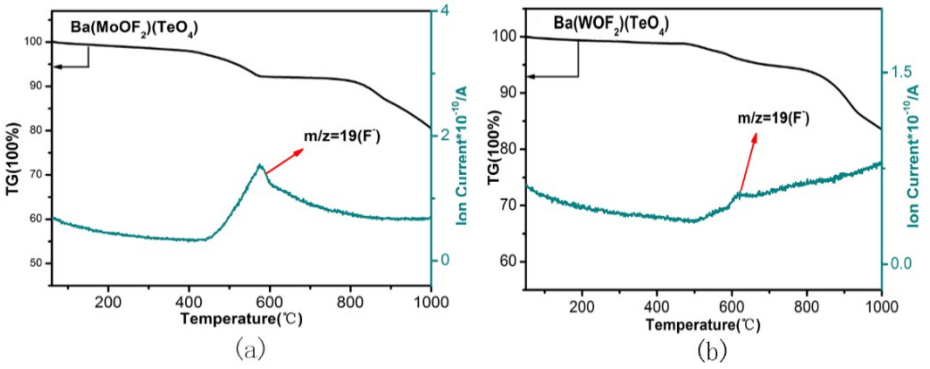

Fig. S2. TG-MS curves of compounds **3** (a) and **4** (b).

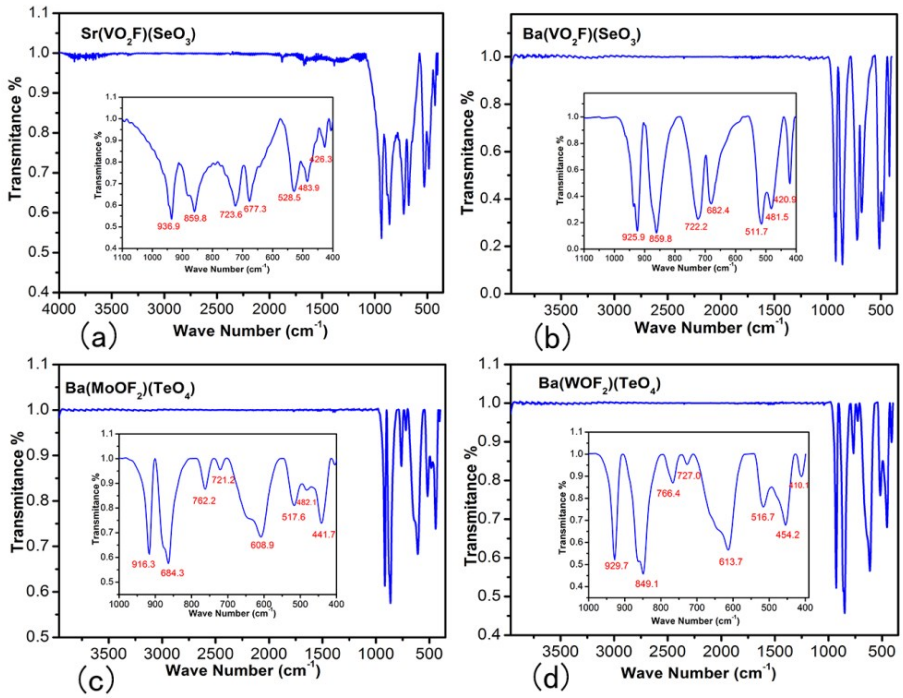

Fig. S3. IR spectra of compounds **1** (a), **2** (b), **3** (c) and **4** (d).

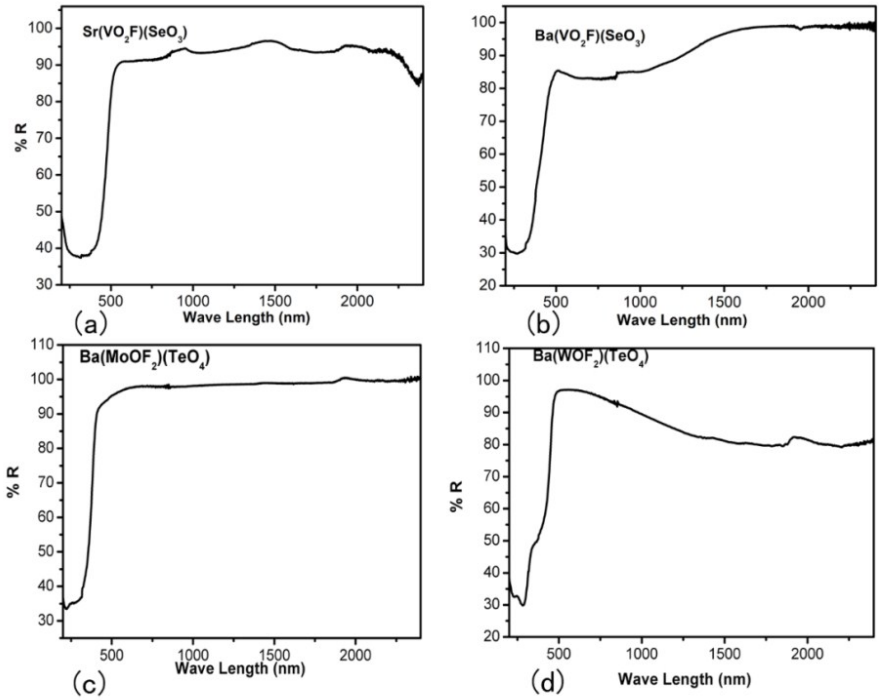

Fig. S4. UV-Vis-NIR spectra of compounds **1** (a), **2** (b), **3** (c) and **4** (d).