Supporting Information

First chiral fluorinated vanadate selenite $Pb_2(V_2O_4F)(VO_2)(SeO_3)_3$ with five asymmetric motifs and large optical properties

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Table S1 Atomic coordinates (× 10^4), equivalent isotropic displacement parameters ($Å^2$ × 10^3) and bond valence sum (BVS) for PVOFS.

Atoms	Wyck.	x	y	z	U_{eq}	BVS
Pb(1)	4a	4890(1)	2811(1)	5755(1)	14(1)	1.95
Pb(2)	4a	5030(1)	4702(1)	7789(1)	15(1)	1.82
Se(1)	4a	5140(3)	-92(1)	4909(1)	8(1)	3.96
Se(2)	4a	1380(2)	2260(1)	7137(1)	6(1)	3.95
Se(3)	4a	-497(2)	3185(1)	8851(1)	6(1)	4.00
V(1)	4a	5179(4)	229(1)	3400(1)	8(1)	5.02
V(2)	4a	4655(4)	1722(1)	8538(1)	7(1)	4.93
V(3)	4a	9466(3)	861(1)	5888(1)	7(1)	4.88
F(1)	4a	10154(18)	5094(5)	7486(3)	18(2)	0.86
O(1)	4a	3729(14)	-975(6)	3613(4)	6(2)	1.90
O(2)	4a	6309(15)	632(7)	4256(4)	12(2)	2.07
O(3)	4a	2636(14)	3524(6)	6915(4)	5(2)	1.94
O(4)	4a	7788(15)	3907(7)	6625(4)	13(2)	1.86
O(5)	4a	3735(14)	5540(6)	6659(4)	8(2)	1.96
O(6)	4a	3859(14)	1729(6)	7534(4)	8(2)	2.08
O(7)	4a	7349(13)	2757(6)	8281(4)	5(2)	1.89
O(8)	4a	5114(19)	1857(6)	9289(3)	19(2)	1.68
O(9)	4a	2240(14)	3180(6)	8424(4)	8(2)	1.92
O(10)	4a	7147(14)	1008(6)	6395(4)	9(2)	1.86
O(11)	4a	8980(15)	1938(6)	5387(4)	12(2)	2.04
O(12)	4a	1961(14)	1613(6)	6423(4)	9(2)	2.23
O(13)	4a	7871(15)	-227(7)	5344(4)	14(2)	2.01
O(14)	4a	8624(15)	4529(6)	8818(4)	13(2)	1.98
O(15)	4a	3471(15)	931(7)	5245(4)	14(2)	1.70

Table S2 Anisotropic displacement parameters ($Å^2 \times 10^3$) for PVOFS.

Atoms	U11	U22	U33	U23	U13	U12
Pb(1)	13(1)	16(1)	12(1)	2(1)	0(1)	2(1)
Pb(2)	16(1)	14(1)	14(1)	1(1)	1(1)	0(1)
Se(1)	13(1)	8(1)	5(1)	0(1)	-1(1)	-2(1)
Se(2)	7(1)	5(1)	5(1)	0(1)	0(1)	0(1)
Se(3)	5(1)	5(1)	7(1)	0(1)	1(1)	-1(1)
V(1)	7(1)	7(1)	11(1)	2(1)	0(1)	-2(1)
V(2)	7(1)	5(1)	7(1)	1(1)	-1(1)	-2(1)
V(3)	12(1)	4(1)	4(1)	-1(1)	-2(1)	1(1)
F(1)	27(4)	19(3)	9(3)	-7(3)	-1(4)	7(4)
O(1)	6(2)	6(2)	6(2)	0(1)	0(1)	-1(1)
O(2)	16(4)	17(4)	4(4)	4(4)	-4(4)	-13(4)
O(3)	5(2)	5(2)	6(2)	1(1)	1(1)	0(1)
O(4)	7(4)	11(4)	21(5)	6(4)	-2(4)	-5(3)
O(5)	4(4)	8(4)	13(4)	0(3)	-1(3)	-1(3)
O(6)	7(2)	8(2)	7(2)	0(1)	0(1)	1(1)
O(7)	4(2)	5(2)	4(2)	0(1)	0(1)	0(1)
O(8)	26(4)	20(4)	11(4)	-3(3)	-3(5)	-7(5)
O(9)	8(4)	4(4)	11(5)	-1(4)	2(3)	-1(3)
O(10)	9(2)	9(2)	9(2)	-1(1)	0(1)	0(1)
O(11)	15(4)	11(4)	10(4)	-1(3)	-1(3)	6(4)
O(12)	8(2)	9(2)	8(2)	-1(1)	0(1)	0(1)
O(13)	14(2)	13(2)	14(2)	0(1)	-1(1)	0(1)
O(14)	13(2)	13(2)	13(2)	0(1)	-1(1)	-1(1)
O(15)	12(4)	12(4)	17(5)	-5(4)	3(4)	2(4)

Table S3 Selected bond lengths (Å) for PVOFS.[a]

Pb(1)-O(11)#1	2.475(8)	Se(3)-O(9)	1.697(8)
Pb(1)-O(11)	2.517(8)	Se(3)-O(7)#3	1.729(8)
Pb(1)-O(12)	2.540(8)	V(1)-O(4)#1	1.635(8)
Pb(1)-O(15)	2.622(8)	V(1)-O(1)	1.702(8)
Pb(1)-O(2)#1	2.662(8)	V(1)-F(1)#1	1.909(6)
Pb(1)-O(4)	2.728(9)	V(1)-O(2)	1.963(8)
Pb(2)-O(10)#2	2.601(8)	V(1)-O(5)#4	2.090(8)
Pb(2)-O(6)#2	2.609(7)	V(1)-O(3)#4	2.093(8)
Pb(2)-O(3)	2.648(8)	V(2)-O(8)	1.611(7)
Pb(2)-O(5)	2.677(8)	V(2)-O(5)#5	1.712(8)
Pb(2)-F(1)#3	2.682(9)	V(2)-O(7)	1.965(8)
Pb(2)-O(9)	2.707(8)	V(2)-O(1)#6	2.001(8)
Se(1)-O(15)	1.673(8)	V(2)-O(6)	2.158(8)
Se(1)-O(13)	1.711(8)	V(2)-O(9)	2.184(8)
Se(1)-O(2)	1.744(8)	V(3)-O(10)	1.631(8)
Se(2)-O(6)	1.676(7)	V(3)-O(11)	1.696(8)
Se(2)-O(12)	1.724(8)	V(3)-O(13)	1.935(9)
Se(2)-O(3)	1.729(8)	V(3)-O(12)#7	1.955(8)
Se(3)-O(14)#3	1.690(8)	V(3)-O(14)#8	1.996(8)

[a] Symmetry codes: #1 x-1/2, -y+1/2, -z+1; #2 -x+1, y+1/2, -z+3/2; #3 x-1, y, z; #4 x+1/2, -y+1/2, -z+1; #5 -x+1, y-1/2, -z+3/2; #6 -x+1/2, -y, z+1/2; #7 x+1, y, z; #8 -x+2, y-1/2, -z+3/2.

Table S4 The reaction parameters of contrast experiments.

Temperature (℃)		180				210				230			
element (mmol)	Pb	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	V	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
	Se	2.0	2.5	4.5	5.0	2.0	2.5	4.5	5.0	2.0	2.5	4.5	5.0
Products		C/D/E	C/D	B/C	B/C	B/E	A/B/E	A/B	A/C	B/E	A/B/E	A/B	A/C/E

A: PVOFS; B: $PbVO_2(SeO_3)F$;[S1] C: $PbSeO_3$ (ICSD #98376); D: PbF_2 (ICSD #161393); E: amorphous.

Reference

[S1] X. L. Cao, F. Kong, C. L. Hu, X. Xu and J. G. Mao, *Inorg. Chem.*, 2014, **53**, 8816-8824.

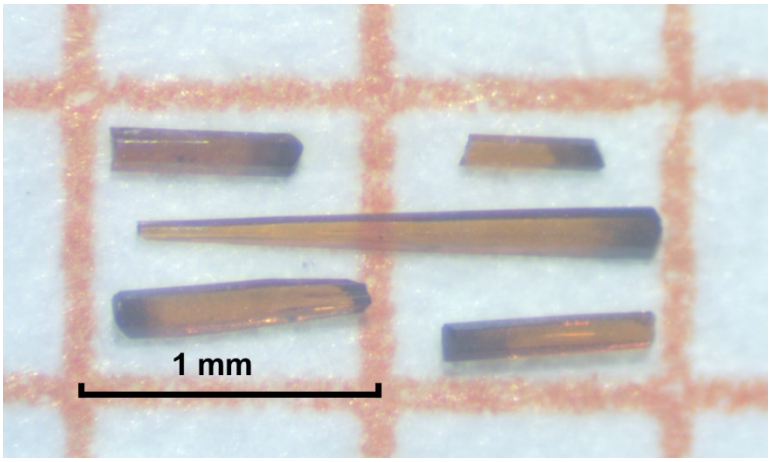

Fig. S1 Photograph of crystals of PVOFS.

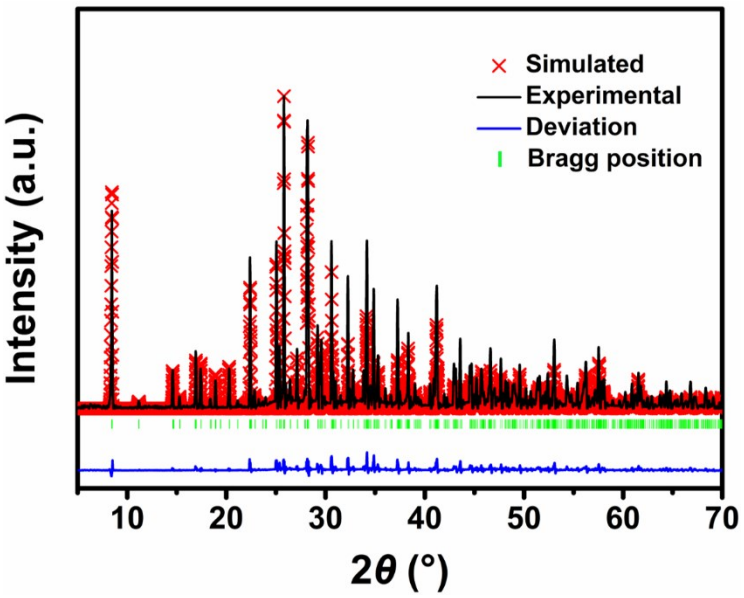

Fig. S2 Experimental and simulated powder X-ray diffraction patterns of PVOFS.

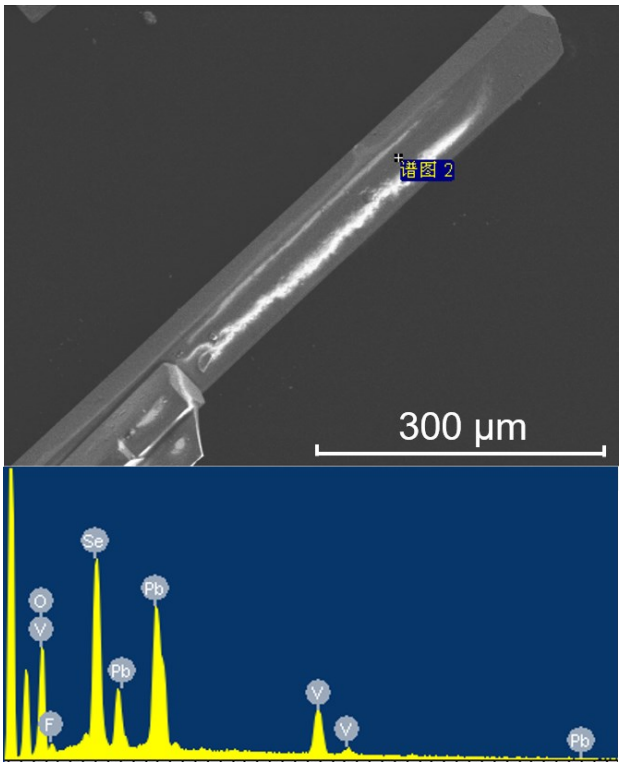

Fig. S3 The energy dispersive spectroscopy analysis of PVOFS.

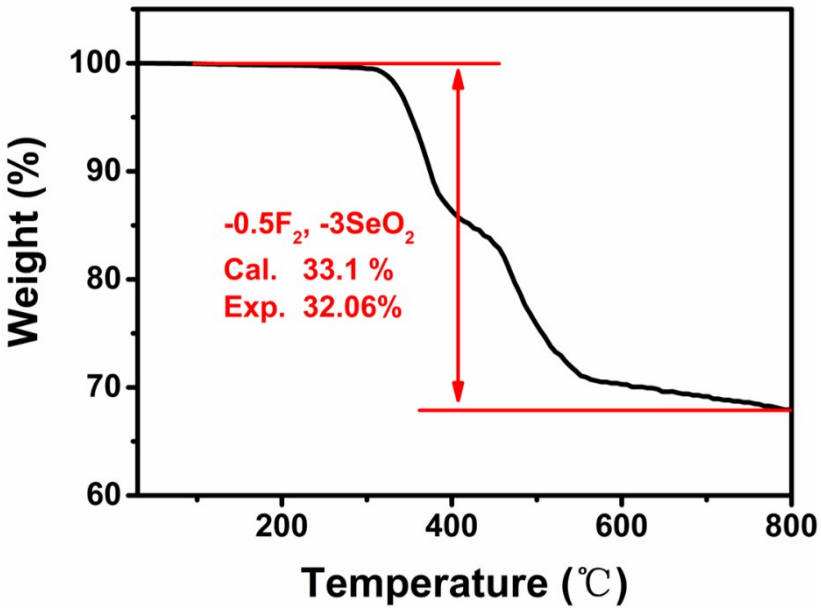

Fig. S4 Thermogravimetric analysis of PVOFS under a nitrogen atmosphere.

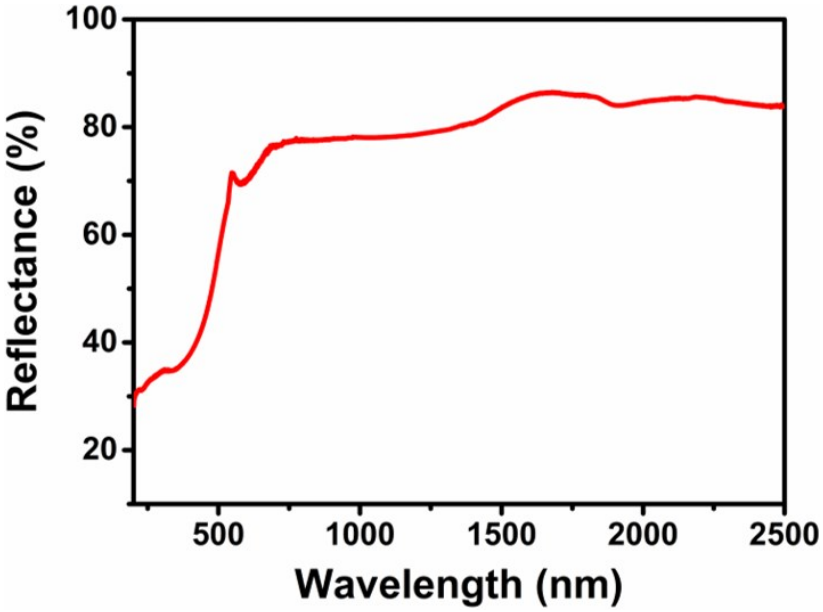

Fig. S5 UV-Vis-NIR diffuse reflectance spectrum of PVOFS.

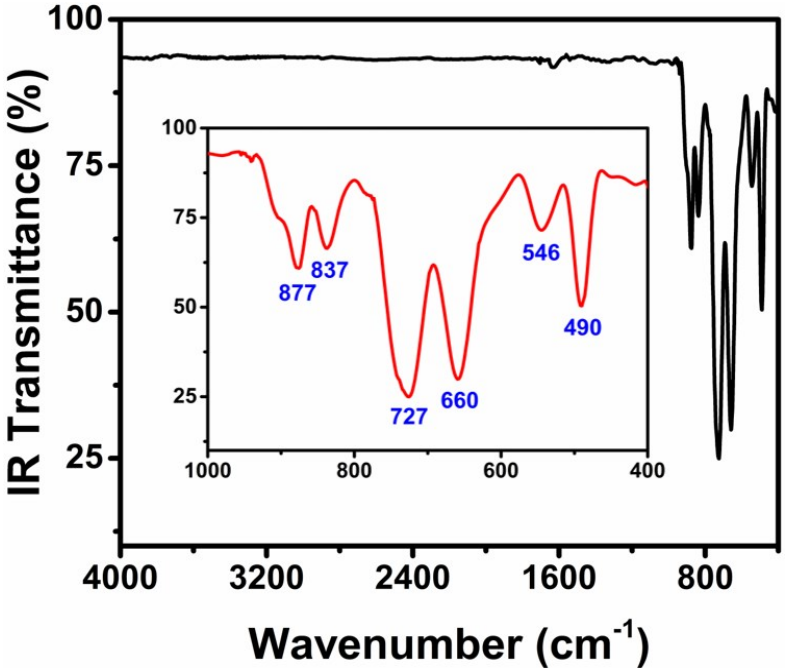

Fig. S6 IR transmittance spectrum of PVOFS.