Electronic Supplementary Information

Two New Tin(IV)-containing Phosphate Fluorides with Two Types of Sn(IV)-P-O-F frameworks and Short Cutoff Edges

Shuaishuai Hu,[a] Zhi Su*[a]

College of Chemistry and Chemical Engineering, Xinjiang Normal University. Urumqi, Xinjiang 830054, China. E-mail: suzhixj@sina.com

EXPERIMENTAL SECTION

Synthesis

The raw materials of KF and SnF_2 were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd, KH_2PO_4 was purchased from Tianjin Baishi Chemical Industry Co., Ltd, KBF_4 was purchased from Tianjin Damao Chemical reagent Co., Ltd. Above reagents are analytical purity.

Crystals of $K_2SnPO_4F_3$ and $K_6Sn(P_2O_7)_2F_2$ were grown by high-temperature solid-phase reaction in the sealed system. First, the mixed KF, SnF_2, KH_2PO_4 and KBF_4 with the molar ratio of 6 : 3 : 4 : 4 for $K_2SnPO_4F_3$ were loaded into a tidy tube, and then made the tube flame-sealed under 10^{-3} Pa. After that, the sealed tube was put in the muffle furnace, heated to 400 °C, and held 10h at this temperature. Subsequently, it was cooled to 300 °C at a rate of 1 °C/h, then cooled to 150 °C at a rate of 2 °C/h, finally lowered to 30 °C at a rate of 10 °C/h. In the cooling process, the $K_2SnPO_4F_3$ crystals were obtained. Another crystal was successfully obtained through the similar process. The solution was prepared for $K_6Sn(P_2O_7)_2F_2$ by melting mixtures of KF, SnF_2, KH_2PO_4 and KBF_4 in a molar ratio of 6 : 3 : 2 : 8.

The polycrystalline samples of $K_2SnPO_4F_3$ and $K_6Sn(P_2O_7)_2F_2$ were synthesized by solid-state reaction. The mixtures of KH_2PO_4, SnF_2 and KF with the molar ratio 1 : 1 : 1 for $K_2SnPO_4F_3$, 4 :1 :2 for $K_6Sn(P_2O_7)_2F_2$, were ground evenly. Subsequently, the $K_2SnPO_4F_3$ mixture was heated to 120 °C slowly and held 4h at this temperature, which was aimed to decompose the phosphate, then elevated to 350 °C and held 6 day. Finally, it was cooled to room temperature naturally. Also, the $K_6Sn(P_2O_7)_2F_2$ mixture was heated to 280 °C slowly and held at this temperature for 3 day, then cooled to room temperature. In this process, the target samples were obtained.

Characterization.

The powder X-ray Diffraction (PXRD) of polycrystalline samples was carried out by Bruker D2 PHASER diffractometer equipped with Cu Kα radiation at room temperature. The scan step width and fixed counting time are 0.02° and 1s/step, respectively. The diffraction patterns were performed in the angular range of 2θ =10–70°. The measurement results for $K_2SnPO_4F_3$ and $K_6Sn(P_2O_7)_2F_2$ are shown in Fig. S8

(ESI†), which indicates that the experimental results agree well with the theoretical ones except several impurity peaks.

The single-crystal XRD data of $K_2SnPO_4F_3$ and $K_6Sn(P_2O_7)_2F_2$ were collected by using a Bruker SMART APEX II 4K CCD diffractometer equipment with Mo Kα radiation (λ=0.71073 Å) at room temperature, and the data were integrated with a SAINT program.[1] The direct methods and full-matrix least-squares program SHELXL were used to solve and refine the crystal structure, respectively.[2] The final structures were rechecked by PLATON to verify the possibility of having the higher symmetric space. The information of crystal data and structural refinements is summarized in Table S1, the atomic coordinates and the equivalent isotropic displacement parameters are given in Tables S2 and S4 (ESI†). The selected bond lengths and angles are listed in the Tables S3 and S5 (ESI†).

Respectively, we mixed the powder samples with dried KBr and ground evenly. And the IR spectra were collected by Shimadzu IRAffinity-1 Fourier transform IR spectrometer with a resolution of 2 cm^{-1} in the range of 400-4000 cm^{-1} at room temperature.

The UV-Vis-NIR diffuse reflectance spectra were obtained by using polytetrafluoroethylene as a standard to collect the data of the title compounds on the Shimadzu SolidSpec-3700DUV spectrophotometer measure at room temperature, and the wavelength range was from 190 to 2500 nm. And the reflectance spectra converted to absorbance with the Kubelka–Munk function to calculate the band gap of title compounds.[3]

Theoretical Calculations.

The electronic and band structures were calculated for title compounds by the CASTEP software,[4] a plane-wave pseudopotential DFT package, with the norm-conserving pseudopotentials.[5-7] The exchange-correlation functional was Perdew-Burke-Emzerhof (PBE) functional within the generalized gradient approximation (GGA).[8] The plane-wave energy cutoff was set at 850.0 eV. Self-consistent field (SCF) calculations were performed with a convergence criterion of 1×10^{-6} eV/atom on the total energy. The k-point separation for each material was set as 0.07 $Å^{-1}$ in the Brillouin

zone. The valence electrons of the elements in $K_2SnPO_4F_3$ and $K_6Sn(P_2O_7)_2F_2$ were calculated as follows: K $3s^2 3p^6 4s^1$, Sn $5s^2 5p^2$, P $3s^2 3p^3$, O $2s^2 2p^4$ and F $2s^2 2p^5$ respectively. The empty bands were set as 3 times the valence bands in the calculation to ensure the convergence of optical properties. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique was employed in geometry optimization during the calculation and the converged criteria are that the residual forces on the atoms, the displacements and the energy change of atoms are less than 0.01 eV/Å, 5×10^{-4} Å and 5.0×10^{-6} eV, respectively. The default values of the CASTEP code were retained for other parameters and convergent criteria.

Table S1 Crystal data and structure refinement for $K_2SnPO_4F_3$ and $K_6Sn(P_2O_7)_2F_2$.

Empirical formula	$K_2SnPO_4F_3$	$K_6Sn(P_2O_7)_2F_2$
Formula weight	348.86	739.17
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a (Å), α (deg.)	10.0393(12)	8.515(3)
b (Å), β (deg.)	9.4153(11), 95.4640(13)	12.400(5), 99.589(4)
c (Å), γ (deg.)	21.602(3)	8.403(3)
Volume (Å^3)	2032.6(4)	874.8(6)
Z, Calculated density (g/cm^3)	12, 3.420	2, 2.806
Absorption coefficient (mm^{-1})	5.257	3.340
F(000)	1944	708
Theta range for data collection (deg.)	1.894 to 27.453	2.426 to 24.998
Limiting indices	$-13 \le h \le 12$, $-6 \le k \le 12$, $-27 \le l \le 28$	$-10 \le h \le 10$, $-14 \le k \le 7$, $-9 \le l \le 9$
Reflections collected / unique	12239/4626 [R_{int} = 0.0380]	4346/1527 [R_{int} = 0.0267]
Completeness	99.70%	99.70%
Refinement method	Full-matrix least-squares on F_o^2	Full-matrix least-squares on F_o^2
Data / restraints / parameters	4626/0/298	1527/0/125
Goodness-of-fit on F_o^2	0.913	1.082
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1 = 0.0315, wR_2 = 0.0549	R_1 = 0.0245, wR_2 = 0.0610
R indices (all data) [a]	R_1 = 0.0489, wR_2 = 0.0608	R_1 = 0.0288, wR_2 = 0.0628
Largest diff. peak and hole (eÅ^{-3})	0.791 and -0.764	0.522 and -0.456

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $K_2SnPO_4F_3$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U(eq)	BVS
K(1)	-407(1)	8413(1)	2252(1)	20(1)	1.282916
K(2)	4904(1)	6384(1)	638(1)	18(1)	1.192665
K(3)	637(1)	1426(1)	1272(1)	22(1)	1.190087
K(4)	7029(1)	9628(1)	3766(1)	25(1)	0.897574
K(5)	2823(1)	352(2)	2985(1)	37(1)	0.784108
K(6)	7569(1)	9860(2)	292(1)	27(1)	1.01138
Sn(1)	677(1)	7164(1)	528(1)	9(1)	4.368166
Sn(2)	4278(1)	2004(1)	1087(1)	10(1)	4.359708
Sn(3)	5888(1)	7847(1)	2272(1)	9(1)	4.33607
P(1)	2058(1)	4043(1)	288(1)	11(1)	5.106152
P(2)	3033(1)	8860(1)	1388(1)	10(1)	5.039987
P(3)	7212(1)	10791(1)	1790(1)	10(1)	5.055351
O(1)	2593(3)	3145(4)	859(2)	21(1)	2.150708
O(2)	3152(3)	10195(4)	975(1)	14(1)	2.185245
O(3)	2535(3)	7636(4)	938(2)	15(1)	2.096459
O(4)	2140(4)	9096(4)	1886(2)	21(1)	1.943859
O(5)	4477(3)	8422(4)	1610(2)	19(1)	2.154366
O(6)	8370(3)	10237(4)	1482(2)	16(1)	2.211317
O(7)	6803(3)	9760(4)	2297(2)	14(1)	2.07433
O(8)	6016(3)	11015(4)	1300(2)	16(1)	2.120641
O(9)	7531(3)	12231(4)	2120(2)	16(1)	2.110797
O(10)	1070(3)	5079(4)	559(2)	16(1)	2.032661
O(11)	3119(3)	4753(4)	-30(2)	19(1)	2.062585
O(12)	1233(4)	3021(4)	-152(2)	29(1)	2.113841
F(1)	1266(3)	7433(3)	-310(1)	22(1)	0.98082
F(2)	41(3)	6780(3)	1346(1)	20(1)	1.119691
F(3)	283(3)	9192(3)	564(1)	22(1)	1.095531
F(4)	4951(3)	8547(3)	2979(1)	19(1)	1.109069
F(5)	6839(3)	7064(3)	1595(1)	25(1)	1.022217
F(6)	4895(3)	6064(3)	2346(1)	26(1)	1.026293
F(7)	3815(3)	2071(4)	1951(1)	27(1)	0.993276
F(8)	4593(3)	1778(3)	209(1)	22(1)	1.027521
F(9)	5251(3)	3809(3)	1196(2)	30(1)	0.992935

Table S3. Selected bond lengths and angles for $K_2SnPO_4F_3$.

K(1)-F(2)	2.562(3)	P(2)-O(4)	1.482(4)
K(1)-F(7)#1	2.567(3)	P(2)-O(5)	1.539(3)
K(1)-O(6)#2	2.615(3)	P(2)-O(2)	1.551(3)
K(1)-F(6)#1	2.677(3)	P(2)-O(3)	1.559(3)
K(1)-O(4)	2.822(4)	P(3)-O(6)	1.488(3)
K(1)-O(9)#3	2.860(4)	P(3)-O(8)	1.539(3)
K(1)-O(7)#2	3.084(4)	P(3)-O(7)	1.548(3)
K(1)-F(5)#2	3.244(3)	P(3)-O(9)	1.550(3)
K(1)-F(9)#1	3.362(3)	F(3)-Sn(1)-F(2)	93.39(12)
K(2)-F(8)#5	2.602(3)	F(3)-Sn(1)-F(1)	89.48(12)
K(2)-O(11)	2.675(3)	F(2)-Sn(1)-F(1)	176.41(12)
K(2)-O(11)#5	2.704(4)	F(3)-Sn(1)-O(10)	175.69(12)
K(2)-F(9)	2.715(3)	F(2)-Sn(1)-O(10)	82.48(13)
K(2)-F(5)	2.775(3)	F(1)-Sn(1)-O(10)	94.69(13)
K(2)-O(3)	2.786(4)	F(3)-Sn(1)-O(12)#9	84.99(13)
K(2)-O(5)	2.908(4)	F(2)-Sn(1)-O(12)#9	88.20(14)
K(3)-F(3)#7	2.606(3)	F(1)-Sn(1)-O(12)#9	89.92(14)
K(3)-O(6)#8	2.614(3)	O(10)-Sn(1)-O(12)#9	96.10(14)
K(3)-F(4)#3	2.671(3)	F(3)-Sn(1)-O(3)	87.11(13)
K(3)-O(1)	2.758(4)	F(2)-Sn(1)-O(3)	90.64(12)
K(3)-F(1)#9	2.893(3)	F(1)-Sn(1)-O(3)	91.65(13)
K(3)-O(2)#7	2.905(3)	O(10)-Sn(1)-O(3)	91.67(13)
K(3)-O(4)#7	2.909(4)	O(12)#9-Sn(1)-O(3)	171.93(14)
K(3)-F(6)#3	3.101(3)	F(9)-Sn(2)-F(8)	94.91(13)
K(4)-F(5)#10	2.707(3)	F(9)-Sn(2)-F(7)	91.03(13)
K(4)-F(4)	2.757(3)	F(8)-Sn(2)-F(7)	173.87(12)
K(4)-O(11)#11	2.787(3)	F(9)-Sn(2)-O(8)#7	87.83(13)
K(4)-F(9)#10	2.831(3)	F(8)-Sn(2)-O(8)#7	87.40(13)
K(4)-F(2)#1	2.896(3)	F(7)-Sn(2)-O(8)#7	94.37(13)
K(4)-F(1)#11	2.937(3)	F(9)-Sn(2)-O(1)	87.96(13)
K(4)-O(9)#6	3.018(4)	F(8)-Sn(2)-O(1)	91.72(13)
K(4)-O(7)	3.160(3)	F(7)-Sn(2)-O(1)	86.95(13)
K(4)-O(12)#11	3.370(4)	O(8)#7-Sn(2)-O(1)	175.60(14)
K(5)-O(4)#7	2.682(3)	F(9)-Sn(2)-O(2)#7	176.30(13)
K(5)-F(4)#7	2.730(3)	F(8)-Sn(2)-O(2)#7	86.21(12)
K(5)-F(2)#3	2.811(3)	F(7)-Sn(2)-O(2)#7	87.76(12)
K(5)-F(6)#3	2.834(3)	O(8)#7-Sn(2)-O(2)#7	95.75(13)
K(5)-F(7)	3.005(3)	O(1)-Sn(2)-O(2)#7	88.48(13)
K(5)-O(3)#3	3.214(4)	F(5)-Sn(3)-F(6)	91.48(13)
K(5)-O(10)#3	3.243(3)	F(5)-Sn(3)-F(4)	177.04(12)
K(5)-O(1)#3	3.307(4)	F(6)-Sn(3)-F(4)	86.54(13)
K(6)-O(6)	2.643(3)	F(5)-Sn(3)-O(5)	86.10(13)
K(6)-O(2)#12	2.764(3)	F(6)-Sn(3)-O(5)	87.63(13)

K(6)-F(8)#5	2.794(3)	F(4)-Sn(3)-O(5)	96.01(13)
K(6)-F(1)#12	2.803(3)	F(5)-Sn(3)-O(7)	95.93(13)
K(6)-F(3)#13	2.805(3)	F(6)-Sn(3)-O(7)	172.50(13)
K(6)-O(12)#5	2.995(4)	F(4)-Sn(3)-O(7)	86.00(13)
K(6)-O(8)	3.001(4)	O(5)-Sn(3)-O(7)	93.94(13)
K(6)-F(3)#12	3.102(3)	F(5)-Sn(3)-O(9)#6	88.21(12)
Sn(1)-F(3)	1.953(3)	F(6)-Sn(3)-O(9)#6	94.25(12)
Sn(1)-F(2)	1.970(3)	F(4)-Sn(3)-O(9)#6	89.74(12)
Sn(1)-F(1)	1.974(3)	O(5)-Sn(3)-O(9)#6	174.05(14)
Sn(1)-O(10)	2.002(3)	O(7)-Sn(3)-O(9)#6	84.93(13)
Sn(1)-O(12)#9	2.018(3)	O(11)-P(1)-O(12)	111.5(2)
Sn(1)-O(3)	2.036(3)	O(11)-P(1)-O(10)	114.0(2)
Sn(2)-F(9)	1.964(3)	O(12)-P(1)-O(10)	107.7(2)
Sn(2)-F(8)	1.964(3)	O(11)-P(1)-O(1)	113.84(19)
Sn(2)-F(7)	1.966(3)	O(12)-P(1)-O(1)	106.0(2)
Sn(2)-O(8)#7	1.992(3)	O(10)-P(1)-O(1)	103.19(19)
Sn(2)-O(1)	2.025(3)	O(4)-P(2)-O(5)	115.5(2)
Sn(2)-O(2)#7	2.046(3)	O(4)-P(2)-O(2)	112.3(2)
Sn(3)-F(5)	1.963(3)	O(5)-P(2)-O(2)	105.99(19)
Sn(3)-F(6)	1.966(3)	O(4)-P(2)-O(3)	112.5(2)
Sn(3)-F(4)	1.982(3)	O(5)-P(2)-O(3)	103.50(19)
Sn(3)-O(5)	1.989(3)	O(2)-P(2)-O(3)	106.18(18)
Sn(3)-O(7)	2.020(3)	O(6)-P(3)-O(8)	109.36(19)
Sn(3)-O(9)#6	2.046(3)	O(6)-P(3)-O(7)	111.62(19)
P(1)-O(11)	1.480(4)	O(8)-P(3)-O(7)	109.32(18)
P(1)-O(12)	1.536(3)	O(6)-P(3)-O(9)	112.1(2)
P(1)-O(10)	1.546(3)	O(8)-P(3)-O(9)	108.01(19)
P(1)-O(1)	1.549(3)	O(7)-P(3)-O(9)	106.31(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,-z+1/2	#2 x-1,y,z	#3 -x+1/2,y-1/2,-z+1/2
#4 x,y+1,z	#5 -x+1,-y+1,-z	#6 -x+3/2,y-1/2,-z+1/2
#7 x,y-1,z	#8 x-1,y-1,z	#9 -x,-y+1,-z
#10 -x+3/2,y+1/2,-z+1/2	#11 x+1/2,-y+3/2,z+1/2	#12 -x+1,-y+2,-z
#13 x+1,y,z	#14 x+1,y+1,z	#15 x-1/2,-y+3/2,z-1/2

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $K_6Sn(P_2O_7)_2F_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U(eq)	BVS
K(1)	9083(1)	7434(1)	433(1)	27(1)	1.03
K(2)	1751(1)	5389(1)	2547(1)	24(1)	1.04
K(3)	4737(1)	7894(1)	896(1)	24(1)	1.06
Sn(1)	5000	5000	0	14(1)	4.33
P(1)	8034(1)	3619(1)	1781(1)	15(1)	5.02
P(2)	7252(1)	5604(1)	3317(1)	15(1)	5.02
O(1)	5662(3)	5763(2)	2117(3)	26(1)	2.04
O(2)	8610(3)	6168(2)	2784(3)	27(1)	2.01
O(3)	7021(3)	4127(2)	254(3)	20(1)	2.19
O(4)	6979(3)	9146(2)	-20(3)	19(1)	2.07
O(5)	7559(3)	4317(2)	3271(3)	15(1)	2.13
O(6)	2505(3)	7496(2)	-2061(3)	24(1)	1.91
O(7)	9755(3)	3754(2)	1740(3)	24(1)	2.04
F(1)	3945(3)	3851(2)	1098(3)	27(1)	0.93

Table S5. Selected bond lengths and angles for $K_6Sn(P_2O_7)_2F_2$.

K(1)-O(2)	2.608(3)	P(2)-O(2)	1.481(3)
K(1)-O(7)#1	2.661(3)	P(2)-O(4)#9	1.486(3)
K(1)-O(4)	2.765(3)	P(2)-O(1)	1.562(3)
K(1)-O(2)#2	2.795(3)	P(2)-O(5)	1.621(3)
K(1)-O(7)#3	2.922(3)	F(1)#4-Sn(1)-F(1)	180
K(1)-F(1)#4	3.119(3)	F(1)#4-Sn(1)-O(1)	89.50(11)
K(1)-O(6)#5	3.301(3)	F(1)-Sn(1)-O(1)	90.50(11)
K(2)-O(7)#7	2.661(3)	F(1)#4-Sn(1)-O(1)#4	90.50(11)
K(2)-O(4)#8	2.667(3)	F(1)-Sn(1)-O(1)#4	89.50(11)
K(2)-O(6)#9	2.709(3)	O(1)-Sn(1)-O(1)#4	180
K(2)-O(3)#4	2.794(3)	F(1)#4-Sn(1)-O(3)	89.41(10)
K(2)-O(2)#7	2.884(3)	F(1)-Sn(1)-O(3)	90.59(10)
K(2)-F(1)	3.061(3)	O(1)-Sn(1)-O(3)	92.89(10)
K(3)-O(4)	2.672(3)	O(1)#4-Sn(1)-O(3)	87.11(10)
K(3)-O(5)#11	2.805(3)	F(1)#4-Sn(1)-O(3)#4	90.59(10)
K(3)-O(6)#9	2.807(3)	F(1)-Sn(1)-O(3)#4	89.41(10)
K(3)-F(1)#11	2.847(3)	O(1)-Sn(1)-O(3)#4	87.11(10)
K(3)-O(1)	2.895(3)	O(1)#4-Sn(1)-O(3)#4	92.89(10)
K(3)-O(6)	2.908(3)	O(3)-Sn(1)-O(3)#4	180
K(3)-O(3)#4	2.996(3)	O(7)-P(1)-O(6)#4	116.23(16)
K(3)-F(1)#4	3.061(3)	O(7)-P(1)-O(3)	110.34(15)
Sn(1)-F(1)#4	1.991(2)	O(6)#4-P(1)-O(3)	111.37(16)
Sn(1)-F(1)	1.991(2)	O(7)-P(1)-O(5)	109.45(14)
Sn(1)-O(1)	2.009(3)	O(6)#4-P(1)-O(5)	104.36(15)
Sn(1)-O(1)#4	2.009(3)	O(3)-P(1)-O(5)	104.22(13)
Sn(1)-O(3)	2.016(2)	O(2)-P(2)-O(4)#9	115.94(15)
Sn(1)-O(3)#4	2.016(2)	O(2)-P(2)-O(1)	112.41(17)
P(1)-O(7)	1.479(3)	O(4)#9-P(2)-O(1)	109.06(15)
P(1)-O(6)#4	1.486(3)	O(2)-P(2)-O(5)	108.82(15)
P(1)-O(3)	1.553(3)	O(4)#9-P(2)-O(5)	106.15(14)
P(1)-O(5)	1.627(2)	O(1)-P(2)-O(5)	103.55(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z #2 x,-y+3/2,z-1/2 #3 -x+2,y+1/2,-z+1/2
#4 -x+1,-y+1,-z #5 x+1,-y+3/2,z+1/2 #6 x+1,y,z
#7 x-1,y,z #8 -x+1,y-1/2,-z+1/2 #9 x,-y+3/2,z+1/2
#10 -x+1,-y+1,-z+1 #11 -x+1,y+1/2,-z+1/2 #12 -x+2,y-1/2,-z+1/2
#13 x-1,-y+3/2,z-1/2

Table S6. The inorganic compounds of tin(IV)-containing phosphates in the ICSD database.

No.	Compounds	Space group	Sn-P-O framework	Absorption edges wavelength(nm)	Band gap(eV)	Reference
1	$(Sn_3O)(Sn_2O)(PO_4)_4$	$P\bar{1}$	3D	N/A	N/A	[9]
2	SnP_2O_7	$Ia\bar{3}$	3D	N/A	N/A	[10]
3	$CaSn_4(PO_4)_6$	*Pnnm*	3D	N/A	N/A	[11]
4	$BaSn(PO_4)_2$	*C*2/*m*	2D	340	3.60 cal.	[12]
5	$SrSn(PO_4)_2$	*C*2/*c*	2D	330	3.76 cal.	[12]
6	$CuSn_2(PO_4)_3$	$R\bar{3}c$	3D	N/A	N/A	[13]
7	$KSnO(PO_4)$	$Pna2_1$	3D	225	5.5 exp.	[14]
8	$KSn_2(PO_4)_3$	$R\bar{3}$	3D	N/A	N/A	[15]
9	$LiSn_2(PO_4)_3$	$R\bar{3}c$	3D	N/A	N/A	[16]
10	$LiSn_2(PO_4)_3$	$P\bar{1}$	3D	N/A	N/A	[16]
11	$NaSn_2(PO_4)_3$	$R\bar{3}$	3D	N/A	N/A	[17]
12	$NaSn_2(PO_4)_3$	$R\bar{3}c$	3D	N/A	N/A	[18]
13	$PbSn(PO_4)_2$	$P2_1/c$	3D	N/A	N/A	[19]
14	$RbSn_2(PO_4)_3$	$R\bar{3}$	3D	N/A	N/A	[20]
15	$Sn(HPO_4)_2(H_2O)$	*C*2/*c*	1D	N/A	N/A	[21]
16	$Sn(HPO_4)_2$	*C*2/*c*	1D	N/A	N/A	[22]
17	$(K_{0.5}Rb_{0.5})(SnO)(PO_4)$	$Pna2_1$	3D	N/A	N/A	[23]
18	$Sn(HPO_4)_2(NH_3)_{0.4}(H_2O)_{0.6}$	$R\bar{3}$	3D	N/A	N/A	[24]
19	$Ag_2SnFe(PO_4)_3$	$R\bar{3}c$	3D	N/A	N/A	[25]
20	$CaSn(H_2PO_2)_6$	$R\bar{3}$	1D	N/A	N/A	[26]
21	$CaSnFe(PO_4)_3$	$R\bar{3}c$	3D	N/A	N/A	[27]
22	$CdSnFe(PO_4)_3$	$R\bar{3}c$	3D	N/A	N/A	[27]
23	$K(Ti_{0.25}Sn_{0.75})O(PO_4)$	$Pna2_1$	3D	N/A	N/A	[28]
24	$K_2SnFe(PO_4)_3$	$P2_13$	3D	N/A	N/A	[29]
25	$K_2YbSn(PO_4)_3$	$P2_13$	3D	N/A	N/A	[29]
26	$K_2AlSn(PO_4)_3$	$P2_13$	3D	N/A	N/A	[30]
27	$Li(Ti_{2-x}Sn_x)(PO_4)_3$	$R\bar{3}c$	3D	N/A	N/A	[31]
28	$Na_{1.168}(Al_{0.148}Sn_{0.852})Sn(PO_4)_3$	$R\bar{3}$	3D	N/A	N/A	[32]
29	$Na_{1.5}Sn_{1.5}Sb_{0.3}(PO_4)_3$	$R\bar{3}$	3D	N/A	N/A	[25]
30	$Na_2FeSn(PO_4)_3$	$R\bar{3}c$	3D	N/A	N/A	[27]
31	$(NH_4)_2Sn(P_4O_{13})$	$P\bar{1}$	1D	N/A	N/A	[33]
32	$SrCrSn(PO_4)_3$	$R\bar{3}$	2D	N/A	N/A	[34]
33	$SrFeSn(PO_4)_3$	$R\bar{3}$	2D	N/A	N/A	[34]
34	$(K_{0.5}Na_{0.5})(Sn_{0.5}Ti_{0.5})O(PO_4)$	$Pna2_1$	3D	N/A	N/A	[35]
35	$(Na_{0.5}Rb_{0.5})(Sn_{0.5}Ti_{0.5})O(PO_4)$	$Pna2_1$	3D	N/A	N/A	[35]
36	$(K_{0.5}Rb_{0.5})(Sn_{0.5}Ti_{0.5})O(PO_4)$	$Pna2_1$	3D	N/A	N/A	[35]
37	$Sn_{0.078}Cu_{0.356}H_{0.4}Al_{0.924}P_{0.924}O_{4.408}$	*P*6/*mcc*	3D	N/A	N/A	[36]
38	$K_2SnPO_4F_3$	$P2_1/c$	2D	192	6.10	This work
39	$K_6Sn(P_2O_7)_2F_2$	$P2_1/c$	0D	196	6.09	This work

N/A = not reported or not available

Table S7. The tin-oxygen-fluorine containing anhydrous inorganic compounds in the ICSD database.

No.	Compounds	Space group	Sn-O/F framework	Groups of tin	Ratio of Sn/F	Reference
1	$Sn(SnOF_5)$	*C*2/*m*	3D	$[Sn_2O_4F_6]$ / $[SnF_4]$	0.4	[37]
2	$Sn_2(SnOF_2)_2$	*C*2/*m*	1D	$[SnO_2F_2]$ / $[SnOF_2]$	1	[38]
3	Sn_4OF_6	$P2_12_12_1$	3D	$[SnOF_3]$ / $[SnOF_2]$ / $[SnF_4]$	0.67	[39]
4	$SnPO_3F$	$P2_1/c$	2D	$[SnO_3]$	1	[40]
5	$(Sn_6F_{10})(NbOF_5)$	*C*2/*c*	3D	$[Sn_2F_6]$ / $[SnF_3]$	1.2	[41]
6	$Sn(FSO_3)_2$	$P2_1/c$	1D	$[SnO_4]$	1	[42]
7	$SnB_2O_3F_2$	*P*31*m*	1D	$[SnO_3]$	0.5	[43]
8	$Sn_3(PO_4)F_3$	*R*3	3D	$[SnO_2F_2]$	1	[44]
9	$KSnSO_4F$	$P\bar{1}$	1D	$[SnO_3F]$	1	[45]
10	$Na_4Sn_4(C_2O_4)_3F_6$	$P\bar{1}$	1D	$[SnO_3F]$ / $[SnO_2F_2]$	0.67	[46]
11	$(NaF_3)(SnSi_3O_9)$	*C*2/*m*	3D	$[SnO_6]$	0.33	[47]
12	$(NH_4)_2Sn_2F_4(NO_3)_2$	*C*2	0D	$[Sn_2F_4]$	0.5	[48]
13	$Na_7(SO_4)_3(SnF_3)$	$P6_3mc$	0D	$[SnF_3]$	0.33	[49]
14	$Sn_{1.24}Ti_{1.94}O_{3.66}(OH)_{1.5}F_{1.42}$	$Fd\bar{3}m$	3D	[Sn (O / F)$_2$]	1	[50]
15	$(NH_4)Sn(C_2O_4)F$	$P2_1/c$	0D	$[SnO_2F]$	1	[51]
16	$(NH_4)SnF(HPO_4)$	*Pnma*	1D	$[SnO_2F]$	1	[52]
17	$(NH_4)SnF(SO_4)$	$P2_1/c$	2D	$[SnO_3F]$	1	[53]
18	$Cs_3(Sn_3F_6)_2H(NO_3)_4$	$P\bar{1}$	0D	$[Sn_3F_6]$	0.5	[54]
19	$NaSnF(HPO_4)$	*Pnma*	1D	$[SnO_2F]$	1	[52]
20	$(CH_3)_3Sn((CH_3)_2SO)_2(FSO_2)_2N$	$P\bar{1}$	0D	$[SnOC_3]$	0.5	[55]
21	$K_2SnPO_4F_3$	$P2_1/c$	2D	$[SnO_3F_3]$	0.33	This work
22	$K_6Sn(P_2O_7)_2F_2$	$P2_1/c$	0D	$[SnO_4F_2]$	0.5	This work

Fig. S1. The coordination of Sn and K atoms in $K_2SnPO_4F_3$.

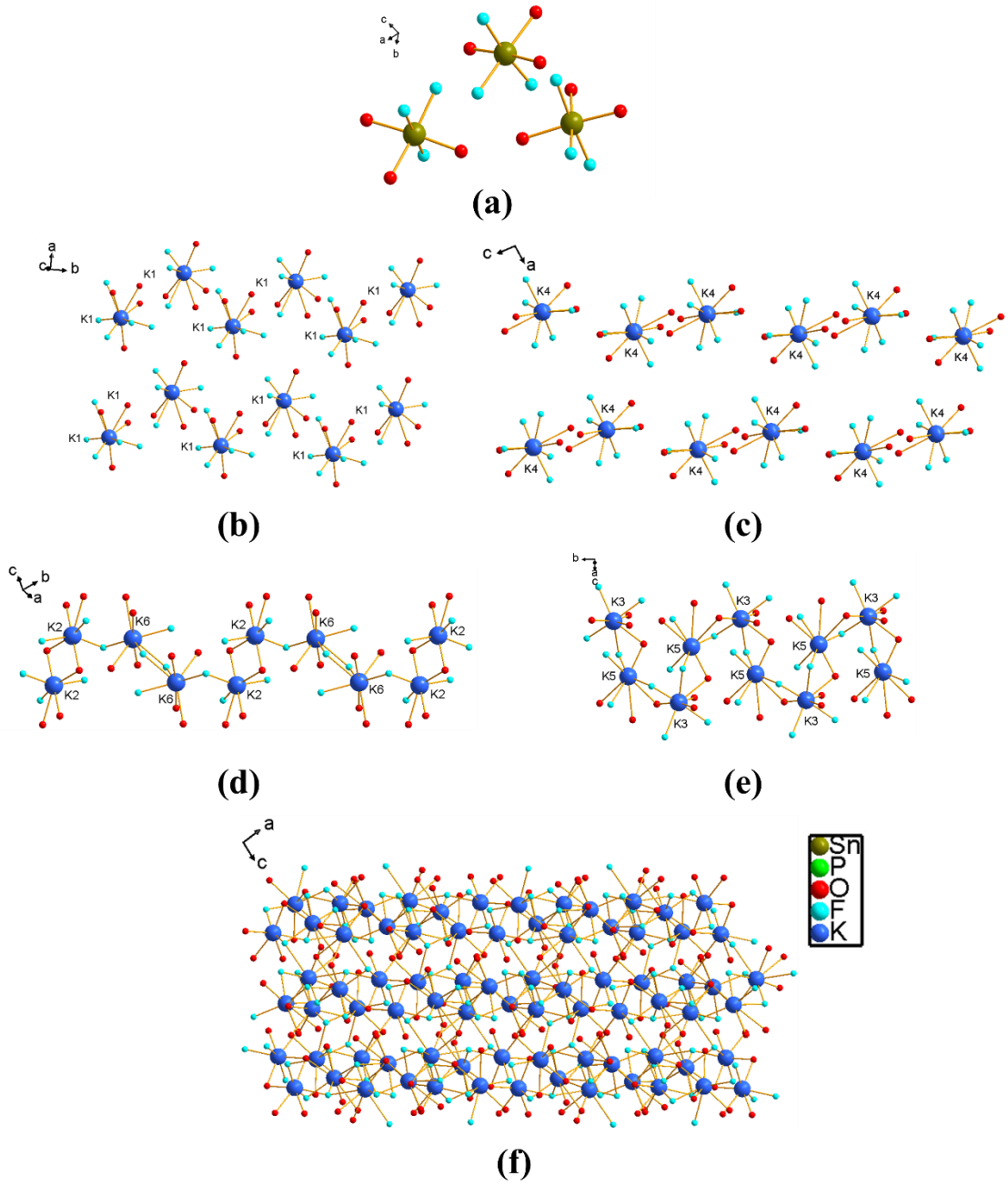


Fig. S2. The coordination of the K atoms in $K_6Sn(P_2O_7)_2F_2$.

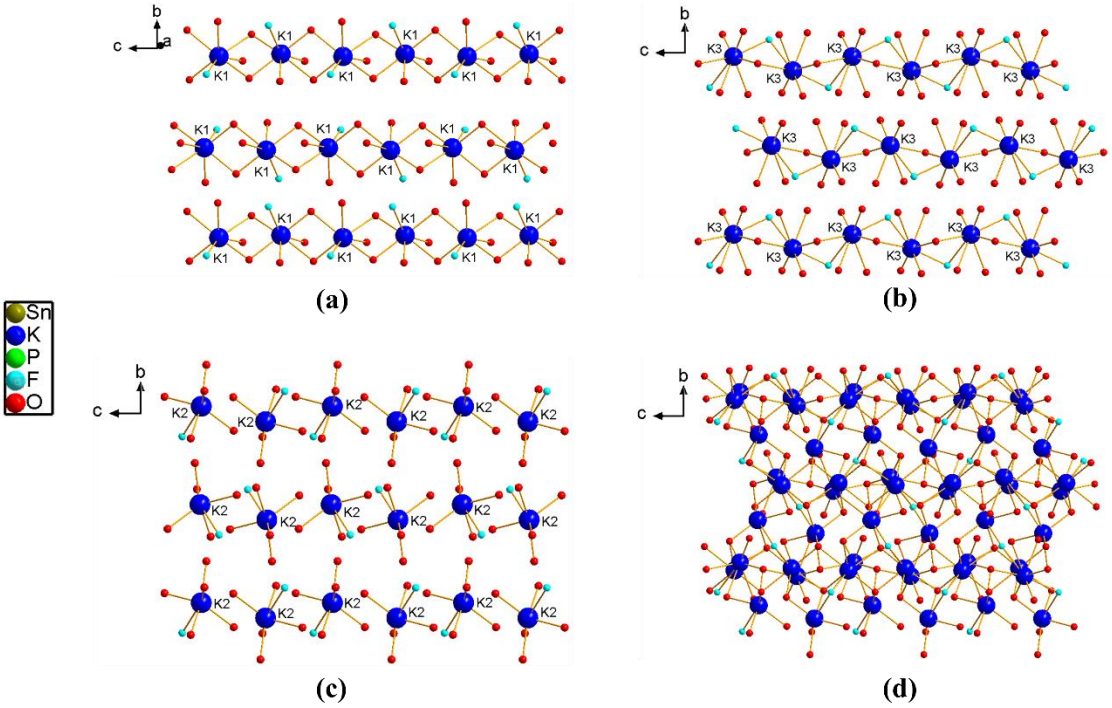


Fig. S3. The IR spectra for $K_2SnPO_4F_3$ and $K_6Sn(P_2O_7)_2F_2$.

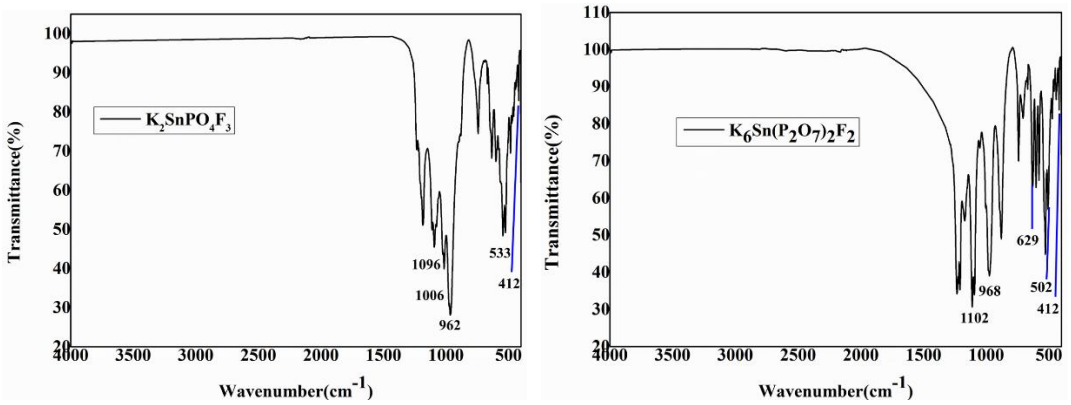


Fig. S4. The UV-Vis-NIR diffuse reflectance spectrum of $K_2SnPO_4F_3$.

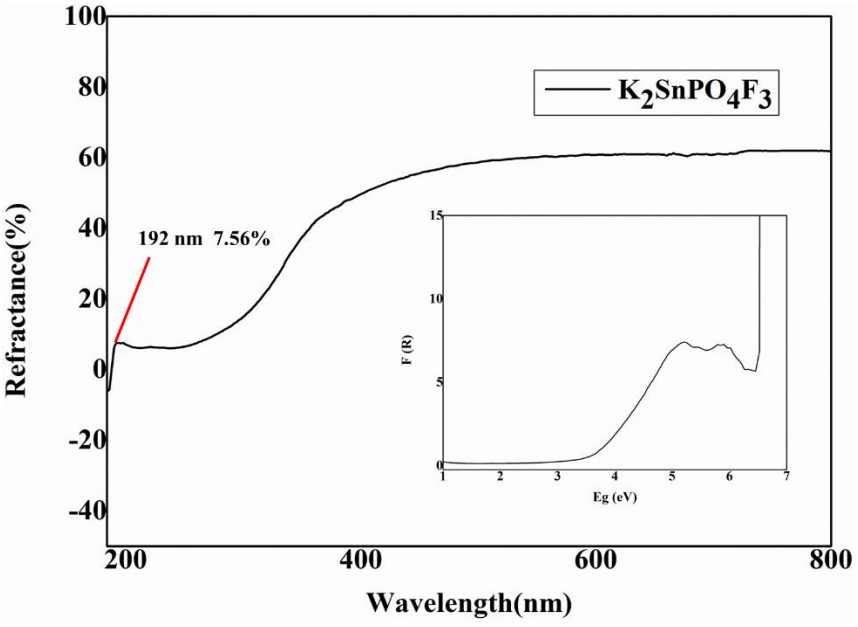


Fig. S5. The UV-Vis-NIR diffuse reflectance spectrum of $K_6Sn(P_2O_7)_2F_2$.

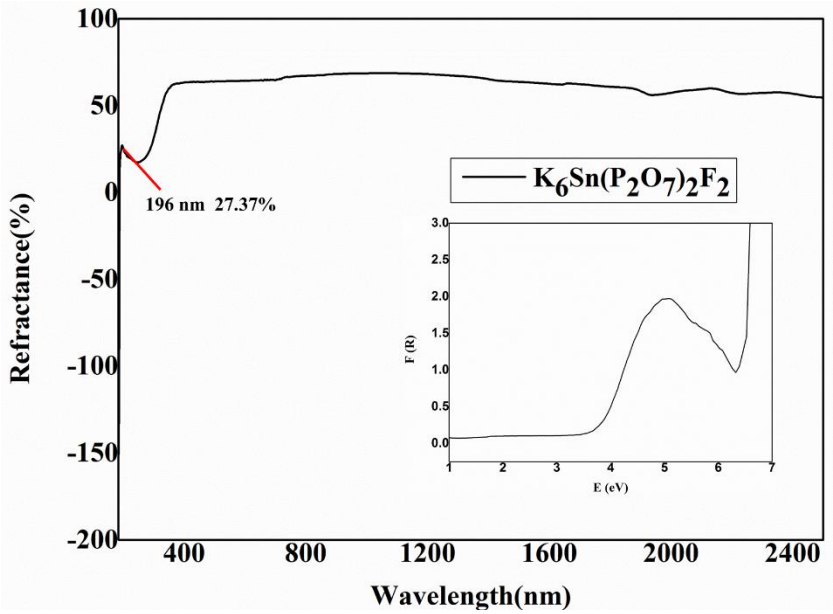


Fig. S6. The calculated band structure by HSE06 for (a) $K_2SnPO_4F_3$ and (b) $K_6Sn(P_2O_7)_2F_2$.

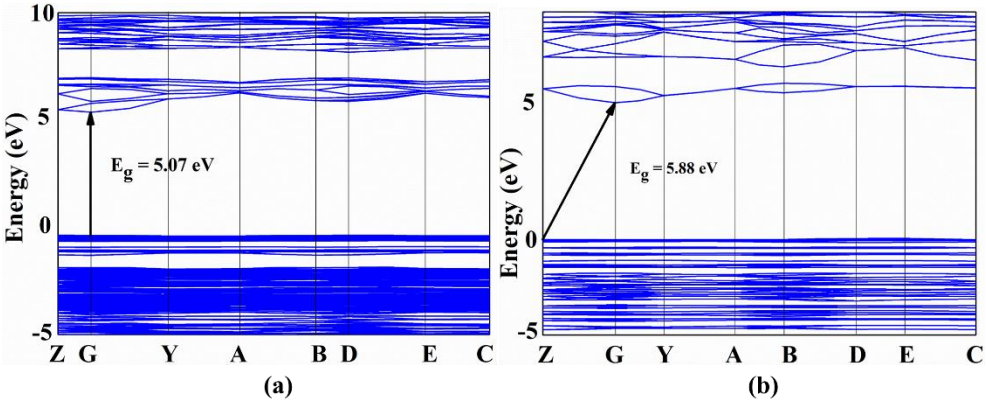


Fig. S7. (a) The band structure of $K_2SnPO_4F_3$; (b) density of states (DOS) of $K_2SnPO_4F_3$.

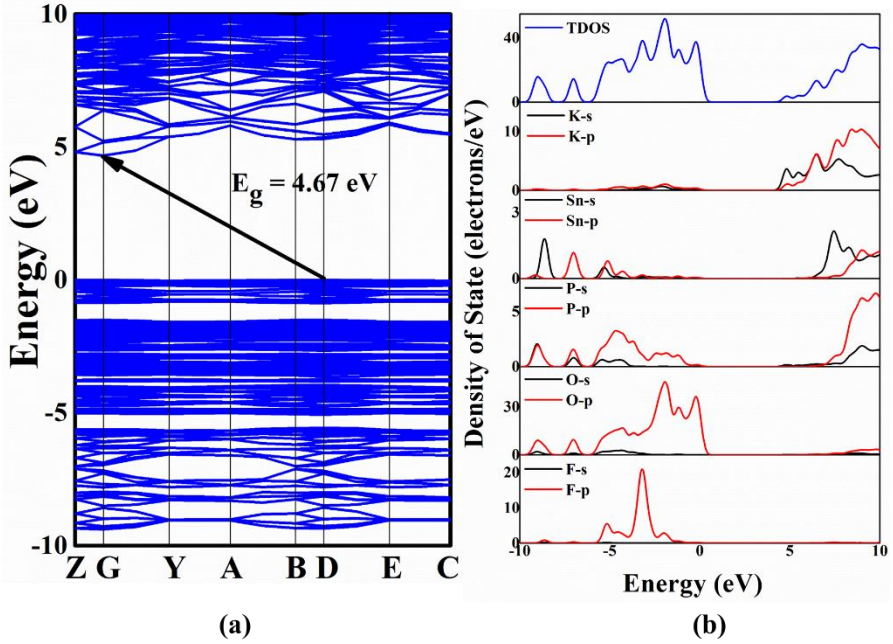
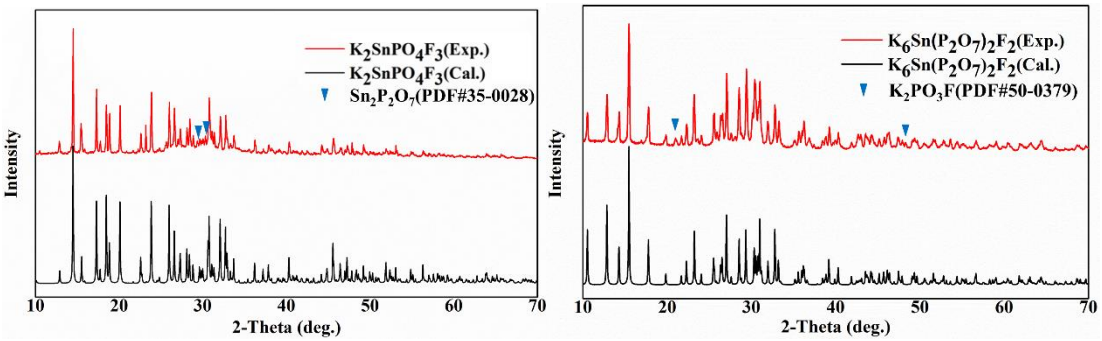


Fig. S8. The calculated and experimental powder X-ray diffraction patterns for $K_2SnPO_4F_3$ and $K_6Sn(P_2O_7)_2F_2$.



Reference

[1] SAINT, Version 7.60A, Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2008.

[2] G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112.

[3] J. Tauc, *Mater. Res. Bull.*, 1970, **5**, 721.

[4] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson and M. C. Payne, *Z. Kristallogr.*, 2005, **220**, 567.

[5] A. M. Rappe, K. M. Rabe, E. Kaxiras and J. D. Joannopoulos, *Phys. Rev. B*, 1990, **41**, 1227.

[6] J. Lin, A. Qteish, M. Payne and V. Heine, *Phys. Rev. B*, 1993, **47**, 4174.

[7] M. H. Lee, Ph.D. Thesis, The University of Cambridge, Cambridge, U.K., 1996.

[8] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

[9] X. J. Yuan, Y. Z. Li, Y. Xu, X. Z. You and R. J. Linhardt, *Eur. J. Inorg. Chem.*, 2007, **6**, 858.

[10] C. H. Huang, O. Knop, D. A. Othen, F. W. D. Woodhams and R. A. Howie, *Can. J. Chem.*, 1975, **53**, 79.

[11] D. Zhao, F. F. Li and A. Y. Zhang, *Z. Kristallogr. NCS*, 2010, **225**, 627.

[12] D. Zhao, H. Zhang, Z. Xie, W. L. Zhang, S. L. Yang and W. D. Cheng, *Dalton Trans.*, 2009, 5310.

[13] A. Serghini, R. Brochu, R. Olazcuaga and P. Gravereau, *Mater. Lett.*, 1995, **22**, 149.

[14] M. L. F. Phillips, W. T. A. Harrison and G. D. Stucky, *Inorg. Chem.*, 1990, **29**, 3245.

[15] H. J. Zhang, *Acta Crystallogr. E,* 2011, **67**, 51.

[16] E. Morin, J. Angenault, J. C. Couturier, M. Quarton, H. He and J. Klinowski, *Eur. J. Solid State Inorg. Chem.*, 1997, **34**, 947.

[17] J. Alamo and J. L. Rodrigo, *Mater. Res. Bull.*, 1992, **27**, 1091.

[18] S. Y. Mao, J. F. Deng, M. R. Li, J. X. Mi, H. H. Chen and J. T. Zhao, *Z. Kristallogr. NCS*, 2004, **219**, 205.

[19] E. Morin1, G. Wallez, S. Jaulmes, J. C. Couturier and M. Quarton, *J. Solid State Chem.*, 1998, **137**, 283.

[20] D. Zhao, F. F. Li, S. Qiu, J. L. Jiao and J. R. Ren, *Acta Crystallogr. E*, 2011, **67**, 32.

[21] S. Bruque, M. A. G. Aranda, E. R. Losilla, P. O. Pastor and P. M. Torres, *Inorg. Chem.*, 1995, **34**, 893.

[22] R. Herak, B. Prelesnik, M. Curic and P. Vasic, J. *Chem. Soc., Dalton Trans.*, 1978, 566.

[23] S. J. Crennell, A. K. Cheetham, J. A. Kadukb and R. H. Jarma, *J. Mater. Chem.*, 1992, **2**, 785.

[24] L. Roces, S. A. Khainakov, J. R. Garcia, P. Pertierra, M. A. Salvado and S. G. Granda, *Inorg. Chem. Commun.*, 2002, **5**, 685.

[25] A. Aatiq, B. Haggouch and R. Tigha, *Global J. Phys. Chem.*, 2011, **2**, 129.

[26] T. Gieschen and H. Reuter, *Acta Crystallogr. E*, 2013, 69, 44.

[27] A. Aatiq, *Powder Diffr.*, 2004, **19**, 272.

[28] O. D. Krotova, N. I. Sorokina, I. A. Verin, V. I. Voronkova, V. K. Yanovskii and V. I. Simonov, *Crystallogr. Rep.*, 2003, **48**, 925.

[29] A. Aatiq, B. Haggouch, R. Bakri, Y. Lakhdar and I. Saadoune, *Powder Diffr.*, 2006, **21**, 214.
[30] H. Y. Li and D. Zhao, *Acta Crystallogr. E*, 2011, **67**, 56.
[31] N. Bounar, A. Benabbas, F. Bourenmad, P. Ropa and J. C. Carru, *Physica B*, 2012, **407**, 403.
[32] P. M. Manso, M. A. G. Aranda, S. Bruque, J. Sanz and E. R. Losilla, *Solid State Ionics*, 2005, **176**, 1613.
[33] L. S. Ivashkevich, A. F. Selevich, A. S. Lyakhov and A. I. Lesnikovich, *Russ. J. Inorg. Chem.*, 2007, **52**, 1274.
[34] G. Buvaneswari, K. V. G. Kutty and U. V. Varadaraju, *Mater. Res. Bull.*, 2004, **39**, 475.
[35] S. J. Crennell, A. K. Cheetham, J. A. Kaduk and R. H. Jarman, *J. Mater. Chem.*, 1992, **2**, 785.
[36] W. R. Flavell, D. G. Nicholson, M. H. Nilsen and K. Stahl, *J. Mater. Chem.*, 2001, **11**, 620.
[37] J. H. Chang and J. Köhler, *Z. Kristallogr. NCS*, 1999, **214**, 147.
[38] B. Darriet and J. Galy, *Acta Crystallogr.*, 1977, **33**, 1489.
[39] I. Abrahams, S. J. Clark, J. D. Donaldson, Z. I. Khan and J. T. Southern, *J. Chem. Soc., Dalton Trans.*, 1994, 2581.
[40] A. F. Berndt, *Acta Cryst.*, 1974, **30**, 529.
[41] I. E. Rakov, Y. E. Gorbunova, Y. V. Kokunov and Y. N. Mikhailov, *Koord. Khim.*, 1993, **19**, 759.
[42] D. C. Adams, T. Birchall, R. Faggiani, R. J. Gillespie and J. E. Vekris, *Can. J. Chem.*, 1991, **69**, 2122.
[43] M. Luo, F. Liang, Y. X. Song, D. Zhao, N. Ye and Z. S. Lin, *J. Am. Chem. Soc.*, 2018, **140**, 6814.
[44] A. F. Berndt, *J. Dent. Res.*, 1972, **51**, 53.
[45] Y. V. Kokunov, D. G. Detkov, Y. E. Gorbunova, M. M. Erahova and Y. N. Mikhailov, *Zh. Neorg. Khim.*, 2001, **46**, 266.
[46] T. O. Salami, P. Y. Zavalij and S. R. J. Oliver, *Acta Crystallogr. E*, 2001, **57**, 111.
[47] C. H. Liao, P. C. Chang, H. M. Kao and K. H. Lii, *Inorg. Chem.*, 2005, **44**, 9335.
[48] Y. V. Kokunov, D. G. Detkov, Y. E. Gorbunova, M. M. Ershova, Y. N. Mikhailov and Y. A. Buslaev, *Dokl. Akad. Nauk*, 2001, **378**, 347.
[49] Y. E. Gorbunova, D. G. Detkov and Y. V. Kokunov, *Zh. Neorg. Khim.*, 2004, **49**, 1459.
[50] Y. H. Xie, S. Yin, H. Yamane, T. Hashimoto, H. Machida and T. Sato, *Chem. Mater.*, 2008, **20**, 4931.
[51] T. O. Salami, K. Marouchkin, P. Y. Zavalij and S. R. J. Oliver, *Chem. Mater.*, 2002, **14**, 4851.
[52] Y. V. Kokunov, D. G. Detkov, Y. E. Gorbunova, M. M. Erahova and Y. N. Mikhailov, *Zh. Neorg. Khim.*, 2002, **47**, 931.
[53] Y. V. Kokunov, D. G. Detkov, Y. E. Gorbunova, M. M. Erahova and Y. N. Mikhailov, *Zh. Neorg. Khim.*, 2001, **46**, 266.
[54] D. G. Detkov, Y. E. Gorbunova, Y. N. Mikhailov and Y. V. Kokunov, *Zh. Neorg.*

Khim., 2003, **48**, 908.
[55] O. Hiemisch, D. Henschel, A. Blaschette and P. G. Jones, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1391.