Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Halogen Regulation Triggers Structural Transformation from Centrosymmetric to Noncentrosymmetric Switches in Tin Phosphate Halides Sn_2PO_4X (X = F, Cl)

Ting Zheng, † Qiang Wang, † JinXuan Ren † Liling Cao, *† Ling Huang, † Daojiang Gao, † Jian Bi, † and Guohong Zou*‡

† College of Chemistry and Materials Science, Sichuan Normal University, Chengdu, 610066, P. R. China.

‡ College of Chemistry, Sichuan University, Chengdu, 610065, P. R. China.

E-mail: llcao21@163.com; zough@scu.edu.cn

CONTENTS

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and calculated Bond Valence Sum for Sn_2PO_4F. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U_{eq} ($Å^2$)	BVS
Sn(1)	2758.7 (19)	7281.7 (13)	8237.2 (4)	21.4 (3)	1.84
Sn(2)	7020 (2)	7392.5 (16)	5461.5 (5)	30.0 (3)	1.68
P(1)	1966 (7)	6478 (5)	6639.7 (13)	22.5 (6)	5.10
O(1)	2280 (20)	8260 (16)	7217 (4)	25.1 (17)	1.99
F(1)	6540 (20)	3662 (16)	5408 (4)	47 (2)	0.87
O(2)	3130 (20)	7576 (15)	5992 (5)	28 (2)	2.00
O(3)	3140 (20)	4046 (17)	6813 (5)	34 (2)	2.00
O(4)	-1309 (19)	6007 (16)	6492 (4)	28.0 (19)	1.97

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and calculated Bond Valence Sum for Sn_2PO_4Cl. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor Sn_2PO_4Cl.

atom	x	y	z	U_{eq} ($Å^2$)	BVS
Sn(1)	1106.9 (4)	4414.0 (7)	1342.0 (8)	19.5 (3)	1.80
Sn(2)	3853.3 (4)	4448.1 (7)	1146.7 (11)	20.6 (3)	1.74
P(1)	2527.8 (13)	6110 (3)	6439 (7)	15.0 (5)	5.02
Cl(1)	4733 (2)	7389 (3)	490 (10)	36.3 (6)	0.57
O(1)	2603 (4)	7871 (7)	6410 (30)	28.2 (17)	2.01
O(2)	1576 (6)	5616 (8)	5110 (20)	27.3 (18)	1.95
O(3)	3436 (6)	5385 (9)	5150 (20)	28.0 (18)	1.93
O(4)	2506 (3)	5607 (9)	9554 (19)	20.7 (19)	2.10

Table S3. Selected Bond lengths (Å) and angles (deg) for Sn_2PO_4F.

Sn1—O1	2.122 (8)	Sn2—O2	2.109 (11)
Sn1—O3[1]	2.162 (11)	Sn2—O4[4]	2.335 (8)
Sn1—O4[2]	2.241 (9)	P1—O1	1.526 (9)
Sn2—F1	2.084 (9)	P1—O2	1.528 (10)
Sn2—F1[3]	2.484 (9)	P1—O3	1.497 (10)
O1—Sn1—O3[1]	86.5 (4)	P1—O4	1.588 (9)
O1—Sn1—O4[2]	87.9 (3)	O2—P1—O4	104.5 (5)
O3[1]—Sn1—O4[2]	82.1 (3)	O3—P1—O1	111.9 (5)
F1—Sn2—F1[3]	69.9 (3)	O3—P1—O2	115.1 (6)
F1—Sn2—O2	88.9 (4)	O3—P1—O4	104.5 (6)
F1—Sn2—O4[4]	75.8 (3)	P1—O1—Sn1	124.8 (5)
O2—Sn2—F1[3]	77.3 (4)	Sn2—F1—Sn2[3]	110.1 (3)
O2—Sn2—O4[4]	82.3 (3)	P1—O2—Sn2	135.3 (6)
O4[4]—Sn2—F1[3]	140.1 (3)	P1—O3—Sn1[5]	136.4 (6)
O1—P1—O2	110.3 (5)	Sn1[6]—O4—Sn2[7]	114.4 (4)
O1—P1—O4	110.0 (5)	P1—O4—Sn1[6]	113.6 (5)

Symmetry codes: (1) 1-*x*, 1/2+*y*, 3/2-*z*; (2) -*x*, 1/2+*y*, 3/2-*z*; (3) 1-*x*, 1-*y*, 1-*z*; (4) 1+*x*, +*y*, +*z*; (5) 1-*x*, -1/2+*y*, 3/2-*z*; (6) -*x*, -1/2+*y*, 3/2-*z*; (7) 1+*x*, +*y*, +*z* .

Table S4. Selected Bond lengths (Å) and angles (deg) for Sn_2PO_4Cl.

Sn1—O1[2]	2.218 (6)	Sn2—Cl1	2.871 (3)
Sn1—O2	2.182 (9)	Sn2—Cl1[4]	3.256 (4)
Sn1—O4[3]	2.332 (6)	P1—O1	1.556 (7)
Sn2—O1[2]	2.419 (6)	P1—O2	1.504 (8)
Sn2—O3	2.157 (10)	P1—O3	1.518 (8)
Sn2—O4[3]	2.228 (6)	P1—O4	1.551 (10)
Sn1—Cl1[1]	2.899 (4)	O2—P1—O3	113.8 (6)
O1[1]—Sn1—O4[3]	68.8 (2)	O2—P1—O4	107.8 (4)
O2—Sn1—Cl1[2]	81.4 (2)	O3—P1—O1	111.3 (5)
O2—Sn1—O1[1]	93.2 (4)	O3—P1—O4	106.4 (4)
O2—Sn1—O4[3]	81.1 (3)	O4—P1—O1	107.2 (6)
O4[3]—Sn1—Cl1[2]	147.9 (2)	Sn1[5]—O1—Sn2[5]	107.0 (3)
Cl1—Sn2—Cl1[4]	105.88 (8)	P1—O1—Sn1[5]	131.6 (3)
O1[1]—Sn2—Cl1[4]	99.3 (2)	P1—O1—Sn2[5]	121.4 (3)
O4[3]—Sn2—Cl1[4]	158.3 (2)	P1—O3—Sn2	137.2 (5)
O4[3]—Sn2—O1[1]	67.1 (2)	Sn2[6]—O4—Sn1[6]	109.7 (3)
O2—P1—O1	109.9 (4)	P1—O4—Sn1[6]	119.7 (3)

Symmetry codes (bond lengths): (1) 1/2-*x*, -1/2+*y*, 1/2+*z*; (2) 1/2-*x*, -1/2+*y*, -1/2+*z*; (3) +*x*, +*y*, -1+*z*; (4) 1-*x*, 1-*y*, 1/2+*z*

Symmetry codes (angles): (1) 1/2-*x*, -1/2+*y*, -1/2+*z*; (2) 1/2-*x*, -1/2+*y*, 1/2+*z*; (3) +*x*, +*y*, -1+*z*; (4) 1-*x*, 1-*y*, 1/2+*z*; (5) 1/2-*x*, 1/2+*y*, 1/2+*z*; (6) +*x*, +*y*, 1+*z*.

Table S5. Crystal data and structure refinement for Sn_2PO_4F and Sn_2PO_4Cl.

Formula	Sn_2PO_4F	Sn_2PO_4Cl

Formula weight	351.35	367.80
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a (Å)	4.6907 (2)	13.5701 (8)
b (Å)	5.5469 (2)	8.8164 (6)
c (Å)	19.9752 (9)	4.7717 (3)
V (Å^3)	519.73 (4)	570.88 (6)
α (°)	90	90
β (°)	89.744 (4)	90
γ (°)	90	90
Z	4	4
D_{calcd}(g·cm^{-3})	4.490	4.279
Temperature (K)	296.69 (10)	297.50 (10)
λ (Å)	0.71073	0.71073
F(000)	624.0	656.0
μ (mm^{-1})	9.860	9.416
GOF on F^2	1.097	1.130
Flack para	/	0.07(4)
R_1,wR_2 (I>2σ(I))[a]	0.0637/0.1760	0.0403/0.1017
R_1,wR_2 (all data)	0.0685/0.1808	0.0460/0.1052

[a]$R_1(F) = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2(F_o^2) = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

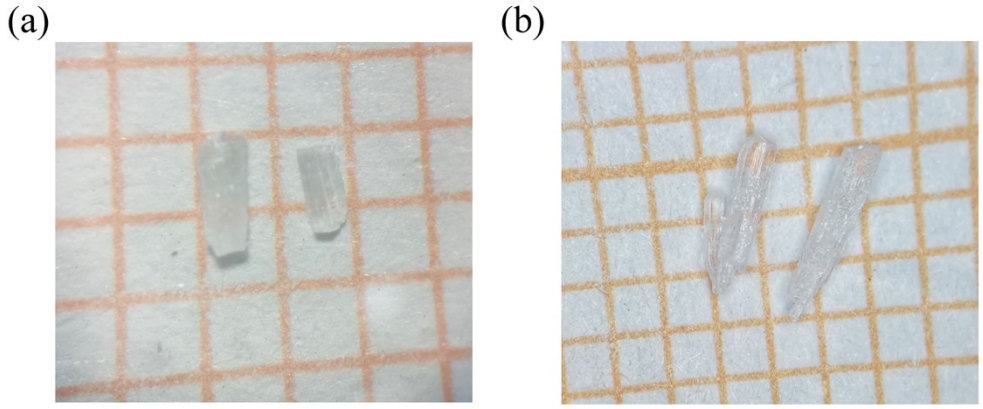

Fig. S1. Photographs of (a) Sn_2PO_4F and (b) Sn_2PO_4Cl.

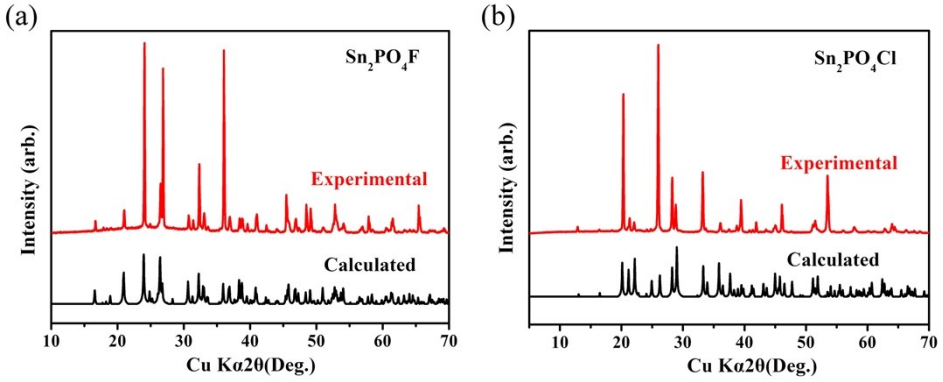

Fig. S2. Experimental and calculated XRD patterns for (a) $Sn_2PO_4F$and (b) Sn_2PO_4Cl.

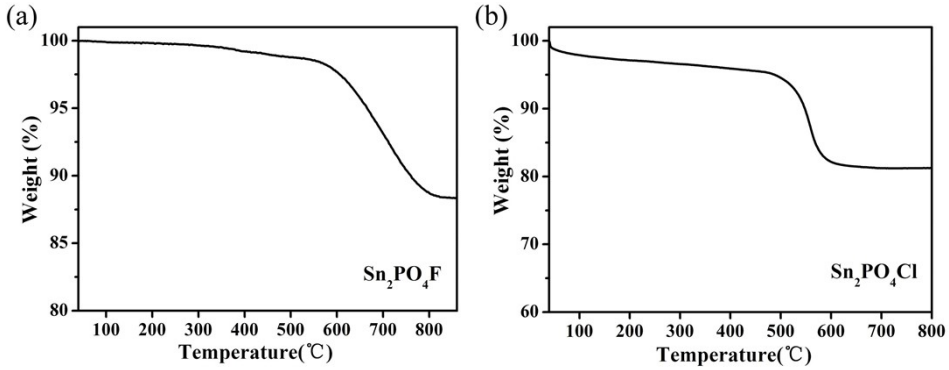

Fig. S3. TGA curves of compounds (a) Sn_2PO_4F and (b) Sn_2PO_4Cl under N_2 air atmosphere.

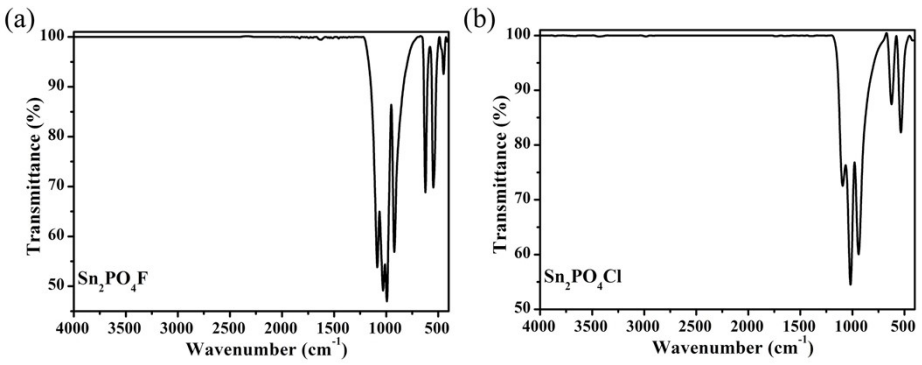

Fig. S4. The IR spectra of compounds (a) Sn_2PO_4F and (b) Sn_2PO_4Cl.

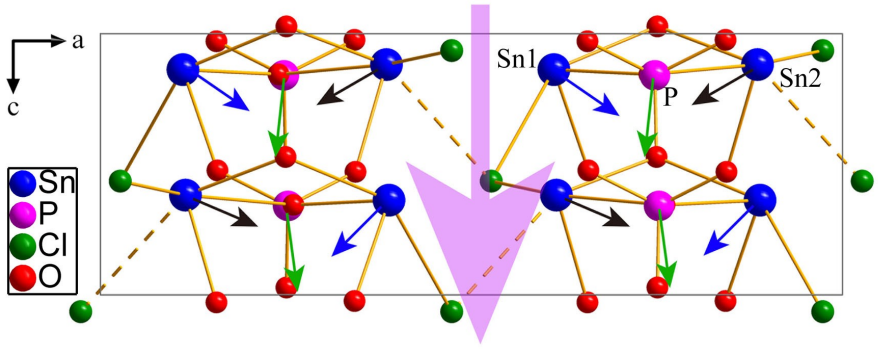

Fig. S5. Projection of the arrangement and dipole orientation of [SnOCl] polyhedra and PO_4 units in the *ac*-plane for Sn_2PO_4Cl. The arrows in black, blue and green represent the local moments and the large bright purple arrow represents the net macroscopic polarization direction.

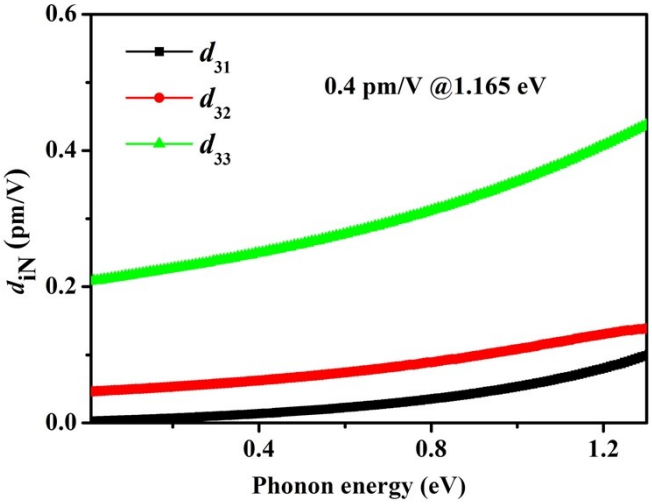

Fig. S6. The calculated frequency dependent second harmonic generation coefficients for Sn_2PO_4Cl.

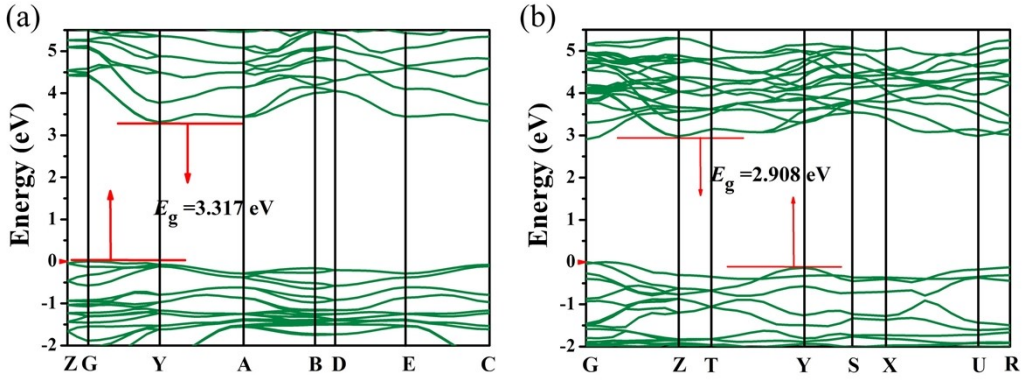

Fig. S7. Calculated band structure for (a) Sn_2PO_4F and (b) Sn_2PO_4Cl (the Fermi level is set at 0 eV).