Supplementary Information

Novel Antimony Phosphates with Enlarged Birefringence Induced by Lone Pair Cations

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1. Experimental Section

Synthesis. The polycrystalline powder of $Cs_2Sb_3O(PO_4)_3$ was prepared via the solid-state reaction in the sealed system. The mixture of Cs_2CO_3， Sb_2O_3 and P_2O_5 with a molar ratio of 2:3:3 was ground and preheated for 6 h at 120 ^{o}C. After sintering at 120 ºC, the sample was ground again and loaded into another neat quartz tube, which was flame-sealed under 10^{-3} Pa. Then the tube was heated at 360 ºC for 24 h and then cooled to 30 ºC at a rate of 3 ºC /min. Finally, white $Cs_2Sb_3O(PO_4)_3$ polycrystalline products were obtained.

Table S1 Crystal data and structure refinement.

Empirical formula	$Cs_2Sb_3O(PO_4)_3$	$(NH_4)_2Sb_4O_2(H_2O)(PO_4)_2[PO_3(OH)]_2$
Formula weight	931.98 g/mol	955.00 g/mol
Temperature	302.0 K	298.0 K
Crystal system	Triclinic	
Space group	$P\bar{1}$ (no. 2)	
Unit cell dimensions	a = 7.2896(2) (Å) b = 9.6583(3) (Å) c = 11.5880(3) (Å) α = 98.7480(10) ° β = 104.7060(10) ° γ = 109.2790(10) °	a = 7.2569(5) (Å) b =7.3904(5) (Å) c = 18.9055(14) (Å) α = 85.297(4) ° β = 81.574(4) ° γ = 70.609(3) °
Volume	719.58(4) Å^3	945.49(12) Å^3
Z	2	2
Density	4.301 g/cm^3	3.354 g/cm^3
Absorption coefficient	10.971 mm^{-1}	6.089 mm^{-1}
F (000)	824	884
Theta range for data collection	1.881 to 27.537 °	2.179 to 27.486 °
Limiting indices	$-9 \le h \le 9$, $-12 \le k \le 12$, $-15 \le l \le 15$	$-9 \le h \le 9$, $-9 \le k \le 9$, $-24 \le l \le 24$
Reflections collected	16977	49817
Independent reflections	3290 [R(int) = 0.0544]	4314 [R(int) = 0.0610]
Completeness to theta	99.3 %	99.6 %
Data/restraints/parameters	3290 / 0 / 190	4314 / 6 / 262
Goodness-of-fit on F^2	1.087	1.132
Final R indexes [$F_o^2 > 2\sigma(F_o^2)$] [a]	R_1 = 0.0227, wR_2 = 0.0509	R_1 = 0.0227, wR_2 = 0.0450
R indexes (all data) [a]	R_1 = 0.0266, wR_2 = 0.0522	R_1 = 0.0288, wR_2 = 0.0508
Largest diff. peak and hole	1.191 and -1.858 e. Å^{-3}	1.237 and -0.950 e. Å^{-3}

[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 (×10^4) and equivalent isotropic displacement parameters (Å×10^3) for CsSbPO. U_{eq} is defined as one-third of the trace the orthogonalised U_{ij} tensor and bond valence sum (BVS).

Atoms	x	y	z	U_{eq}[a]	BVS[b]
Sb(1)	8746(1)	1270(1)	6308(1)	15(1)	3.01
Sb(2)	9931(1)	7365(1)	9569(1)	15(1)	3.10
Sb(3)	5745(1)	4046(1)	8116(1)	15(1)	2.80
Cs(1)	8697(1)	6252(1)	5806(1)	25(1)	1.11
Cs(2)	4855(1)	-1317(1)	7932(1)	29(1)	1.25
P(1)	11112(2)	491(1)	8534(1)	14(1)	4.98
P(2)	1695(2)	4701(1)	8334(1)	13(1)	5.07
P(3)	5213(2)	2157(1)	5404(1)	16(1)	4.97
O(1)	11686(5)	1321(4)	9898(3)	19(1)	2.09
O(2)	5122(5)	3537(4)	6243(3)	19(1)	2.24
O(3)	7501(5)	6113(4)	8164(3)	17(1)	2.29
O(4)	3348(6)	4654(4)	7712(4)	31(1)	2.11
O(5)	8997(5)	571(4)	7853(3)	18(1)	2.30
O(6)	1558(5)	6231(4)	8380(3)	21(1)	2.06
O(7)	5956(5)	1201(3)	6266(3)	16(1)	2.14
O(8)	12605(6)	1143(4)	7898(4)	26(1)	1.52
O(9)	6786(6)	2691(4)	4781(3)	26(1)	2.20
O(10)	10710(6)	-1199(4)	8443(3)	22(1)	1.96
O(11)	3034(5)	1213(4)	4539(3)	26(1)	1.90
O(12)	-371(5)	3464(4)	7497(4)	27(1)	1.60
O(13)	2290(6)	4400(4)	9593(3)	30(1)	1.95

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

[b] BVS are calculated by using bond-valence theory ($S_i = \exp[(R_o - R_i)/B]$, where R_o is an empirical constant, R_i is the length of bond (in angstroms), and B = 0.37

Table S3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$\times 10^3$) for NH_4SbPOH.

Atoms	*x*	*y*	*z*	U_{eq}[a]
Sb(1)	9479(1)	8918(1)	8819(1)	14(1)
Sb(2)	6509(1)	6161(1)	8790(1)	14(1)
Sb(3)	8375(1)	9150(1)	6170(1)	14(1)
Sb(4)	5619(1)	6121(1)	6175(1)	15(1)
P(1)	10065(1)	5632(1)	7346(1)	14(1)
P(2)	7117(1)	2391(1)	9916(1)	12(1)
P(3)	2333(1)	7048(1)	5024(1)	12(1)
P(4)	6311(2)	11246(1)	7741(1)	15(1)
O(1)	4892(4)	2985(4)	10151(1)	17(1)
O(2)	7930(4)	221(4)	9776(1)	16(1)
O(3)	81(4)	7866(4)	5151(1)	18(1)
O(4)	10478(4)	7244(4)	7661(2)	23(1)
O(5)	8668(4)	6698(4)	9129(1)	14(1)
O(6)	6296(4)	8405(4)	5850(1)	13(1)
O(7)	8993(4)	6265(4)	6681(2)	22(1)
O(8)	6714(4)	9920(4)	8417(2)	20(1)
O(9)	7514(4)	3428(4)	9186(1)	19(1)
O(10)	2997(4)	4927(4)	4825(1)	18(1)
O(11)	4573(4)	13009(4)	7929(2)	26(1)
O(12)	8849(5)	4703(4)	7906(2)	22(1)
O(13)	6027(4)	10151(4)	7141(2)	22(1)
O(14)	3205(4)	8164(4)	4432(2)	22(1)
O(15)	12033(4)	4038(4)	7076(2)	26(1)
O(16)	8145(4)	2870(4)	10476(2)	22(1)
O(17)	3073(4)	7182(4)	5741(2)	21(1)
O(18)	3419(5)	8425(5)	6996(2)	41(1)
O(19)	8229(4)	11764(4)	7467(2)	23(1)
N(1)	12052(5)	3178(5)	9218(2)	23(1)
N(2)	2704(5)	11768(5)	5835(2)	24(1)

Table S4 Selected bond lengths (Å) for CsSbPO.

Sb(1)-O(5)	1.995(3)	Cs(2)-O(1)#10	3.077(3)
Sb(1)-O(7)	2.000(3)	Cs(2)-O(3)#11	3.613(3)
Sb(1)-O(11)#2	2.233(3)	Cs(2)-O(4)#11	3.626(4)
Sb(1)-O(12)#3	2.136(3)	Cs(2)-O(5)	3.001(3)
Sb(2)-O(1)#6	2.122(3)	Cs(2)-O(6)#11	2.984(3)
Sb(2)-O(3)	1.943(3)	Cs(2)-O(7)	3.348(3)
Sb(2)-O(6)#3	2.394(3)	Cs(2)-O(8)#9	3.302(4)
Sb(2)-O(10)#4	2.087(3)	Cs(2)-O(9)#2	2.974(4)
Sb(2)-O(13)#7	2.440(4)	Cs(2)-O(10)#9	3.257(4)
Sb(3)-O(2)	2.046(3)	Cs(2)-O(11)#2	3.577(4)
Sb(3)-O(3)	1.967(3)	P(1)-O(1)	1.541(3)
Sb(3)-O(4)	1.990(4)	P(1)-O(5)	1.576(3)
Cs(1)-O(2)#8	3.255(3)	P(1)-O(8)	1.490(4)
Cs(1)-O(2)	3.238(4)	P(1)-O(10)	1.542(3)
Cs(1)-O(3)	3.080(3)	P(2)-O(4)	1.563(4)
Cs(1)-O(6)#3	3.183(4)	P(2)-O(6)	1.508(3)
Cs(1)-O(9)	3.152(4)	P(2)-O(12)	1.534(3)
Cs(1)-O(9)#1	3.387(4)	P(2)-O(13)	1.513(4)
Cs(1)-O(10)#4	3.256(3)	P(3)-O(2)	1.556(3)
Cs(1)-O(11)#8	3.134(3)	P(3)-O(7)	1.575(3)
Cs(1)-O(12)#3	3.700(4)	P(3)-O(9)	1.498(4)
		P(3)-O(11)	1.522(4)

Table S5 Selected bond lengths (Å) for $NH_4SbPOH_。$

Sb(1)-O(2)#1	2.105(3)	P(2)-O(2)	1.544(3)
Sb(1)-O(4)	2.497(3)	P(2)-O(9)	1.558(3)
Sb(1)-O(5)	1.940(2)	P(2)-O(16)	1.507(3)
Sb(1)-O(8)	2.126(3)	P(3)-O(3)	1.532(3)
Sb(1)-O(16)#2	2.317(3)	P(3)-O(10)	1.540(3)
Sb(2)-O(1)#3	2.150(3)	P(3)-O(14)	1.524(3)
Sb(2)-O(5)	1.942(3)	P(3)-O(17)	1.551(3)
Sb(2)-O(9)	2.026(3)	P(4)-O(8)	1.547(3)
Sb(2)-O(12)	2.257(3)	P(4)-O(11)	1.506(3)
Sb(3)-O(3)#4	2.228(3)	P(4)-O(13)	1.521(3)
Sb(3)-O(6)	1.953(3)	P(4)-O(19)	1.569(3)
Sb(3)-O(7)	2.198(3)	O(15)-H(15)	0.9351
Sb(3)-O(13)	2.299(3)	O(18)-H(18A)	0.8672
Sb(3)-O(14)#5	2.247(3)	O(18)-H(18B)	0.8550
Sb(4)-O(6)	1.939(2)	O(19)-H(19)	0.9322
Sb(4)-O(10)#6	2.086(3)	N(1)-H(1A)	0.9595
Sb(4)-O(17)	2.020(3)	N(1)-H(1B)	0.9622
Sb(4)-O(18)	2.400(4)	N(1)-H(1C)	0.9656
P(1)-O(4)	1.507(3)	N(1)-H(1D)	0.9580
P(1)-O(7)	1.534(3)	N(2)-H(2A)	0.9604
P(1)-O(12)	1.543(3)	N(2)-H(2B)	0.9550
P(1)-O(15)	1.567(3)	N(2)-H(2C)	0.9527
P(2)-O(1)	1.533(3)	N(2)-H(2D)	0.9607

Table S6 Hydrogen bonds for NH_4SbPOH [Å and °]. D, donor; H, hydrogen; A, acceptor.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(18)-H(18A)...O(13)	0.87	1.89	2.664(5)	148.2
N(1)-H(1A)...O(1)#4	0.96	2.07	2.865(4)	139.2
N(1)-H(1C)...O(11)#9	0.97	1.86	2.810(5)	165.5
N(2)-H(2A)...O(15)#10	0.96	1.95	2.885(5)	162.7
N(2)-H(2B)...O(3)#11	0.95	1.96	2.880(4)	160.9

Symmetry transformations used to generate equivalent atoms:

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

Table S7 The Distortion Index of CsSbPO and NH_4SbPOH.

compound	Group	Distortion index
$Cs_2Sb_3O(PO_4)_3$	$P(1)O_4$	0.01535
	$P(2)O_4$	0.01246
	$P(3)O_4$	0.01810
	$Sb(3)O_3$	0.01498
	$Sb(1)O_4$	0.04462
	$Sb(2)O_5$	0.08009
NHSbPOH	$P(1)O_3OH$	0.01121
	$P(2)O_3$	0.01021
	$P(3)O_4$	0.00575
	$P(4)O_3OH$	0.01442
	$Sb(1)O_5$	0.07650
	$Sb(2)O_4$	0.05231
	$Sb(3)O_5$	0.04240
	$Sb(4)O_3H_2O$	0.06833

Table S8 The obtained Born effective charges in CsSbPO.

Crystal	elemental	q_{xx}	q_{yy}	q_{zz}	$\Delta q(q_{yy}-q_{zz})$
CsSbPO	O1	-0.91603	-2.45537	-1.7271	-0.72827
	O2	-0.84124	-1.73875	-2.81918	1.08043
	O3	-2.17503	-1.77026	-0.99661	-0.77365
	O4	-3.2474	-1.10017	-1.14533	0.04516
	O5	-1.27591	-1.7733	-2.32666	0.55336
	O6	-1.36653	-1.95625	-1.23308	-0.72317
	O7	-2.03045	-1.88448	-1.08447	-0.80001
	O8	-1.35825	-1.47513	-1.4256	-0.04953
	O9	-1.48817	-1.40344	-1.69843	0.29499
	O10	-1.11705	-2.3106	-2.38719	0.07659
	O11	-2.21471	-1.28636	-1.11654	-0.16982
	O12	-2.49427	-1.90572	-1.22718	-0.67854
	O13	-1.26402	-1.17047	-3.01791	1.84744
	P1	2.91133	4.25158	3.74288	0.5087
	P2	4.30216	3.32964	3.73334	-0.4037
	P3	3.58727	3.35572	3.24701	0.10871
	Sb1	**3.16883**	**2.99614**	**2.39575**	**0.60039**
	Sb2	**2.31193**	**3.18183**	**3.89649**	**-0.71466**
	Sb3	**2.87607**	**2.31521**	**2.5791**	**-0.26389**
	Cs1	1.23771	1.48769	1.31267	0.17502
	Cs2	1.39378	1.31249	1.29804	0.01445

Table S9 The obtained Born effective charges in NH_4SbPOH.

Crystal	elemental	q_{xx}	q_{yy}	q_{zz}	$\Delta q(q_{zz}-q_{xx})$
NH_4SbPOH	H1	1.17736	0.49328	0.81375	-0.36361
	H2	0.5867	0.8708	0.73186	0.14516
	H3	1.1988	0.54596	0.3479	-0.8509
	H4	0.4155	1.29375	0.4835	0.068
	H5	0.373	0.29915	0.42278	0.04978
	H6	0.3078	0.68671	0.40959	0.10179
	H7	0.44653	0.24905	1.27572	0.82919
	H8	1.19585	0.38294	0.2368	-0.95905
	H9	0.44215	0.51601	0.56669	0.12454
	H10	0.28445	0.34642	0.2915	0.00705
	H11	0.8509	0.43462	0.41996	-0.43094
	H12	0.24715	1.17501	0.48362	0.23647
	N1	-0.8615	-0.53681	-0.88011	-0.01861
	N2	-0.60599	-0.96896	-0.52479	0.0812
	O1	-2.02166	-0.93322	-2.67769	-0.65603
	O2	-0.93863	-2.31762	-2.40679	-1.46816
	O3	-3.21667	-0.77107	-1.77503	1.44164
	O4	-1.47109	-1.92704	-1.56384	-0.09275
	O5	-1.06645	-2.92946	-0.86102	0.20543
	O6	-2.0466	-1.9053	-1.0943	0.9523
	O7	-1.0005	-1.40873	-2.82703	-1.82653
	O8	-1.75322	-1.15544	-2.15568	-0.40246
	O9	-1.01551	-2.60033	-1.67983	-0.66432
	O10	-1.30839	-1.75125	-2.36203	-1.05364
	O11	-2.20934	-1.20918	-1.65793	0.55141
	O12	-1.9359	-1.56165	-2.0024	-0.0665

	O13	-1.23923	-1.78396	-1.87557	-0.63634
	O14	-1.30875	-1.7044	-1.52378	-0.21503
	O15	-2.28941	-1.38308	-1.25139	1.03802
	O16	-1.90955	-1.29612	-1.4441	0.46545
	O17	-2.15976	-0.88138	-2.29924	-0.13948
	O18	-1.45256	-1.65803	-1.24889	0.20367
	O19	-1.07733	-1.96291	-0.99267	0.08466
	P1	3.58214	3.32151	3.86898	0.28684
	P2	3.41176	4.2061	3.71624	0.30448
	P3	4.31958	3.34718	3.89194	-0.42764
	P4	3.17373	3.46462	3.64375	0.47002
	Sb1	**2.14819**	**3.33164**	**3.14818**	**0.99999**
	Sb2	**2.34542**	**2.99525**	**3.7544**	**1.40898**
	Sb3	**3.36745**	**2.26384**	**3.27536**	**-0.09209**
	Sb4	**3.01381**	**2.46177**	**3.32159**	**0.30778**

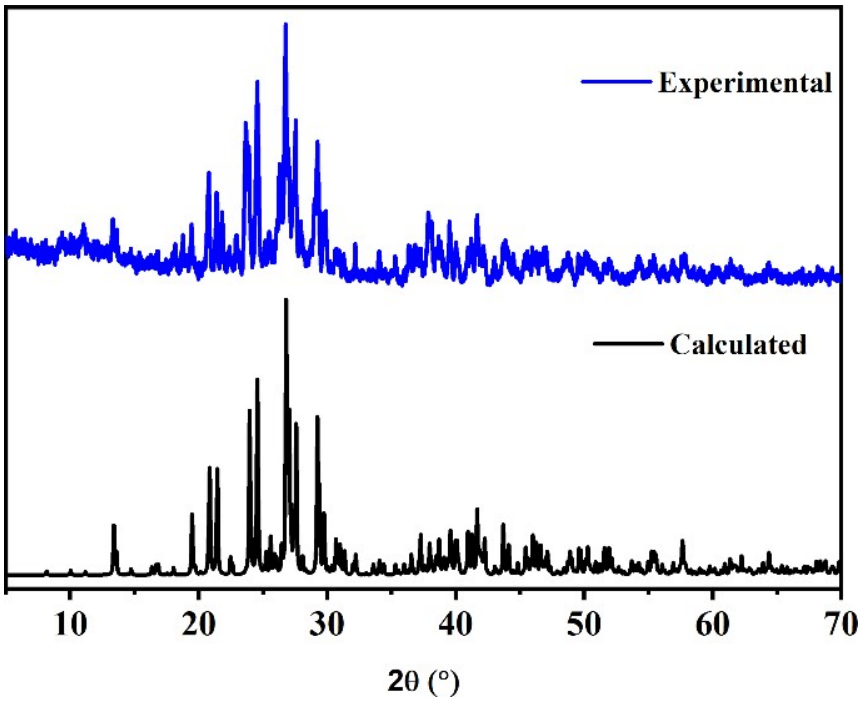

Figure S1 The XRD patterns of CsSbPO.

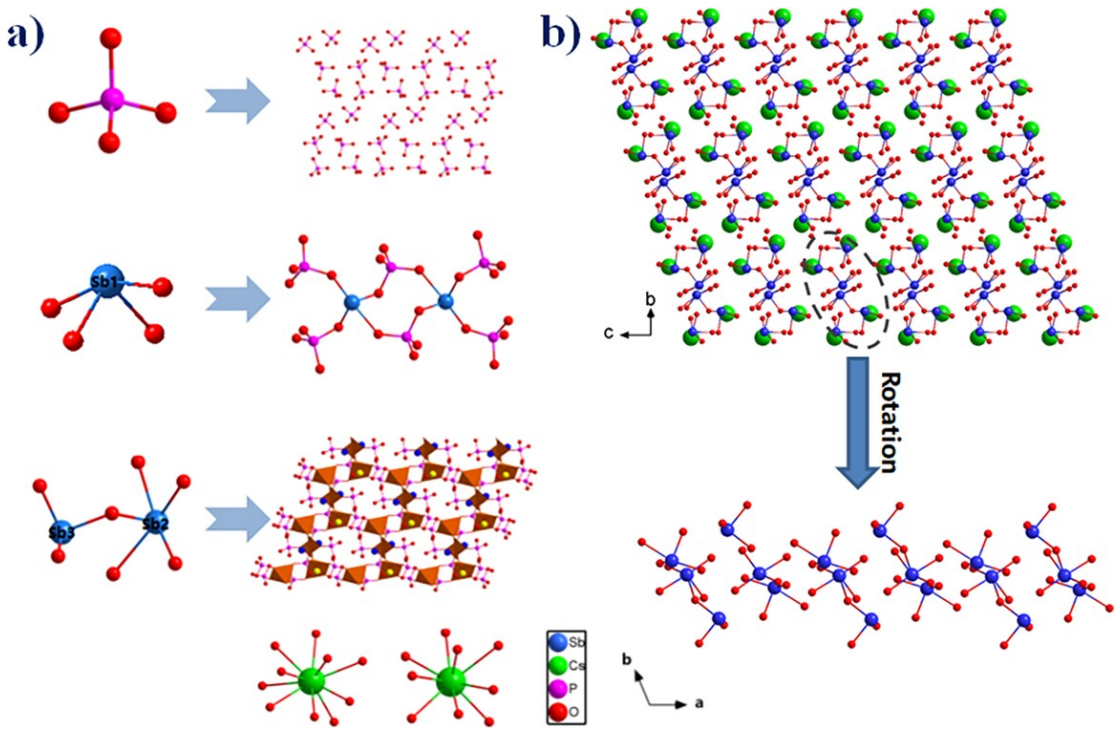

Figure S2 (a) 0D [PO_4], 0D [$Sb_2P_6O_{24}$] cluster, 2D layer of [Sb-P-O] and Coordination modes of [CsO_9] and [CsO_{10}] polyhedron; (b) Overall arrangement of cations.

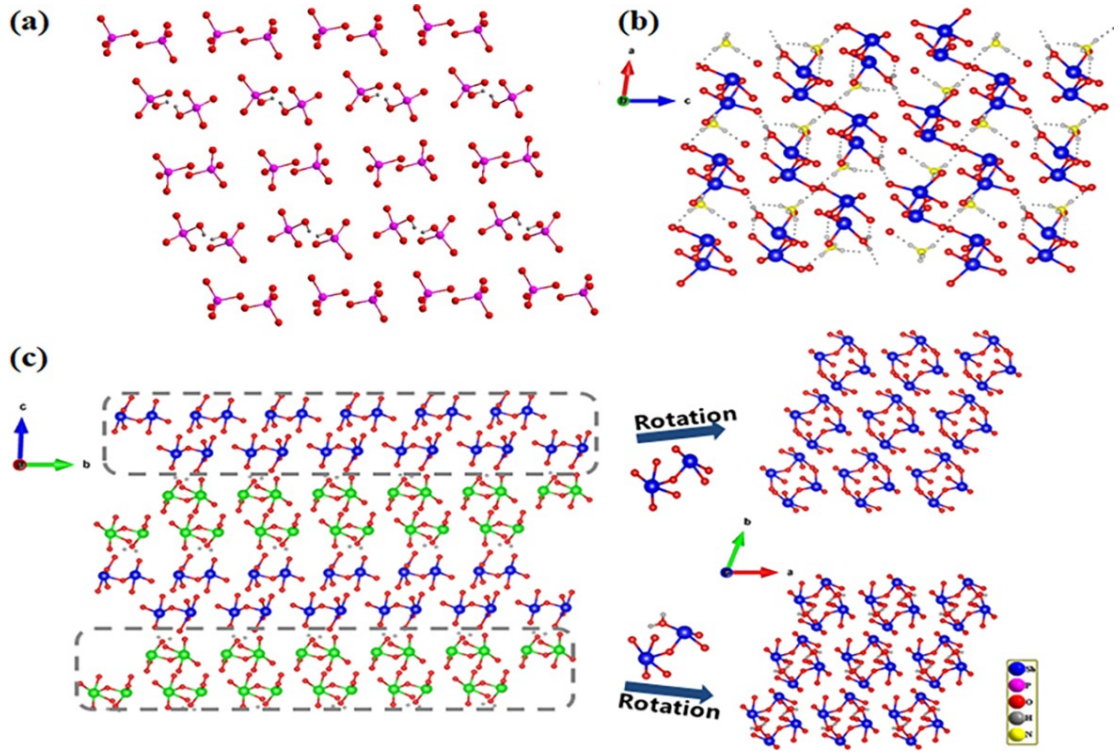

Figure S3 (a) PO_4 overall alignment; (b) Sb-O view in the ac plane and N-H arrangement; (c) Sb cation arrangement ([Sb_2O_8] dimer: blue, [$Sb_2O_7(H_2O)$] dimer: green).

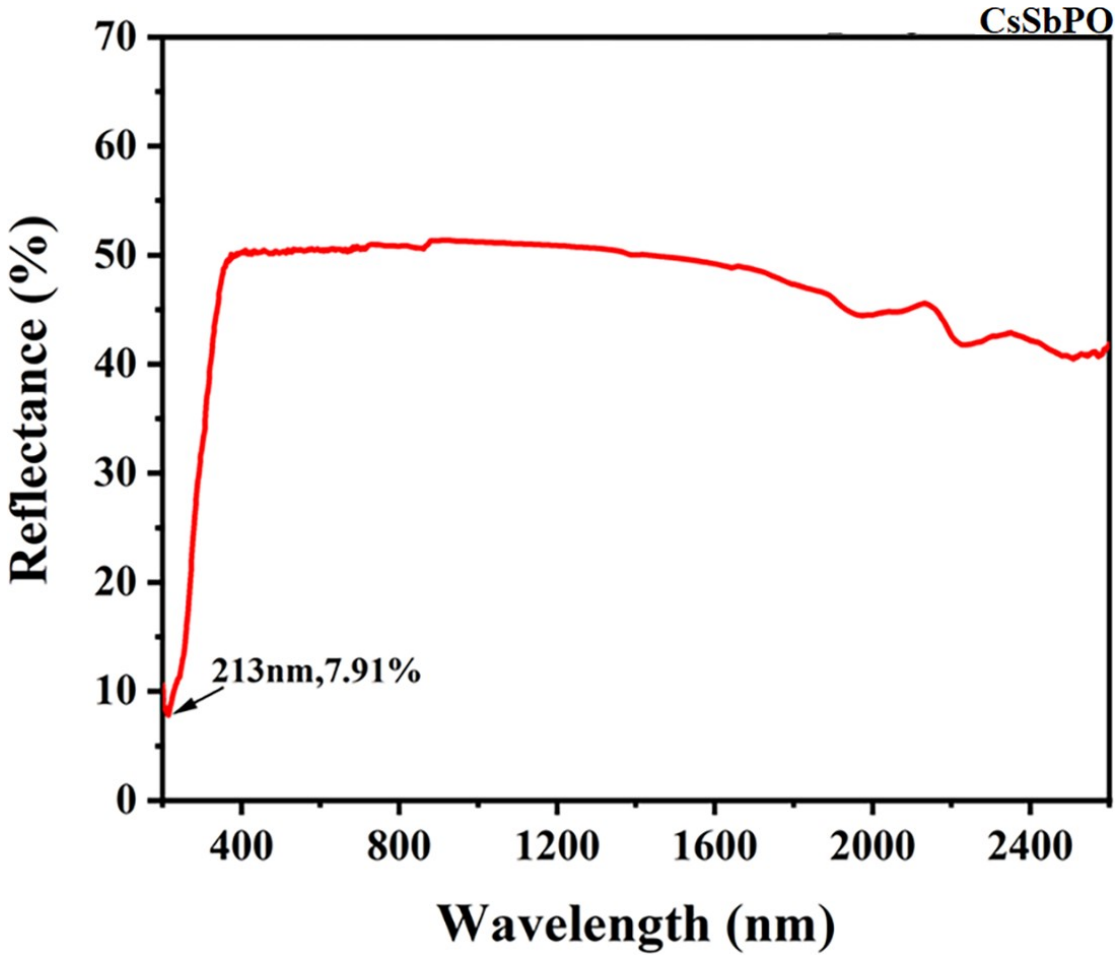

Figure S4 The UV-vis-NIR diffuse reflectance spectrum of CsSbPO.

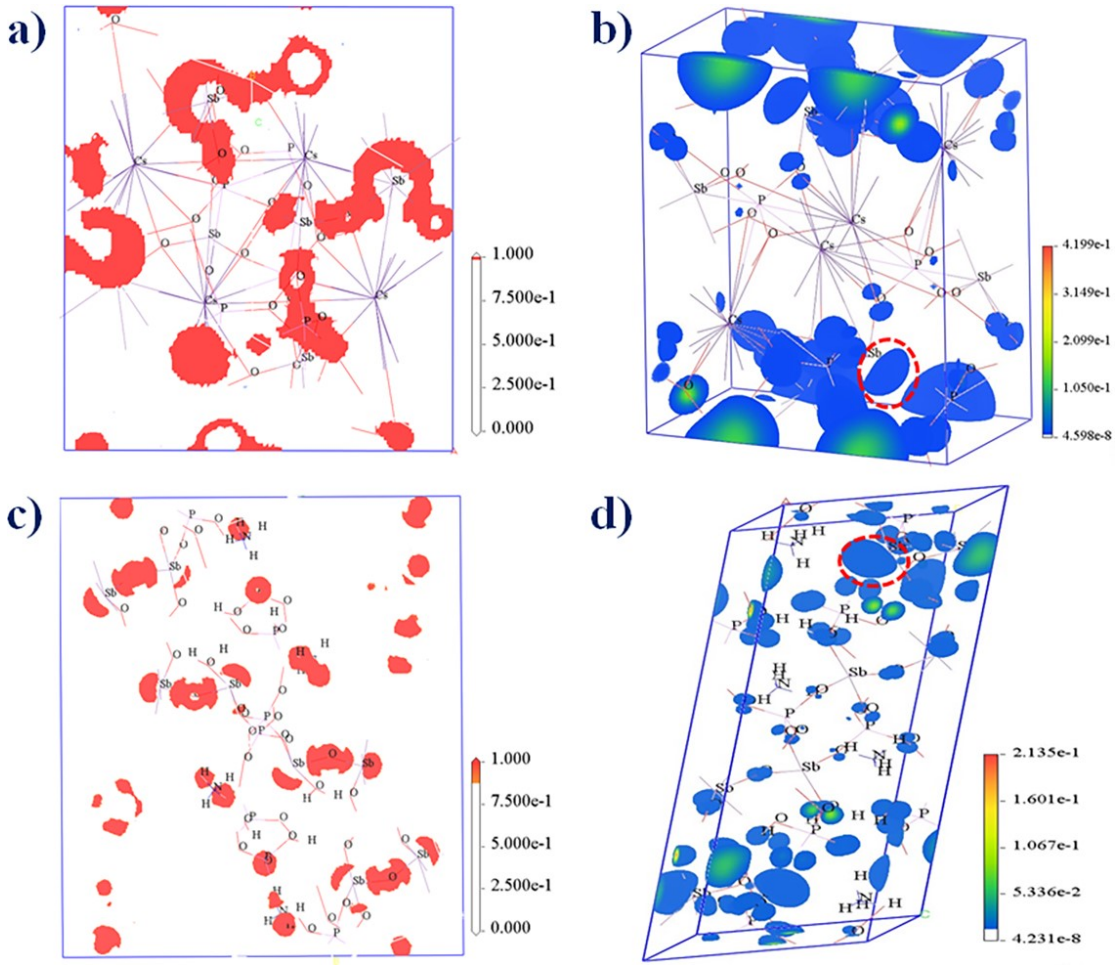

Figure S5 Election localization function (ELF) diagrams of (a) CsSbPO and (c) NH_4SbPOH. The whole crystal orbitals near the Fermi level of (b) CsSbPO and (d) NH_4SbPOH.