Electronic Supplementary Information (ESI)

Experimental and Theoretical Studies of the Ternary Thiophosphate $PbPS_3$ Featuring Ethane-Like $[P_2S_6]^{4-}$ Unit

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Theoretical Calculations of $M^{I}_{2n}/M^{II}_{n}P_nS_{3n}$ (M^{I} = K, Rb, n = 2; M^{II} = Ca, Sr, Ba, Sn, n = 2).

Utilizing the plane wave pseudopotential method implemented in the CASTEP package, the first-principles calculations of $M^{I}_{2n}/M^{II}_{n}P_nS_{3n}$ (M^{I} = K, Rb, n = 2; M^{II} = Ca, Sr, Ba, Sn, n = 2) based on the density functional theory (DFT) were carried out.[1, 2] For the $K_4P_2S_6$,[3] $Rb_4P_2S_6$,[3] $Ca_2P_2S_6$,[4] $Sr_2P_2S_6$,[4] $Ba_2P_2S_6$,[5] and $Sn_2P_2S_6$,[6] the energy cutoff was chosen to be 910.0, 720.0, 880.0, 720.0, 720.0, and 720.0 eV, respectively, and the Monkhorst-Pack k-point grid was set by 4 × 3 × 3, 3 × 3 × 4, 4 × 3 × 3, 4 × 3 × 3, 3 × 4 × 4, and 4 × 3 × 2 in the Brillouin Zone (BZ),[7, 8] respectively. In order to model the e□ective interactions between valence electrons and the atom cores, the valence electrons were set as $3s^2$ $3p^3$ configuration for P, $3s^2$ $3p^4$ for S, $3s^2$ $3p^6$ $4s^1$ for K, $4s^2$ $4p6$ $5s^1$ for Rb, $3s^2$ $3p^6$ $4s^2$ for Ca, $4s^2$ $4p^6$ $5s^2$ for Sr, $5s^2$ $5p^6$ $6s^2$ for Ba, and $5s^2$ $5p^2$ for Sn, respectively.

Table S1. Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for $PbPS_3$.

Atoms	Wyckoff position	Occupancy	*x*	*y*	*z*	U_{eq}	*BVS*
Pb(1)	4e	1	9607(1)	6172(1)	7494(1)	22(1)	1.812
P(1)	4e	1	4387(2)	6096(2)	5654(1)	9(1)	3.888
S(1)	4e	1	6551(2)	8017(2)	5561(2)	14(1)	1.973
S(2)	4e	1	1810(2)	6939(2)	4644(2)	13(1)	1.877
S(3)	4e	1	3990(2)	5052(2)	7610(2)	15(1)	1.850
GII (vu)							**0.131**

The concept of GII[9, 10] can be derived from the bond valence concepts, which represents the tension of lattice parameters and is always used to estimate the rationality of the structure. To a reliable structure, its GII value should be limited at 0.05-0.2 in general. As for the title compound, $PbPS_3$, the calculated GII value is 0.131 vu, indicating that the crystal structure was reasonable.

Table S2. Selected bond distances (Å) and angles (deg) for $PbPS_3$.

Atoms	Bond Distances (Å) or Angles (deg)	Atoms	Bond Distances (Å) or Angles (deg)
Pb(1)-S(1)	3.0100(17)	S(3)$^{\#1}$-Pb(1)-S(2)$^{\#1}$	67.24(4)
Pb(1)-S(3)$^{\#1}$	3.011(2)	S(3)$^{\#2}$-Pb(1)-S(2)$^{\#1}$	69.52(4)
Pb(1)-S(3)$^{\#2}$	3.040(2)	S(1)$^{\#3}$-Pb(1)-S(2)$^{\#1}$	140.62(4)
Pb(1)-S(1)$^{\#3}$	3.0893(19)	S(2)$^{\#4}$-Pb(1)-S(2)$^{\#1}$	140.36(3)
Pb(1)-S(2)$^{\#4}$	3.1129(17)	S(1)-Pb(1)-S(1)$^{\#4}$	134.99(3)
Pb(1)-S(2)$^{\#1}$	3.1370(18)	S(3)$^{\#1}$-Pb(1)-S(1)$^{\#4}$	69.94(4)
Pb(1)-S(1)$^{\#4}$	3.1806(19)	S(3)$^{\#2}$-Pb(1)-S(1)$^{\#4}$	74.50(4)
Pb(1)-S(2)$^{\#5}$	3.1922(19)	S(1)$^{\#3}$-Pb(1)-S(1)$^{\#4}$	73.04(5)
P(1)-S(1)	2.027(2)	S(2)$^{\#4}$-Pb(1)-S(1)$^{\#4}$	63.71(5)
P(1)-S(3)	2.020(2)	S(2)$^{\#1}$-Pb(1)-S(1)$^{\#4}$	123.68(5)
P(1)-S(2)	2.025(2)	S(1)-Pb(1)-S(2)$^{\#5}$	76.85(5)
P(1)-P(1)#5	2.213(3)	S(3)$^{\#1}$-Pb(1)-S(2)$^{\#5}$	94.92(4)
S(1)-Pb(1)-S(3)$^{\#1}$	140.89(4)	S(3)$^{\#2}$-Pb(1)-S(2)$^{\#5}$	139.08(4)
S(1)-Pb(1)-S(3)$^{\#2}$	75.25(5)	S(1)$^{\#3}$-Pb(1)-S(2)$^{\#5}$	75.30(5)
S(3)#1-Pb(1)-S(3)$^{\#2}$	88.38(3)	S(2)$^{\#4}$-Pb(1)-S(2)$^{\#5}$	124.66(3)
S(1)-Pb(1)-S(1)$^{\#3}$	122.17(4)	S(2)$^{\#1}$-Pb(1)-S(2)$^{\#5}$	74.32(5)
S(3)$^{\#1}$-Pb(1)-S(1)$^{\#3}$	91.21(4)	S(1)#4-Pb(1)-S(2)$^{\#5}$	144.33(4)
S(3)$^{\#2}$-Pb(1)-S(1)$^{\#3}$	145.52(4)	S(3)-P(1)-S(2)	114.70(9)
S(1)-Pb(1)-S(2)$^{\#4}$	77.60(5)	S(3)-P(1)-S(1)	114.93(9)
S(3)$^{\#1}$-Pb(1)-S(2)$^{\#4}$	133.56(4)	S(2)-P(1)-S(1)	110.12(10)
S(3)$^{\#2}$-Pb(1)-S(2)$^{\#4}$	77.12(5)	S(3)-P(1)-P(1)$^{\#5}$	106.29(11)
S(1)$^{\#3}$-Pb(1)-S(2)$^{\#4}$	78.39(5)	S(2)-P(1)-P(1)$^{\#5}$	106.51(10)
S(1)-Pb(1)-S(2)$^{\#1}$	73.75(5)	S(1)-P(1)-P(1)$^{\#5}$	103.18(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y-1/2,-z+3/2	#2 -x+3/2,y+1/2,-z+3/2	#3 x+1,y,z
#4 x+1/2,-y+3/2,z+1/2	#5 -x+1,-y+1,-z+1	#6 x-1,y,z
#7 x-1/2,-y+3/2,z-1/2		

Table S3. Mulliken atomic populations of $PbPS_3$.

Charge Q (in| e |)			
Atom	Pb	P	S
population	0.80	0.55	0.44 - 0.45

Table S4. Crystallographic information of $M^{I}_{2n}M^{II}_{n}P_nS_{3n}$ (M^{I} = K, Rb, n = 2; M^{II} = Ca, Sr, Ba, Sn, Pb, n = 1, 2).

Compound	Space Group	Z	Cell Parameter	P-S Unit	MS_x	Structural Dimension	ICSD Number
$K_4P_2S_6$[3]		4	a = 13.243(3) Å, b = 11.946(2) Å, c = 8.3955(17) Å, β = 91.44(3) °		KS_6, KS_7		426905
$Rb_4P_2S_6$[3]		4	a = 13.538(3) Å, b = 12.310(3) Å, c = 8.7510(18) Å, β = 92.46(3) °		RbS_7, RbS_8		426908
$Ca_2P_2S_6$[4]		2	a = 6.532(2) Å, b = 7.281(2) Å, c = 11.101(4) Å, β = 124.00(4) °		CaS_8		405192
$Sr_2P_2S_6$[4]	$P2_1/c$	2	a = 6.643(2) Å, b = 7.557(3) Å, c = 11.397(3) Å, β = 124.07(2) °	Isolated $[P_2S_6]^{4-}$	SrS_8	3D	405191
$Ba_2P_2S_6$[5]		2	a = 9.966(1) Å, b = 7.580(2) Å, c = 6.737(2) Å, β = 91.17(3) °		BaS_9		412764
$Sn_2P_2S_6$[6]		2	a = 6.518(1) Å, b = 7.463(1) Å, c = 11.475(2) Å, β = 125.72(1) °		SnS_8		72835
$PbPS_3$[a]		4	a = 6.603(3) Å, b = 7.456(4) Å, c = 9.401(5) Å, β = 91.618(6) °		PbS_8		-

[a] This work.

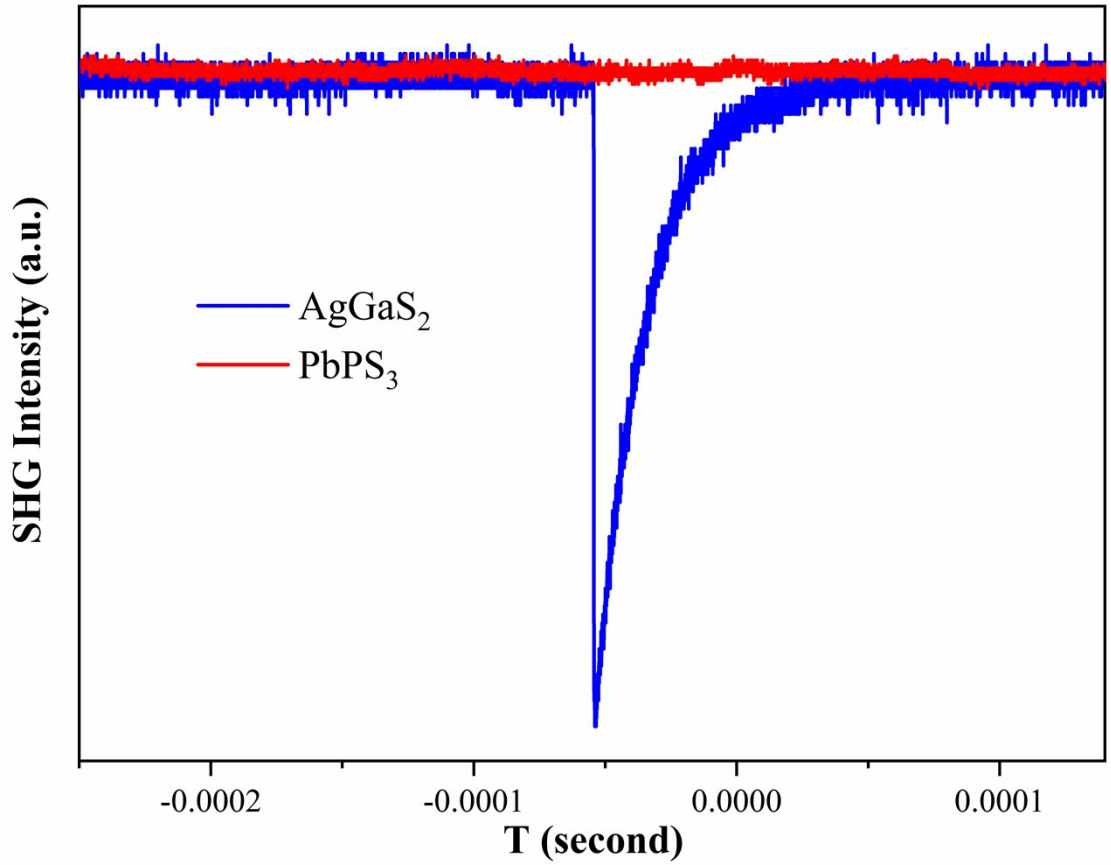

Figure S1. The results of second harmonic generation (SHG) measurement of $PbPS_3$ and $AgGaS_2$.

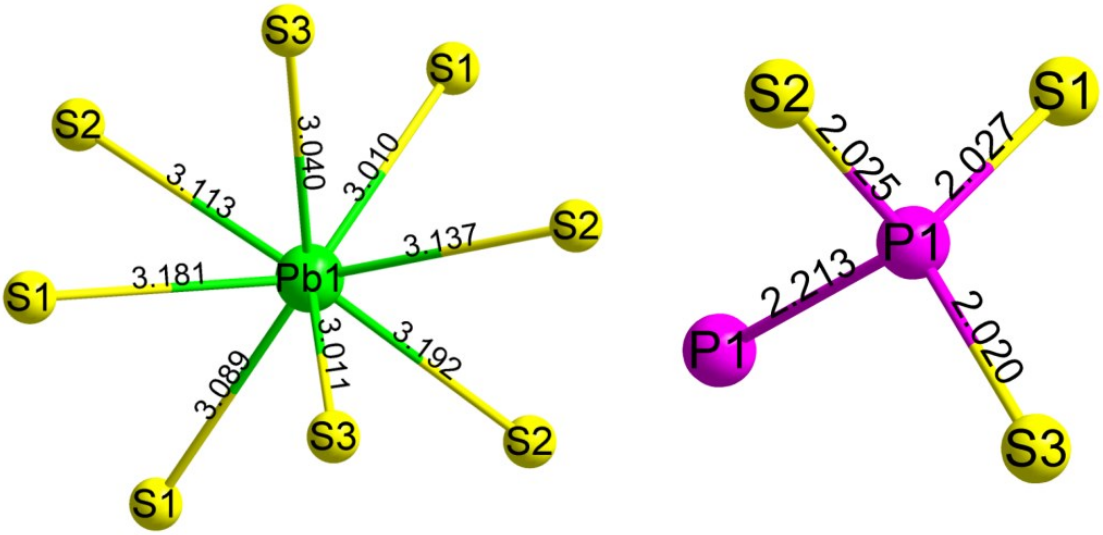

Figure S2. Coordination environments and bond lengths in $PbPS_3$.

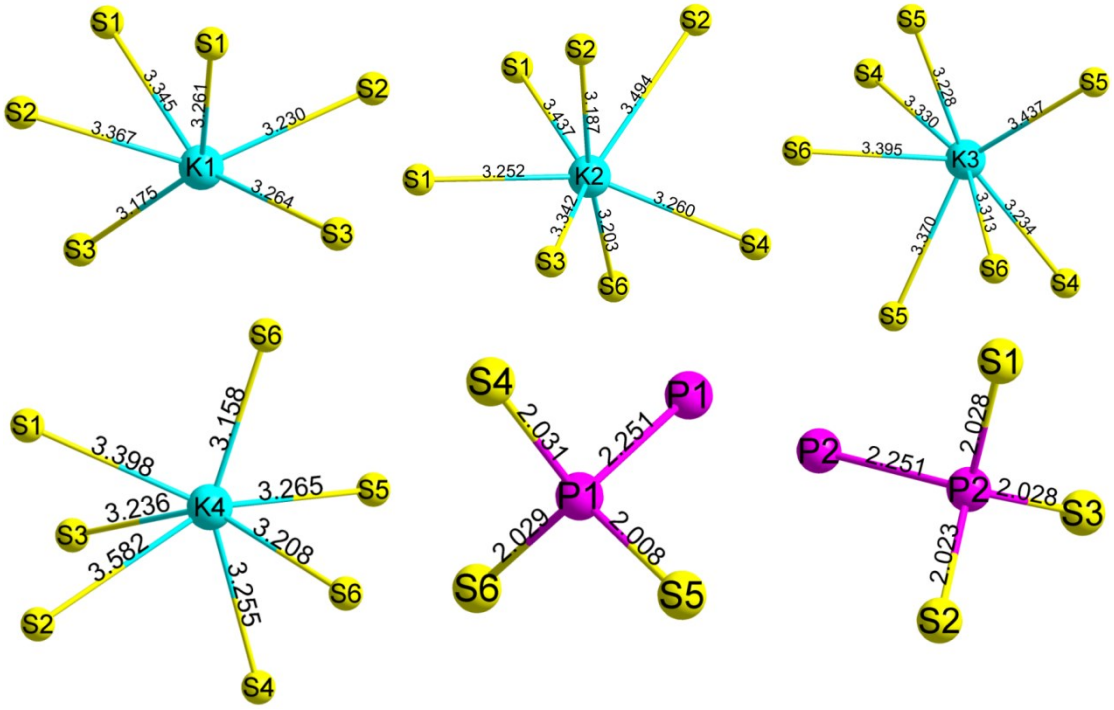

Figure S3. Coordination environments and bond lengths in $K_4P_2S_6$.

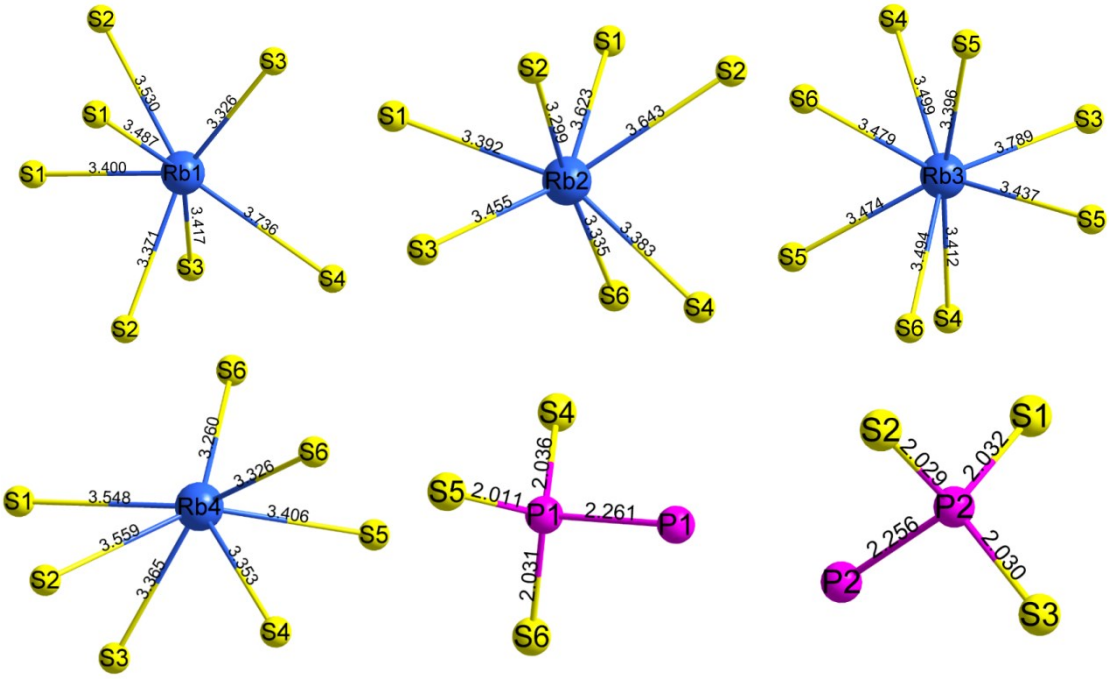

Figure S4. Coordination environments and bond lengths in $Rb_4P_2S_6$.

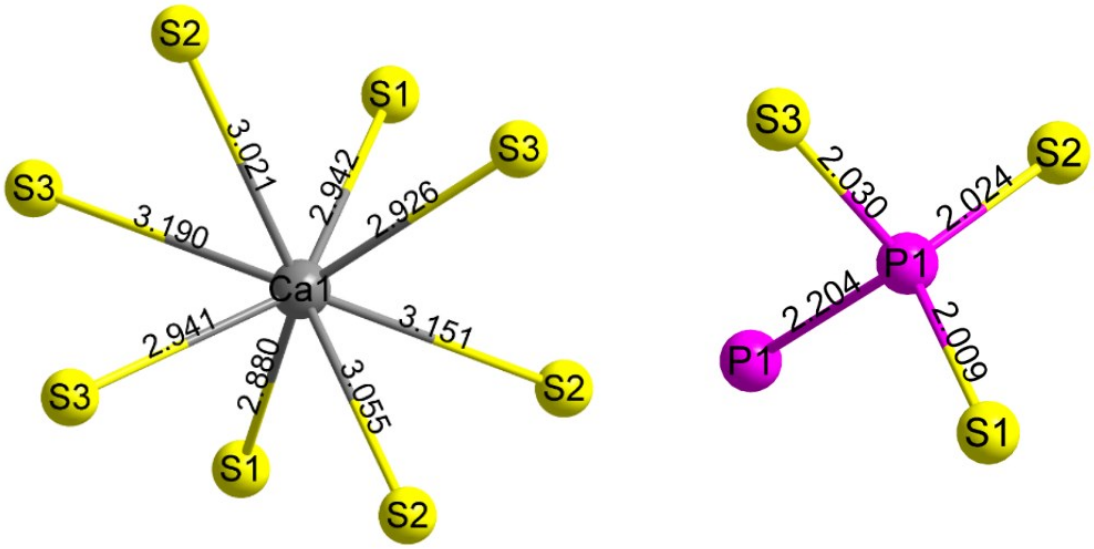

Figure S5. Coordination environments and bond lengths in $Ca_2P_2S_6$.

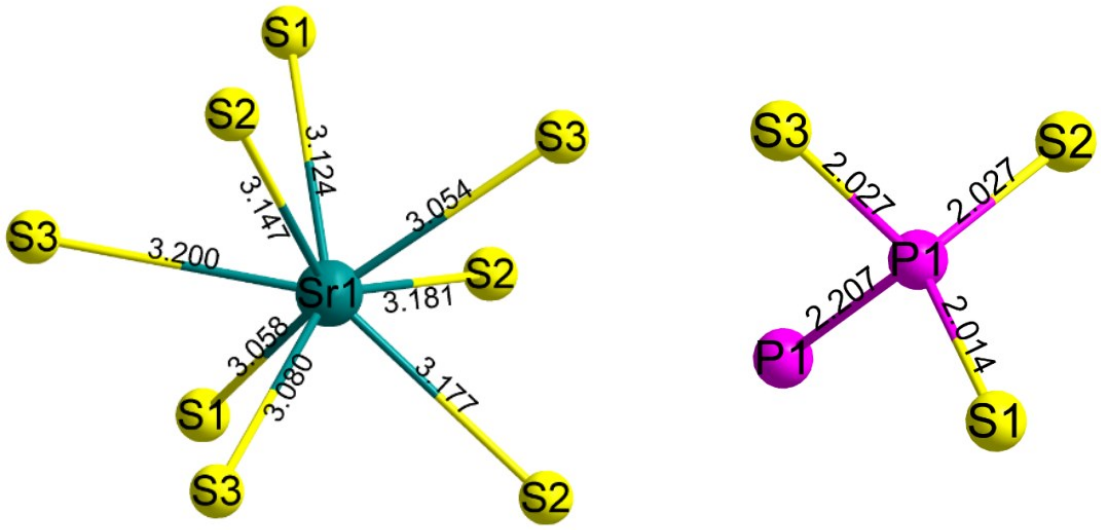

Figure S6. Coordination environments and bond lengths in $Sr_2P_2S_6$.

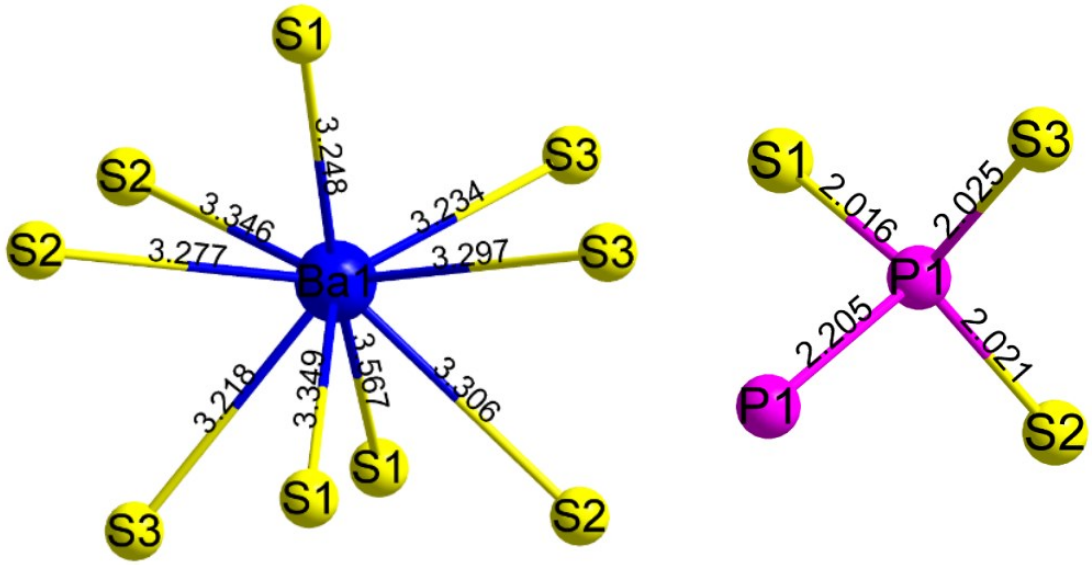

Figure S7. Coordination environments and bond lengths in $Ba_2P_2S_6$.

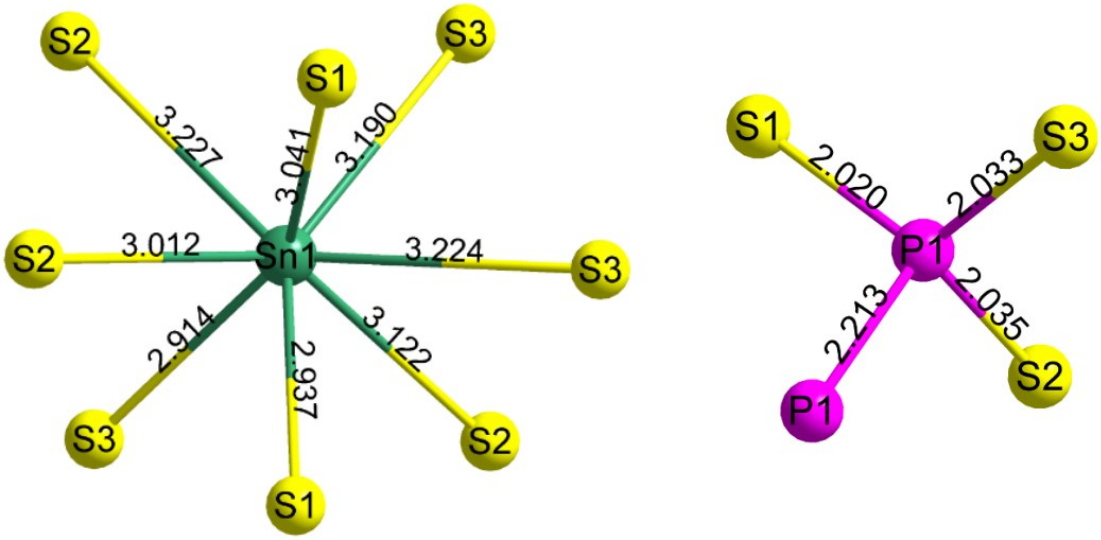

Figure S8. Coordination environments and bond lengths in $Sn_2P_2S_6$.

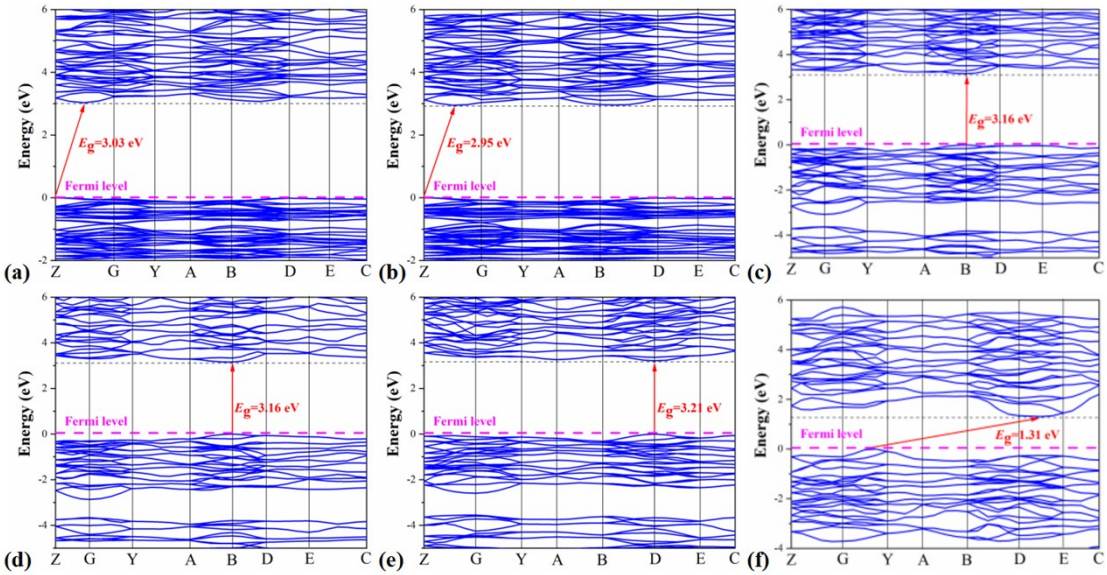

Figure S9. The calculated band gap of $K_4P_2S_6$ (a), $Rb_4P_2S_6$ (b), $Ca_2P_2S_6$ (c), $Sr_2P_2S_6$ (d), $Ba_2P_2S_6$, and $Sn_2P_2S_6$ (f).

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