SUPPORTING INFORMATION

Pb_3SBrI_3: The first Pb-based chalcohalide with multiple halogens features unique two-dimensional structure composed by diverse Pb-centered polyhedra

Mei Yan, Ru-Ling Tang, * Wenfeng Zhou, Wenlong Liu, and Sheng-Ping Guo*

School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, P. R. China

Corresponding authors: rltang@yzu.edu.cn, spguo@yzu.edu.cn

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Tables and Figures

Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (U_{eq}, Å^2 × 10^3) for Pb_3SBrI_3.

atom	Wyckoff site	*x*	*y*	*z*	U_{eq}/Å^2
Pb(1)	2*e*	3000.9(9)	7500	9323.6(7)	28.6(3)
Pb(2)	2*e*	7045.6(10)	7500	7828.8(6)	30.3(3)
Pb(3)	2*e*	2495.1(11)	2500	5444.9(7)	32.9(3)
I(1)	2*e*	9476.5(16)	2500	8671.4(12)	29.3(4)
I(2)	2*e*	-421.9(17)	2500	3725.1(12)	31.0(4)
I(3)	2*e*	4058.2(17)	2500	7685.0(11)	31.5(4)
Br(1)	2*e*	3478(2)	-2500	4209.3(16)	24.0(5)
S(1)	2*e*	6280(6)	7500	9535(4)	18.7(10)

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

Table S2. Important bond lengths (Å) and bond angles (°) for Pb_3SBrI_3.

Bond	Dist./Å	Bond	Angle/Å
Pb(1)–S(1)	2.753(5)	S(1)–Pb(1)–S(1)#1	79.48(11)
Pb(1)–S(1)#1	2.799(3)	I(1)#3–Pb(2)–I(1)	90.74(5)
Pb(1)–S(1)#2	2.799(3)	I(1)#3–Pb(2)–I(3)	159.28(5)
Pb(1)–I(1)	3.158(13)	I(1)–Pb(2)–I(3)	89.23(3)
Pb(2)–I(1)#3	3.158(13)	I(3)–Pb(2)–I(3)#3	83.60(4)
Pb(2)–I(3)	3.372(13)	S(1)–Pb(2)–I(1)	83.41(8)
Pb(2)–I(3)#3	3.372(13)	S(1)–Pb(2)–I(3)	76.00(8)
Pb(2)–S(1)	2.668(5)	I(2)–Pb(3)–I(2)#4	83.76(4)
Pb(3)–I(2)#4	3.213(13)	I(2)–Pb(3)–I(3)	153.79(5)
Pb(3)–I(2)#5	3.213(13)	I(2)#5–Pb(3)–I(3)	77.62(4)
Pb(3)–I(2)	3.211(2)	Br(1)–Pb(3)–I(2)	78.24(5)
Pb(3)–I(3)	3.302(2)	Br(1)#3–Pb(3)–I(2)#4	161.66(6)
Pb(3)–Br(1)#3	3.078(16)	Br(1)–Pb(3)–I(2)#4	85.87(4)
Pb(3)–Br(1)	3.078(16)	Br(1)–Pb(3)–I(3)	118.09(5)

Symmetry transformations used to generate equivalent atoms: #1 1-*x*, -*y*, 2-*z*; #2 1-*x*, 1-*y*, 2-*z*; #3 +*x*, 1+*y*, +*z*; #4 -*x*, -*y*, 1-*z*; #5 -*x*, 1-*y*, 1-*z*; #6 +*x*, -1+*y*, +*z*.

Table S3. Pb-based chalcohalides.

Compound	Crystal system	Space group	Pb-based units	Structural dimensionality	Ref.
$Pb_7S_2Br_{10}$	Hexagonal	$P6_3/m$	$Pb(Br/S)_3$, $PbBr_5(Br/S)_3$	3D	1
Pb_4SeBr_6	Orthorhombic	$Imm2$	$PbSeBr_6$, $PbSe_2Br_6$, $PbBr_7$	3D	2
$Pb_5S_2I_6$	Monoclinic	$C2/m$	PbI_7, $PbSI_6$, PbS_3I_3	3D	1
$Pb_2BiS_2I_3$	Orthorhombic	$Cmcm$	PbS_3, PbS_6I_3	3D	3
$Pb_2SbS_2I_3$	Orthorhombic	$Cmcm$	PbS_3, PbS_6I_3	3D	4
$Pb_{22}Sb_{26}S_{60}Cl$	Triclinic	$P\bar{1}$	PbS_5, PbS_7, PbS_6I, PbS_8	3D	5
$Pb_{23}Sb_{25}S_{60}Cl$	Triclinic	$P\bar{1}$	PbS_5, PbS_7, PbS_8, PbS_6Cl	3D	5
$Pb_{10}Sb_{10}S_{23}Cl_4$	Triclinic	$P2/m$	PbS_7, PbS_5Cl_2	3D	6
$Pb_{12.65}Sb_{11.35}S_{28.35}Cl_{2.65}$	Monoclinic	$C2/m$	$(Pb/Sb)S_3$, $(Pb/Sb)S_5$, PbS_5, PbS_6, $(Pb/Sb)S_7$, PbS_8, PbS_6Cl_2	3D	7
$Cu_{3.12}Pb_{0.12}Bi_{2.88}S_5I_2$	Orthorhombic	$Cmcm$	$(Bi/Pb)S_6$	3D	8
$Pb_{3.45}Sb_{2.55}S_{6.55}Cl_{1.45}$	Orthorhombic	$Pnma$	$PbS_2(S/Cl)_4Cl_2$, $Pb(S/Cl)_2$, $Pb(S/Cl)_2Cl$	3D	6
$Pb_{4.32}Sb_{3.68}S_{8.68}Cl_{2.32}$	Orthorhombic	$Pnma$	$(Pb/Sb)S_5$, PbS_6Cl_2, PbS_7	3D	9
$Hg_2PbI_2S_2$	Tetragonal	$P4/nnc$	PbS_4I_3	3D	10
Pb_2AsS_3I	Tetragonal	$Pnma$	PbS_4I_2, PbS_4I_3	3D	11
$Pb_4As_2S_6ICl$	Orthorhombic	$Pmn2_1$	PbS_6I_2, PbS_6I_3	3D	12
$Ba_4Ge_2PbS_8Br_2$	Orthorhombic	$Pnma$	PbS_5Br	3D	13
$Ba_4Ge_2PbSe_8Br_2$	Orthorhombic	$Pnma$	$PbSe_5Br$	3D	13
Pb_3SBrI_3	Monoclinic	$P2_1/m$	PbS_3, $PbSI_4$, $PbBr_2I_4$	2D	This work

Table S4. Chalcohalides contain multiple halogens.

Compound	Space group	Functional units	S/X ratio	Dimensionality	Ref.
$Hg_5Ag_4S_5(I/Br)_2Cl_2$	$P2_12_12_1$	$AgS_3(I/Br)$, $AgSCl(Br/I)_2$	5:4	3D	14
$Hg_3S_2Br_{1.5}Cl_{0.5}$	$C2/m$	HgS_2Br, HgS_2BrCl, HgS_2Br_2	1:1	3D	15
$Hg_3S_2Br_{1.5}Cl_{0.5}$	$Pm\bar{3}n$	HgS_2Br/Cl, $HgS_2(Br/Cl)_2$	1:1	3D	15
$Hg_3S_2Br_{0.5}Cl_{1.5}$	$C2/m$	HgS_2Cl, $HgS_2(Cl/Br)_2Br$, $HgS_2(Cl/Br)Cl$, $HgS_2(Cl/Br)$	1:1	3D	16
$Hg_3S_2Br_{0.5}Cl_{1.5}$	$Pm\bar{3}n$	$HgS_2(Cl/Br)_2Cl$, HgS_2	1:1	3D	16
$Hg_6S_4IBr_2Cl$	$Pmna$	HgS_2Cl, HgS_4, $HgS_2Br_2I_2$, HgS_2BrI_2	1:1	3D	17
$Pb_4As_2S_6ICl$	$Pma2_1$	PbS_3, PbS_2Cl, $PbAsS_6ICl$	3:1	3D	12
Pb_3SBrI_3	$P2_1/m$	PbS_3, $PbSI_4$, $PbBr_2I_4$	1:4	2D	This work

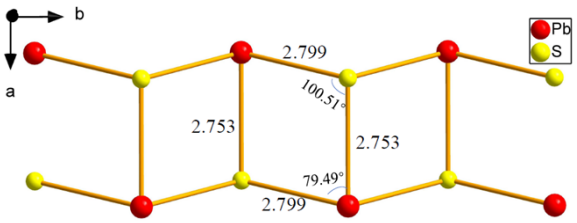

Figure S1. Unique stepped layers shape formed by adjacent parallelograms extending along the *b*-axis.

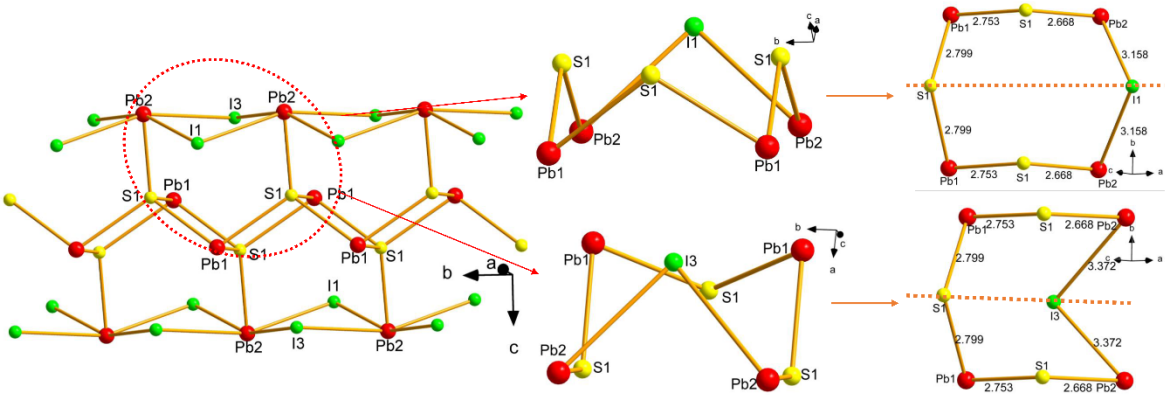

Figure S2. Two seesaw-like $[Pb_4S_3I]^+$ units in the $[Pb_3I_4S_2]_\infty$ neutral layer.

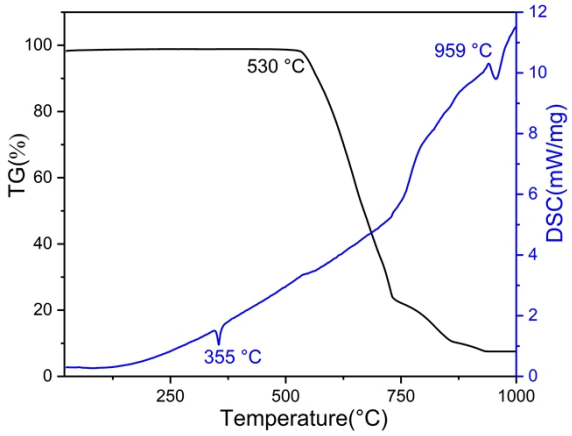

Figure S3. The TG-DSC curves of Pb_3SBrI_3.

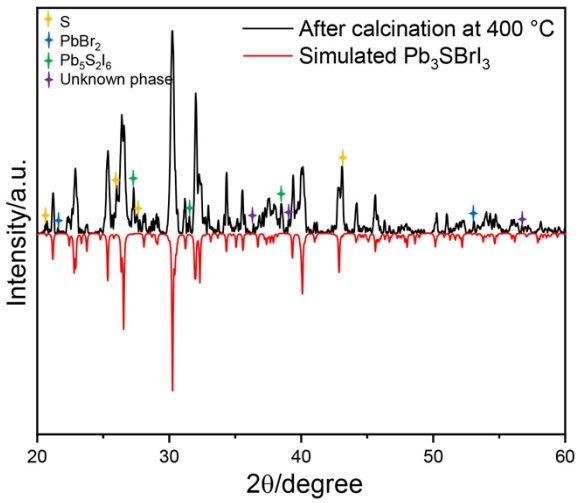

Figure S4. Simulated and experimental XRD pattern of powder calcinated at 400 ℃.

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