

Supporting Information

Synthesis, Structure, and Optical Properties of Antiperovskite-derived $\text{Ba}_2\text{MQ}_3\text{X}$ ($M = \text{As}, \text{Sb}$; $Q = \text{S}, \text{Se}$; $X = \text{Cl}, \text{Br}, \text{I}$) Chalcogenides

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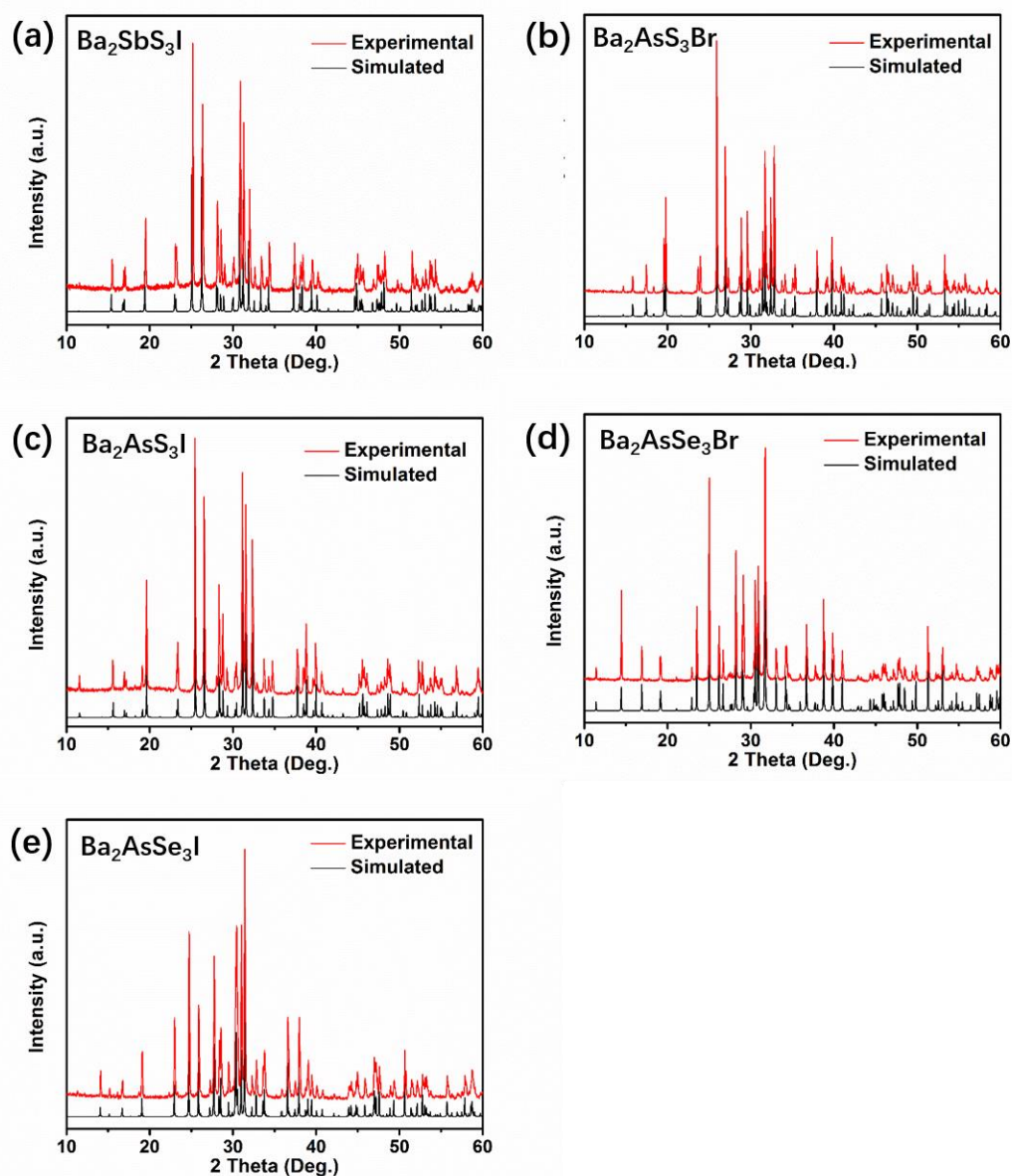
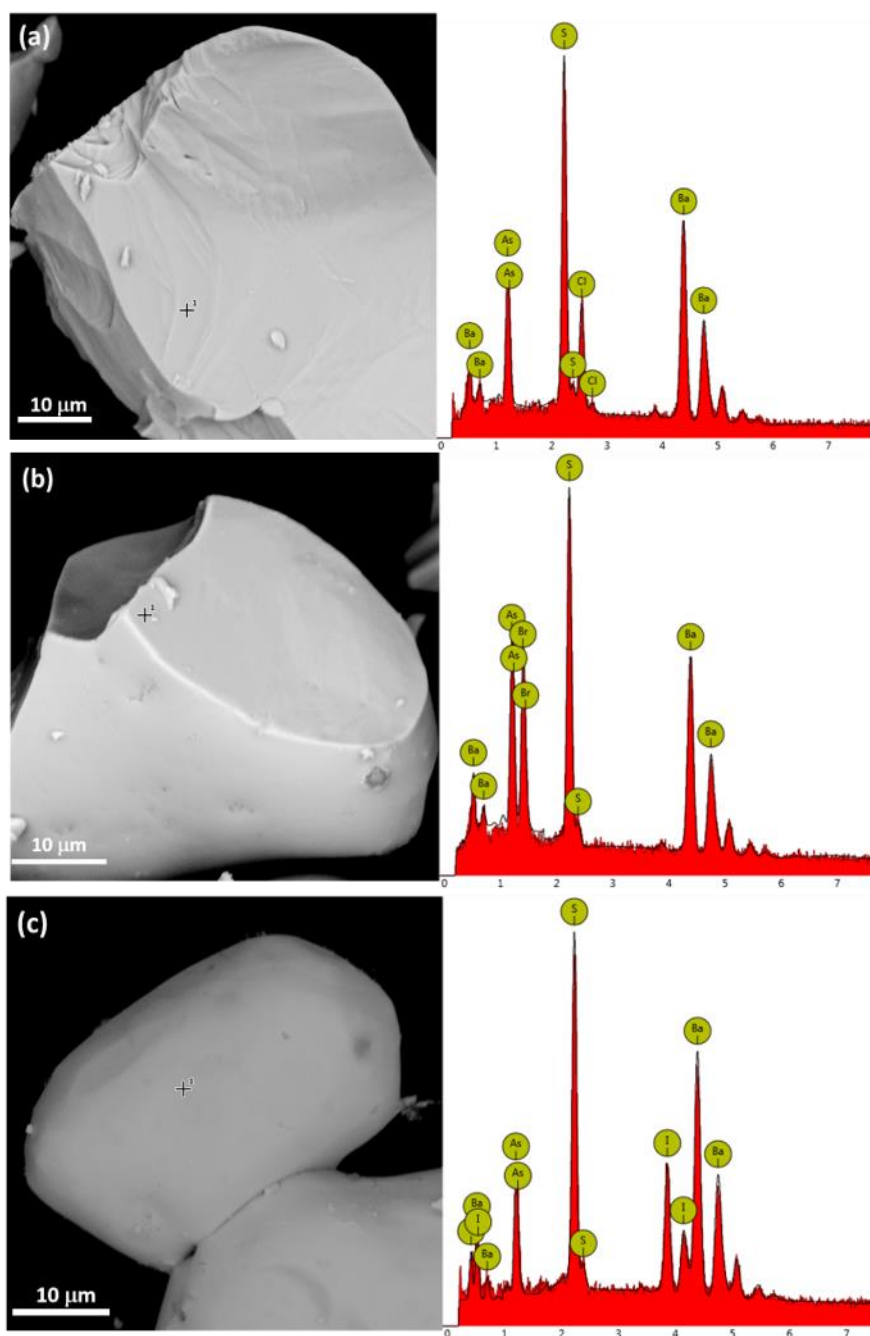


Figure S1. Simulated (black) and experimental (red) PXRD patterns of (a) $\text{Ba}_2\text{SbS}_3\text{I}$, (b) $\text{Ba}_2\text{AsS}_3\text{Br}$, (c) $\text{Ba}_2\text{AsS}_3\text{I}$, (d) $\text{Ba}_2\text{AsSe}_3\text{Br}$, (e) $\text{Ba}_2\text{AsSe}_3\text{I}$.



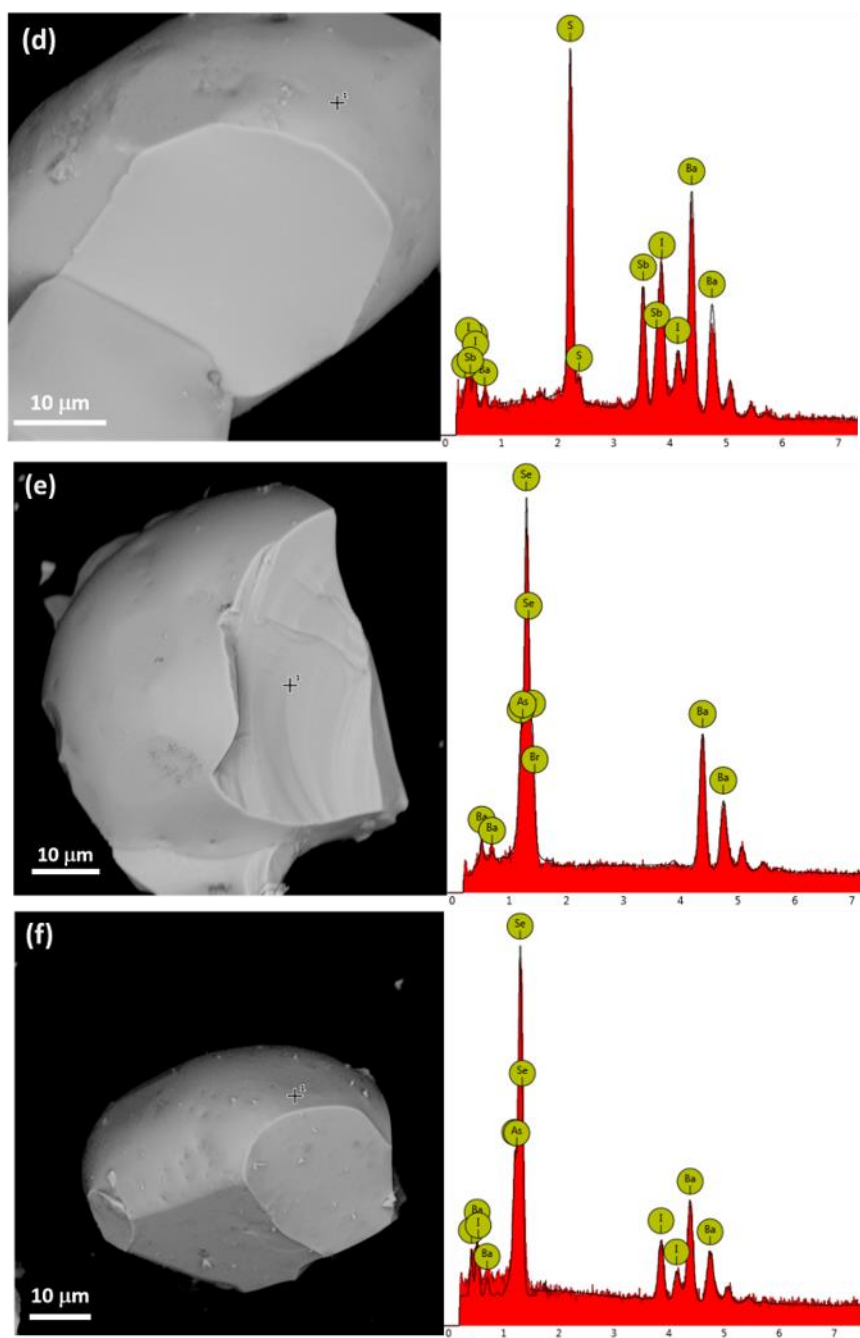


Figure S2. SEM images and EDS spectrum of (a) $\text{Ba}_2\text{AsS}_3\text{Cl}$ (b) $\text{Ba}_2\text{AsS}_3\text{Br}$ (c) $\text{Ba}_2\text{AsS}_3\text{I}$ (d) $\text{Ba}_2\text{SbS}_3\text{Cl}$ (e) $\text{Ba}_2\text{AsSe}_3\text{Br}$ and (f) $\text{Ba}_2\text{AsSe}_3\text{I}$

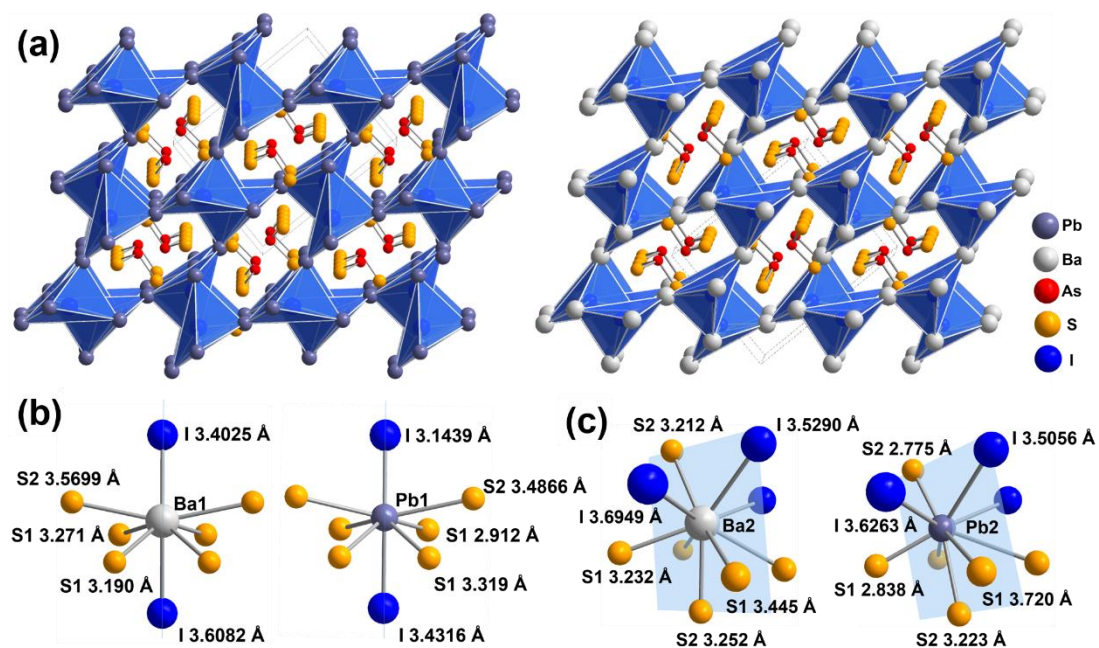


Figure S3. Schematic diagrams of (a) crystal structures of $\text{Pb}_2\text{AsS}_3\text{I}$ and $\text{Ba}_2\text{AsS}_3\text{I}$ and the coordination environments of (b) Pb1 and Ba1, (c) Pb2 and Ba2. Light blue lines and planes represent the symmetry element m perpendicular to the b -axis.

Table S1 Selected bond lengths (Å) and angles (°) for Ba₂AsS₃X (X = Cl, Br, I),
Ba₂AsSe₃X (X = Br, I) and Ba₂SbS₃I

Ba ₂ AsS ₃ Cl	Ba1-S1 × 2	3.1755(7)	Ba2-S2	3.117(2)
	Ba1-S1 × 2	3.1822(7)	Ba2-S2	3.218(2)
	Ba1-S2 × 2	3.4679(2)	Ba2-S1 × 2	3.3100(7)
	Ba1-Cl	3.154(2)	Ba2-S1 × 2	3.4230(7)
	Ba1-Cl	3.514(2)	Ba2-Cl	3.214(2)
	As-S1 × 2	2.2296(7)	Ba2-Cl × 2	3.5378(3)
	As-S2	2.228(2)		
	S1-As-S1	97.93(4)	S1-As-S2 × 2	99.82(3)
Ba ₂ AsS ₃ Br	Ba1-S1 × 2	3.1776(7)	Ba2-S2	3.230(2)
	Ba1-S1 × 2	3.2129(7)	Ba2-S2	3.1477(9)
	Ba1-S2 × 2	3.4987(4)	Ba2-S1 × 2	3.2728(7)
	Ba1-Br	3.2585(5)	Ba2-S1 × 2	3.4274(7)
	Ba1-Br	3.5352(5)	Ba2-Br	3.3466(7)
	As-S1 × 2	2.2351(7)	Ba2-Br × 2	3.5825(4)
	As-S2	2.232(2)		
	S1-As-S1	97.09(2)	S1-As-S2 × 2	99.86(2)
Ba ₂ AsS ₃ I	Ba1-S1 × 2	3.190(2)	Ba2-S2	3.212(2)
	Ba1-S1 × 2	3.271(2)	Ba2-S2	3.252(2)
	Ba1-S2 × 2	3.5699(4)	Ba2-S1 × 2	3.232(2)
	Ba1-I	3.4025(7)	Ba2-S1 × 2	3.445(2)
	Ba1-I	3.6082(7)	Ba2-I	3.5290(6)
	As-S1 × 2	2.240(2)	Ba2-I × 2	3.6949(3)
	As-S2	2.236(2)		
	S1-As-S1	94.04(7)	S1-As-S2 × 2	99.93(5)

Ba ₂ AsSe ₃ Br	Ba1-Se1 × 2	3.3125(3)	Ba2-Se2	3.2336(4)
	Ba1-Se1 × 2	3.2986(3)	Ba2-Se2	3.3202(5)
	Ba1-Se2 × 2	3.6242(2)	Ba2-Se1 × 2	3.4157(3)
	Ba1-Br	3.2815(5)	Ba2-Se1 × 2	3.4974(3)
	Ba1-Br	3.6346(5)	Ba2-Br	3.4974(3)
	As-Se1 × 2	2.3733(4)	Ba2-Br × 2	3.6992(2)
	As-Se2	2.3703(6)		
	Se1-As-Se1	97.03(2)	Se1-As-Se2×2	99.58(2)
Ba ₂ AsSe ₃ I	Ba1-Se1 × 2	3.3040(4)	Ba2-Se2	3.2927(5)
	Ba1-Se1 × 2	3.3627(4)	Ba2-Se2	3.3459(6)
	Ba1-Se2 × 2	3.6822(4)	Ba2-Se1 × 2	3.3677(4)
	Ba1-I	3.4358(6)	Ba2-Se1 × 2	3.5104(4)
	Ba1-I	3.6923(7)	Ba2-I	3.5394(4)
	As-Se1 × 2	2.3804(4)	Ba2-I × 2	3.7839(4)
	As-Se2	2.3750(5)		
	Se1-As-Se1	95.78(2)	Se1-As-Se2×2	99.68(2)
Ba ₂ SbS ₃ I	Ba1-S1 × 2	3.2199(7)	Ba2-S2	3.195(2)
	Ba1-S1 × 2	3.2429(7)	Ba2-S2	3.290(2)
	Ba1-S2 × 2	3.6608(3)	Ba2-S1 × 2	3.2514(7)
	Ba1-I	3.5835(4)	Ba2-S1 × 2	3.4990(7)
	Ba1-I	3.4249(4)	Ba2-I	3.5824(4)
	Sb-S1 × 2	2.4080(7)	Ba2-I × 2	3.7677(2)
	Sb-S2	2.389(2)		

	S1-Sb-S1	93.25(4)	S1-Sb-S2 ×2	97.41(2)
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Table S2 Element percentages of title compounds identified by EDS analysis

	Ba	M (As/Sb)	Q (S/Se)	X (Cl/Br/I)
Ba ₂ AsS ₃ Cl	33.4	19.6	36.2	10.8
Ba ₂ AsS ₃ Br	28.7	19.9	35.3	16.1
Ba ₂ AsS ₃ I	32.4	18.2	33.9	15.5
Ba ₂ SbS ₃ I	33.5	15.6	34.6	16.3
Ba ₂ AsSe ₃ Br	27.8	16.1	41.8	14.3
Ba ₂ AsSe ₃ I	21.3	21.7	46.2	10.8

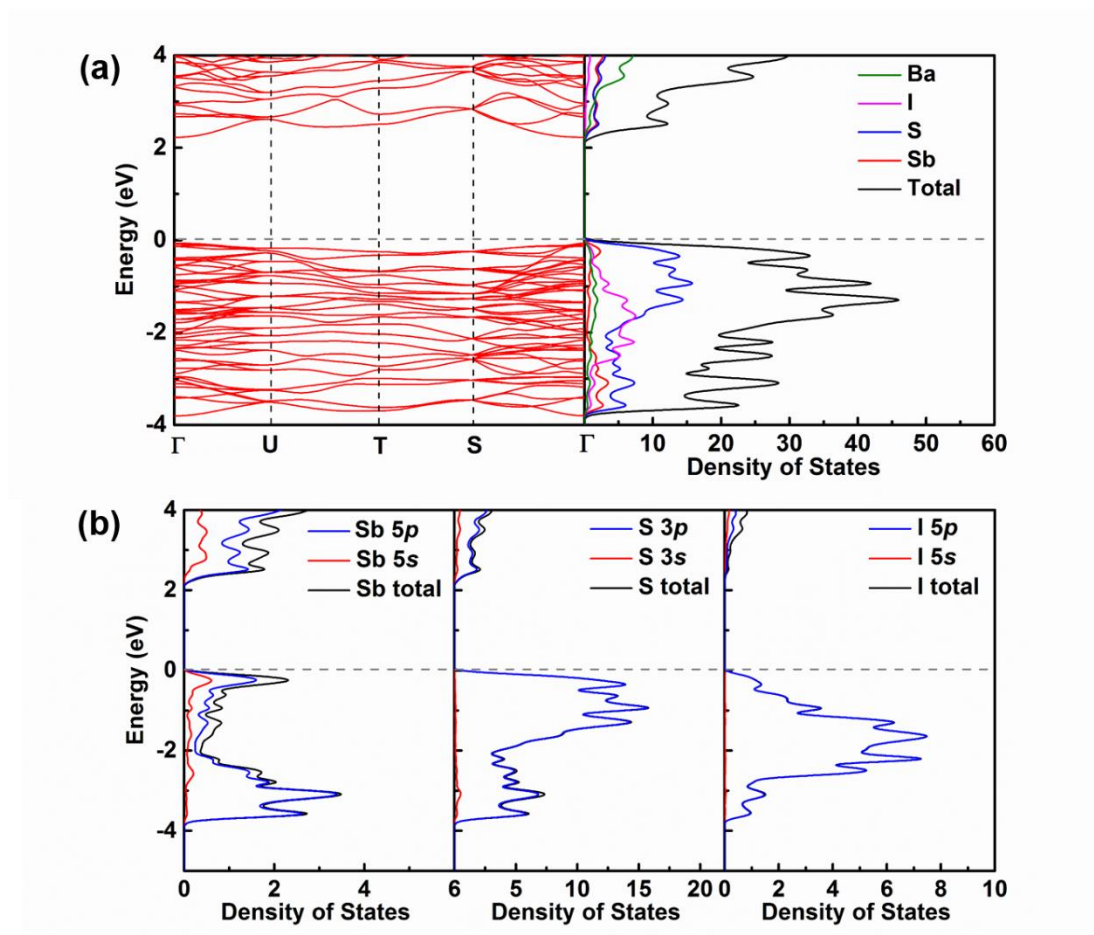


Figure S4. (a) Band structure (left) and DOS (right) of Ba₂SbS₃I. (b) Partial DOS of Sb, S and I.

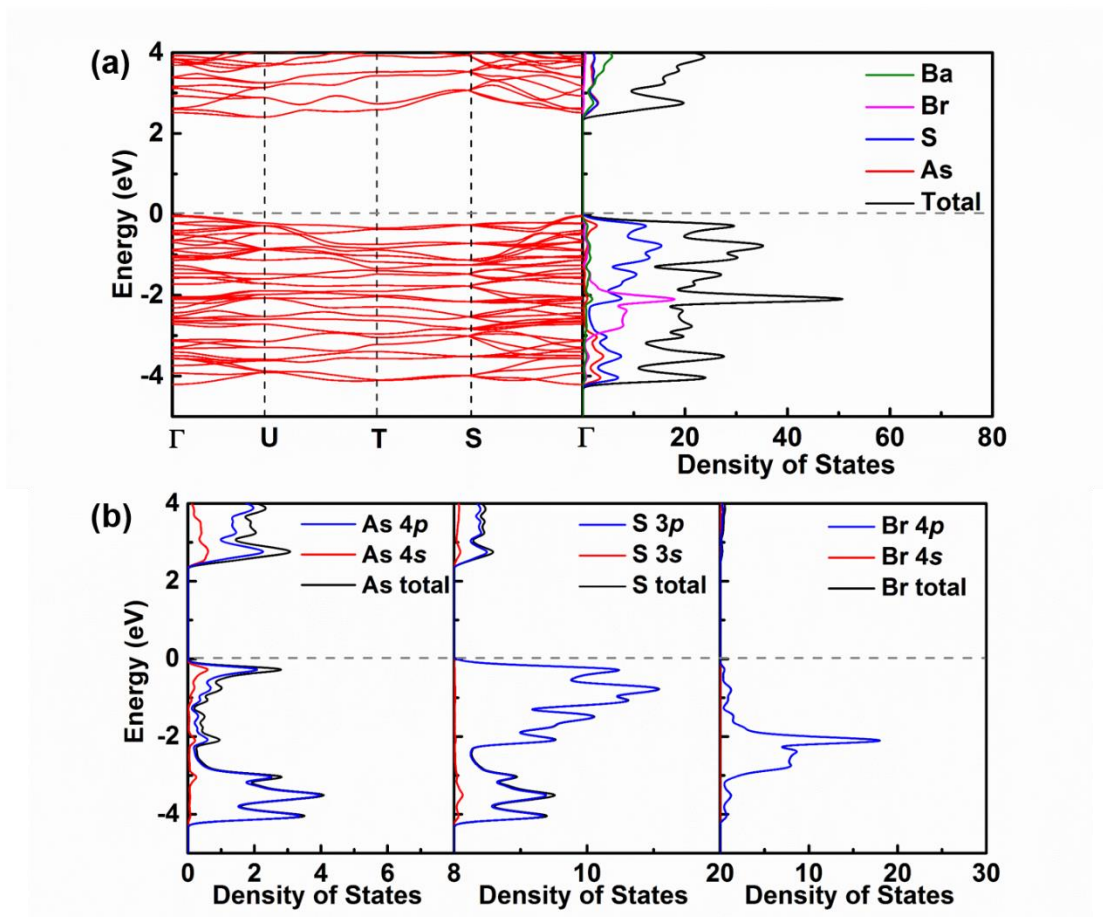


Figure S5. (a) Band structure (left) and DOS (right) of $\text{Ba}_2\text{AsS}_3\text{Br}$. (b) Partial DOS of As, S and Br

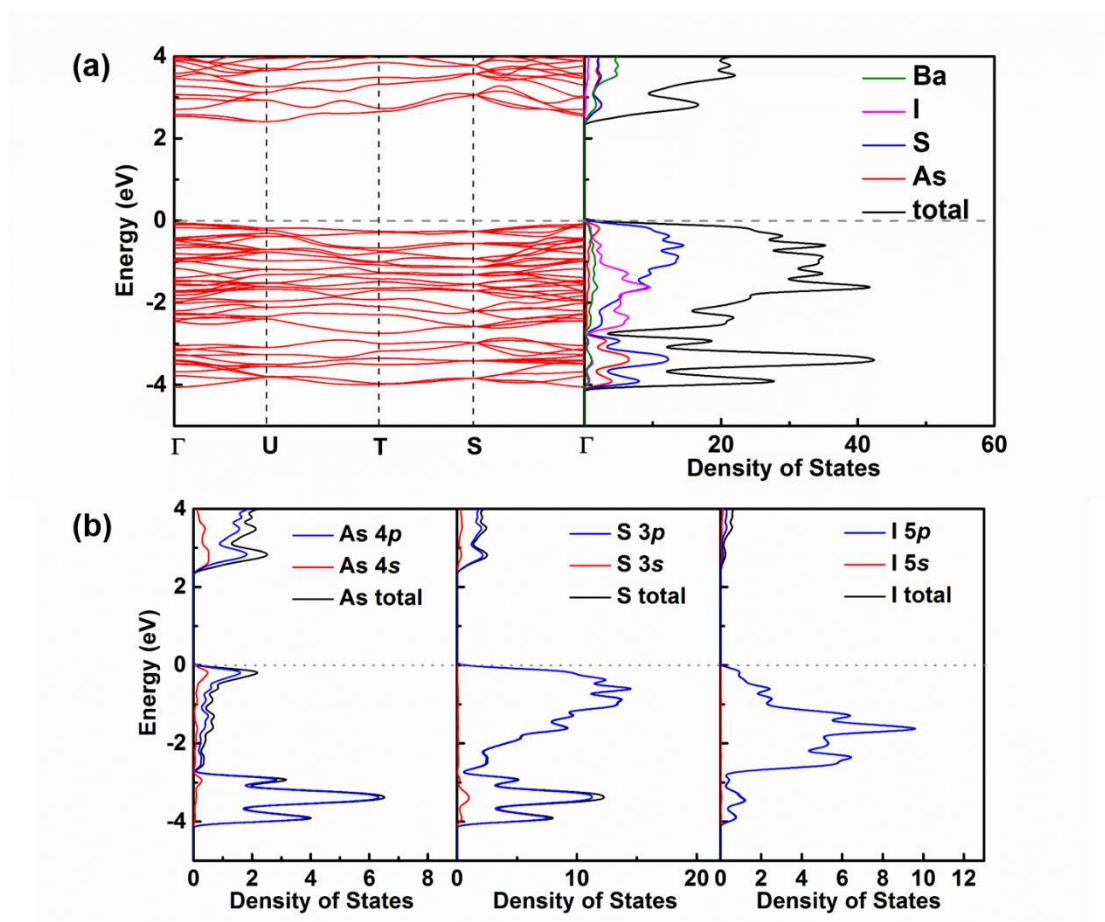


Figure S6. (a) Band structure (left) and DOS (right) of $\text{Ba}_2\text{AsS}_3\text{I}$. (b) Partial DOS of As, S and I.

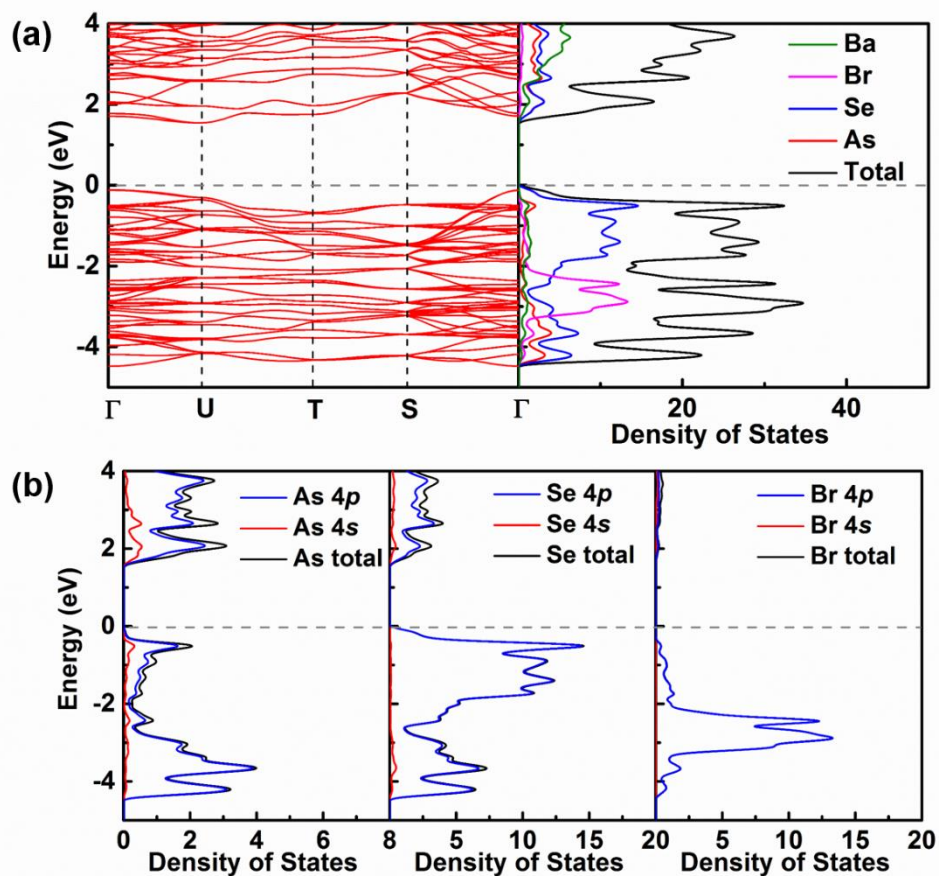


Figure S7. (a) Band structure (left) and DOS (right) of $\text{Ba}_2\text{AsSe}_3\text{Br}$. (b) Partial DOS of As, Se and Br.

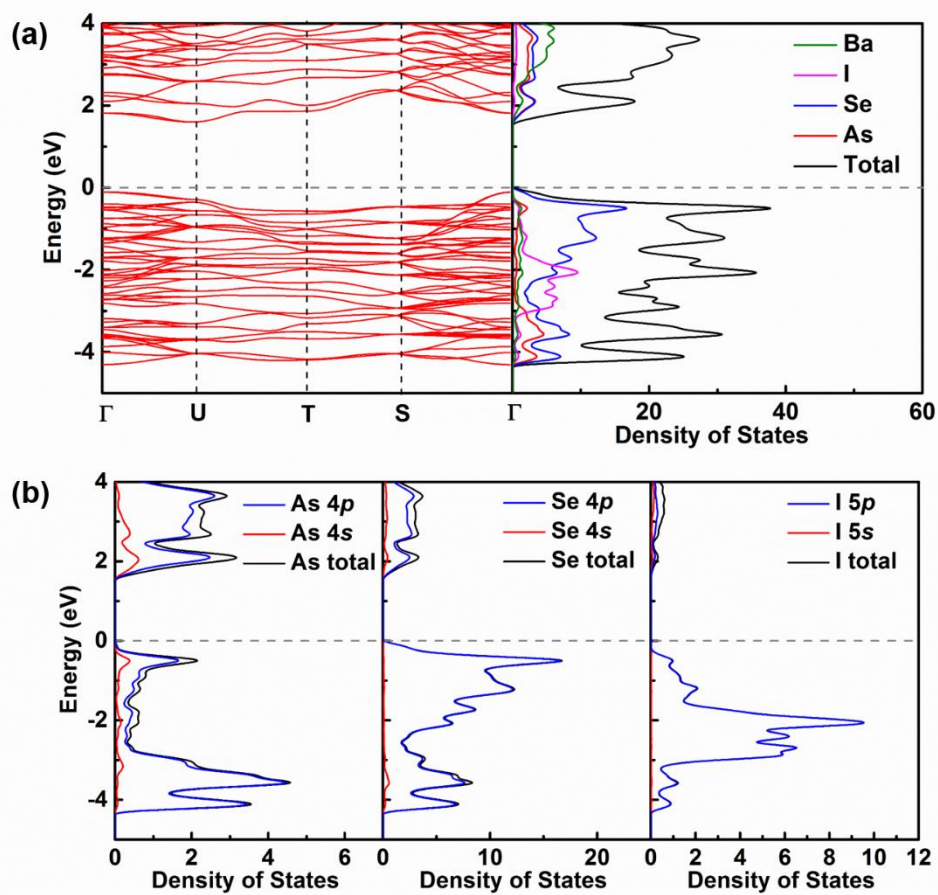


Figure S8. (a) Band structure (left) and DOS (right) of $\text{Ba}_2\text{AsSe}_3\text{I}$. (b) Partial DOS of As, Se and I.

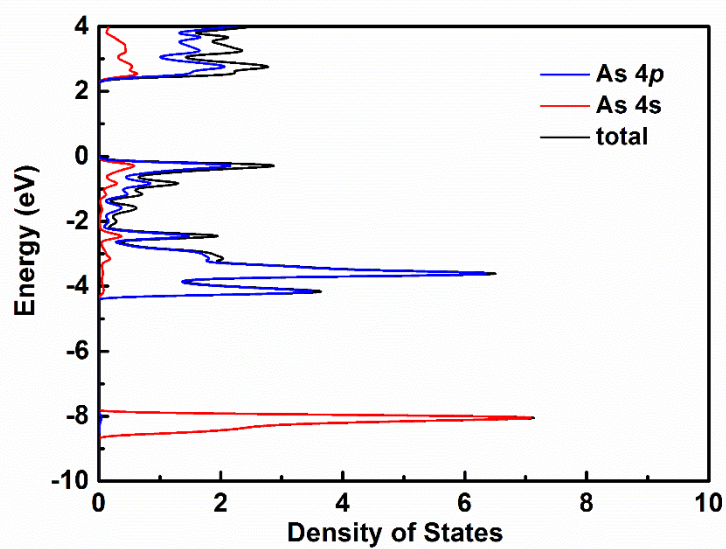


Figure S9. Partial DOS of As in $\text{Ba}_2\text{AsS}_3\text{Cl}$ in larger energy range.