Two new members in the quaternary Cs−Ag−As−S family with different arrangements of Ag–S and As–S asymmetric building units: syntheses, structures, and theoretical studies

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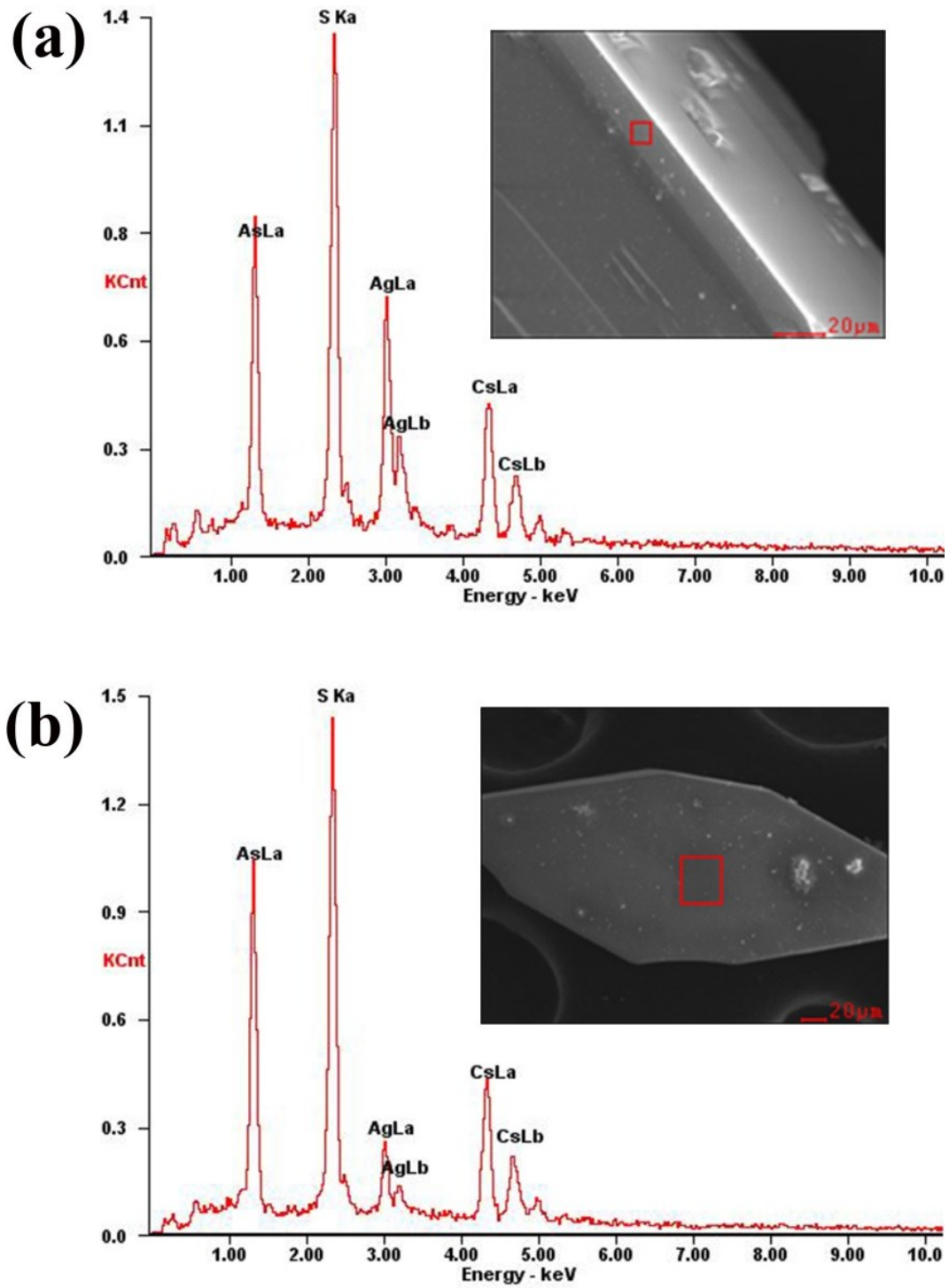

Figure S1. EDX analysis of (a) **I** and (b) **II**.

Point-1				Point-2			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
As L	20.05	45.14	4.94	As L	19.25	43.72	4.82
S K	19.02	18.33	2.00	S K	20.09	19.53	2.15
Ag L	27.25	18.24	1.99	Ag L	27.55	18.60	2.05
Cs L	33.68	18.29	2	Cs L	33.11	18.14	2
Total	100.00			Total	100.00		
Point-3				Point-4			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
As L	20.12	45.15	5.01	As L	19.01	43.43	4.62
S K	19.58	18.81	2.09	S K	19.88	19.44	2.07
Ag L	27.02	18.03	2.00	Ag L	26.97	18.32	1.95
Cs L	33.28	18.02	2	Cs L	34.14	18.82	2
Total	100.00			Total	100.00		
Point-5							
Element	Weight%	Atomic%	Formula				
As L	20.23	45.33	5.03	Average formula of **I**: $Cs_2Ag_{2.0\,(7)}\ As_{1.9\,(9)}\ S_{4.8\,(8)}$			
S K	19.52	18.73	2.08				
Ag L	26.92	17.93	1.99				
Cs L	33.33	18.01	2				
Total	100.00						

Point-1				Point-2			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
As L	24.13	49.86	8.15	As L	23.95	49.79	7.87
S K	28.85	25.51	4.17	S K	28.01	24.92	3.94
Ag L	10.22	6.28	1.03	Ag L	10.19	6.30	0.99
Cs L	36.80	18.35	3	Cs L	37.85	18.99	3
Total	100.00			Total	100.00		
Point-3				Point-4			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
As L	23.88	49.73	7.77	As L	24.52	50.62	8.05
S K	27.96	24.92	3.89	S K	27.55	24.34	3.87
Ag L	9.92	6.14	0.96	Ag L	10.06	6.17	0.98
Cs L	38.24	19.21	3	Cs L	37.87	18.86	3
Total	100.00			Total	100.00		
Point-5							
Element	Weight%	Atomic%	Formula				
As L	24.22	50.09	8.10	Average formula of **II**: $Cs_3Ag_{1.0\,(1)}\ As_{3.9\,(9)}\ S_{7.9\,(8)}$			
S K	28.21	24.97	4.04				
Ag L	10.38	6.38	1.03				
Cs L	37.19	18.56	3				
Total	100.00						

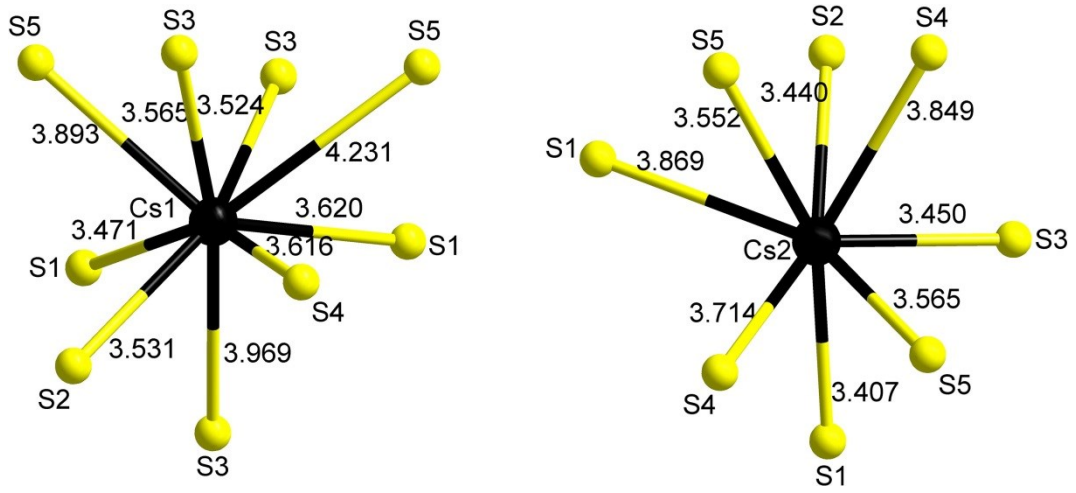

Figure S2. Coordination environment of Cs atoms including Cs−S bonds in the compound **I**.

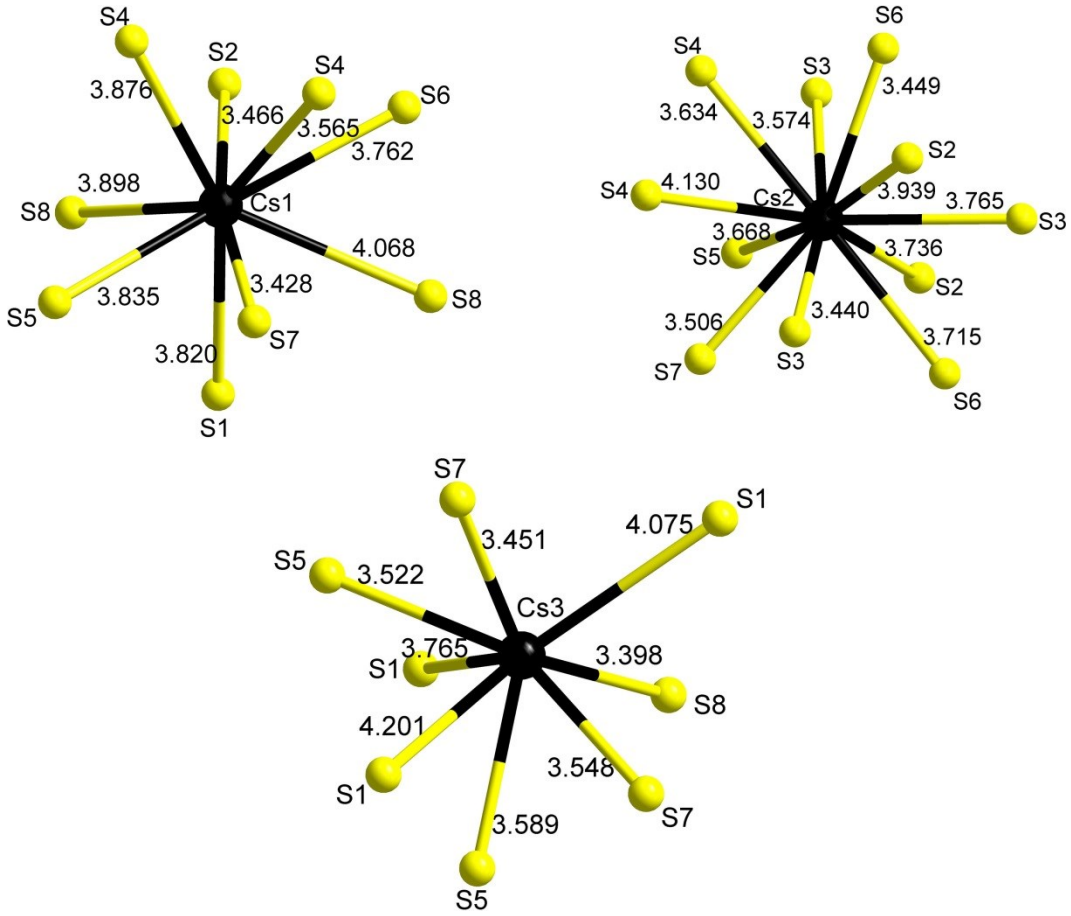

Figure S3. Coordination environment of Cs atoms including Cs−S bonds in the compound **II**.

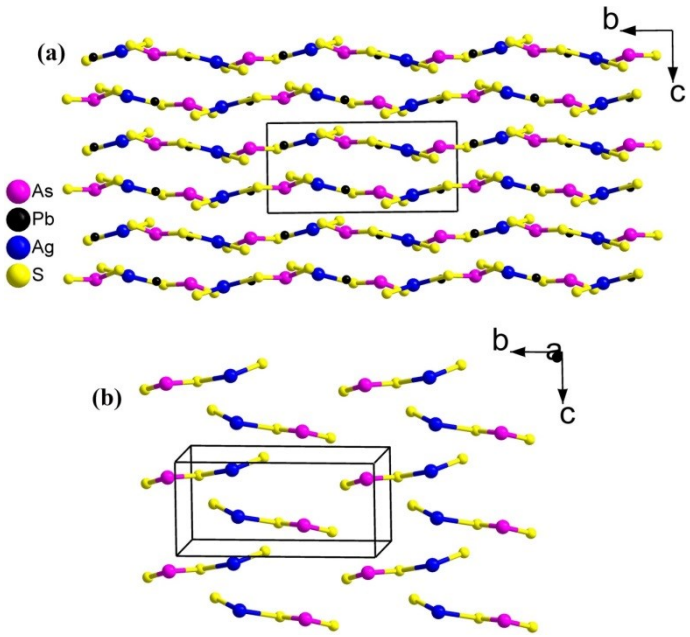

Figure S4. (a) Structure of $PbAgAsS_3$ viewed from the *bc* plane. (b) The arrangement of $[AgAsS_3]$ clusters in the structure.

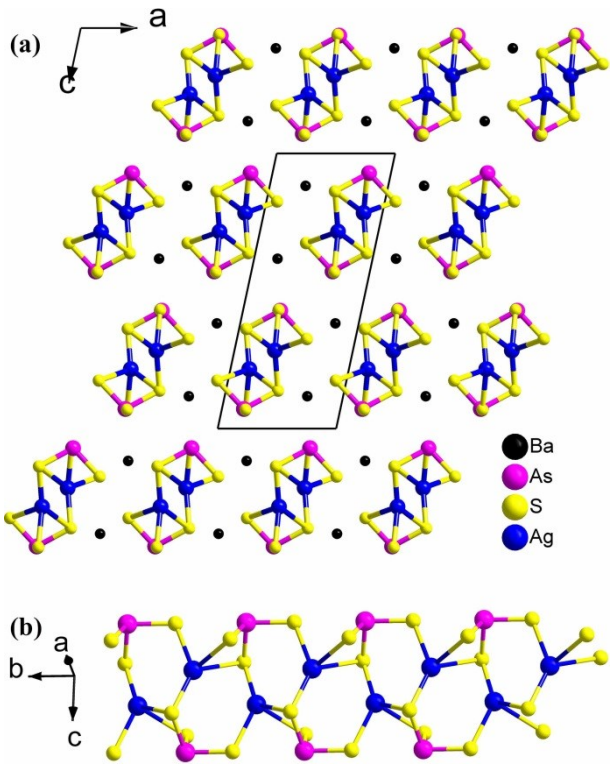

Figure S5. (a) Structure of $BaAgAsS_3$ viewed from the *ac* plane. (b) The 1D $[AgAsS_3]^{2-}$ chain in the structure.

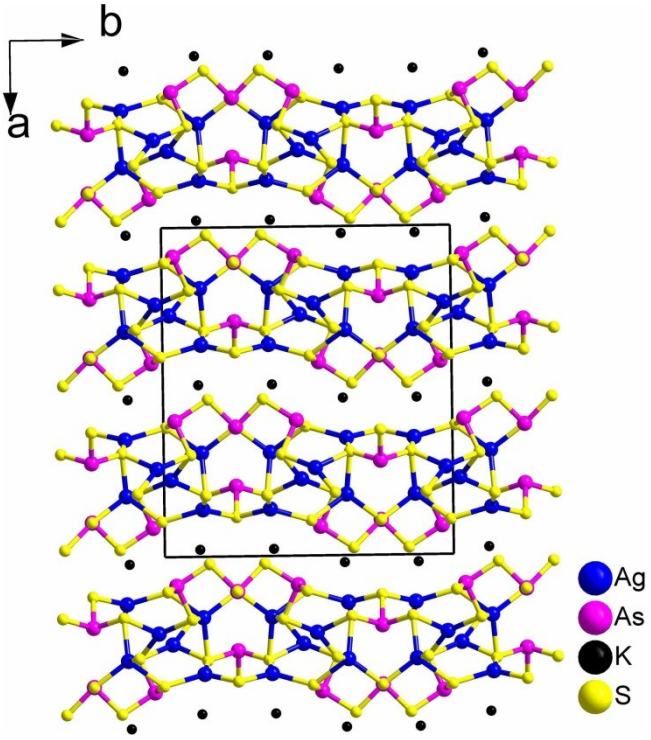

Figure S6. Structure of KAg_2AsS_3 viewed from the *ab* plane.

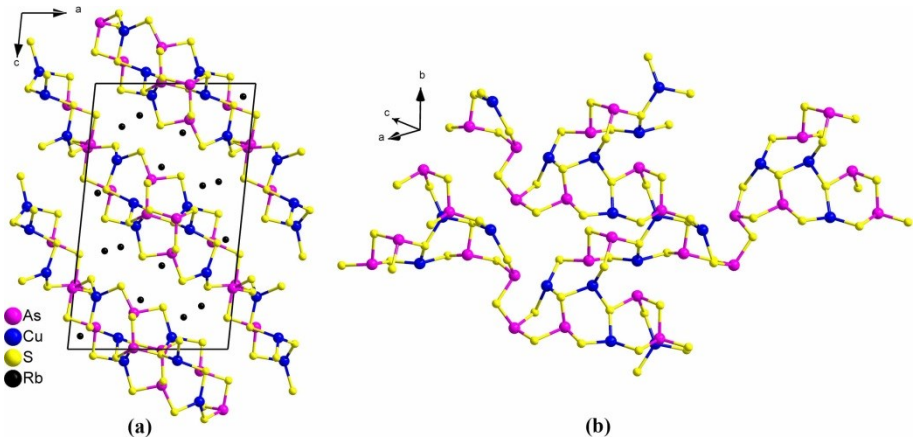

Figure S7. (a) Structure of $Rb_8Cu_6As_8S_{19}$ viewed from the *ac* plane. (b) The 2D $[Cu_6As_8S_{19}]^{8-}$ layer in the structure.

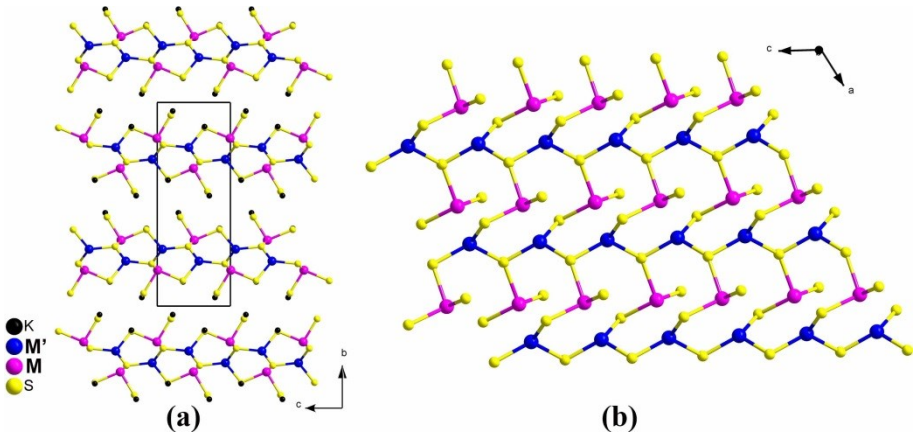

Figure S8. (a) Structure of KM'_2MS_3 (M' = Cu, Ag; M= As, Sb) viewed from the *bc* plane. (b) The 2D $[M'_2MS_3]^-$ layer in the structure.

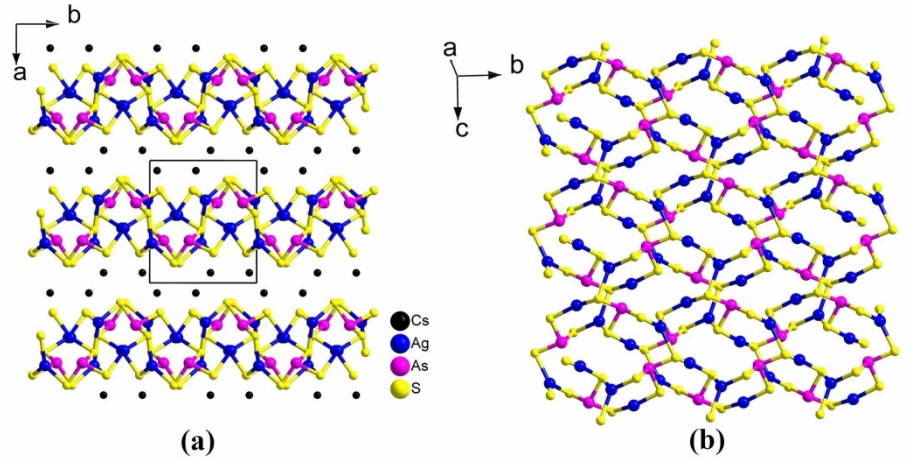

Figure S9. (a) Structure of $CsAg_2AsS_3$ viewed from the *ab* plane. (b) The 2D $[Ag_2AsS_3]^-$ layer in the structure.

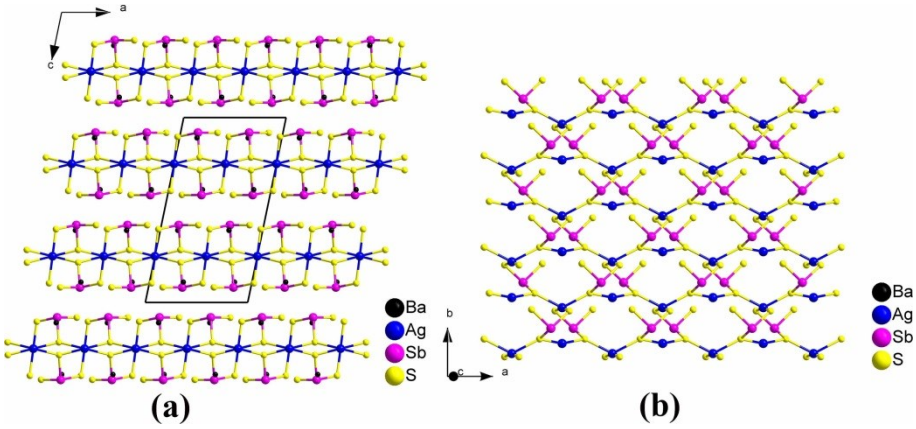

Figure S10. (a) Structure of $BaAgSbS_3$ viewed from the *ac* plane. (b) The 2D $[AgSbS_3]^{2-}$ layer in the structure.

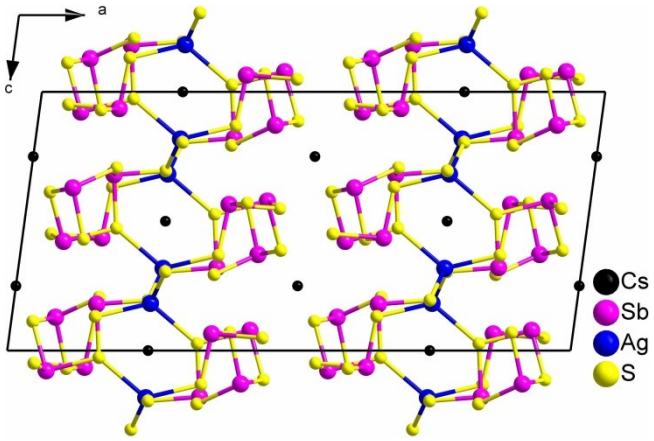

Figure S11. Structure of $CsAgSb_4S_7$ viewed from the *ac* plane.

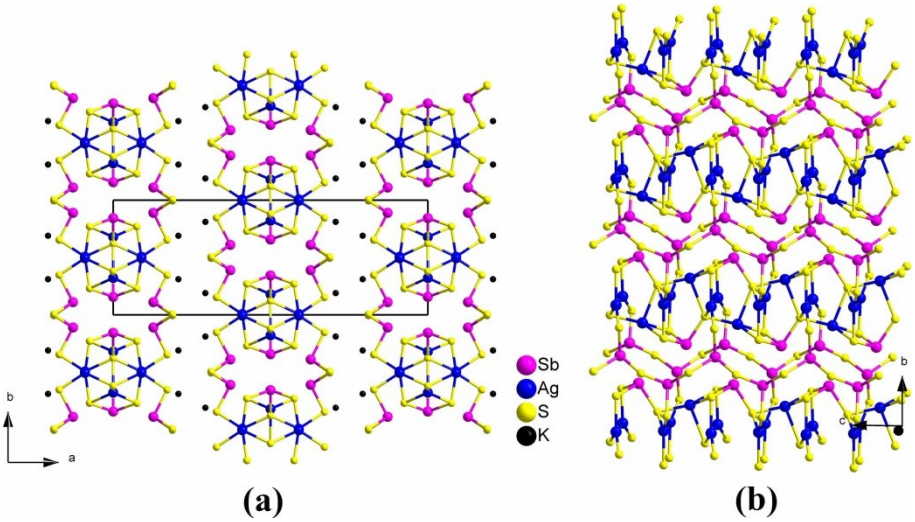

Figure S12. (a) Structure of $K_2Ag_3Sb_3S_7$ viewed from the *ab* plane. (b) The 2D $[Ag_3Sb_3S_7]^{2-}$ layer in the structure.

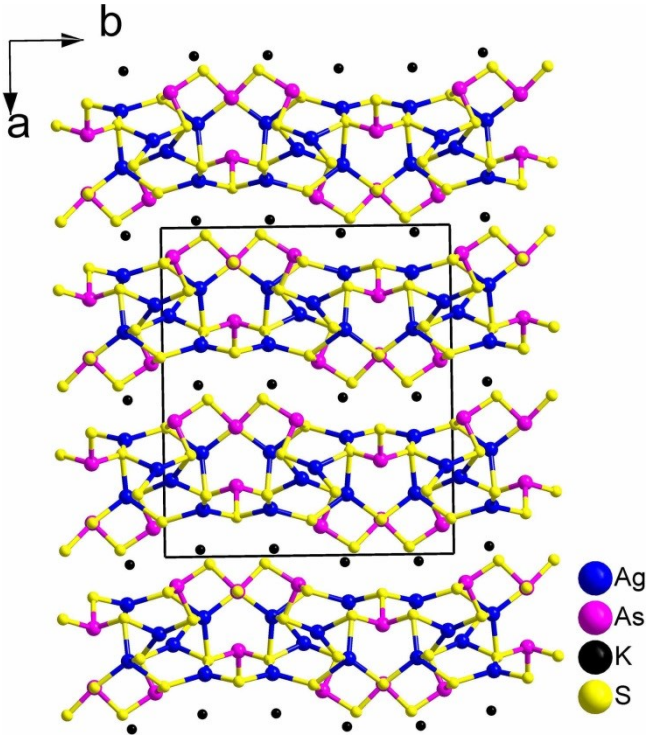

Figure S13. 2D layered structure of $KAg_3As_2S_5$ along the [110] direction.

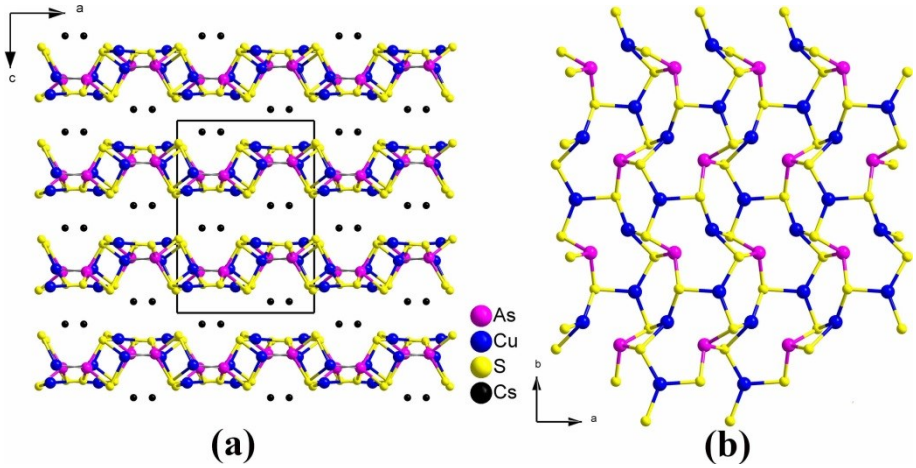

Figure S14. (a) Structure of $CsCu_2AsS_3$ viewed from the *ab* plane. (b) The 2D $[Cu_2AsS_3]^-$ layer in the structure.

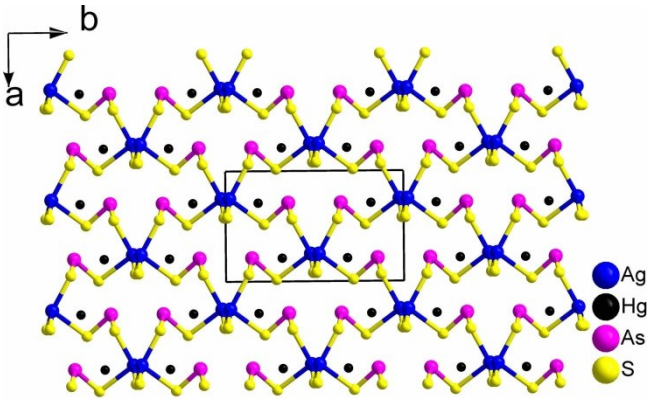

Figure S15. Structure of $HgAgAsS_3$ viewed from the *ab* plane.

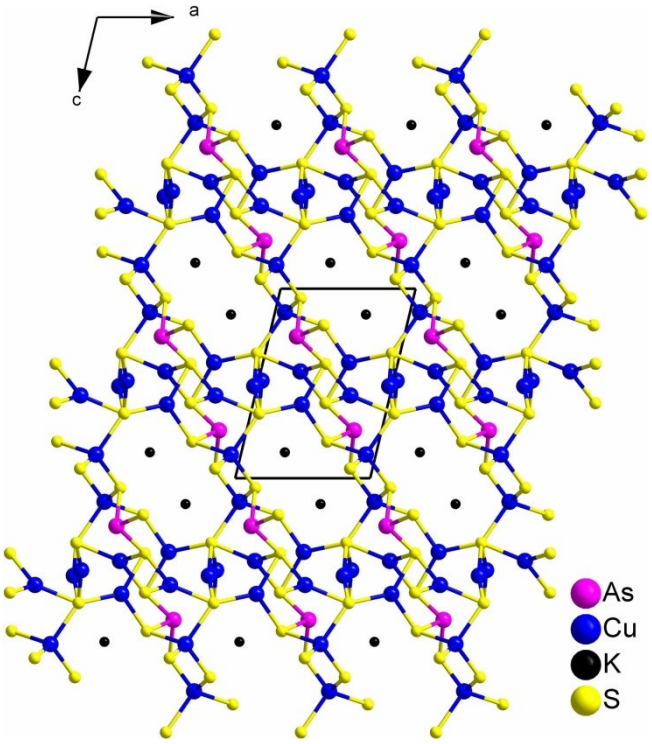

Figure S16. Structure of KCu_4AsS_4 viewed from the *ac* plane.

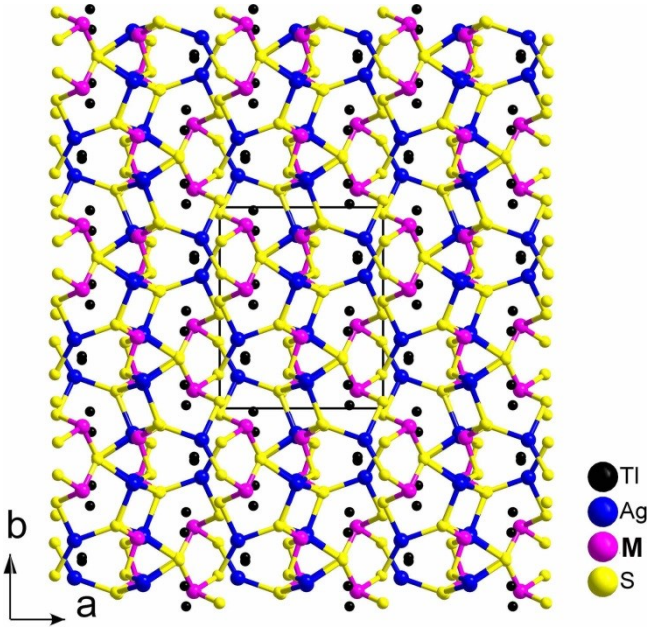

Figure S17. Structure of $Tl_3Ag_3M_2S_6$ (M= As, Sb) viewed from the *ab* plane.

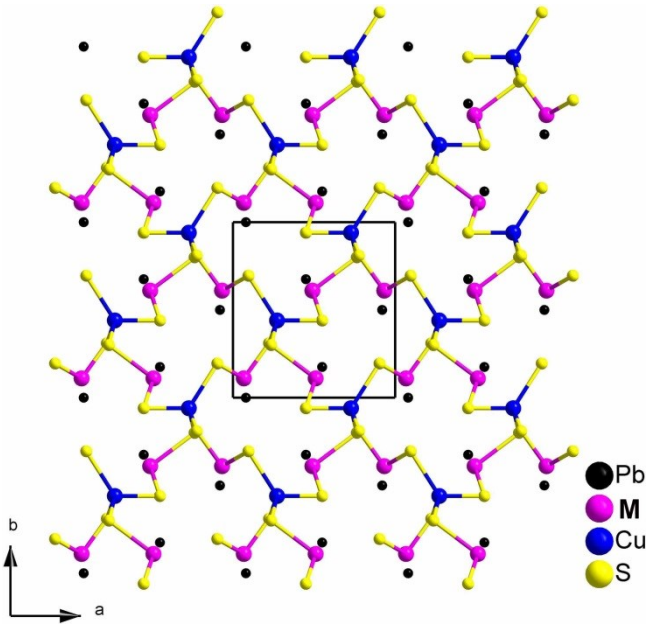

Figure S18. Structure of $PbCuMS_3$ (M= As, Sb) viewed from the *ab* plane.

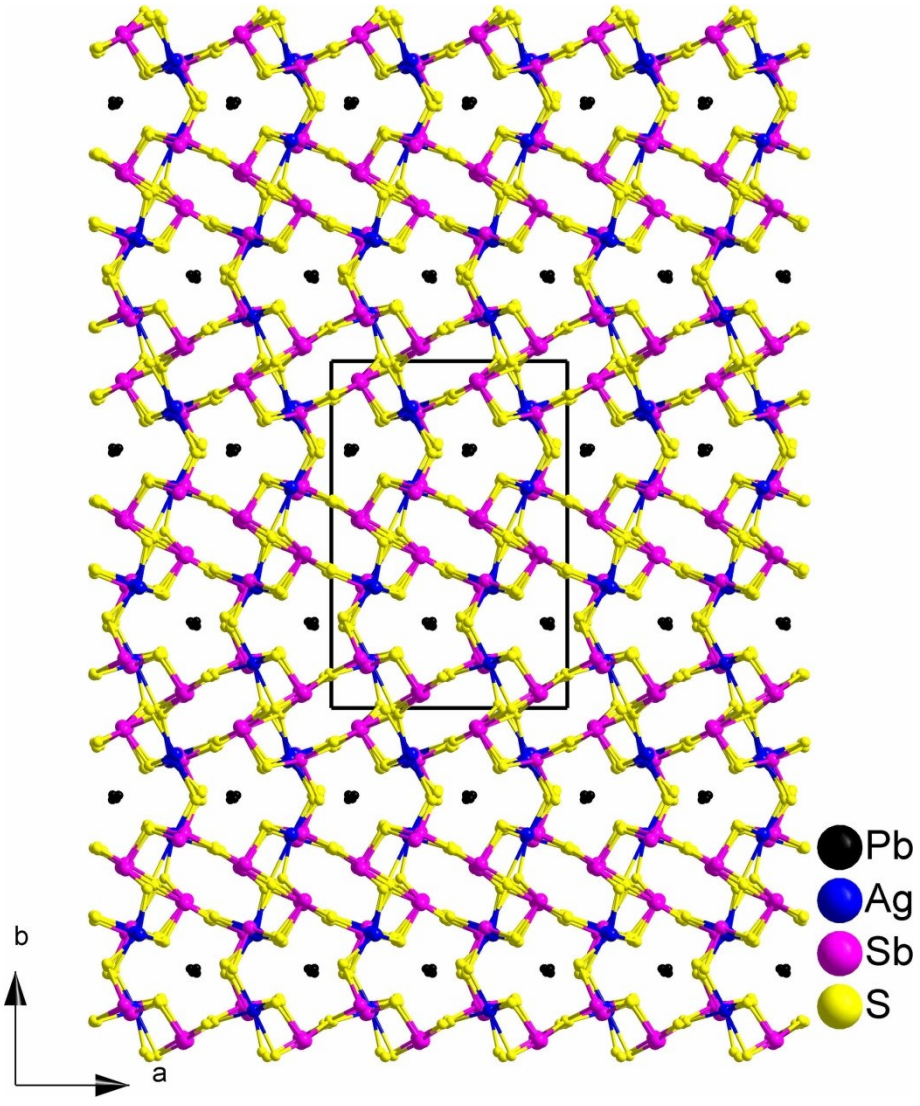

Figure S19. Structure of $PbAgSb_3S_6$ viewed from the *ab* plane.

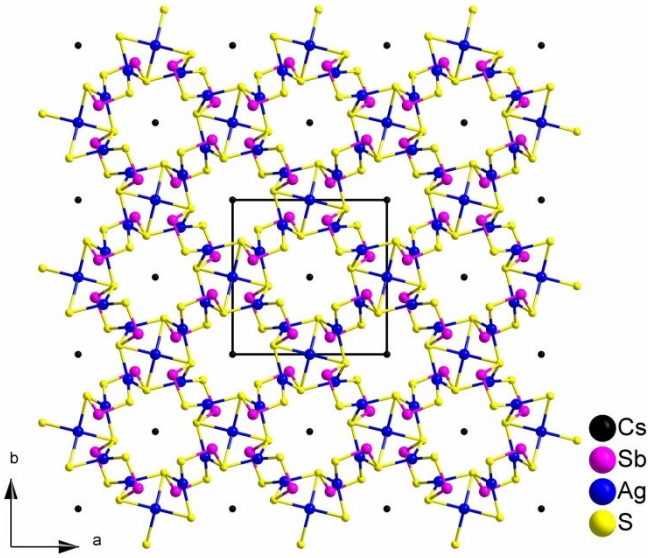

Figure S20. Structure of $Cs_3Ag_9Sb_4S_{12}$ viewed from the *ab* plane.

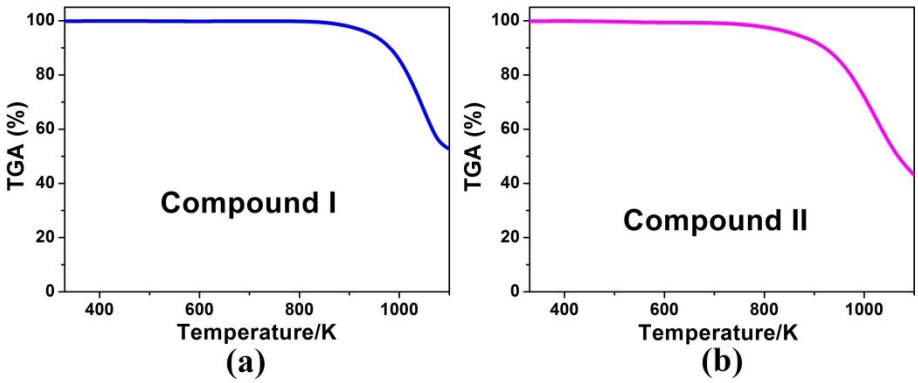

Figure S21. TGA diagrams of (a) **I** and (b) **II**.

Table S1. Selected bond lengths (Å) and angles (deg) for $Cs_2Ag_2As_2S_5$ (**I**).

Cs(1)–S(1)	3.4710(18)	Cs(2)–S(4)	3.8487(18)
Cs(1)–S(3)	3.524(2)	Cs(2)–S(1)	3.869(2)
Cs(1)–S(2)	3.5310(17)	Ag(1)–S(1)	2.4989(16)
Cs(1)–S(3)	3.5657(17)	Ag(1)–S(2)	2.5838(16)
Cs(1)–S(4)	3.6165(19)	Ag(1)–S(4)	2.5890(16)
Cs(1)–S(1)	3.6196(18)	Ag(2)–S(3)	2.5016(17)
Cs(1)–S(5)	3.8927(18)	Ag(2)–S(4)	2.5260(15)
Cs(1)–S(3)	3.9690(17)	Ag(2)–S(2)	2.5486(16)
Cs(2)–S(1)	3.4067(19)	As(1)–S(2)	2.2378(16)
Cs(2)–S(2)	3.4403(19)	As(1)–S(4)	2.2496(18)
Cs(2)–S(3)	3.4498(16)	As(1)–S(5)	2.2965(15)
Cs(2)–S(5)	3.5517(18)	As(2)–S(1)	2.2034(16)
Cs(2)–S(5)	3.565(2)	As(2)–S(3)	2.2040(15)
Cs(2)–S(4)	3.7136(17)	As(2)–S(5)	2.3134(18)
S(1)–Ag(1)–S(2)	109.93(5)	S(2)–As(1)–S(4)	101.25(6)
S(1)–Ag(1)–S(4)	111.42(5)	S(2)–As(1)–S(5)	106.31(6)
S(2)–Ag(1)–S(4)	119.89(5)	S(4)–As(1)–S(5)	96.20(6)
S(3)–Ag(2)–S(4)	124.63(5)	S(1)–As(2)–S(3)	103.93(6)
S(3)–Ag(2)–S(2)	115.98(5)	S(1)–As(2)–S(5)	99.01(6)
S(4)–Ag(2)–S(2)	118.10(6)	S(3)–As(2)–S(5)	100.96(6)

Table S2. Selected bond lengths (Å) and angles (deg) for $Cs_3AgAs_4S_8$ (**II**).

Cs(1)–S(7)	3.428(5)	Cs(3)–S(5)	3.589(5)
Cs(1)–S(2)	3.467(5)	Cs(3)–S(1)	3.765(6)
Cs(1)–S(4)	3.565(5)	Cs(3)–S(1)	4.075(6)
Cs(1)–S(6)	3.763(5)	As(4)–S(4)	2.167(5)
Cs(1)–S(1)	3.819(5)	As(4)–S(3)	2.321(5)
Cs(1)–S(5)	3.834(5)	As(4)–S(6)	2.399(5)
Cs(1)–S(4)	3.876(6)	As(1)–S(7)	2.161(5)
Cs(1)–S(8)	3.898(6)	As(1)–S(3)	2.276(6)
Cs(1)–S(8)	4.068(6)	As(1)–S(5)	2.368(5)
Cs(2)–S(3)	3.440(5)	As(2)–S(1)	2.234(5)
Cs(2)–S(6)	3.449(5)	As(2)–S(5)	2.287(5)
Cs(2)–S(7)	3.507(5)	As(2)–S(2)	2.299(5)
Cs(2)–S(3)	3.574(5)	As(3)–S(8)	2.199(5)
Cs(2)–S(4)	3.635(5)	As(3)–S(6)	2.239(5)
Cs(2)–S(5)	3.668(5)	As(3)–S(2)	2.298(5)
Cs(2)–S(6)	3.715(5)	Ag(1)–S(1)	2.672(6)
Cs(2)–S(2)	3.736(5)	Ag(1)–S(1)	2.672(6)
Cs(2)–S(3)	3.764(6)	Ag(1)–S(8)	2.700(6)
Cs(2)–S(2)	3.940(5)	Ag(1)–S(8)	2.700(6)
Cs(3)–S(8)	3.397(5)	Ag(2)–S(1)	2.611(6)
Cs(3)–S(7)	3.452(5)	Ag(2)–S(1)	2.611(6)
Cs(3)–S(5)	3.522(5)	Ag(2)–S(8)	2.638(6)
Cs(3)–S(7)	3.548(5)	Ag(2)–S(8)	2.638(6)
S(7)–As(1)–S(3)	102.53(19)	S(3)–As(4)–S(6)	88.58(17)
S(7)–As(1)–S(5)	98.43(17)	S(1)–Ag(1)–S(1)	100.8(2)
S(3)–As(1)–S(5)	94.83(18)	S(1)–Ag(1)–S(8)	109.82(17)
S(1)–As(2)–S(5)	101.6(2)	S(1)–Ag(1)–S(8)	123.29(15)
S(1)–As(2)–S(2)	107.5(2)	S(8)–Ag(1)–S(8)	91.7(2)
S(5)–As(2)–S(2)	98.90(19)	S(1)–Ag(1)–Ag(2)	50.38(12)
S(8)–As(3)–S(6)	99.6(2)	S(8)–Ag(1)–Ag(2)	134.13(12)
S(8)–As(3)–S(2)	103.7(2)	S(1)–Ag(2)–S(1)	104.1(3)
S(6)–As(3)–S(2)	96.38(18)	S(1)–Ag(2)–S(8)	121.82(15)
S(4)–As(4)–S(3)	103.08(19)	S(1)–Ag(2)–S(8)	107.91(18)
S(4)–As(4)–S(6)	98.9(2)	S(8)–Ag(2)–S(8)	94.5(3)

Table S3. Band Valence in $Cs_2Ag_2As_2S_5$ (**I**) and $Cs_3AgAs_4S_8$ (**II**).

$Cs_2Ag_2As_2S_5$ (**I**)		$Cs_3AgAs_4S_8$ (**II**)	
Site	**Valence**	**Site**	**Valence**
Cs1	1.12	Cs1	1.03
Cs2	1.03	Cs2	1.05
Ag1	0.92	Cs3	1.19
Ag2	1.00	Ag1	0.96
As1	3.09	Ag2	1.02
As2	3.29	As1	3.11
		As2	2.99
		As3	3.24
		As4	2.91

Table S4. Structural features of selected quaternary sulfides in the X−M'−M−S (X = cations; M' = Cu and Ag; M = As and Sb) system.

Compounds	Crystal system	Space group	Structural dimension	ABUs	Units link mode	Ref.
$PbAgAsS_3$	monoclinic	$P2_1/c$ (14)	0D	$[AgS_2]$, $[AsS_2]$	corner-sharing	1
$BaAgAsS_3$	monoclinic	$P2_1/c$ (14)	1D	$[AgS_4]$, $[AsS_3]$	corner- and edge-sharing	2
$Cs_2Ag_2As_2S_5$	triclinic	$P\bar{1}$（no. 2）	2D	$[AgS_3]$, $[AsS_3]$	corner-sharing	This work
$Cs_2Cu_2Sb_2S_5$	triclinic	$P\bar{1}$（no. 2）	2D	$[CuS_4]$, $[SbS_3]$	corner- and edge-sharing	3
KAg_2AsS_3	triclinic	$P\bar{1}$（no. 2）	2D	$[AgS_3]$, $[AsS_3]$	corner-sharing	4
$Rb_8Cu_6As_8S_{19}$	triclinic	$P\bar{1}$（no. 2）	2D	$[CuS_3]$, $[AsS_3]$	corner-sharing	3
KAg_2SbS_3	triclinic	$P\bar{1}$（no. 2）	2D	$[AgS_3]$, $[SbS_3]$	corner-sharing	5
KCu_2SbS_3	triclinic	$P\bar{1}$（no. 2）	2D	$[CuS_3]$, $[SbS_3]$	corner-sharing	6
KCu_2AsS_3	triclinic	$P\bar{1}$（no. 2）	2D	$[CuS_3]$, $[AsS_3]$	corner-sharing	7
$Cs_3AgAs_4S_8$	monoclinic	$C2/c$（no. 12）	2D	$[AgS_4]$, $[AsS_3]$	corner- and edge-sharing	This work
$Rb_2Cu_2Sb_2S_5$	monoclinic	$P2_1/c$ (14)	2D	$[CuS_3]$, $[CuS_4]$, $[SbS_3]$	corner-sharing	3
$CsAg_2AsS_3$	monoclinic	$P2_1/c$ (14)	2D	$[AgS_2]$, $[AgS_3]$, $[AsS_3]$	corner-sharing	8
K_2CuSbS_3	monoclinic	$P2_1/c$ (14)	2D	$[CuS_3]$, $[SbS_3]$	corner-sharing	9
$BaAgSbS_3$	monoclinic	$C2/c$ (15)	2D	$[AgS_2]$, $[AgS_3]$, $[SbS_3]$	corner-sharing	10
$CsAgSb_4S_7$	monoclinic	$C2/c$ (15)	2D	$[AgS_4]$, $[SbS_3]$	corner-sharing	11
$K_2Ag_3Sb_3S_7$	orthorhombic	$Cmc2_1$ (36)	2D	$[AgS_3]$, $[AgS_4]$, $[SbS_3]$	corner- and edge-sharing	5
$KAg_3As_2S_5$	orthorhombic	*Pnma* (62)	2D	$[AgS_3]$, $[AgS_4]$, $[AsS_3]$	corner-sharing	12
$CsCu_2AsS_3$	orthorhombic	*Pbca* (63)	2D	$[CuS_3]$, $[AsS_3]$	corner-sharing	13
$HgAgAsS_3$	monoclinic	*Cc* (9)	3D	$[AgS_4]$, $[AsS_3]$	corner-sharing	14
KCu_4AsS_4	monoclinic	$P2_1$ (9)	3D	$[CuS_2]$, $[CuS_3]$, $[AsS_3]$	corner-sharing	13
$Tl_3Ag_3As_2S_6$	monoclinic	$P2_1/c$ (14)	3D	$[AgS_3]$, $[AgS_4]$, $[AsS_3]$	corner-sharing	15
$Tl_3Ag_3Sb_2S_6$	monoclinic	$P2_1/c$ (14)	3D	$[AgS_3]$, $[AgS_4]$, $[SbS_3]$	corner-sharing	15
$PbCuAsS_3$	orthorhombic	$Pmn2_1$ (31)	3D	$[CuS_4]$, $[AsS_3]$	corner-sharing	16
$PbCuSbS_3$	orthorhombic	$Pmn2_1$ (31)	3D	$[CuS_4]$, $[SbS_3]$	corner-sharing	17
$PbAgSb_3S_6$	orthorhombic	$Pna2_1$ (33)	3D	$[AgS_4]$, $[SbS_3]$, $[SbS_4]$	corner- and edge-sharing	18
$Cs_3Ag_9Sb_4S_{12}$	tetragonal	*I4/m* (87)	3D	$[AgS_3]$, $[AgS_4]$, $[SbS_3]$	corner- and edge-sharing	8

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