Electronic Supplementary Information

A wide band gap selenohalide $Cs_9Si_8Se_{20}Cl$ with unprecedented [$CsSe_7Cl$] mixed anionic units

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Table S1 Crystal data and structure refinements for $Cs_9Si_8Se_{20}Cl$.

Empirical formula	**$Cs_9Si_8Se_{20}Cl$**
Formula weight	3035.472
Temperature (K)	296.15
Crystal system, space group	trigonal, $P\bar{3}$
a(Å)	10.6055(5)
b(Å)	10.6055(5)
c(Å)	13.8678(9)
Volume(Å^3)	1350.83(13)
Z	1
Absorption coefficient(mm^{-1})	19.705
***F*(000)**	1302.9
Radiation	Mo K_α (λ = 0.71073)
Data / restraints / parameters	1711 / 0 / 59
Index ranges	$-10 \le h \le 12$, $-13 \le k \le 13$, $-16 \le l \le 15$
Completeness(%)	99.9
Independent reflections	1711 [R_{int} = 0.0618, R_{sigma} = 0.0540]
GOF on F^2	1.002
2θ range for data collection/°	4.44 to 54.38
Reflections collected	6972
Final *R* indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1 = 0.0341, wR_2 = 0.0558
***R* indices (all data)**[a]	R_1 = 0.0574, wR_2 = 0.0634
Largest diff. peak and hole(e/Å^3)	1.23/-1.25

[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), equivalent isotropic displacement parameters (Å^2 × 10^3), and bond valence calculations (BVSs) for $Cs_9Si_8Se_{20}Cl$.

Atom	Wyckoff	*x*	*y*	*z*	U(eq)	BVSs[a]
Cs(1)	6*g*	3019.5(5)	665.1(5)	3648.1(4)	45.71(17)	1.04
Cs(2)	1*a*	0	0	10000	51.4(3)	0.86
Cs(3)	2*d*	3333.3	-3333.3	9207.7(7)	58.7(3)	0.80
Si(1)	2*d*	6666.7	3333.3	5753(2)	27.7(7)	4.00
Si(2)	*6g*	4599(2)	1369(2)	7962.6(15)	32.5(5)	3.97
Se(1)	*6g*	4635.3(7)	1275.9(7)	6296.5(5)	32.14(19)	2.11
Se(2)	*6g*	4667.7(8)	3440.6(8)	8524.5(5)	34.44(19)	2.03
Se(3)	*2d*	6666.7	3333.3	4188.2(9)	39.5(3)	1.92
Se(4)	*6g*	2588.6(8)	-471.3(8)	8466.8(6)	47.3(2)	1.82
Cl(1)	1*b*	0	0	5000	44.6(11)	0.97
		GII[b]			0.107	

[a] The bond valence sum is calculated by bond-valence theory (S_{ij} = exp[(R_0-R)/B, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and B = 0.37).

[b] The global instability index (GII) calculated using:

$$G = \sqrt{\frac{\sum_{i=1}^{n}(BVS - v_i)}{N}}$$

Where N is the number of atoms in the formula unit. The GII is calculated as 0.107, which is lower than 0.2, indicating the rationality of the structure.

Table S3 Bond lengths for $Cs_9Si_8Se_{20}Cl$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cs(1)	Se(1)	3.9667(9)	Cs(2)	Se(4)#1	3.6987(8)
Cs(1)	Se(1)#5	3.9433(9)	Cs(3)	Se(2)#9	3.8261(11)
Cs(1)	Se(1)#2	3.7081(8)	Cs(3)	Se(2)#7	3.8261(11)
Cs(1)	Se(1)#3	4.0432(8)	Cs(3)	Se(2)#10	3.8261(11)
Cs(1)	Se(2)#2	3.7684(9)	Cs(3)	Se(4)#11	3.6456(9)
Cs(1)	Se(3)	3.5474(6)	Cs(3)	Se(4)#12	3.6456(9)
Cs(1)	Se(4)#3	3.5606(10)	Cs(3)	Se(4)	3.6456(9)
Cs(1)	Cl(1)	3.4653(5)	Si(1)	Se(3)	2.171(4)
Cs(2)	Se(4)#6	3.6987(8)	Si(1)#13	Se(1)	2.2953(13)
Cs(2)	Se(4)#7	3.6987(8)	Si(2)	Se(1)	2.314(2)
Cs(2)	Se(4)#8	3.6987(8)	Si(2)	Se(2)	2.298(2)
Cs(2)	Se(4)	3.6987(8)	Si(2)#14	Se(2)	2.295(2)
Cs(2)	Se(4)#4	3.6987(8)	Si(2)	Se(4)	2.164(2)

Symmetry transformations used to generate equivalent atoms:

#1 +Y-X,-X,+Z #2 +Y,-X+Y,1-Z #3 -Y+X,+X,1-Z #4 -Y,+X-Y,+Z

#5 1-X,-Y,1-Z #6 -X,-Y,2-Z #7 +Y,-X+Y,2-Z #8 -Y+X,+X,2-Z

#9 1-X,-Y,2-Z #10 -Y+X,-1+X,2-Z #11 1+Y-X,-X,+Z

#12 -Y,-1+X-Y,+Z #13 1-Y,+X-Y,+Z #14 1+Y-X,1-X,+Z

Table S4 Bond angles for $Cs_9Si_8Se_{20}Cl$.

Atom	Atom	Atom	Angle/ °	Atom	Atom	Atom	Angle/ °
Se(2)#1	Cs(1)	Se(1)#1	61.787(17)	Se(4)#8	Cs(2)	Se(4)#7	90.245(19)
Se(2)#1	Cs(1)	Se(1)#1	57.584(16)	Se(4)#8	Cs(2)	Se(4)#3	89.755(19)
Se(2)#1	Cs(1)	Se(1)	132.121(19)	Se(4)	Cs(2)	Se(4)#7	89.755(19)
Se(2)#1	Cs(1)	Se(1)#2	126.67(2)	Se(4)#3	Cs(2)	Se(4)	90.245(18)
Se(3)	Cs(1)	Se(1)#1	129.134(18)	Se(4)#5	Cs(2)	Se(4)#8	90.245(19)
Se(3)	Cs(1)	Se(1)#2	70.815(13)	Se(2)#5	Cs(3)	Se(2)#9	59.11(2)
Se(3)	Cs(1)	Se(1)	57.63(2)	Se(2)#10	Cs(3)	Se(2)#9	59.11(2)
Se(3)	Cs(1)	Se(1)#4	72.035(13)	Se(2)#10	Cs(3)	Se(2)#5	59.11(2)
Se(3)	Cs(1)	Se(2)#1	102.79(2)	Se(4)#11	Cs(3)	Se(2)#10	72.613(18)
Se(4)#2	Cs(1)	Se(1)#2	56.613(17)	Se(4)	Cs(3)	Se(2)#5	72.613(18)
Se(4)#2	Cs(1)	Se(1)1	142.06(2)	Se(4)#11	Cs(3)	Se(2)#9	112.55(2)
Se(4)#2	Cs(1)	Se(1)#4	119.02(2)	Se(4)	Cs(3)	Se(2)#9	127.62(2)
Se(4)#2	Cs(1)	Se(1)#1	122.19(2)	Se(4)#12	Cs(3)	Se(2)#9	72.613(18)
Se(4)#2	Cs(1)	Se(2)#1	71.085(18)	Se(4)	Cs(3)	Se(2)#10	112.55(2)
Se(4)#2	Cs(1)	Se(3)	91.20(2)	Se(4)#12	Cs(3)	Se(2)#10	127.62(2)
Cl(1)	Cs(1)	Se(1)#1	82.892(14)	Se(4)#11	Cs(3)	Se(2)#5	127.62(2)
Cl(1)	Cs(1)	Se(1)#4	130.023(17)	Se(4)#12	Cs(3)	Se(2)#5	112.55(2)
Cl(1)	Cs(1)	Se(1)	79.172(14)	Se(4)#11	Cs(3)	Se(4)#12	112.385(18)
Cl(1)	Cs(1)	Se(1)#2	78.103(14)	Se(4)#11	Cs(3)	Se(4)	112.385(17)
Cl(1)	Cs(1)	Se(2)#1	131.886(18)	Se(4)	Cs(3)	Se(4)#12	112.385(17)
Cl(1)	Cs(1)	Se(3)	125.19(2)	Se(1)	Si(1)	Se(1)#15	109.79(8)
Cl(1)	Cs(1)	Se(4)#2	107.904(19)	Se(1)#13	Si(1)	Se(1)#15	109.79(8)
Se(4)#5	Cs(2)	Se(4)#6	180	Se(1)#13	Si(1)	Se(1)	109.79(8)
Se(4)#5	Cs(2)	Se(4)	89.755(19)	Se(3)	Si(1)	Se(1)#15	109.15(8)
Se(4)#5	Cs(2)	Se(4)#7	90.245(18)	Se(3)	Si(1)	Se(1)	109.15(8)
Se(4)#3	Cs(2)	Se(4)#7	180	Se(3)	Si(1)	Se(1)#13	109.15(8)
Se(4)#6	Cs(2)	Se(4)#7	89.755(18)	Se(2)#13	Si(2)	Se(1)	107.54(8)
Se(4)#8	Cs(2)	Se(4)#6	89.755(18)	Se(2)#13	Si(2)	Se(1)	112.71(8)

Se(4)#3	Cs(2)	Se(4)#6	90.245(19)	Se(4)	Si(2)	Se(1)	108.31(9)
Se(4)#8	Cs(2)	Se(4)	180	Se(4)	Si(2)	Se(2)#13	110.35(9)
Se(4)#6	Cs(2)	Se(4)	90.245(19)	Se(4)	Si(2)	Se(2)	107.38(8)
Se(4)#5	Cs(2)	Se(4)#3	89.755(18)				

Symmetry transformations used to generate equivalent atoms:

#1 +Y,-X+Y,1-Z #2 -Y+X,+X,1-Z #3 +Y-X,-X,+Z #4 1-X,-Y,1-Z

#5 +Y,-X+Y,2-Z #6 -Y,+X-Y,+Z #7 -Y+X,+X,2-Z #8 -X,-Y,2-Z

#9 1-X,-Y,2-Z #10 -Y+X,-1+X,2-Z #11 -Y,-1+X-Y,+Z #12 1+Y-X,-X,+Z

#13 1-Y,+X-Y,+Z #14 1+Y,1-X+Y,2-Z #15 1+Y-X,1-X,+Z #16 -X,-Y,1-Z

Table S5 Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Cs_9Si_8Se_{20}Cl$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs(1)	45.7(3)	38.7(3)	51.1(3)	19.9(2)	5.2(2)	-0.6(2)
Cs(2)	54.8(5)	54.8(5)	44.6(8)	27.4(2)	0	0
Cs(3)	61.0(4)	61.0(4)	54.0(6)	30.5(2)	0	0
Se(1)	29.0(4)	28.2(4)	34.6(4)	10.8(3)	-0.5(3)	-0.7(3)
Se(2)	32.8(4)	35.2(4)	36.6(4)	17.9(3)	4.0(3)	-1.2(3)
Se(3)	43.5(5)	43.5(5)	31.5(7)	21.7(2)	0	0
Se(4)	35.0(4)	37.6(5)	53.2(5)	6.0(4)	11.8(4)	4.1(4)
Si(1)	40.0(16)	40.0(16)	54(3)	20.0(8)	0	0
Si(2)	26.0(10)	26.0(10)	31.2(19)	13.0(5)	0	0
Cl(1)	29.0(10)	30.1(11)	35.9(11)	12.8(9)	2.6(9)	0.8(9)

Table S6 The calculated hyperpolarizability, polarizability anisotropy, and HOMO–LUMO gap for typical Si–Se units.

Unit	Hyperpolarizability (10^{-30} esu)	Polarizability anisotropy (Å^3)	HOMO–LUMO gap (eV)	Ref.
[$SiSe_4$]	0.20815	12.331	4.686	1
[$SiSe_6$]	57.37714	3.03975	4.882	2
[α-Si_2Se_6]	75.07554	59.98494	4.634	3
[β-Si_2Se_6]	0.1946	107.3089	3.694	4
[Si_2Se_7]	36.54961	16.37671	4.324	5
[α-Si_2Se_8]	278.04398	102.89523	3.395	6
[β-Si_2Se_8]	2.37182	158.41212	3.62	7
[Si_3Se_9]	145.32187	13.9644	4.142	8
[Si_4Se_{10}]	157.35553	14.33184	4.24	9

Table S7 The optimized structures (Cartesian coordinates) for the [$SiSe_4$] unit.

Atoms (5)	**Symmetry**	***x/a***	***y/b***	***z/c***
Si1 (#5)	*x, y, z*	0	0	0
Se2 (#6)	*x, y, z*	0.16166	0.16166	0.20865
Se2 (#7)	*y, -x, -z*	0.16166	-0.16171	-0.20871
Se2 (#8)	*-x, -y, z*	-0.16171	-0.16171	0.20865
Se2 (#9)	*-y, x, -z*	-0.16171	0.16166	-0.20871

Table S8 The optimized structures (Cartesian coordinates) for the [$SiSe_6$] unit.

Atoms (7)	**Symmetry**	***x/a***	***y/b***	***z/c***
Si1 (#5)	*x, y, z*	0.25835	0	0.27449
Se1 (#6)	*x, y, z*	0.37449	0.00001	0.03278
Se1 (#7)	*1/2-x, -1/2+y, -z*	45704	-0.5	-0.03277
Se1 (#8)	*1/2-x, 1/2+y, -z*	45704	45722	-0.03277
Se2 (#9)	*x, y, z*	0.1135	0.00001	0.45105
Se2 (#10)	*1/2-x, -1/2+y, 1-z*	0.38645	-0.5	0.54895
Se2 (#11)	*1/2-x, 1/2+y, 1-z*	0.38645	45722	0.54895

Table S9 The optimized structures (Cartesian coordinates) for the [α-Si_2Se_6] unit.

Atoms (8)	**Symmetry**	***x/a***	***y/b***	***z/c***
Si1 (#5)	*x, y, z*	0.65888	0.30301	0.55492
Se1 (#6)	*x, y, z*	0.73002	0.46922	0.7316
Se2 (#7)	*x, y, z*	0.76566	0.29319	0.28336
Se3 (#8)	*x, y, z*	0.76957	0.14884	0.74661
Si1 (#9)	*1-x, y, 1-z*	0.3411	0.30302	0.44504
Se1 (#10)	*1-x, y, 1-z*	0.26996	0.46923	0.26839
Se2 (#11)	*1-x, y, 1-z*	0.23432	0.2932	0.71663
Se3 (#12)	*1-x, y, 1-z*	0.23041	0.14885	0.25337

Table S10 The optimized structures (Cartesian coordinates) for the [β-Si_2Se_6] unit.

Atoms (8)	**Symmetry**	***x/a***	***y/b***	***z/c***
Si1 (#5)	*x, y, z*	0.65397	0.34603	0
Se1 (#6)	*x, y, z*	0.77518	0.22481	0.14923
Se1 (#7)	*1-y, 1-x, -z*	0.77518	0.22481	-0.14924
Se2 (#8)	*x, y, z*	0.33225	0.33229	0
Se2 (#9)	*1-x, 1-y, z*	0.6677	0.66774	0
Si1 (#10)	*1-x, 1-y, z*	0.34598	0.65401	-0.00001
Se1 (#11)	*1-x, 1-y, z*	0.22482	0.77522	0.14922
Se1 (#12)	*y, x, -z*	0.22482	0.77522	-0.14925

Table S11 The optimized structures (Cartesian coordinates) for the [Si_2Se_7] unit.

Atoms (9)	**Symmetry**	***x/a***	***y/b***	***z/c***
Si (#5)	*x, y, z*	0.34331	0.41951	0.13965
Se1 (#6)	*x, y, z*	0.13125	0.37495	0.17873
Se2 (#7)	*x, y, z*	0.30465	0.56526	0.03048
Se3 (#8)	*x, y, z*	0.44741	0.2436	0.10537
Se4 (#9)	*1/2+x, 1/2+y, z*	45722	0.53767	45728
Si1 (#10)	*1-x, y, 1/2-z*	0.65668	0.4195	0.36033
Se1 (#11)	*1-x, y, 1/2-z*	0.86875	0.37494	0.32129
Se2 (#12)	*1-x, y, 1/2-z*	0.69535	0.56524	0.46955
Se3 (#13)	*1-x, y, 1/2-z*	0.55259	0.24359	0.39466

Table S12 The optimized structures (Cartesian coordinates) for the [α-Si_2Se_8] unit.

Atoms (10)	**Symmetry**	***x/a***	***y/b***	***z/c***
Si1 (#5)	*x, y, z*	0.88703	0.27604	0.97445
Se2 (#6)	*1+x, y, 1+z*	1.14183	0.31864	1.07871
Se3 (#7)	*x, 1/2-y, 1/2+z*	0.94249	0.18357	0.86411
Se6 (#8)	*x, y, 1+z*	0.66356	0.23319	1.05796
Se8 (#9)	*x, 1/2-y, 1/2+z*	0.80449	0.39371	0.88804
Se5 (#10)	*1-x, 1-y, 1-z*	0.52395	0.35038	0.78087
Si2 (#11)	*1-x, 1-y, 1-z*	0.39643	0.47452	0.73108
Se1 (#12)	*x, 3/2-y, 1/2+z*	0.59636	0.54368	0.6529
Se4 (#13)	*1-x, 1-y, 1-z*	0.32732	0.53391	0.86622
Se7 (#14)	*1-x, 1-y, 1-z*	0.14086	0.43387	0.6269

Table S13 The optimized structures (Cartesian coordinates) for the [β-Si_2Se_8] unit.

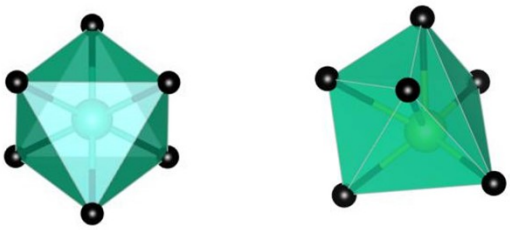
Atoms (10)	**Symmetry**	***x/a***	***y/b***	***z/c***
Si1 (#5)	*x, y, z*	0.15601	0	-0.29924
Se3 (#6)	*x, y, z*	0.08987	0.24544	-0.46272
Se3 (#7)	*x, -y, z*	0.08987	-0.2454	-0.46272
Se1 (#8)	*x, y, z*	0.31357	0.00002	-0.26918
Se2 (#9)	*x, y, z*	0.12564	0.00002	-0.10628
Se3 (#10)	*-x, y, -1-z*	-0.08991	0.2454	-0.53728
Se3 (#11)	*-x, -y, -1-z*	-0.08991	-0.24544	-0.53728
Si1 (#12)	*-x, y, -1-z*	-0.15598	0	-0.70076
Se1 (#13)	*-x, y, -1-z*	-0.31361	0.00002	-0.73082
Se2 (#14)	*-x, y, -1-z*	-0.12568	0.00002	-0.89373

Table S14 The optimized structures (Cartesian coordinates) for the [Si_3Se_9] unit.

Atoms (12)	Symmetry	*x/a*	*y/b*	*z/c*
Si1 (#5)	*x, y, z*	0.45562	0.34006	0.19301
Se1 (#6)	*x, y, z*	0.26535	0.33717	0.28372
Se2 (#7)	*x, y, z*	0.42153	0.33858	0.01498
Se3 (#8)	*x, y, z*	0.44778	0.12098	0.25797
Se3 (#9)	*1-x+y, 1-x, z*	0.67324	0.55226	0.25797
Si1 (#10)	*1-y, x-y, z*	0.65991	0.11553	0.19298
Si1 (#11)	*1-x+y, 1-x, z*	0.88446	0.54437	0.19298
Se1 (#12)	*1-y, x-y, z*	0.66281	-0.0718	0.28375
Se2 (#13)	*1-y, x-y, z*	0.66141	0.08292	0.01501
Se3 (#14)	*1-y, x-y, z*	0.879	0.32676	0.25799
Se1 (#15)	*1-x+y, 1-x, z*	1.07175	0.73465	0.28375
Se2 (#16)	*1-x+y, 1-x, z*	0.91702	0.57846	0.01501

Table S15 The optimized structures (Cartesian coordinates) for the [Si_4Se_{10}] unit.

Atoms (14)	Symmetry	*x/a*	*y/b*	*z/c*
Si1 (#5)	*x, y, z*	0.43625	0.20445	0.37961
Se2 (#6)	*x, y, z*	0.38437	0.12922	0.52325
Se3 (#7)	*1/2-x, 1/2-y, -z*	0.32877	0.28376	0.23267
Se4 (#8)	*1/2+x, 1/2-y, 1/2+z*	0.54276	0.28284	0.53253
Se6 (#9)	*x, y, z*	45722	0.1175	45728
Si2 (#10)	*1/2-x, 1/2-y, -z*	0.3953	0.36789	0.10208
Si2 (#11)	*1/2+x, 1/2-y, 1/2+z*	0.60465	0.36789	0.39798
Si1 (#12)	*1-x, y, 1/2-z*	0.5637	0.20444	0.12039
Se1 (#13)	*1/2-x, 1/2-y, -z*	0.29643	0.4414	-0.0492
Se4 (#14)	*1/2-x, 1/2-y, -z*	0.4572	0.28283	-0.03254
Se5 (#15)	*1/2-x, 1/2-y, -z*	45722	0.45074	45728
Se1 (#16)	*1/2+x, 1/2-y, 1/2+z*	0.70354	0.4414	0.54919
Se3 (#17)	*1/2+x, 1/2-y, 1/2+z*	0.67119	0.28375	0.26733
Se2 (#18)	*1-x, y, 1/2-z*	0.61558	0.12921	-0.02326



[Cs2Se$_6$] regular octahedral unit **[Cs3Se$_6$] distorted octahedral unit**

Figure S1 The coordination modes of Cs2 and Cs3.

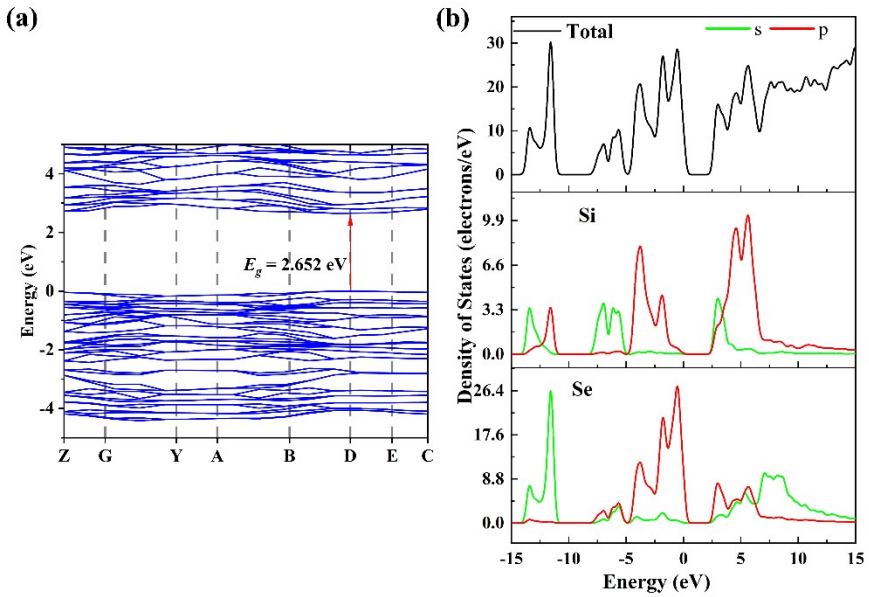


Figure S2 (a) The calculated GGA band gap, and (b) total and partial density of states of $SiSe_2$.

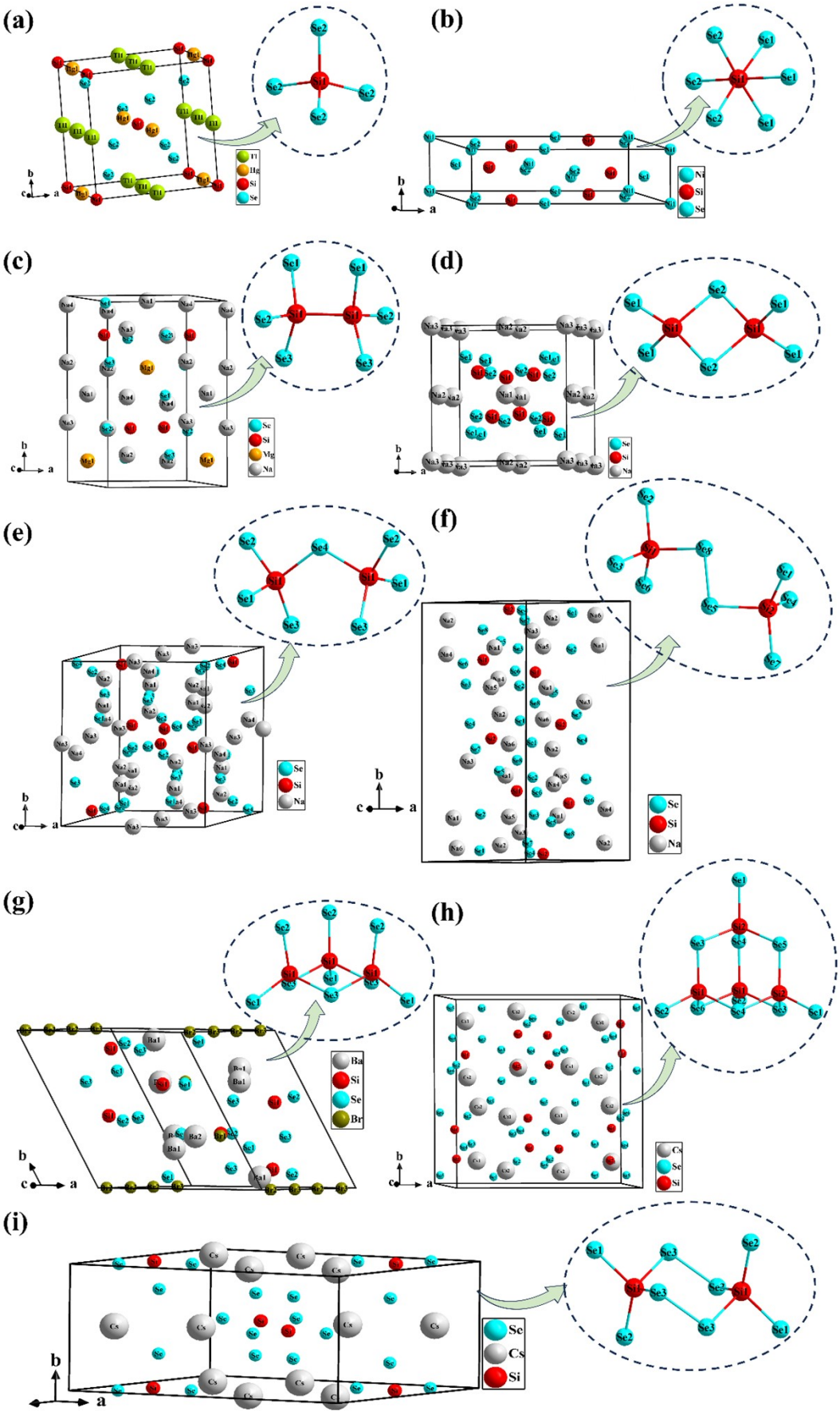

(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)

Figure S3. The graphical representation (with atomic numbers) for the investigated models: (a) the [$SiSe_4$] unit,[1] (b) the [$SiSe_6$] unit,[2] (c) the [α-Si_2Se_6] unit,[3] (d) the [β-Si_2Se_6] unit,[4] (e) the [Si_2Se_7] unit,[5] (f) the [α-Si_2Se_8] unit,[6] (g) the [Si_3Se_9] unit,[8] (h) the [Si_4Se_{10}] unit,[9] (i) the [β-Si_2Se_8] unit.[7]

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