Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Tuning electronic and optical properties in a new class of covalent organic frameworks

Supporting Information

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Table S1. The calculated enthalpies of formation (ΔH; kJ mol^{-1}*f.u.*$^{-1}$) according to eq 1 for the [$(X_4Y)(O_2B\text{-}C_6H_4\text{-}BO_2)_3$] (X=C/Si; Y=C, Si, Ge, Sn, and Pb) compounds. 1*f.u.*= [$(X_4Y)(O_2B\text{-}C_6H_4\text{-}BO_2)_3$]

$(X_4Y)(O_2B\text{-}C_6H_4\text{-}BO_2)_3$	(C, C)	(C, Si)	(C, Ge)	(C, Sn)	(C, Pb)
ΔH (kJ mol^{-1}*f.u.* ^{1})	-46.47	-47.61	-46.32	-41.67	-37.57
$(X_4Y)(O_2B\text{-}C_6H_4\text{-}BO_2)_3$	(Si, C)	(Si, Si)	(Si, Ge)	(Si, Sn)	(Si, Pb)
ΔH (kJ mol^{-1}*f.u.* ^{1})	-75.90	-70.60	-70.86	-65.82	-62.86

Table S2. Optimized equilibrium lattice constant (*a* (Å)), bulk modulus (B_0 (GPa)), and its pressure derivative (B_0’) for novel materials (X, Y), (X = C/Si; Y = C, Si, Ge, Sn, and Pb) as well as that of prototypical MOF-5.

(X, Y)	***a* (Å)**	**B_0 (GPa)**[a]	**B_0’**[a]
(C, C)	24.0980	21.84(21.86)[21.87]	3.53(3.55)[3.54]
(C, Si)	24.2861	21.66(21.69)[21.68]	2.69(2.71)[2.71]
(C, Ge)	24.3361	21.54(21.56)[21.55]	2.59(2.60)[2.61]
(C, Sn)	24.4613	21.46(21.48)[21.49]	3.77(3.78)[3.80]
(C, Pb)	24.4991	21.38(21.40)[21.41]	3.98(4.00)[4.01]
(Si, C)	25.4826	19.28(19.29)[19.29]	4.33(4.33)[4.34]
(Si, Si)	25.8116	18.79(18.80)[18.80]	4.49(4.51)[4.52]
(Si, Ge)	25.8341	18.70(18.72)[18.71]	2.20(2.21)[2.22]
(Si, Sn)	25.9704	18.40(18.41)[18.41]	3.10(3.11)[3.11]
(Si, Pb)	25.9983	18.23(18.25)[18.25]	5.04(5.04)[5.05]
MOF-5	<25.6690>[b]<25.8849>[c]26.0443[d]	15.37(15.37)[15.37][d]	5.06(5.13)[5.17][d]

[a] Data without brackets from Murnaghan EOS; data (in parentheses) from Birch-Murnaghan 3rd-order EOS; data [in brackets] from Universal EOS.

[b] and [c] <in double braces> are the experimental lattice parameters of single crystals of as-synthesized and fully desolvated MOF-5 from ref[1], respectively.

[d] The lattice parameter of MOF-5 from PBE-GGA VASP calculations in ref[2].

Table S3. Optimized bond lengths (Å) and angles (°) for novel COFs materials (X, Y), (X = C/Si; Y = C, Si, Ge, Sn, and Pb) series at their equilibrium volumes in the cubic *Fm-3m* symmetry (no. 225). The atomic labels are followed that in Fig. 1.

(X, Y)	X-Y	X-O	O-B	B-C1	C1-C2	C2-C2	C2-H	X-Y-X	Y-X-O	X-O-B	O-B-C1	B-C1-C2	C1-C2-C2	C1-C2-H
(C, C)	1.718	1.396	1.359	1.557	1.408	1.393	1.092	109.471	115.885	129.455	120.075	120.804	120.804	119.303
(C, Si)	1.896	1.409	1.386	1.559	1.408	1.392	1.092	109.471	112.526	129.536	116.798	120.867	120.867	119.276
(C, Ge)	1.947	1.408	1.393	1.561	1.409	1.392	1.092	109.471	111.338	130.005	116.079	120.933	120.933	119.219
(C, Sn)	2.054	1.416	1.412	1.564	1.409	1.392	1.092	109.471	109.244	130.406	114.386	121.010	121.010	119.206
(C, Pb)	2.091	1.420	1.419	1.564	1.409	1.392	1.091	109.471	108.545	130.450	113.731	121.057	121.057	119.204
(Si, C)	1.902	1.632	1.379	1.560	1.409	1.393	1.092	109.471	112.356	133.371	120.462	121.001	121.001	119.063
(Si, Si)	2.187	1.650	1.405	1.567	1.409	1.393	1.091	109.471	106.402	135.869	117.006	121.056	121.056	119.061
(Si, Ge)	2.207	1.652	1.406	1.568	1.409	1.393	1.091	109.471	105.935	136.124	116.795	121.102	121.102	119.046
(Si, Sn)	2.323	1.662	1.417	1.569	1.409	1.393	1.091	109.471	103.329	137.707	115.771	121.137	121.137	119.022
(Si, Pb)	2.332	1.662	1.418	1.572	1.409	1.393	1.091	109.471	103.134	137.787	115.656	121.246	121.246	118.961

As a further analysis of the newly designed ten COFs, the geometry parameters (optimized bond lengths (Å) and angles (°)) for the whole series were listed in **Table S3** and plotted in **Fig. S1** for a vivid evolution picture of bond lengths and angles *vs.* different atoms of group IVa. Interestingly, some general trend and change rule can be revealed for bond lengths and angles. We can clearly see (in **Table S3** and **Fig. S1**) that the bond lengths of X-Y are increasing when one moves X from C to Si, and Y from C to Pb. This is consistent with the fact that crystal lattice is increasing when one moves X from C to Si, and Y from C to Pb. The bond lengths of X-O and O-B are only slightly increasing, whereas the B-C1, C1-C2, C2-C2, and C2-H bond lengths are essentially identical. Interestingly, the angle ∠X-Y-X keeps constant (109.471°) independent of composition, which can be ascribed to the local T_d symmetry of X_4Y node. The ∠X-O-B angles are increasing, whereas the ∠Y-X-O and ∠O-B-C1 angles are decreasing when one moves X from C to Si, and Y from C to Pb.

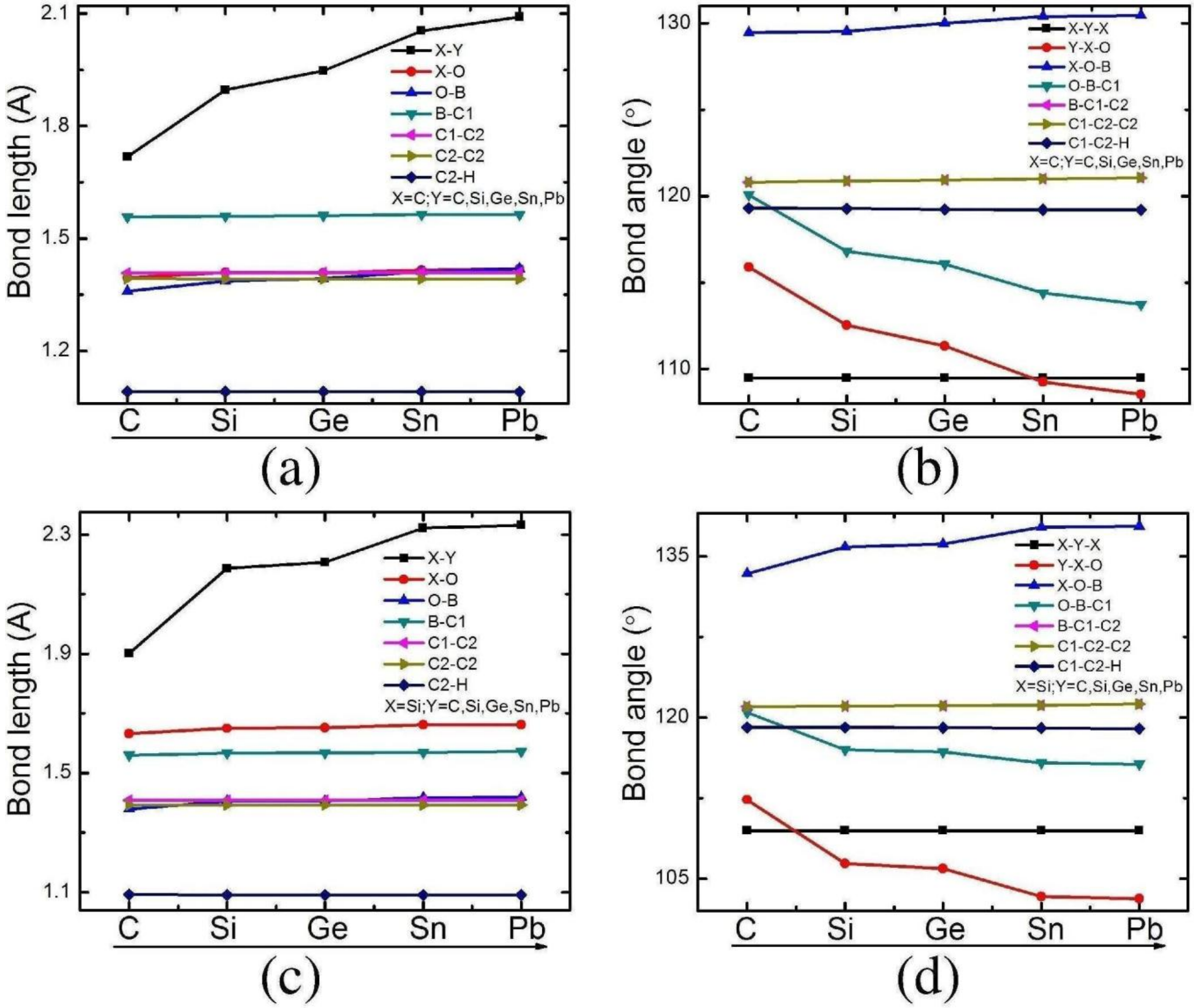


Figure S1. The evolution of bond lengths and angles *vs.* different atoms of group IVa of novel materials (X, Y), (X = C/Si; Y = C, Si, Ge, Sn, and Pb) at the equilibrium volume. (a)/(b) and (c)/(d) are the change trend of bond lengths/angles of subsystems (C, Y) and (Si, Y), respectively.

Table S4. Estimated band gap values (Theo. E_g (in eV)) for the novel materials (X, Y) (X = C/Si; Y = C, Si, Ge, Sn, and Pb), experimental and theoretical band gap values (Expt. and Theo. E_g) for prototypical MOF-5, as well as the corresponding wavelength (**λ** in nm) of absorption lights. Note that **λ** = hc/E in nm; h is Planck constant (in eV·s), c is the speed of light (i.e., 3×10^8 m/s or 3×10^{17} nm/s), E is the energy (in eV), here corresponding to a certain band gap of a specific material.

(X, Y)	Theo. E_g (eV)	**λ (nm)**	**(X, Y)**	Theo. E_g (eV)	**λ (nm)**
(C, C)	3.7821	328.0	(Si, C)	3.7037	335.0
(C, Si)	3.6799	337.2	(Si, Si)	3.6197	342.8
(C, Ge)	3.6603	339.0	(Si, Ge)	3.5003	354.5
(C, Sn)	3.5311	351.4	(Si, Sn)	2.9210	424.8
(C, Pb)	3.1630	392.3	(Si, Pb)	2.7003	459.5
MOF-5	3.558 (Theo.)[2]	348.7	MOF-5	3.4-4.0 (Expt.)[3-5]	364.9-310.2

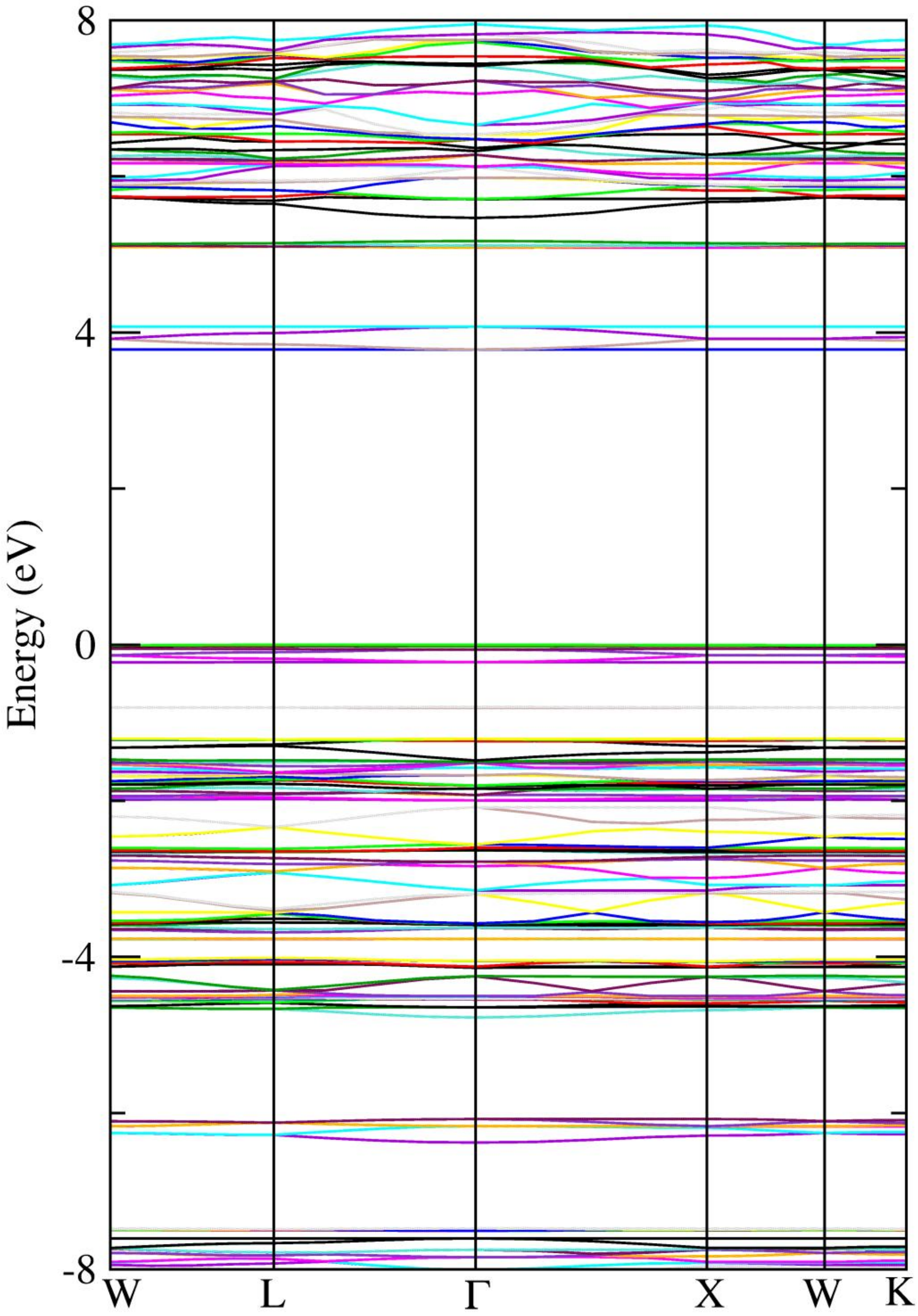


Figure S2. The electronic band structure of (C, C). The Fermi level is set to zero and placed in the valence band maximum.

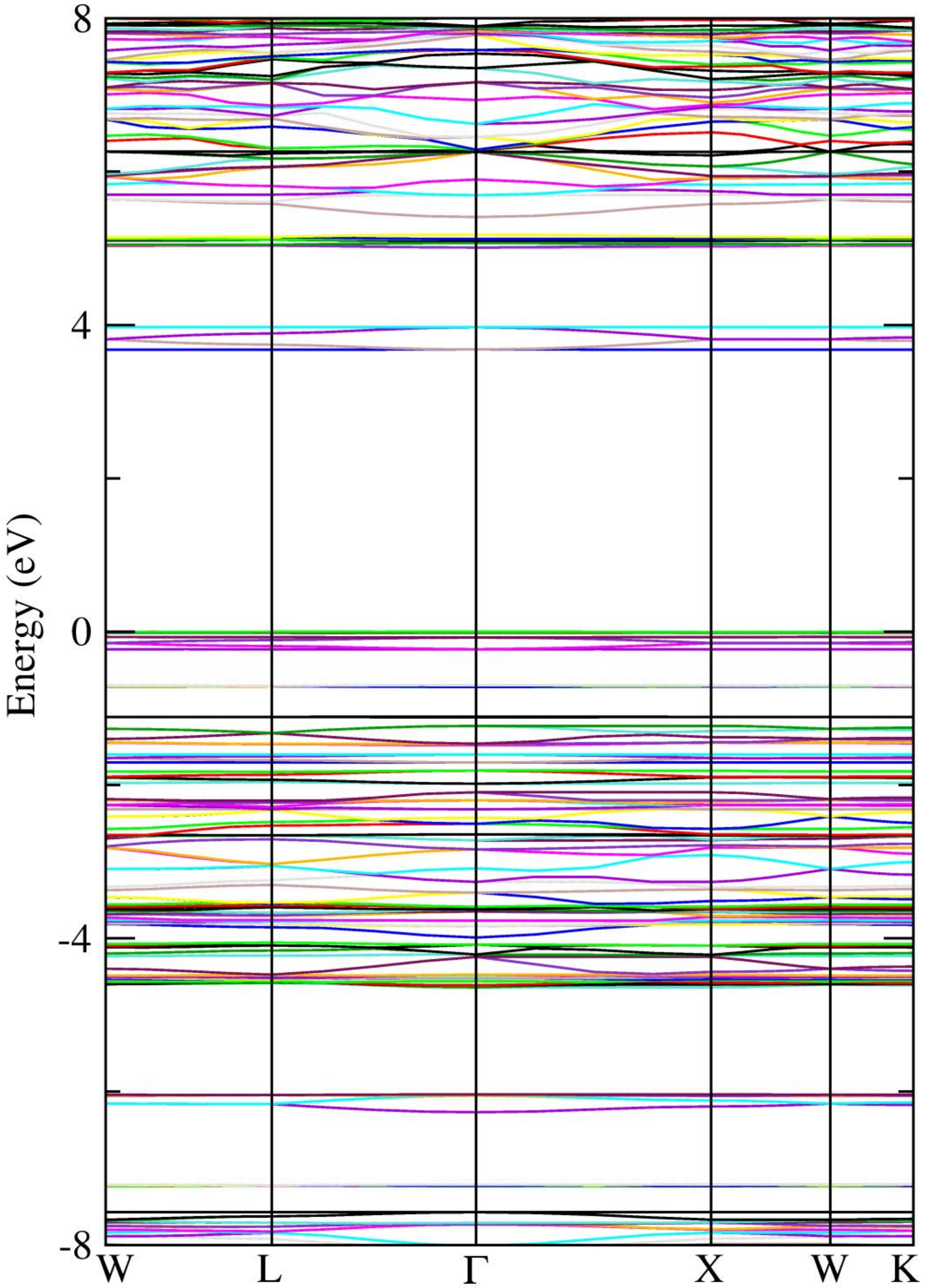


Figure S3. The electronic band structure of (C, Si). The Fermi level is set to zero and placed in the valence band maximum.

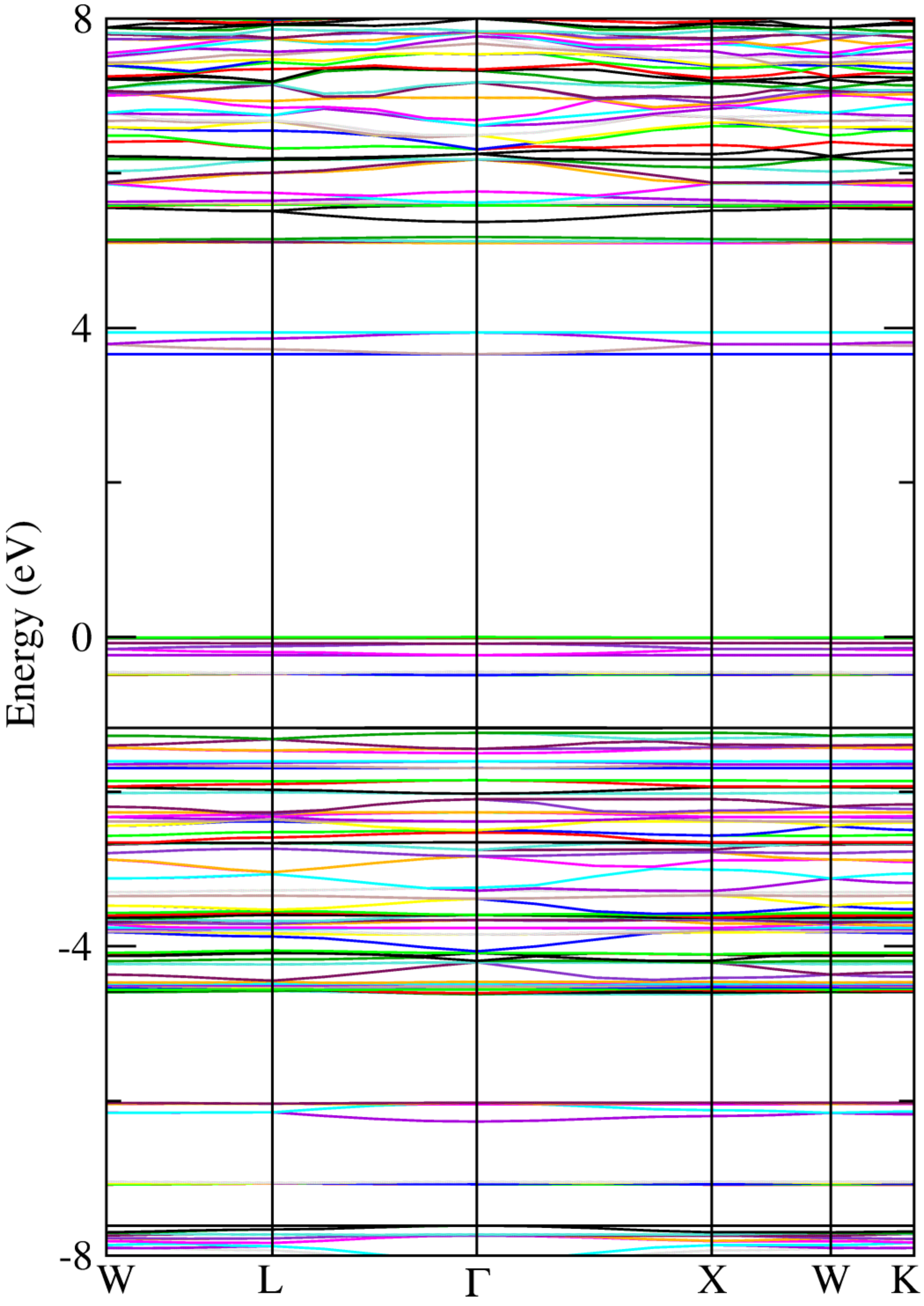


Figure S4. The electronic band structure of (C, Ge). The Fermi level is set to zero and placed in the valence band maximum.

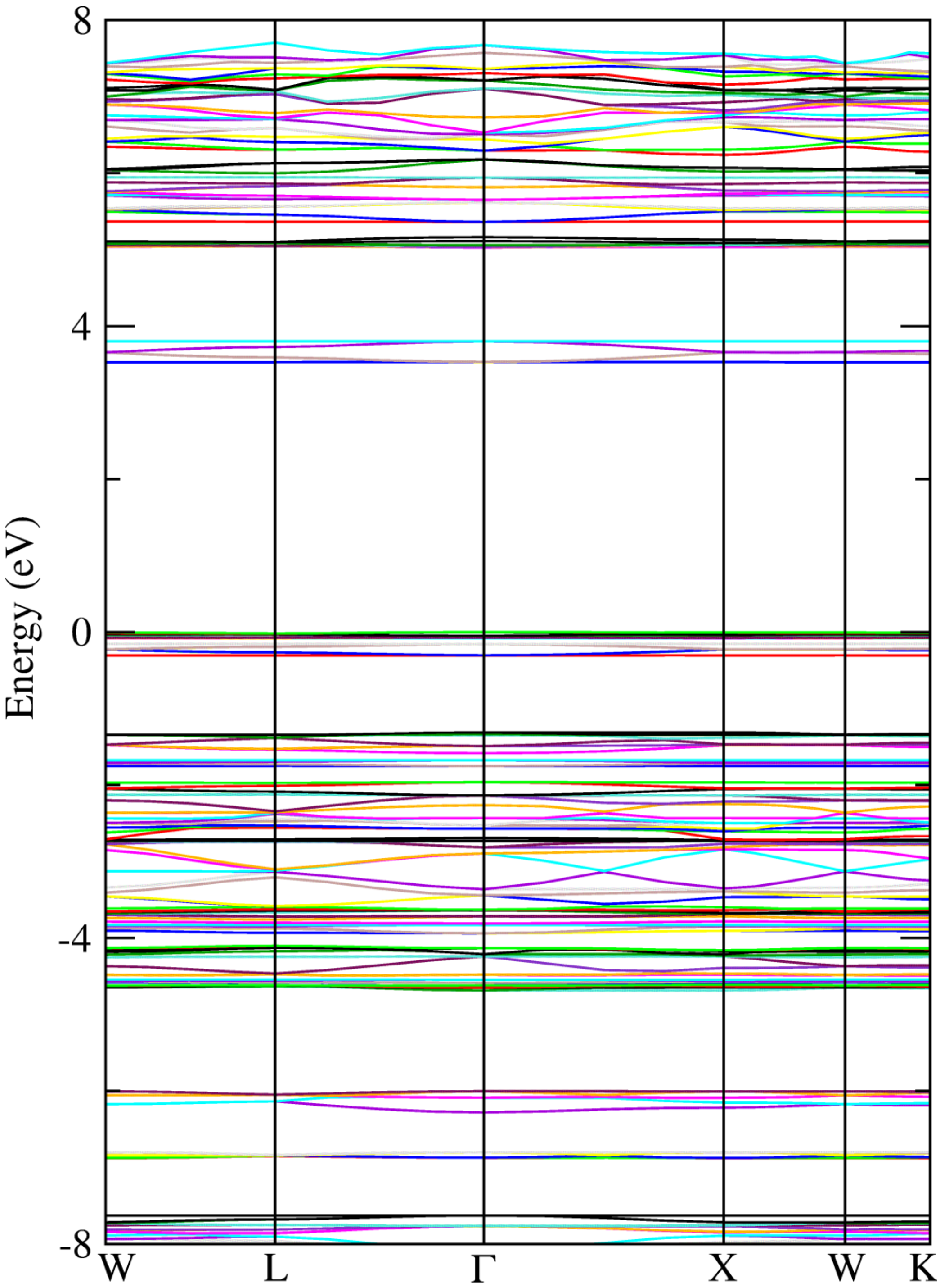


Figure S5. The electronic band structure of (C, Sn). The Fermi level is set to zero and placed in the valence band maximum.

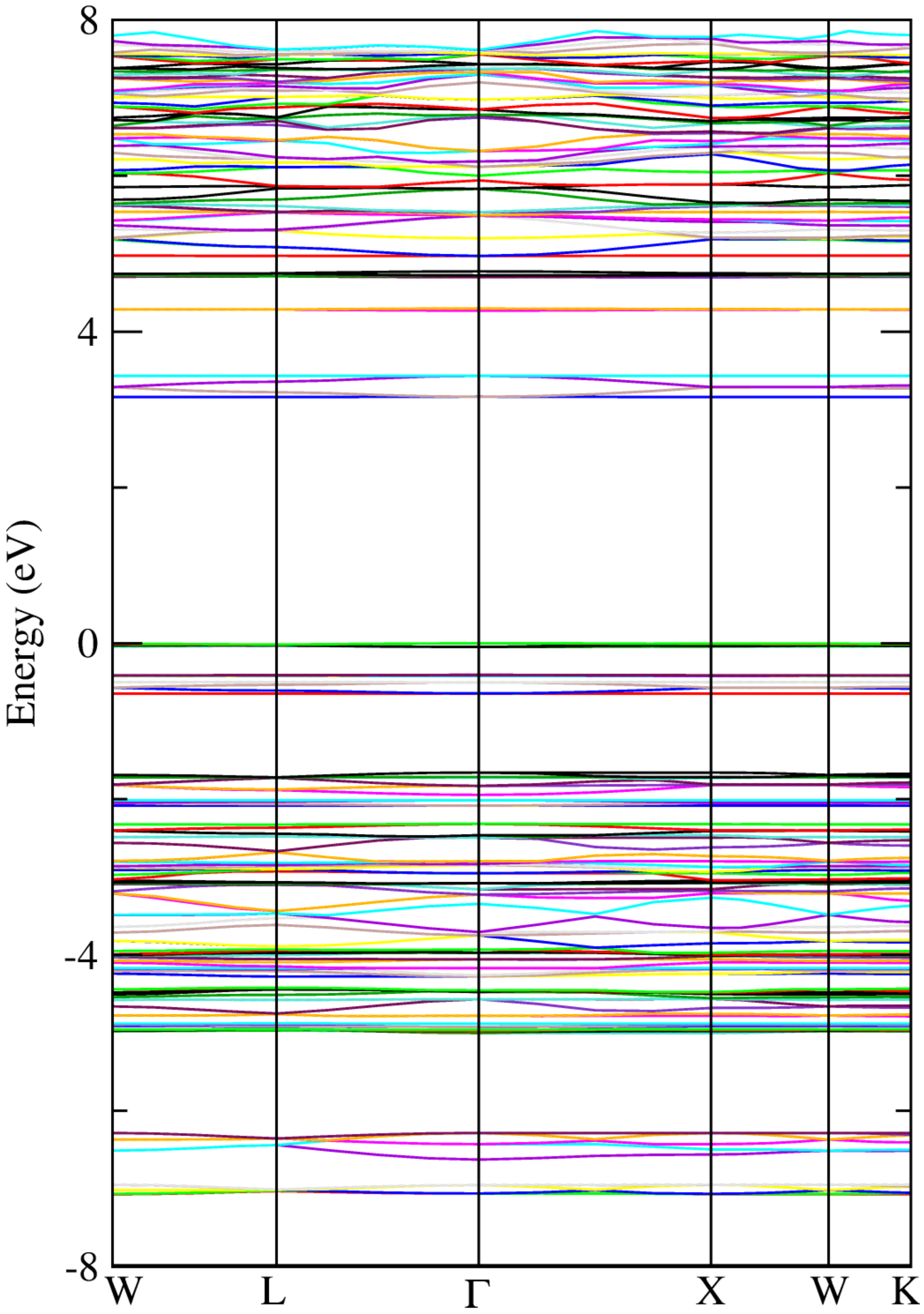


Figure S6. The electronic band structure of (C, Pb). The Fermi level is set to zero and placed in the valence band maximum.

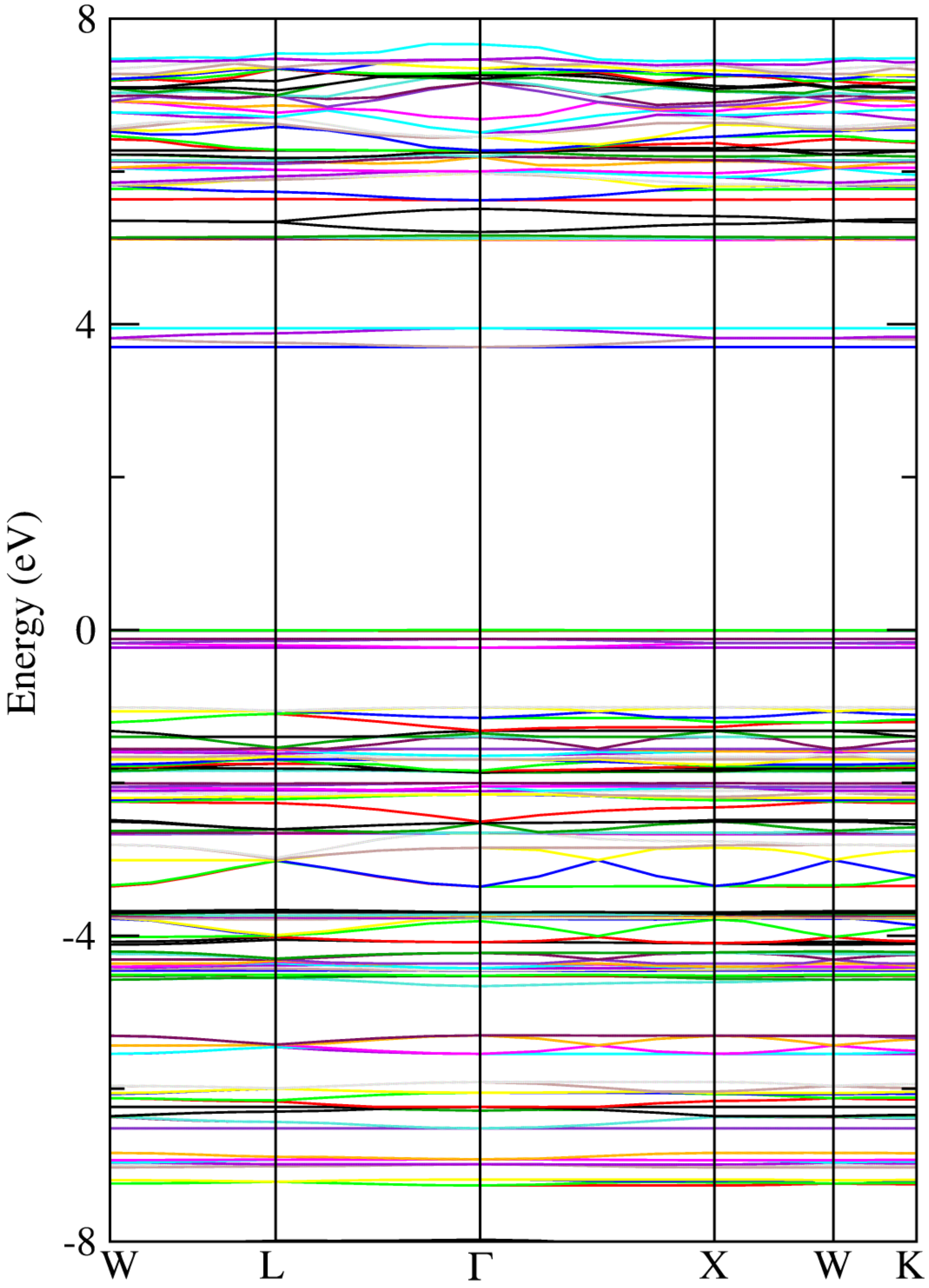


Figure S7. The electronic band structure of (Si, C). The Fermi level is set to zero and placed in the valence band maximum.

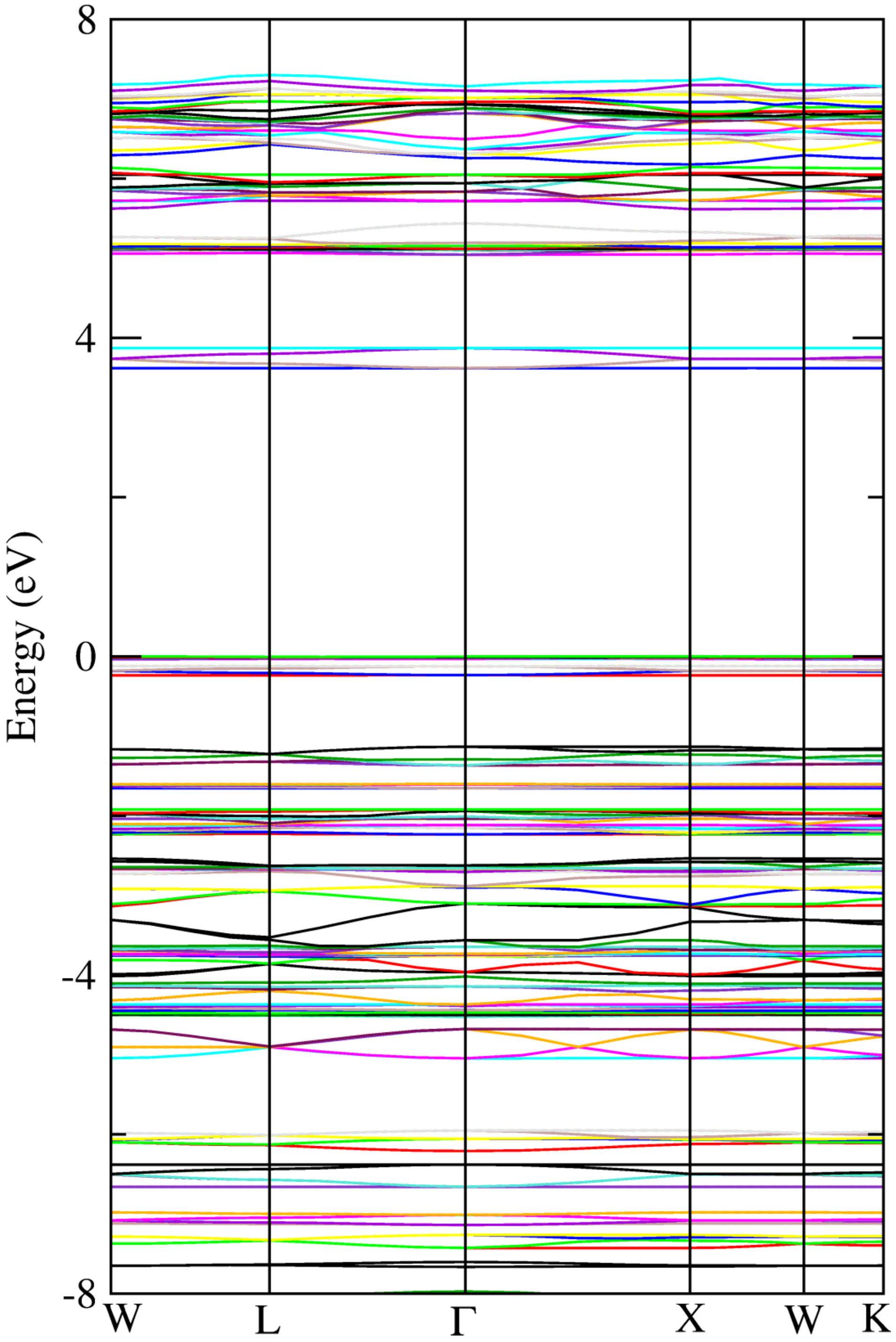


Figure S8. The electronic band structure of (Si, Si). The Fermi level is set to zero and placed in the valence band maximum.

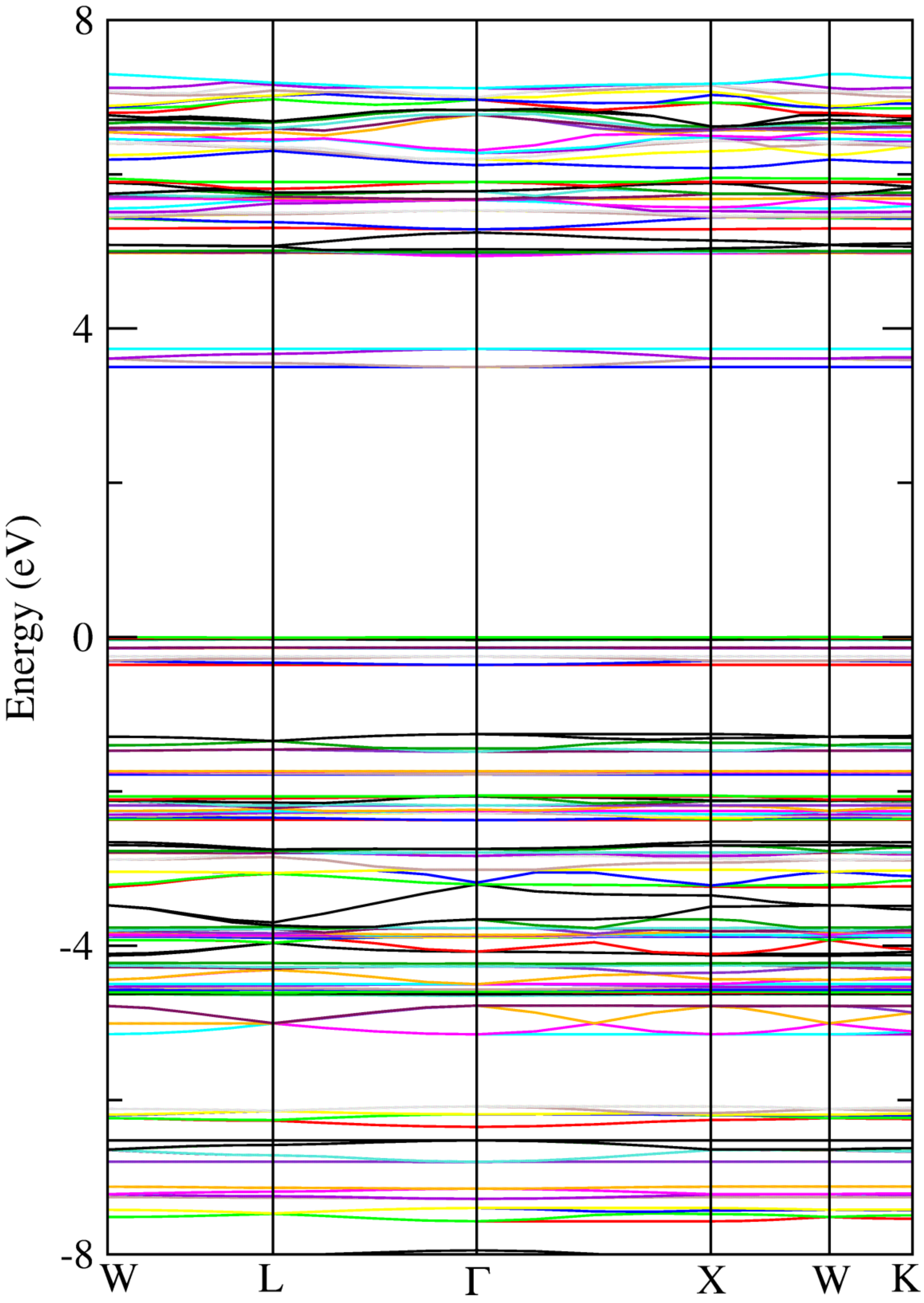


Figure S9. The electronic band structure of (Si, Ge). The Fermi level is set to zero and placed in the valence band maximum.

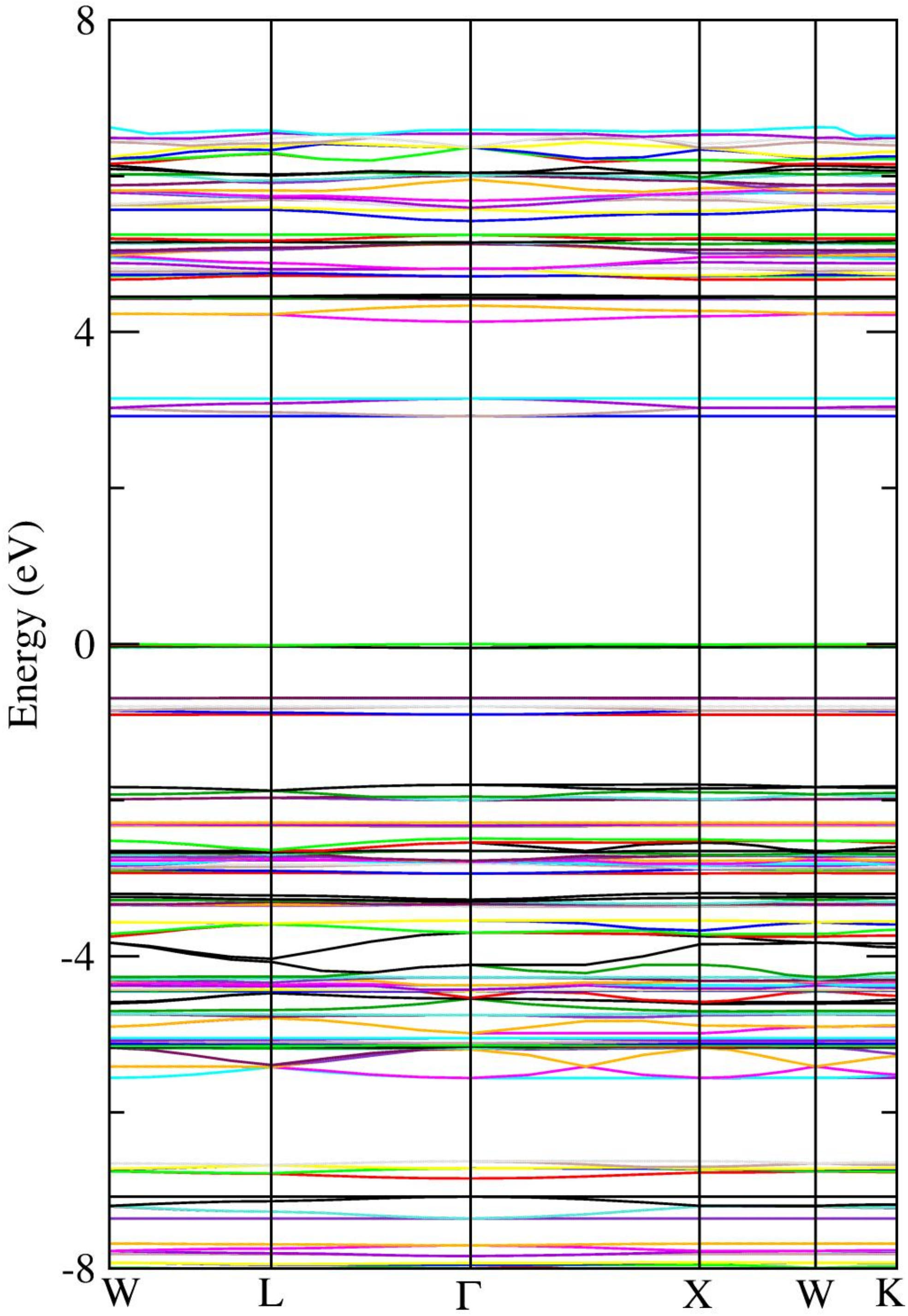


Figure S10. The electronic band structure of (Si, Sn). The Fermi level is set to zero and placed in the valence band maximum.

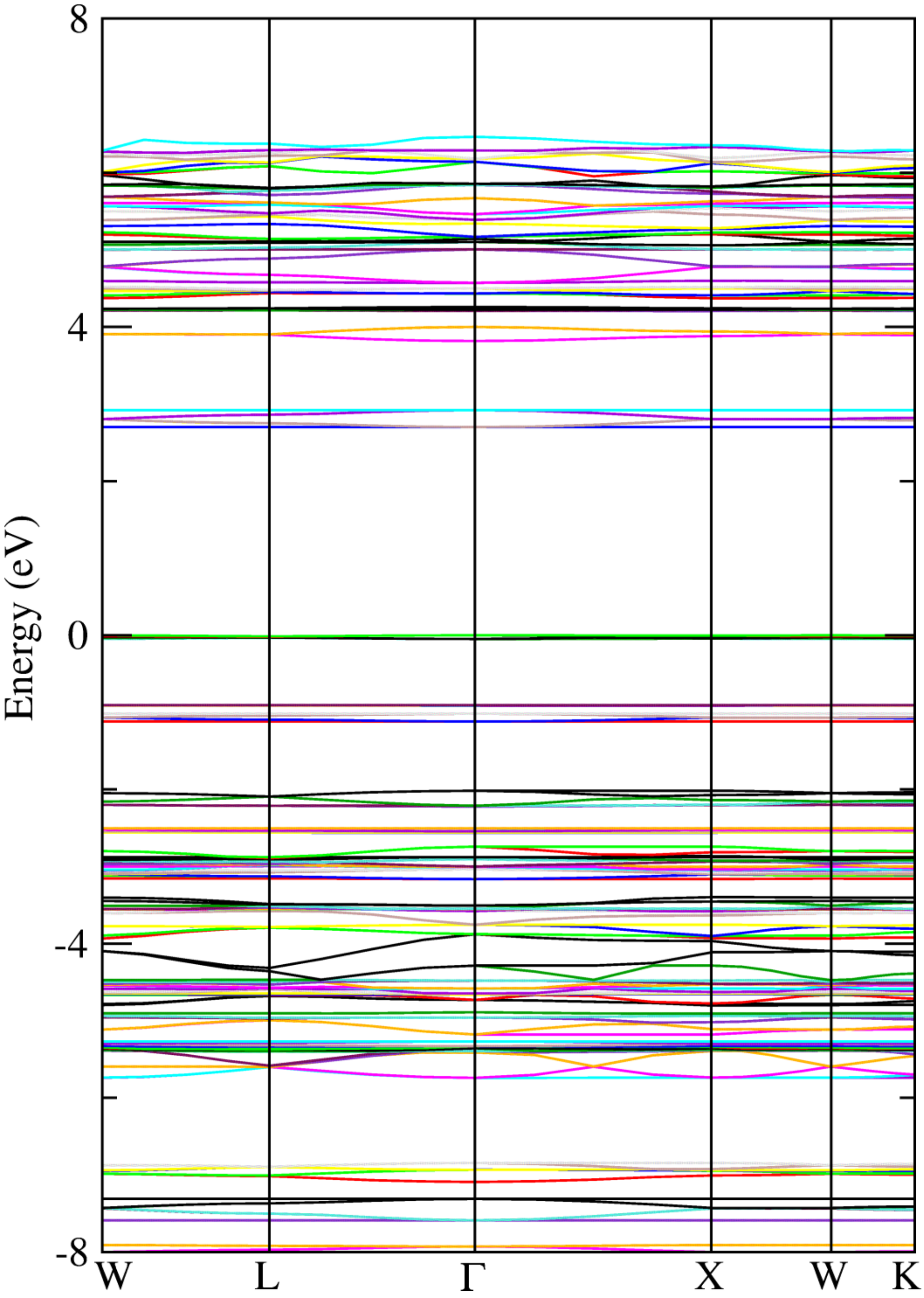


Figure S11. The electronic band structure of (Si, Pb). The Fermi level is set to zero and placed in the valence band maximum.

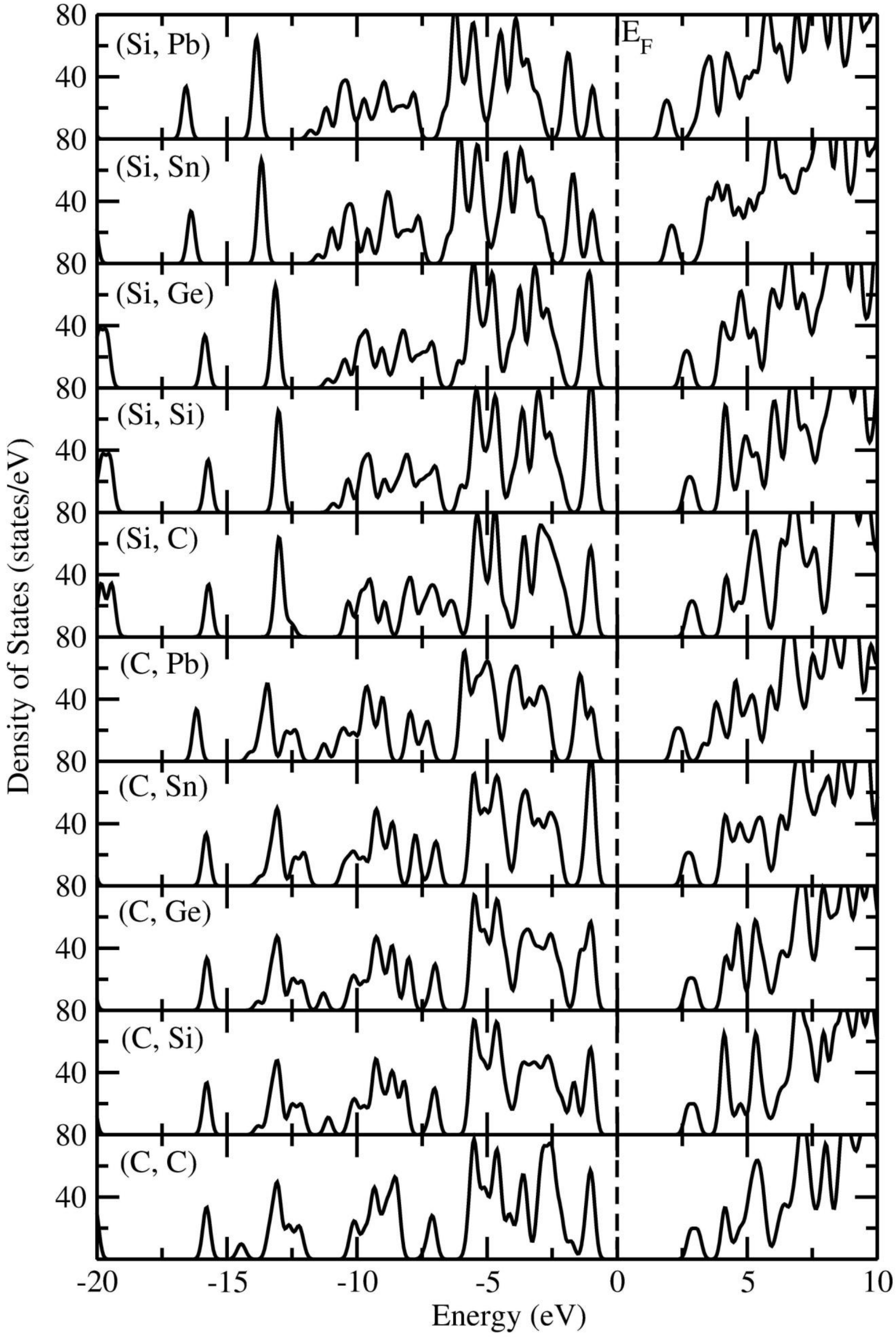


Figure S12. Calculated total density of states (TDOS) for (X, Y), (X=C/Si; Y=C, Si, Ge, Sn, and Pb) in the equilibrium cubic structure with *Fm*-*3m* symmetry (no. 225).

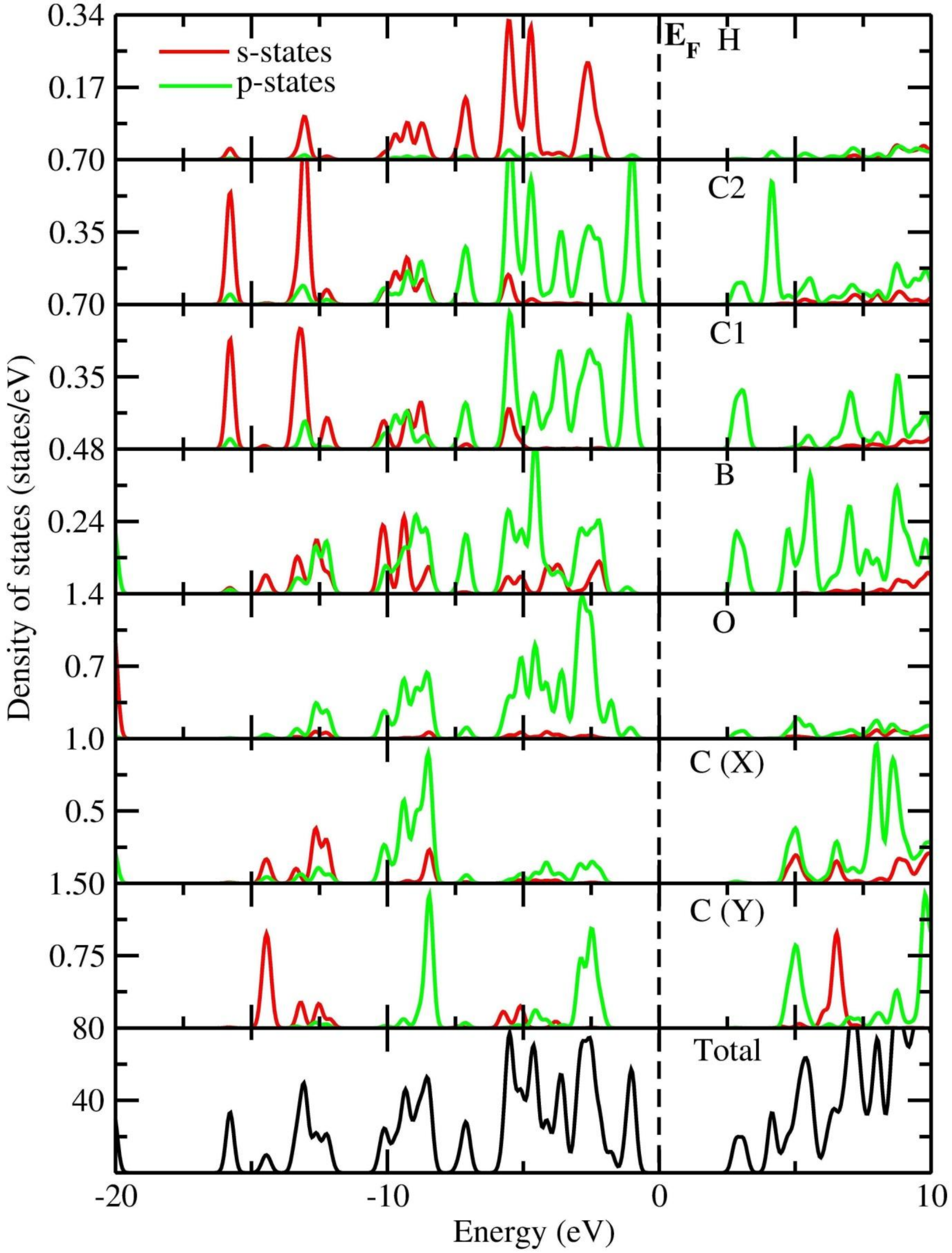


Figure S13. The calculated total density of states (TDOS) and partial density of states (PDOS) for (C, C) in the cubic *Fm-3m* symmetry (no. 225). The atomic labels in the table are followed that in Fig. 1.

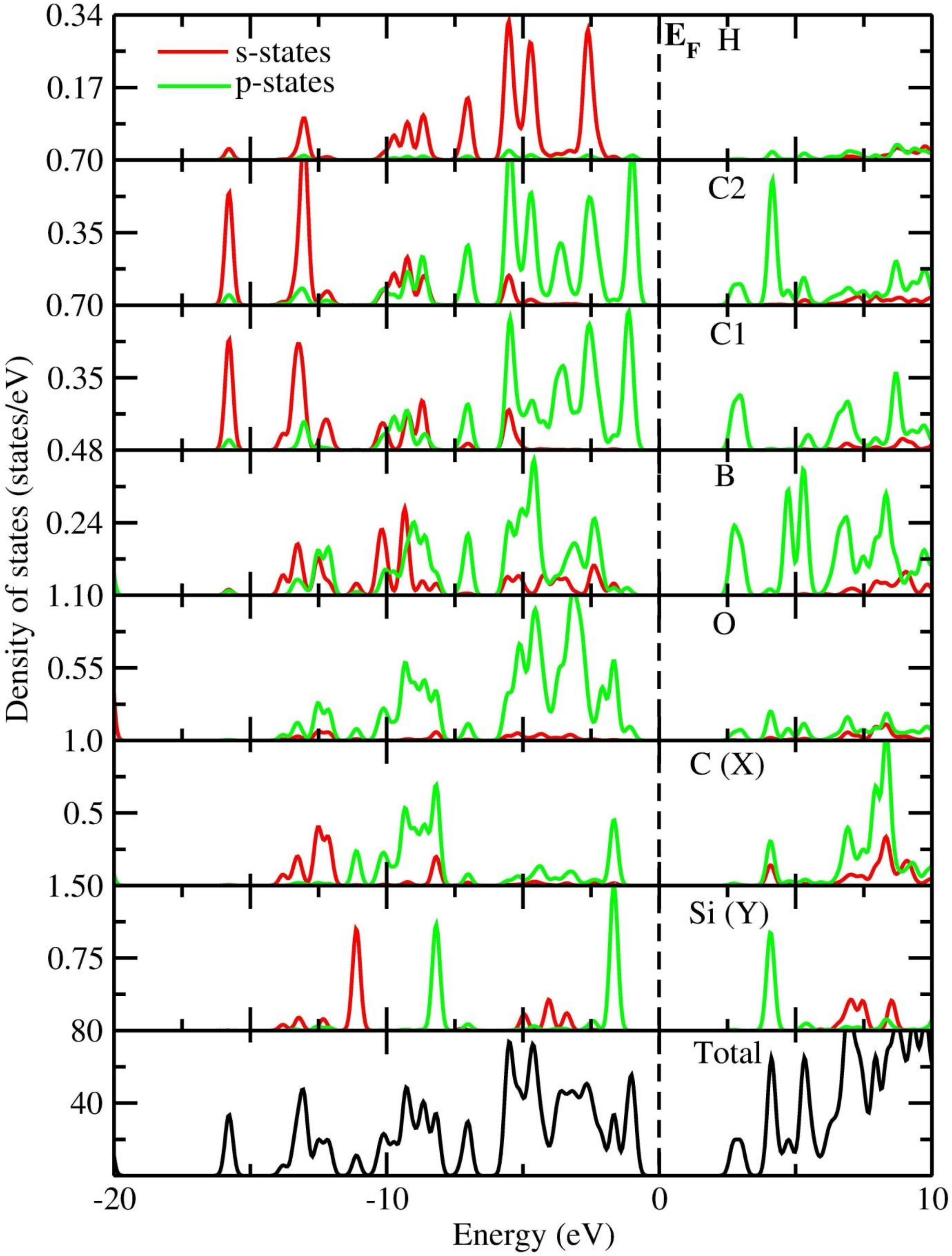


Figure S14. The calculated total density of states (TDOS) and partial density of states (PDOS) for (C, Si) in the cubic *Fm-3m* symmetry (no. 225)

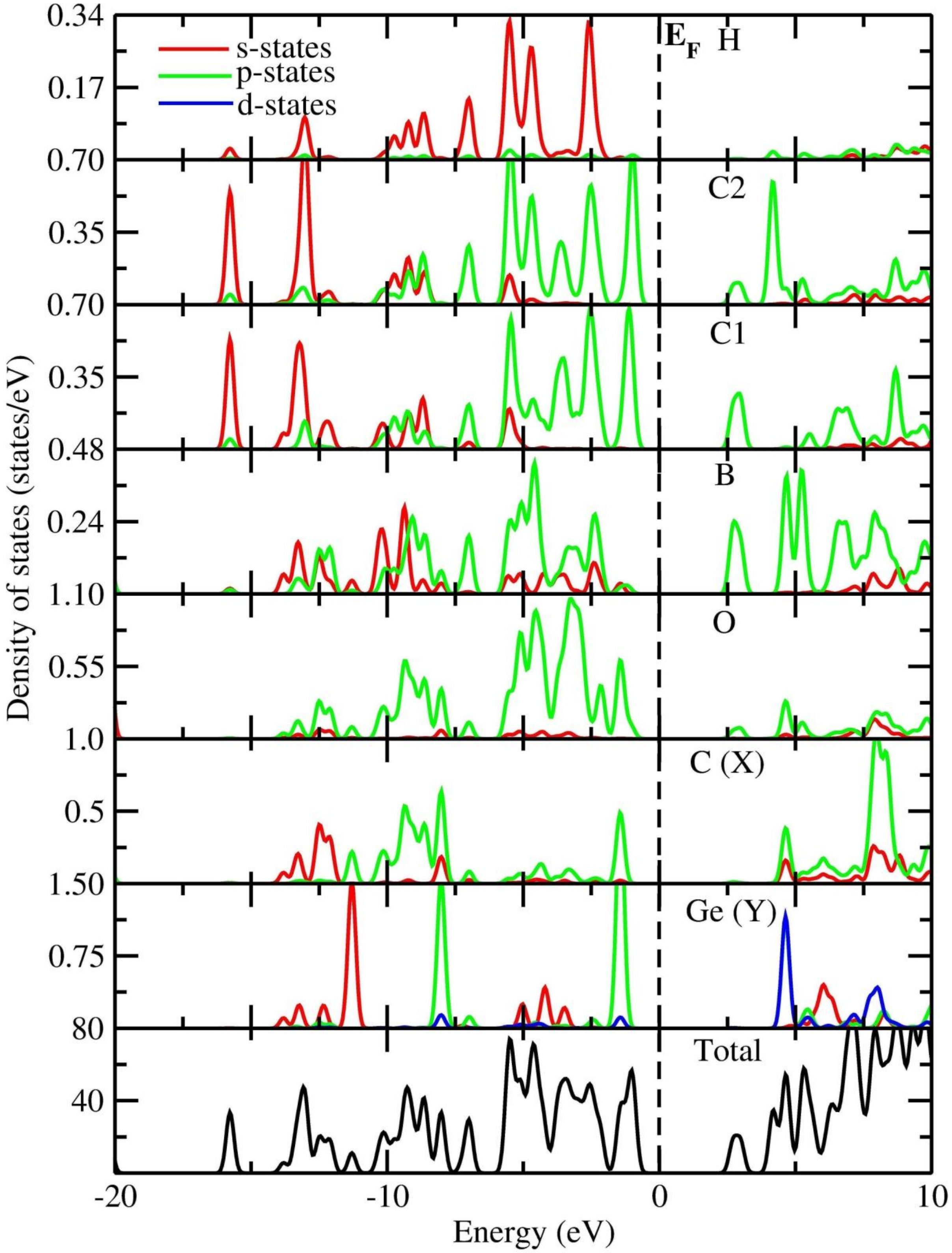


Figure S15. The calculated total density of states (TDOS) and partial density of states (PDOS) for (C, Ge) in the cubic *Fm-3m* symmetry (no. 225)

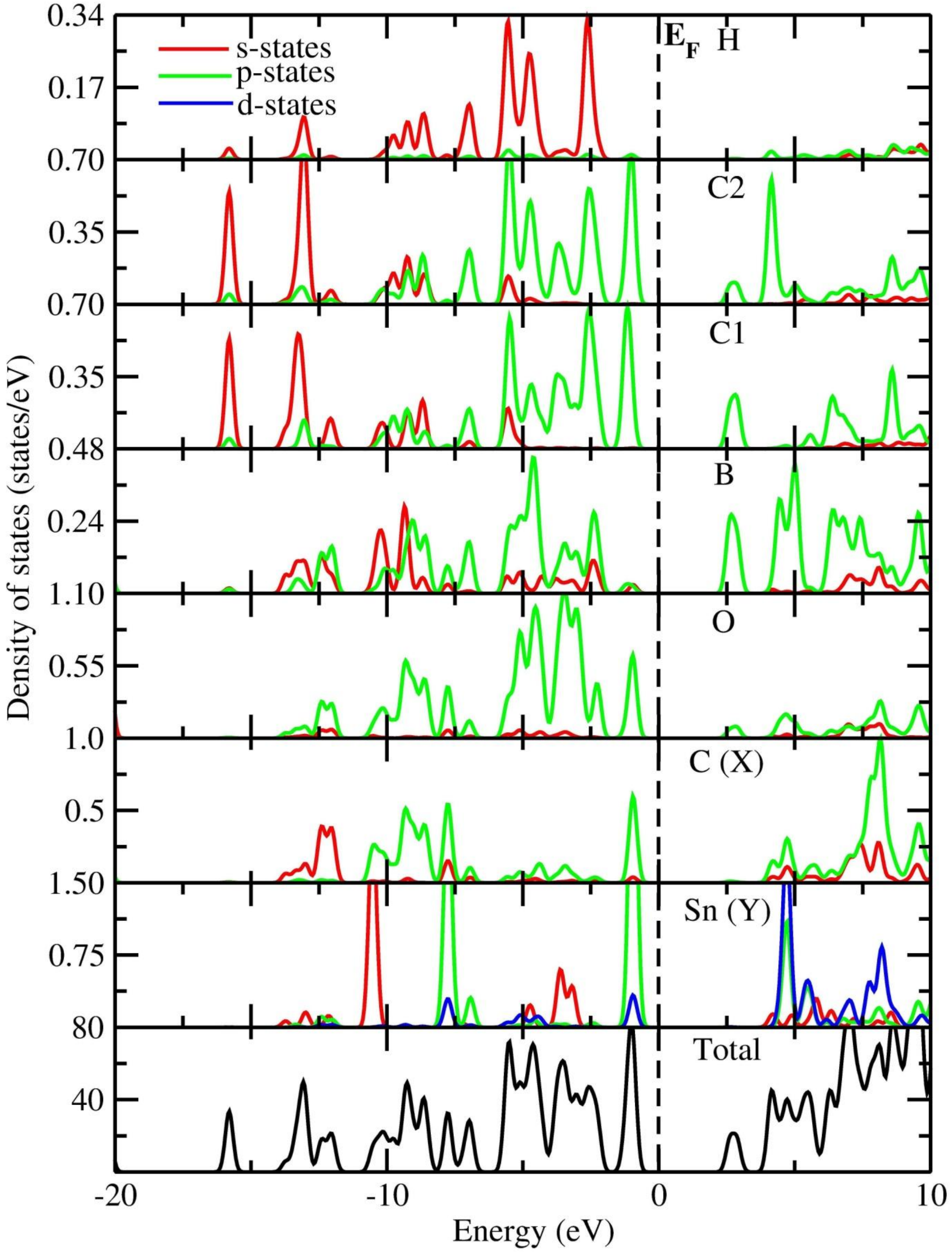


Figure S16. The calculated total density of states (TDOS) and partial density of states (PDOS) for (C, Sn) in the cubic *Fm-3m* symmetry (no. 225)

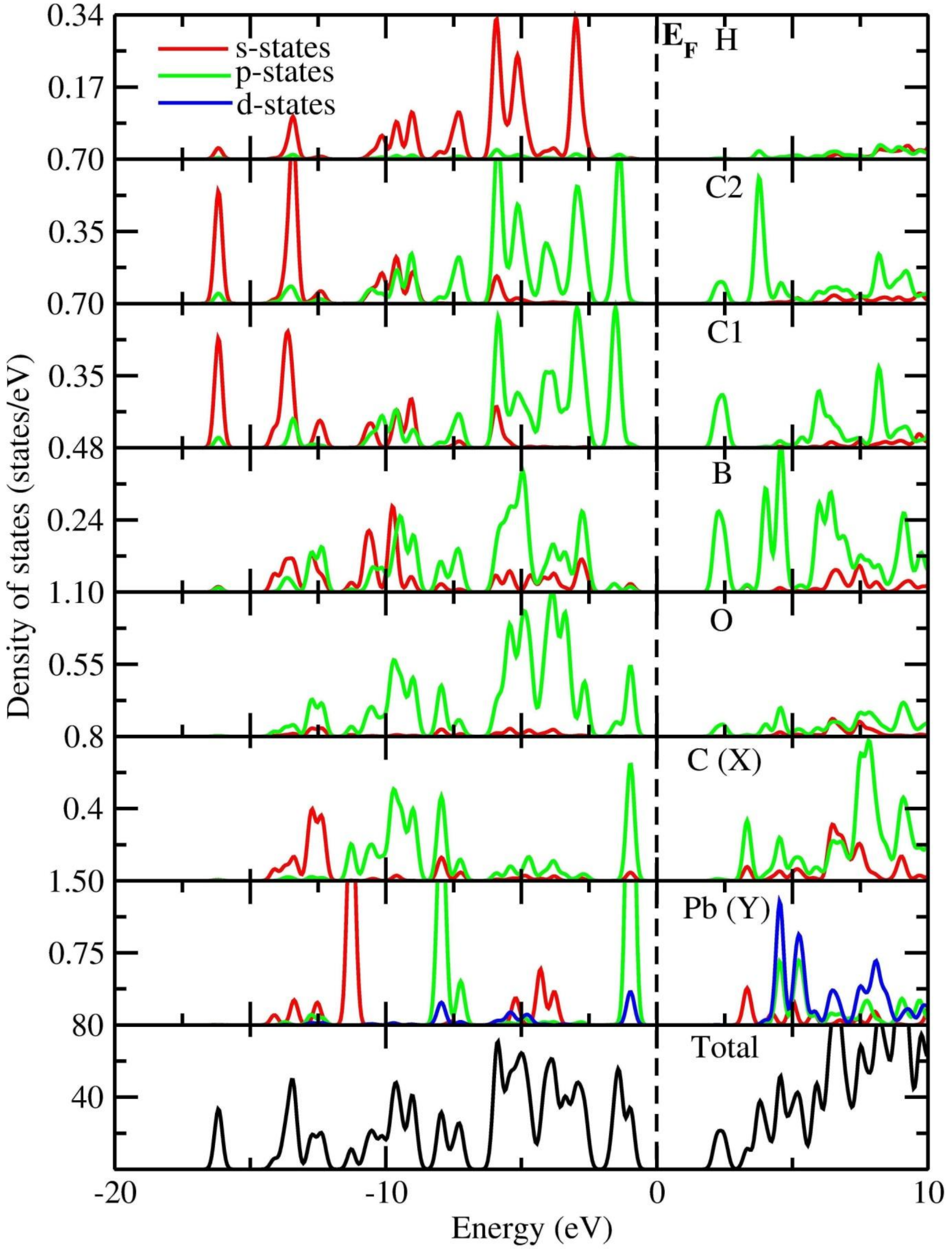


Figure S17. The calculated total density of states (TDOS) and partial density of states (PDOS) for (C, Pb) in the cubic *Fm-3m* symmetry (no. 225)

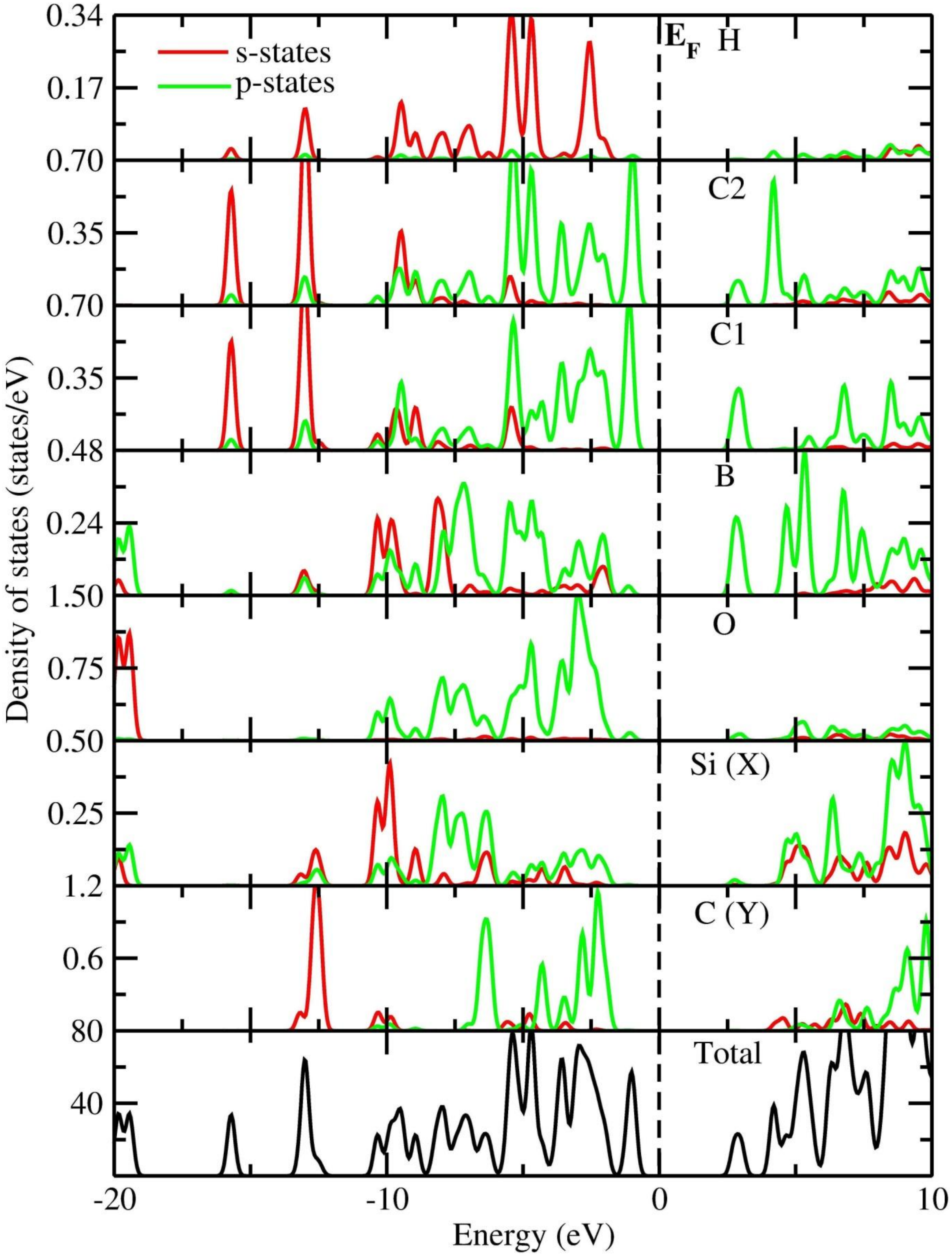


Figure S18. The calculated total density of states (TDOS) and partial density of states (PDOS) for (Si, C) in the cubic *Fm-3m* symmetry (no. 225)

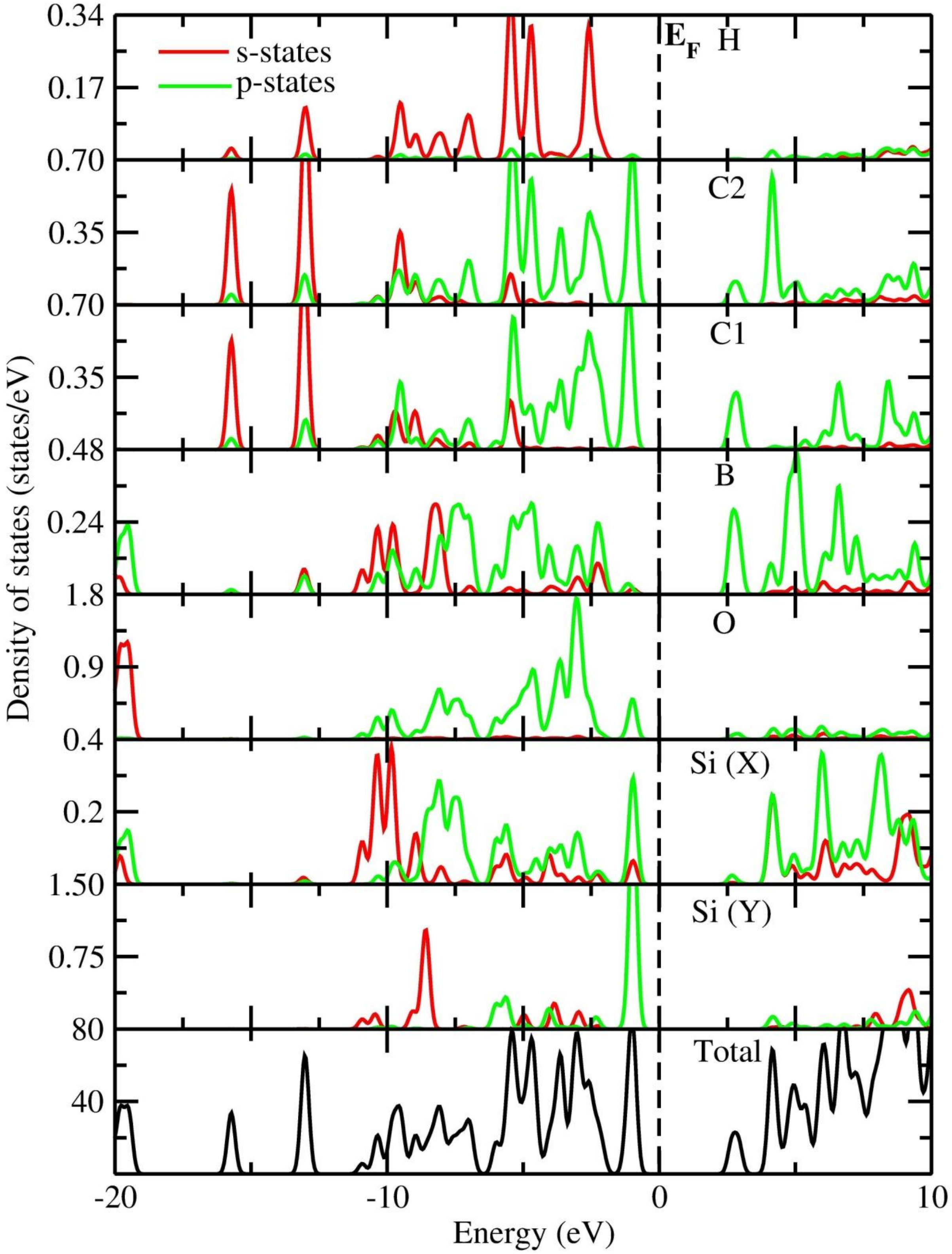


Figure S19. The calculated total density of states (TDOS) and partial density of states (PDOS) for (Si, Si) in the cubic *Fm-3m* symmetry (no. 225)

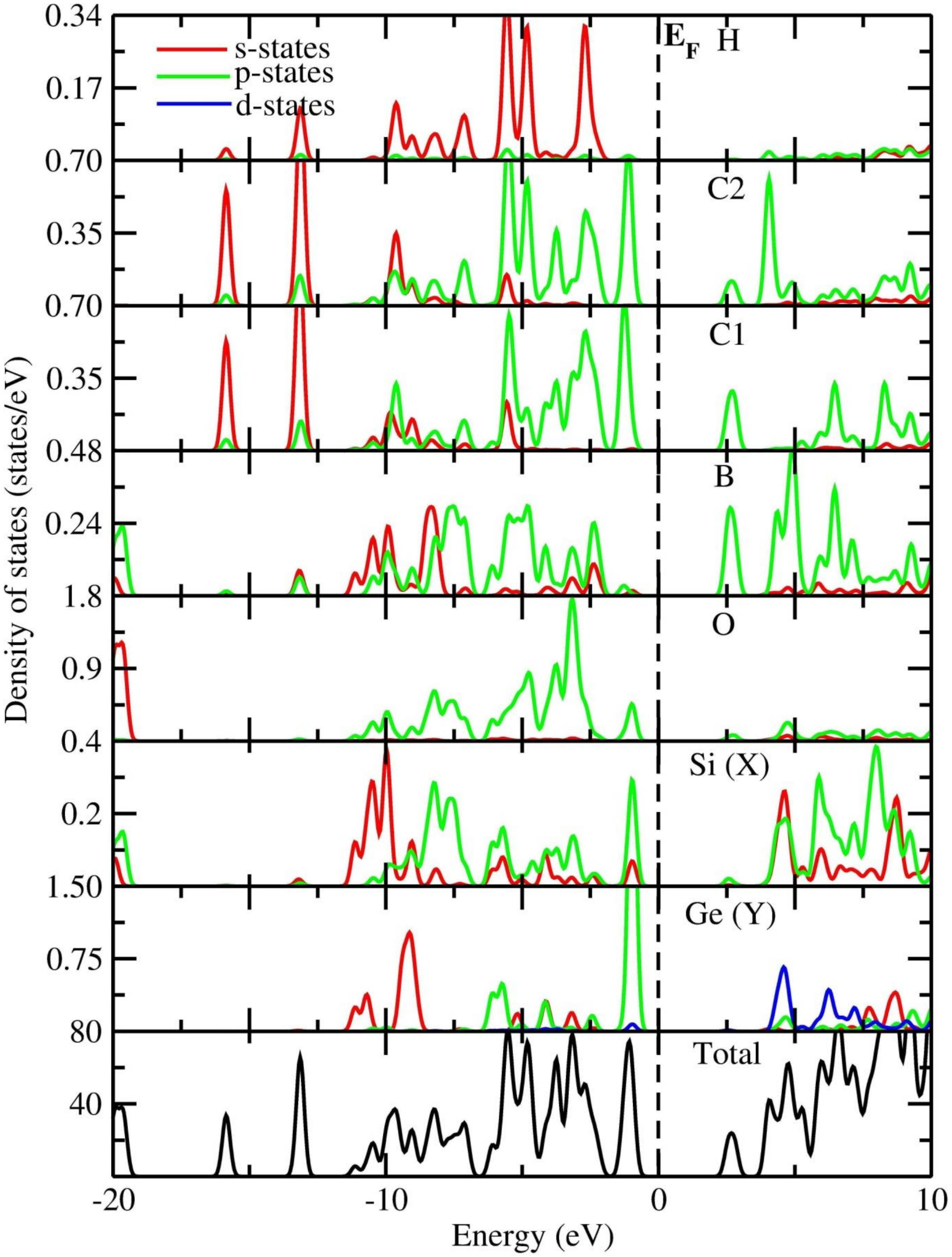


Figure S20. The calculated total density of states (TDOS) and partial density of states (PDOS) for (Si, Ge) in the cubic *Fm-3m* symmetry (no. 225)

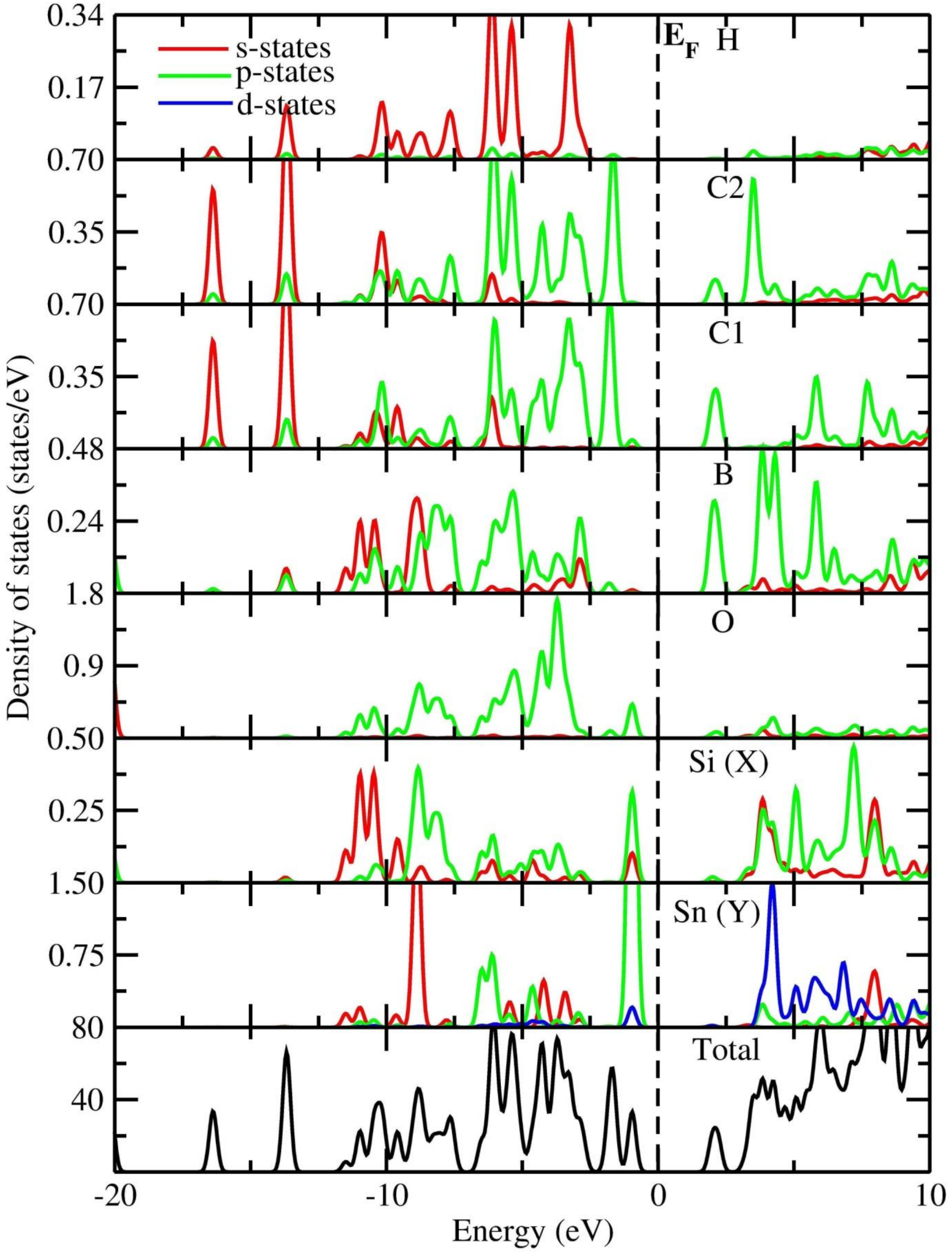


Figure S21. The calculated total density of states (TDOS) and partial density of states (PDOS) for (Si, Sn) in the cubic *Fm-3m* symmetry (no. 225)

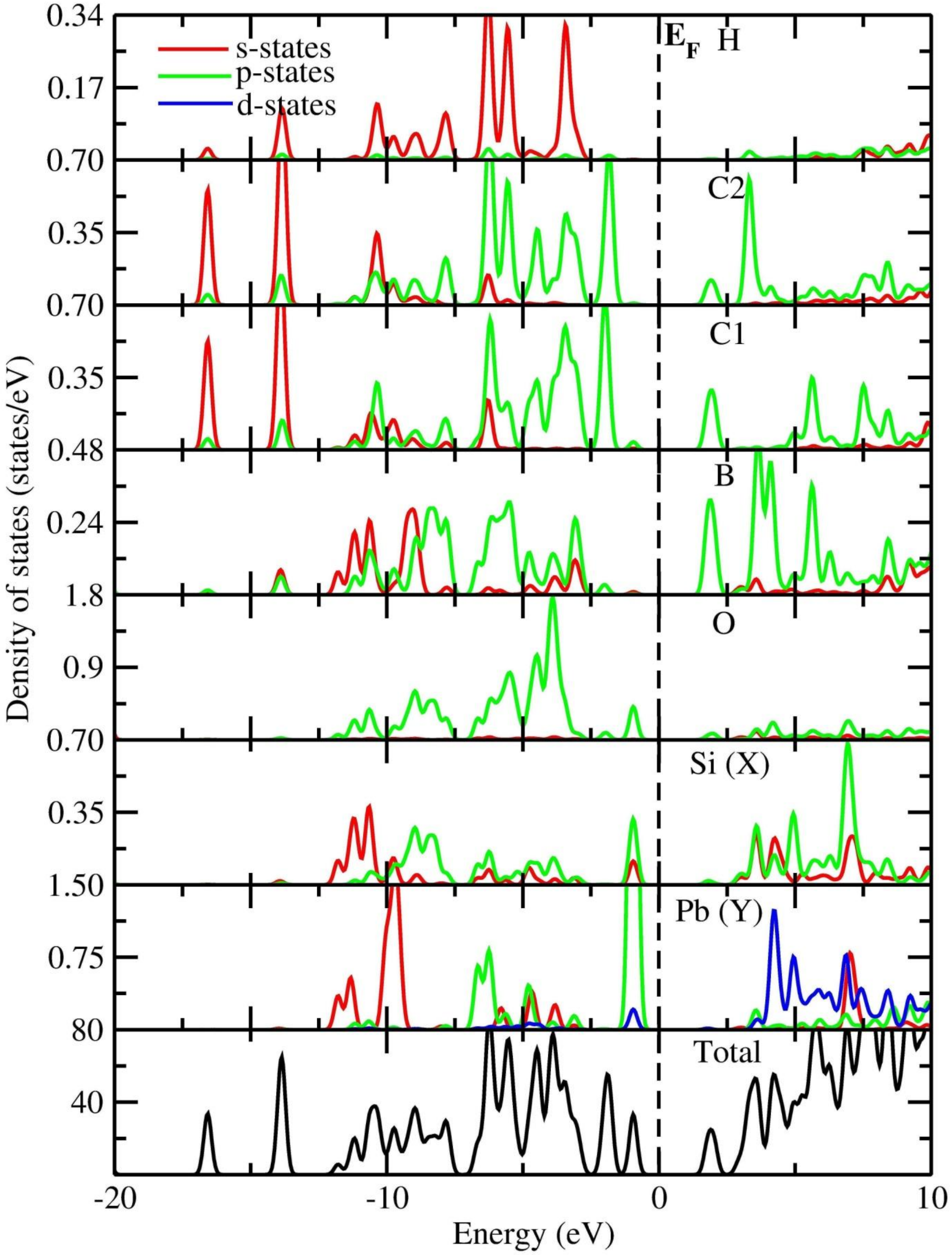


Figure S22. The calculated total density of states (TDOS) and partial density of states (PDOS) for (Si, Pb) in the cubic *Fm-3m* symmetry (no. 225)

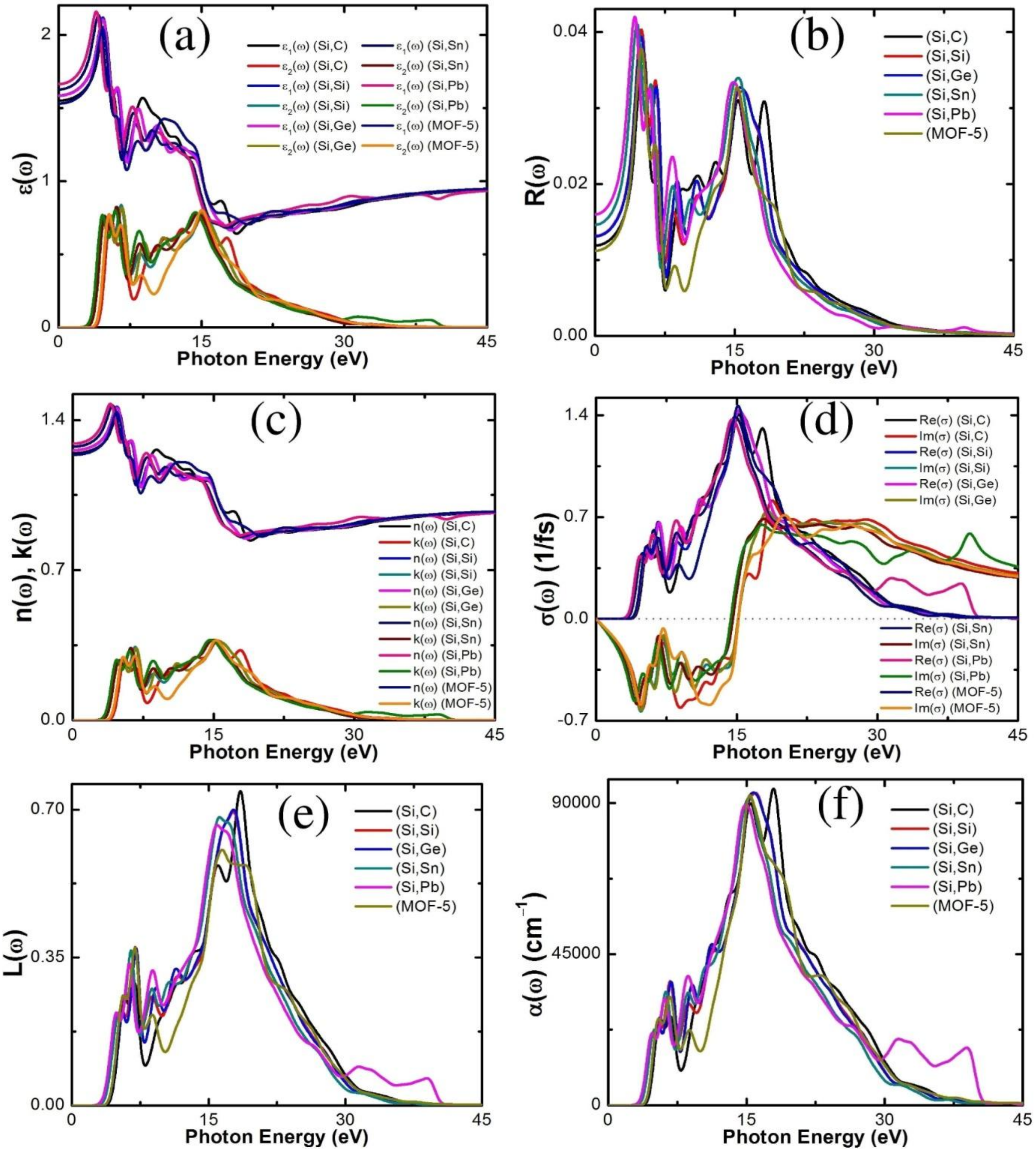


Figure S23. Calculated optical properties for (Si, Y) (Y=C, Si, Ge, Sn, and Pb) as well as that of prototypical MOF-5: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

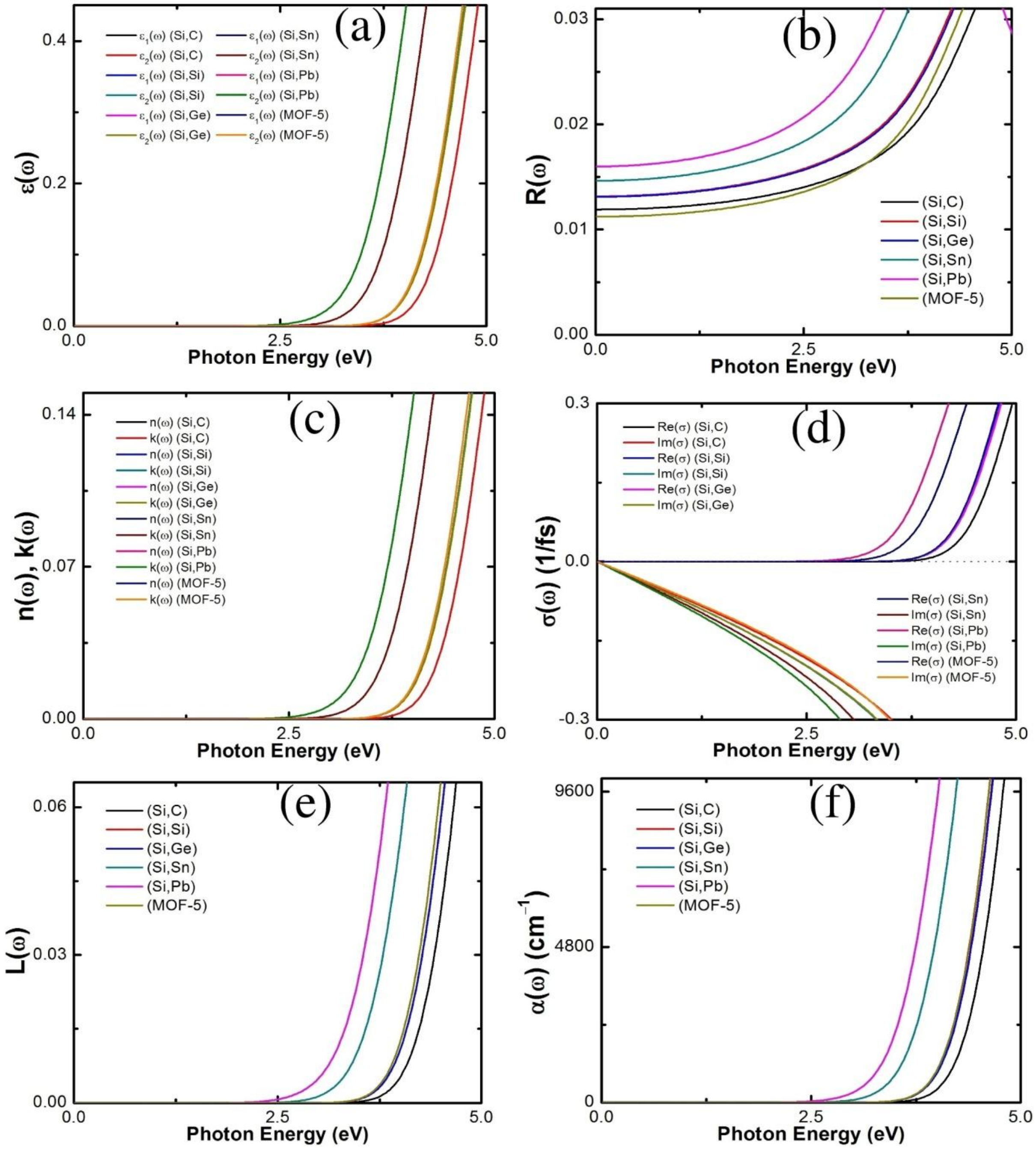


Figure S24. For having clear pictures of the initial optical response of the calculated COFs materials, we display the insets (0 ~ 5 eV) of optical properties (Fig. S23) for (Si, Y) (Y=C, Si, Ge, Sn, and Pb) as well as that of prototypical MOF-5: (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

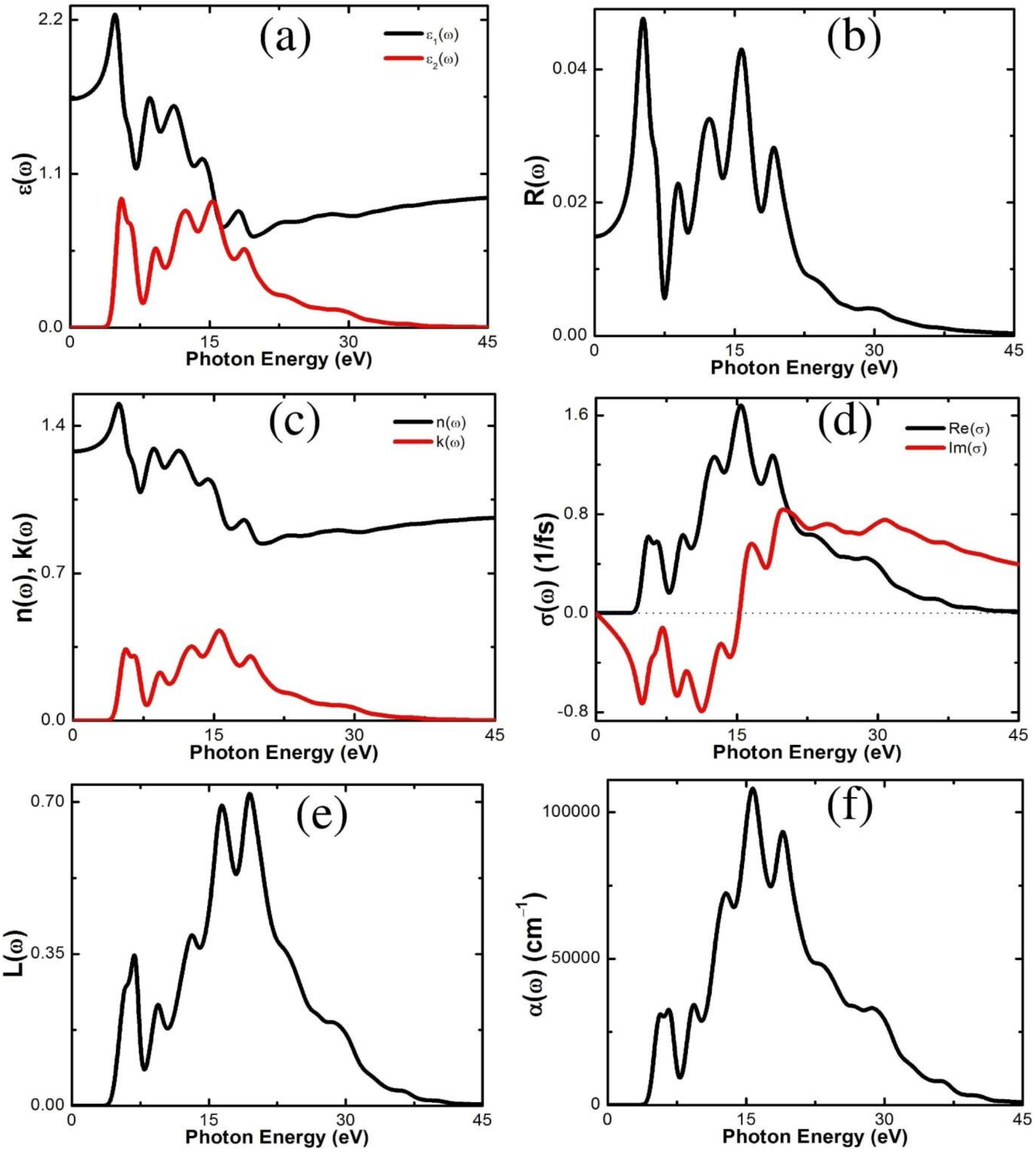


Figure S25. Calculated optical properties for (C, C): (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

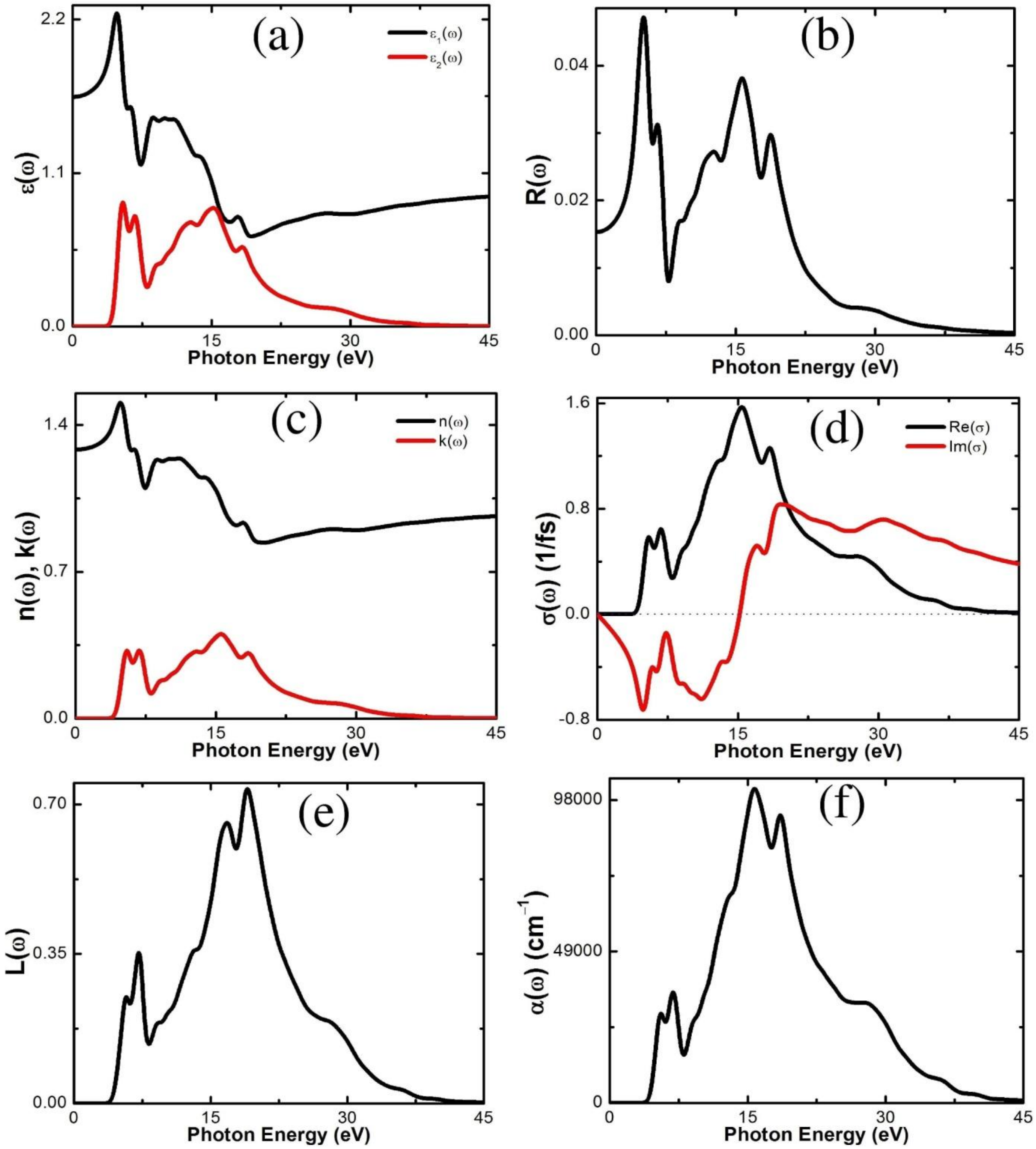


Figure S26. Calculated optical properties for (C, Si): (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

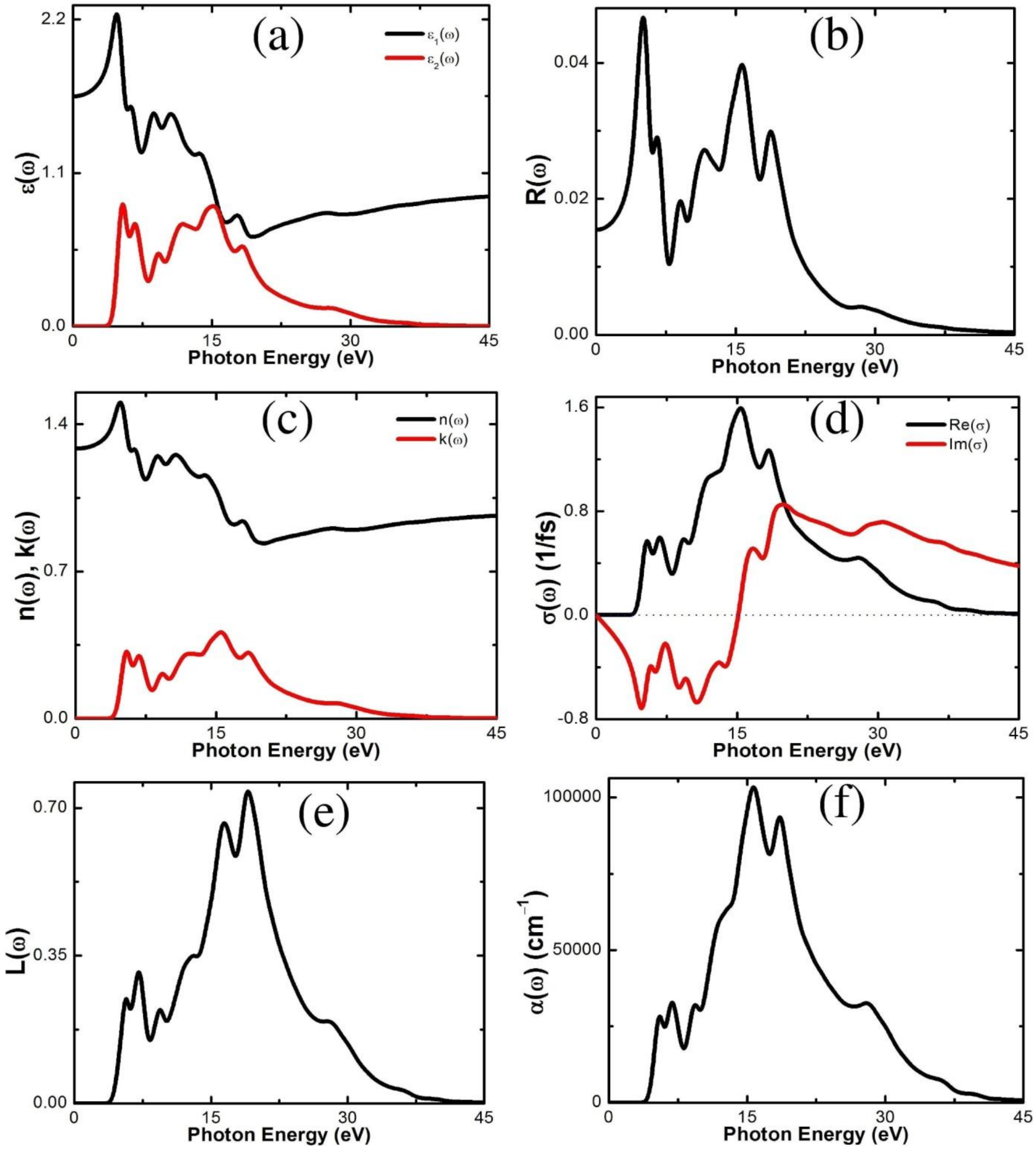


Figure S27. Calculated optical properties for (C, Ge): (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

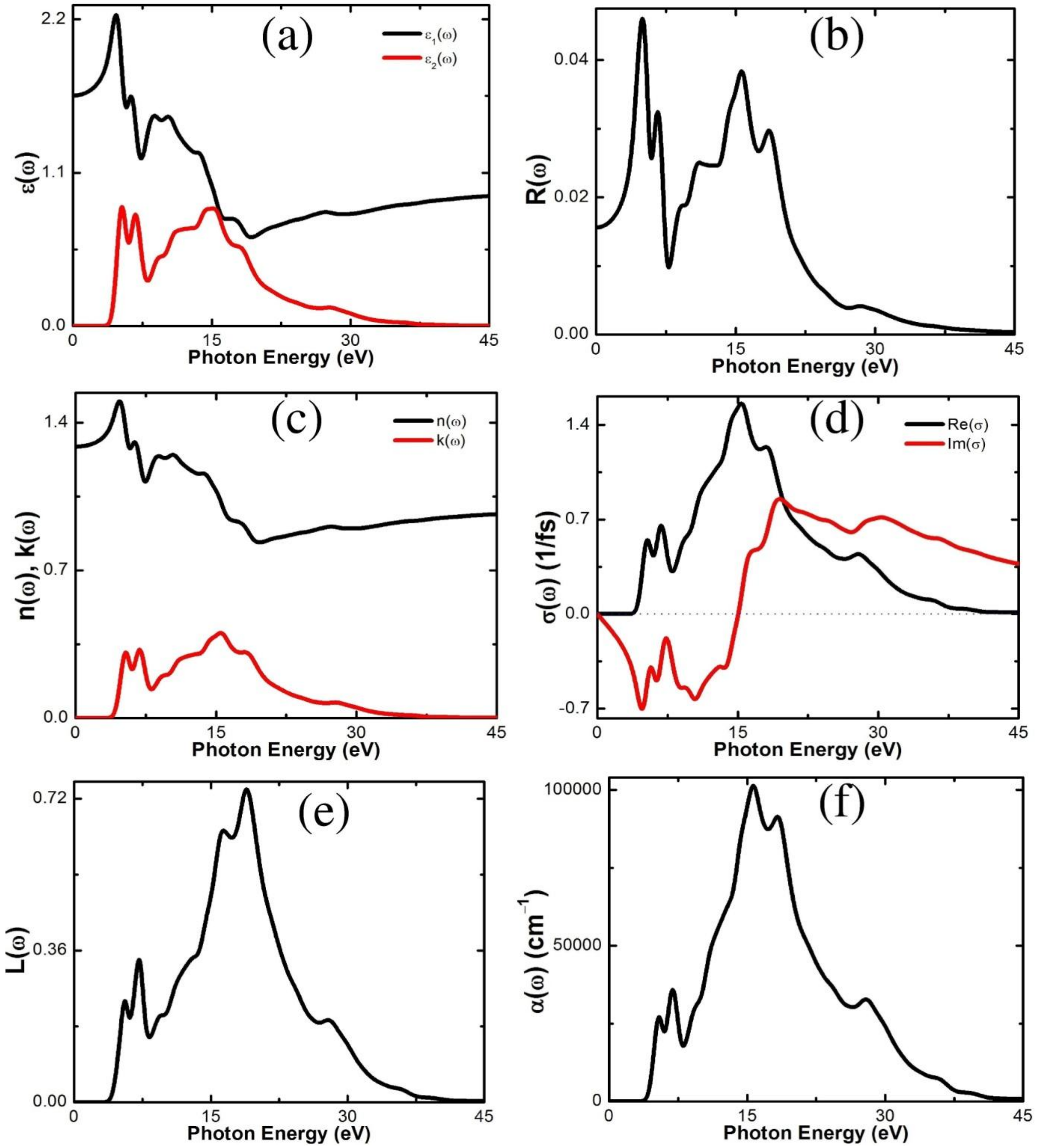


Figure S28. Calculated optical properties for (C, Sn): (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

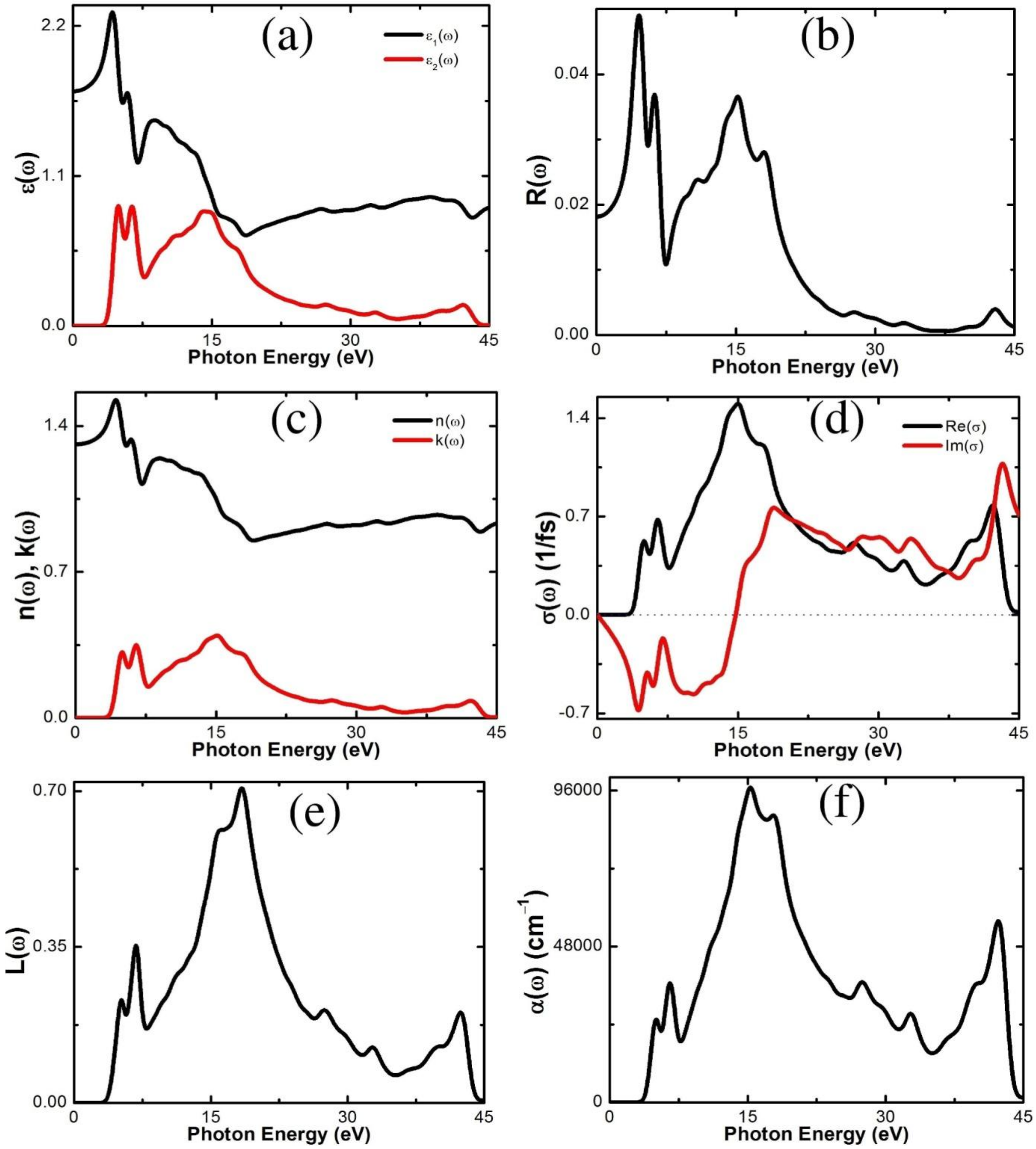


Figure S29. Calculated optical properties for (C, Pb): (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

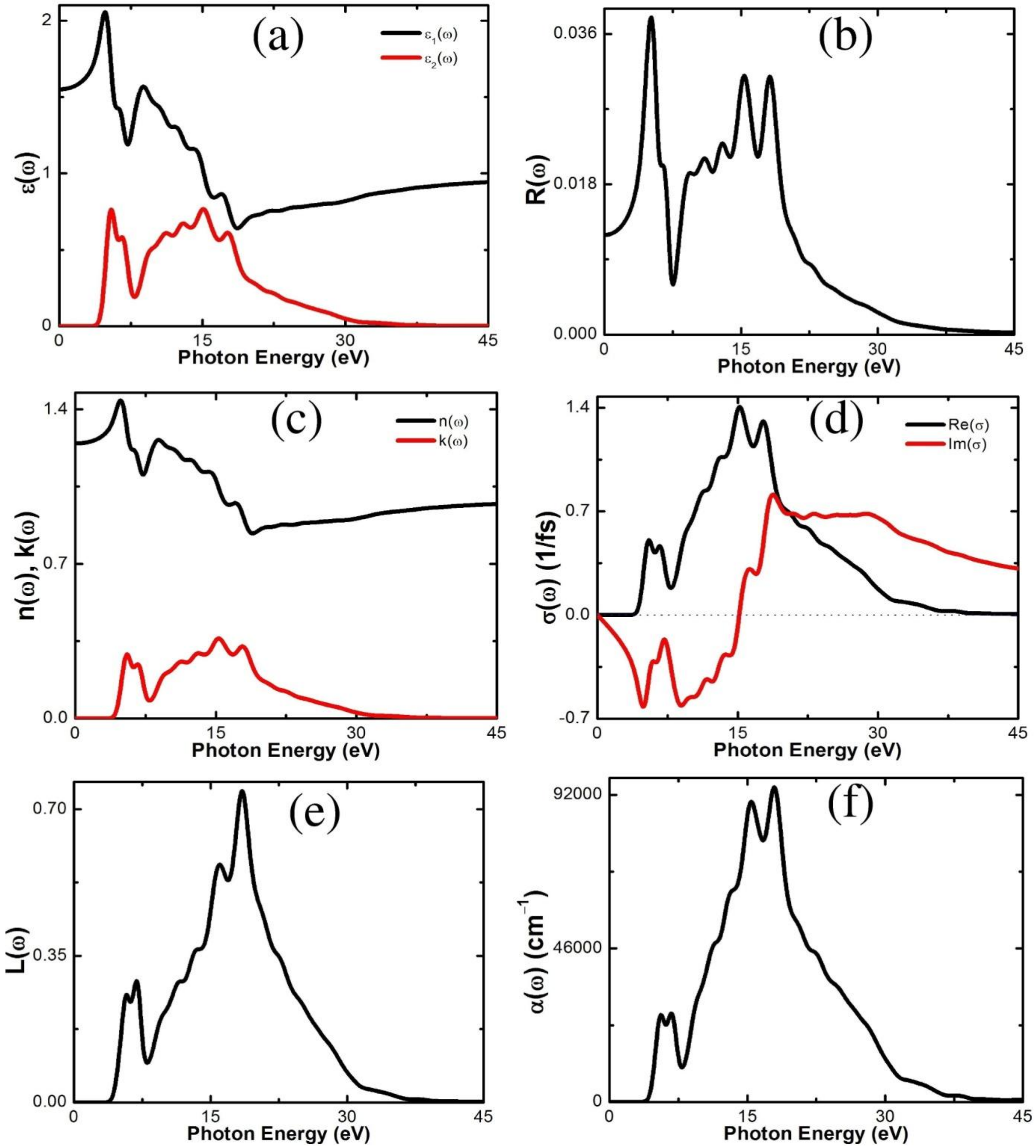


Figure S30. Calculated optical properties for (Si, C): (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

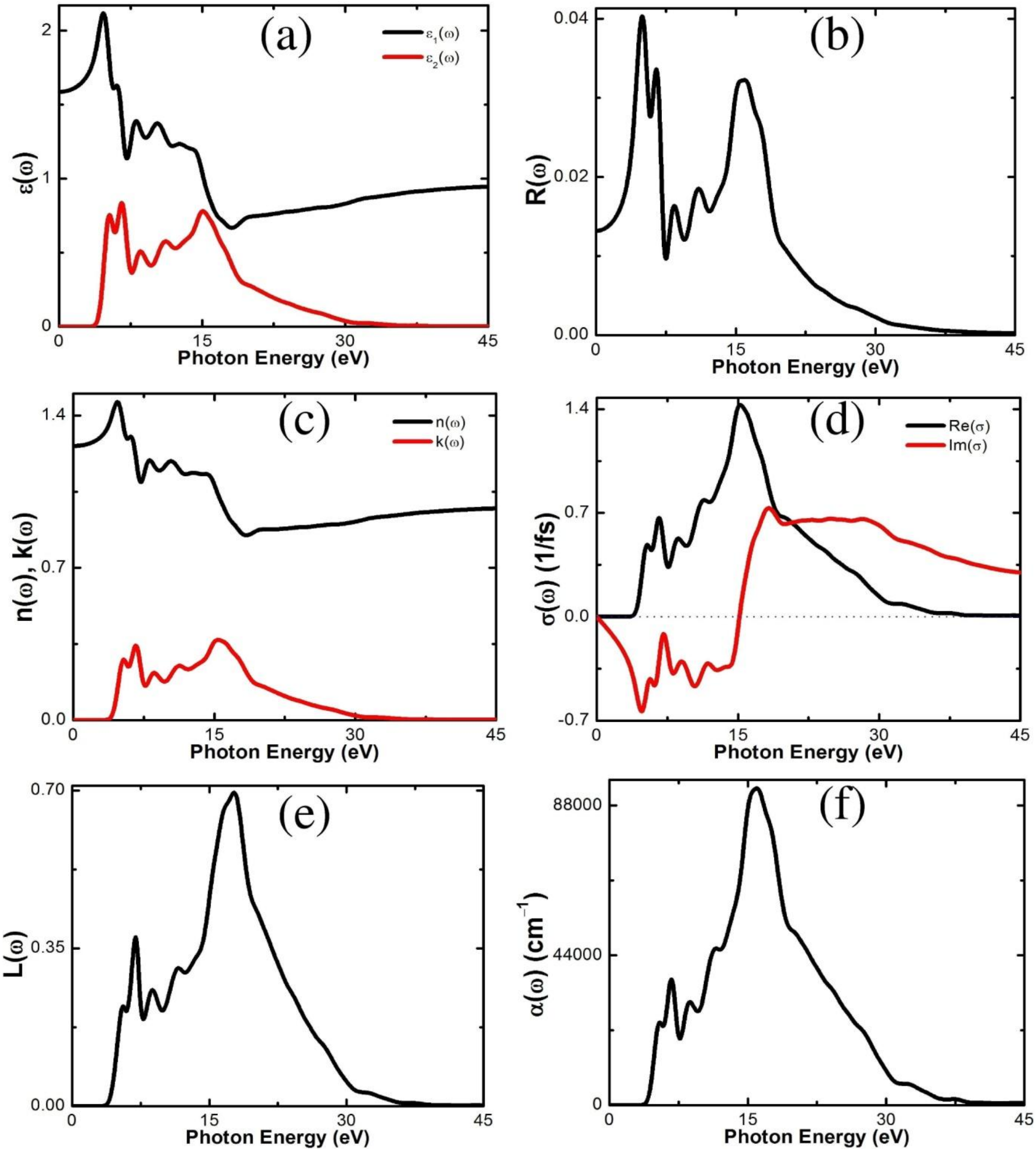


Figure S31. Calculated optical properties for (Si, Si): (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

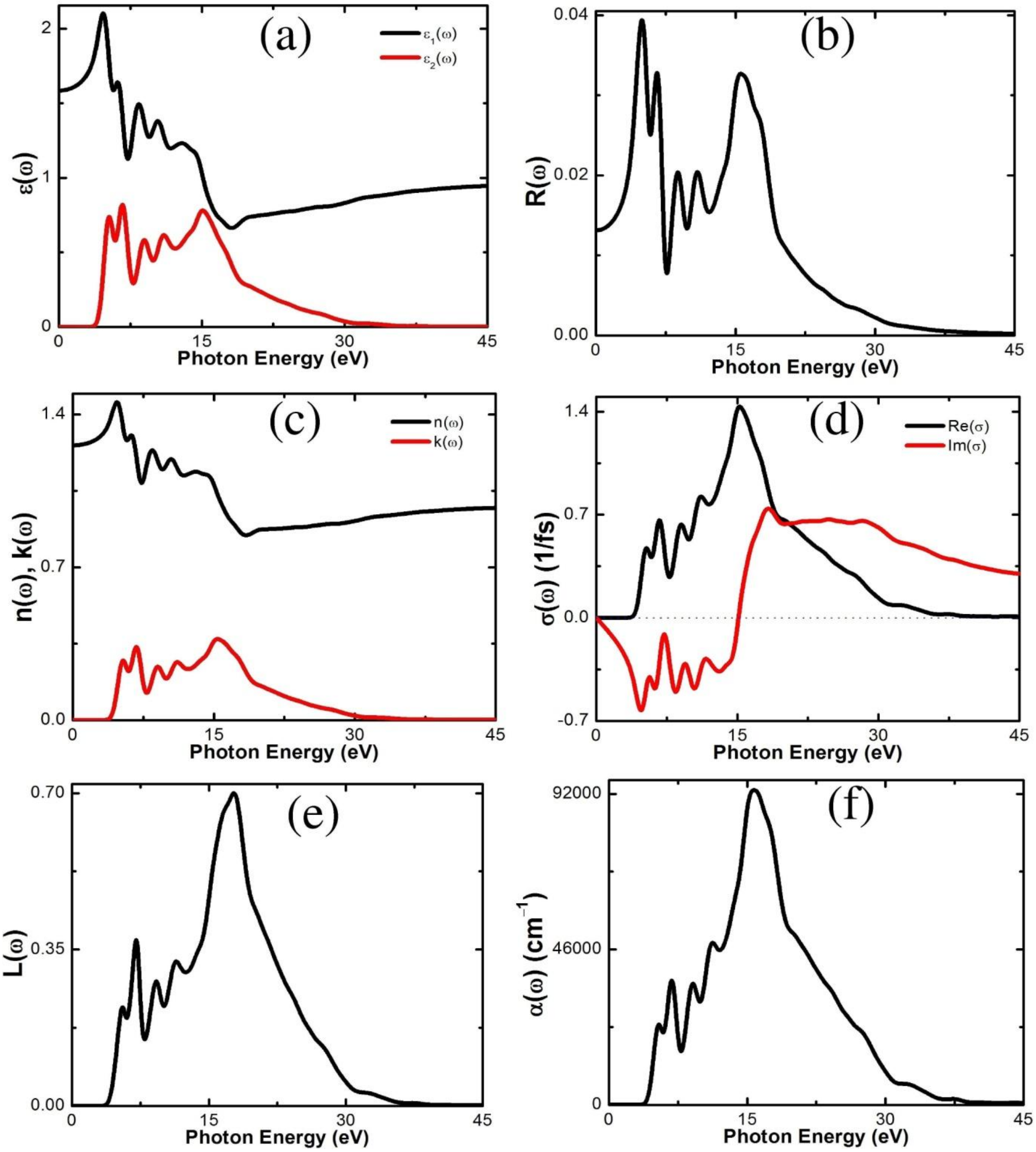


Figure S32. Calculated optical properties for (Si, Ge): (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

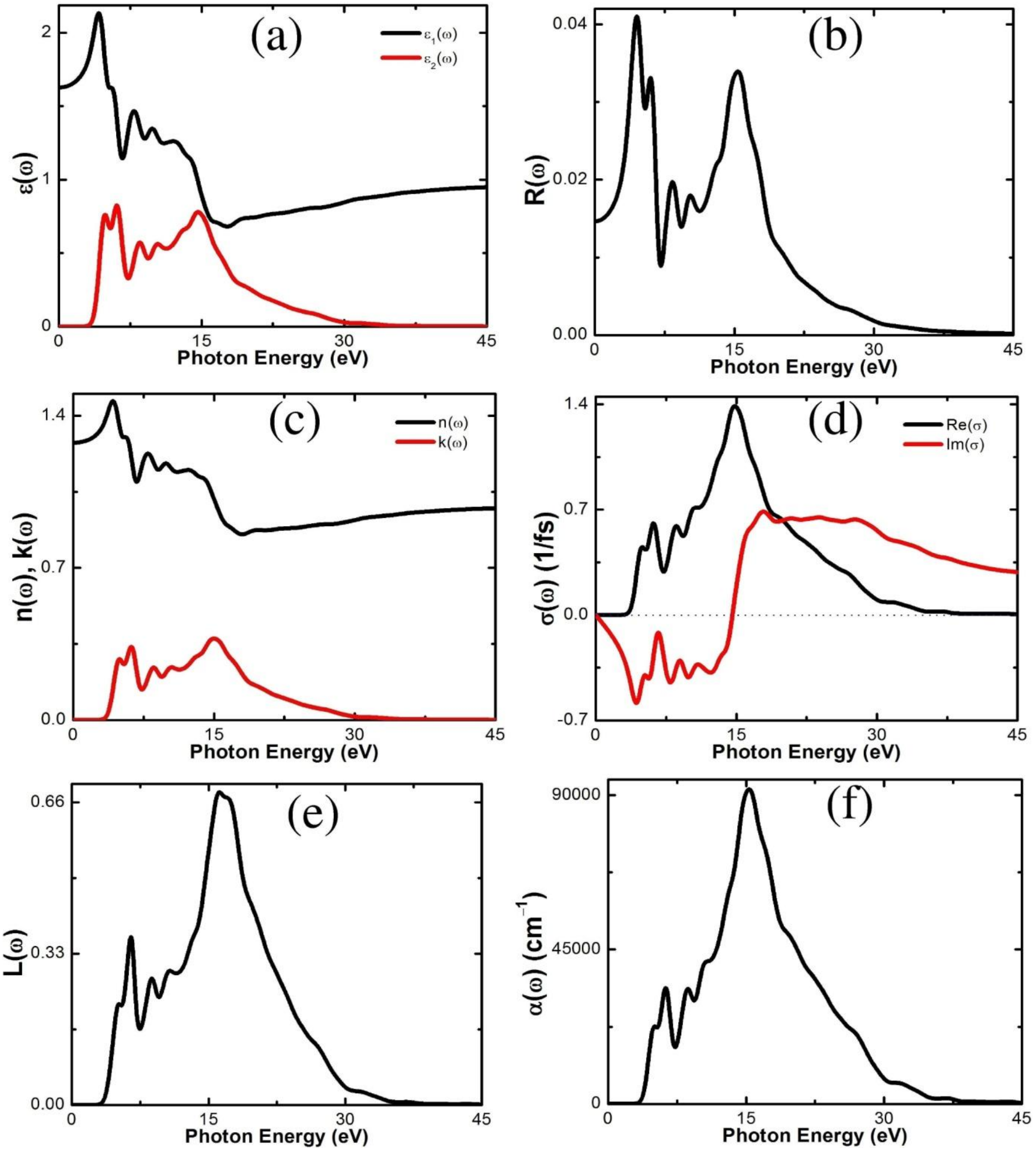


Figure S33. Calculated optical properties for (Si, Sn): (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

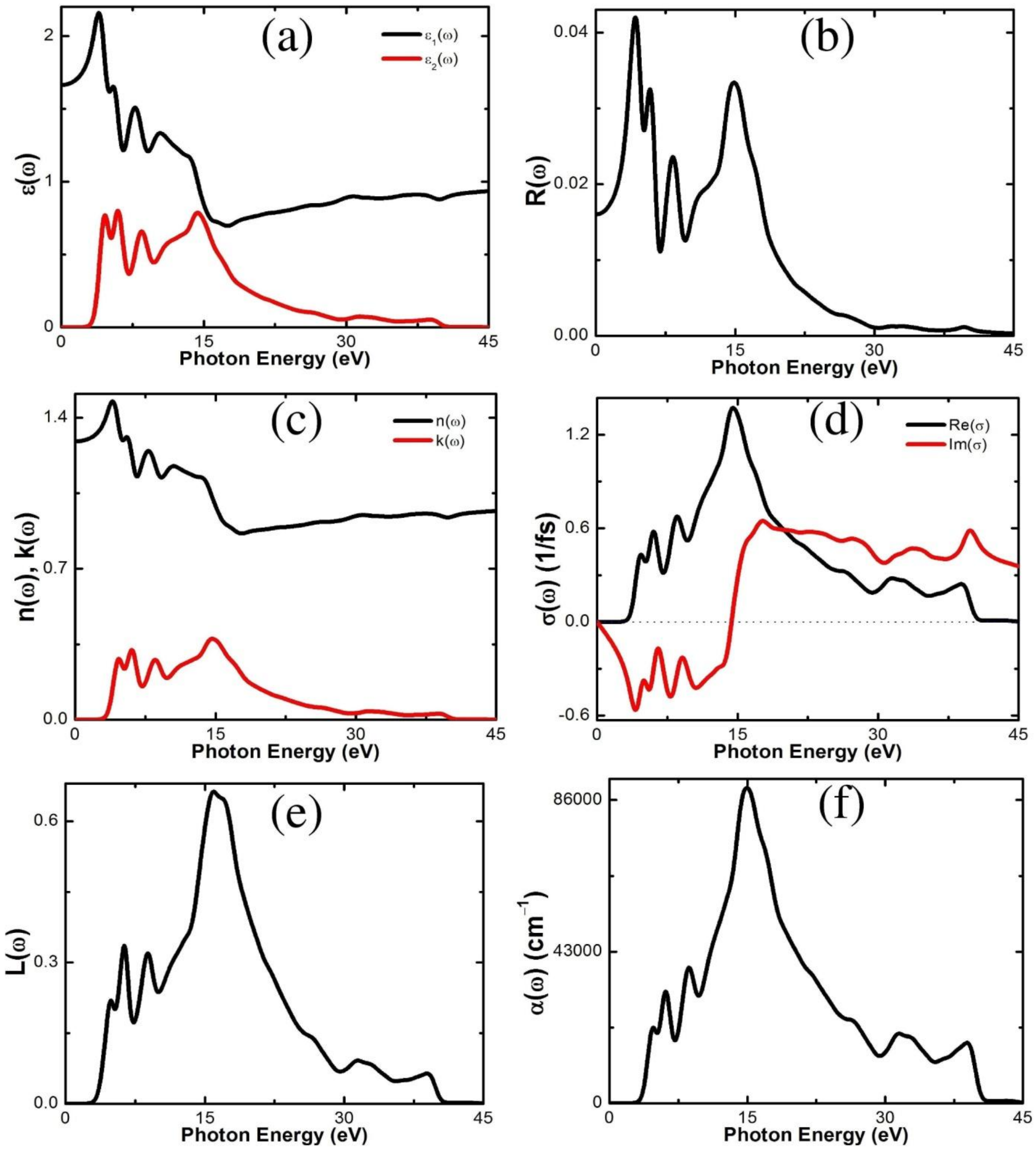


Figure S34. Calculated optical properties for (Si, Pb): (a) dielectric function ε(ω), (b) reflectivity R(ω), (c) refractive index **n**(ω); extinction coefficient **k**(ω), (d) optical conductivity σ(ω), (e) energy loss function L(ω), and (f) absorption α(ω).

Table S5. The calculated Mulliken effective charges (MEC, given in terms of *e*), bond overlap populations (BOP), and Bader charges (BC, *e*) for ten hypothetical materials $(X_4Y)(O_2B\text{-}C_6H_4\text{-}BO_2)_3$ (X=C/Si; Y=C, Si, Ge, Sn, and Pb). Atoms in $(X_4Y)(O_2B\text{-}C_6H_4\text{-}BO_2)_3$ are numbered according to the labels in Figure 1.

Materials (X, Y)	Atomic site	MEC (*e*)	BOP	BC (*e*)
(C, C)	C (X)	+0.64	0.71 (X-Y)	+2.9907
	C (Y)	-0.21		-0.0746
	O	-0.60	0.63 (O-X)	-1.9797
	B	+1.02	0.73 (B-O)	+3.0000
	C1	-0.27	0.84 (C1-B)	-1.0940
	C2	-0.27	1.08 (C2-C1)	+0.0095
			1.11 (C2-C2)	
	H	+0.30	0.87 (H-C2)	+0.0265
(C, Si)	C (X)	+0.34	0.74 (X-Y)	+1.7346
	Si (Y)	+1.12		+4.0029
	O	-0.59	0.57 (O-X)	-1.9004
	B	+0.98	0.75 (B-O)	+3.0000
	C1	-0.26	0.85 (C1-B)	-1.0909
	C2	-0.27	1.08 (C2-C1)	-0.0021
			1.11 (C2-C2)	
	H	+0.30	0.87 (H-C2)	+0.0361
(C, Ge)	C (X)	+0.41	0.70 (X-Y)	+1.7605
	Ge (Y)	+0.98		+4.0029
	O	-0.59	0.58 (O-X)	-1.9088
	B	+0.96	0.76 (B-O)	+3.0000
	C1	-0.26	0.86 (C1-B)	-1.0898
	C2	-0.27	1.08 (C2-C1)	-0.0085
			1.11 (C2-C2)	
	H	+0.29	0.88 (H-C2)	+0.0418

(C, Sn)	C (X)	+0.36	0.70 (X-Y)	+1.7712
	Sn (Y)	+1.29		+3.7711
	O	-0.59	0.56 (O-X)	-1.8896
	B	+0.93	0.77 (B-O)	+3.0000
	C1	-0.25	0.87 (C1-B)	-1.0947
	C2	-0.27	1.08 (C2-C1)	-0.0225
			1.11 (C2-C2)	
	H	+0.29	0.88 (H-C2)	+0.0547
(C, Pb)	C (X)	+0.37	0.64 (X-Y)	+1.9463
	Pb (Y)	+1.22		+3.1837
	O	-0.58	0.56 (O-X)	-1.8979
	B	+0.93	0.77 (B-O)	+3.0000
	C1	-0.25	0.87 (C1-B)	-1.0966
	C2	-0.27	1.08 (C2-C1)	-0.0265
			1.11 (C2-C2)	
	H	+0.29	0.88 (H-C2)	+0.0586
(Si, C)	Si (X)	+2.12	0.65 (X-Y)	+4.0023
	C (Y)	-1.63		-3.9130
	O	-0.95	0.53 (O-X)	-1.9927
	B	+0.98	0.75 (B-O)	+3.0000
	C1	-0.27	0.85 (C1-B)	-1.0167
	C2	-0.27	1.08 (C2-C1)	-0.0563
			1.11 (C2-C2)	
	H	+0.29	0.87 (H-C2)	+0.0493
(Si, Si)	Si (X)	+1.91	0.74 (X-Y)	+2.0304
	Si (Y)	-0.97		+4.0032
	O	-0.93	0.49 (O-X)	-1.9952
	B	+0.98	0.76 (B-O)	+3.0000
	C1	-0.26	0.86 (C1-B)	-1.0883

	C2	-0.27	1.08 (C2-C1)	-0.0164
			1.11 (C2-C2)	
	H	+0.29	0.87 (H-C2)	+0.0454
(Si, Ge)	Si (X)	+1.93	0.70 (X-Y)	+2.0525
	Ge (Y)	-0.96		+4.0063
	O	-0.93	0.50 (O-X)	-2.0022
	B	+0.96	0.76 (B-O)	+3.0000
	C1	-0.26	0.87 (C1-B)	-1.0854
	C2	-0.27	1.08 (C2-C1)	-0.0220
			1.11 (C2-C2)	
	H	+0.29	0.88 (H-C2)	+0.0488
(Si, Sn)	Si (X)	+1.84	0.76 (X-Y)	+2.0669
	Sn (Y)	-0.65		+4.0367
	O	-0.92	0.49 (O-X)	-2.0076
	B	+0.96	0.77 (B-O)	+3.0000
	C1	-0.26	0.87 (C1-B)	-1.0912
	C2	-0.27	1.08 (C2-C1)	-0.0208
			1.11 (C2-C2)	
	H	+0.28	0.88 (H-C2)	+0.0486
(Si, Pb)	Si (X)	+1.86	0.72 (X-Y)	+2.2494
	Pb (Y)	-0.76		+3.4156
	O	-0.92	0.50 (O-X)	-2.0163
	B	+0.96	0.77 (B-O)	+3.0000
	C1	-0.26	0.87 (C1-B)	-1.0896
	C2	-0.27	1.08 (C2-C1)	-0.0231
			1.11 (C2-C2)	
	H	+0.28	0.88 (H-C2)	+0.0497

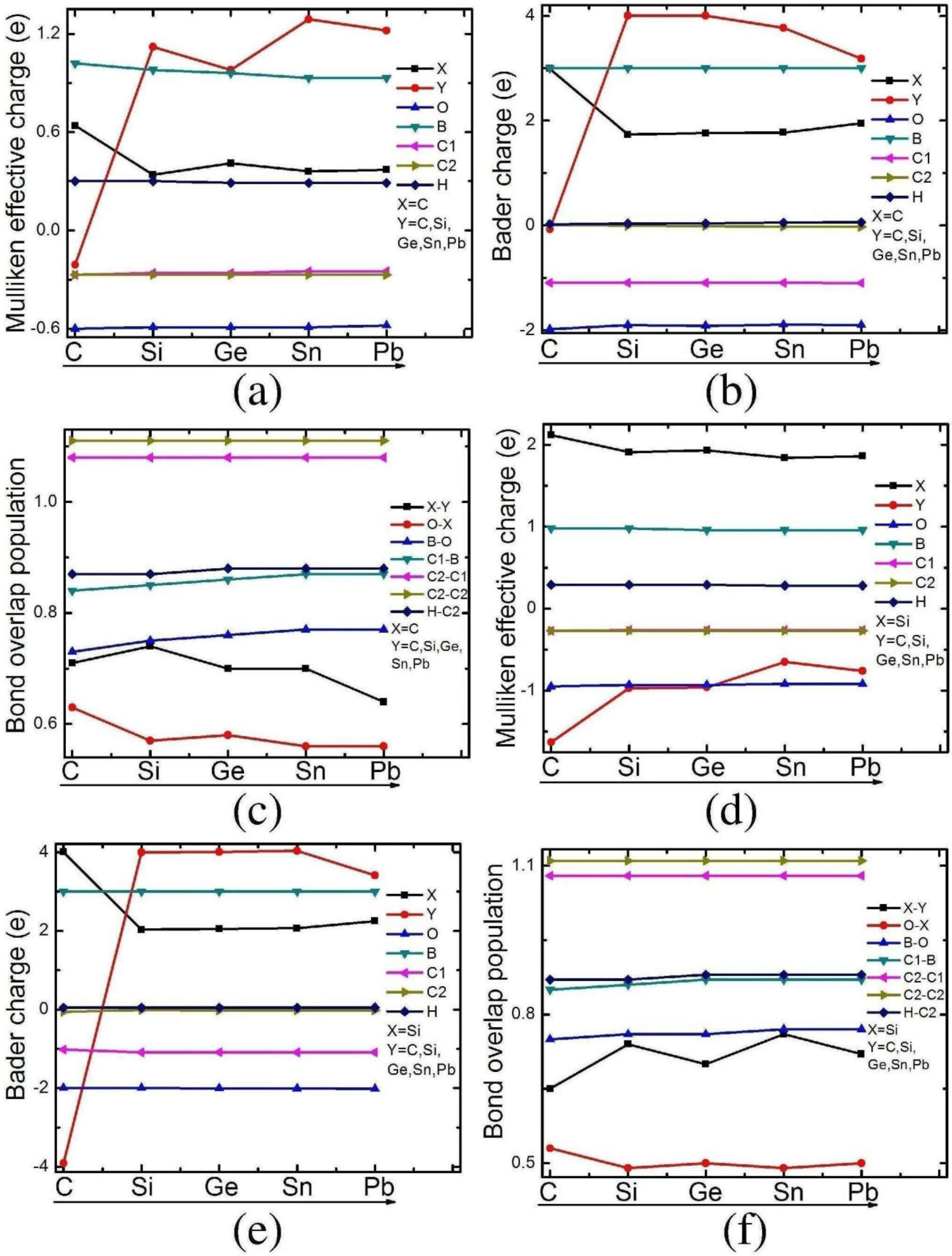


Figure S35. The evolution trend of MEC (*e*), BC (*e*), and BOP for $(X_4Y)(O_2B\text{-}C_6H_4\text{-}BO_2)_3$, (X = C/Si; Y = C, Si, Ge, Sn, and Pb). For subsystem (C, Y), plots (a), (b), and (c) are MEC, BC, and BOP, respectively. For subsystem (Si, Y), plots (d), (e), and (f) are MEC, BC, and BOP, respectively.

Table S6. The electron configurations of atoms for $(X_4Y)(O_2B\text{-}C_6H_4\text{-}BO_2)_3$ (X=C/Si; Y=C, Si, Ge, Sn, and Pb) from atomic populations (Mulliken) with CASTEP code.

Materials (X, Y)	Atom	*s*	*p*	*d*	Total	Charge (e)
(C, C)	C (X)	1.03	2.33	0.00	3.36	0.64
	C (Y)	1.26	2.95	0.00	4.21	-0.21
	O	1.75	4.85	0.00	6.60	-0.60
	B	0.52	1.46	0.00	1.98	1.02
	C1	1.16	3.11	0.00	4.27	-0.27
	C2	1.19	3.09	0.00	4.27	-0.27
	H	0.70	0.00	0.00	0.70	0.30
(C, Si)	C (X)	1.11	2.55	0.00	3.66	0.34
	Si (Y)	1.03	1.85	0.00	2.88	1.12
	O	1.76	4.83	0.00	6.59	-0.59
	B	0.54	1.48	0.00	2.02	0.98
	C1	1.16	3.10	0.00	4.26	-0.26
	C2	1.19	3.09	0.00	4.27	-0.27
	H	0.70	0.00	0.00	0.70	0.30
(C, Ge)	C (X)	1.09	2.50	0.00	3.59	0.41
	Ge (Y)	1.05	1.98	0.00	3.02	0.98
	O	1.76	4.83	0.00	6.59	-0.59
	B	0.56	1.48	0.00	2.04	0.96
	C1	1.16	3.10	0.00	4.26	-0.26
	C2	1.18	3.08	0.00	4.27	-0.27
	H	0.71	0.00	0.00	0.71	0.29
(C, Sn)	C (X)	1.10	2.54	0.00	3.64	0.36
	Sn (Y)	0.99	1.73	0.00	2.71	1.29
	O	1.76	4.83	0.00	6.59	-0.59
	B	0.58	1.49	0.00	2.07	0.93
	C1	1.16	3.10	0.00	4.25	-0.25

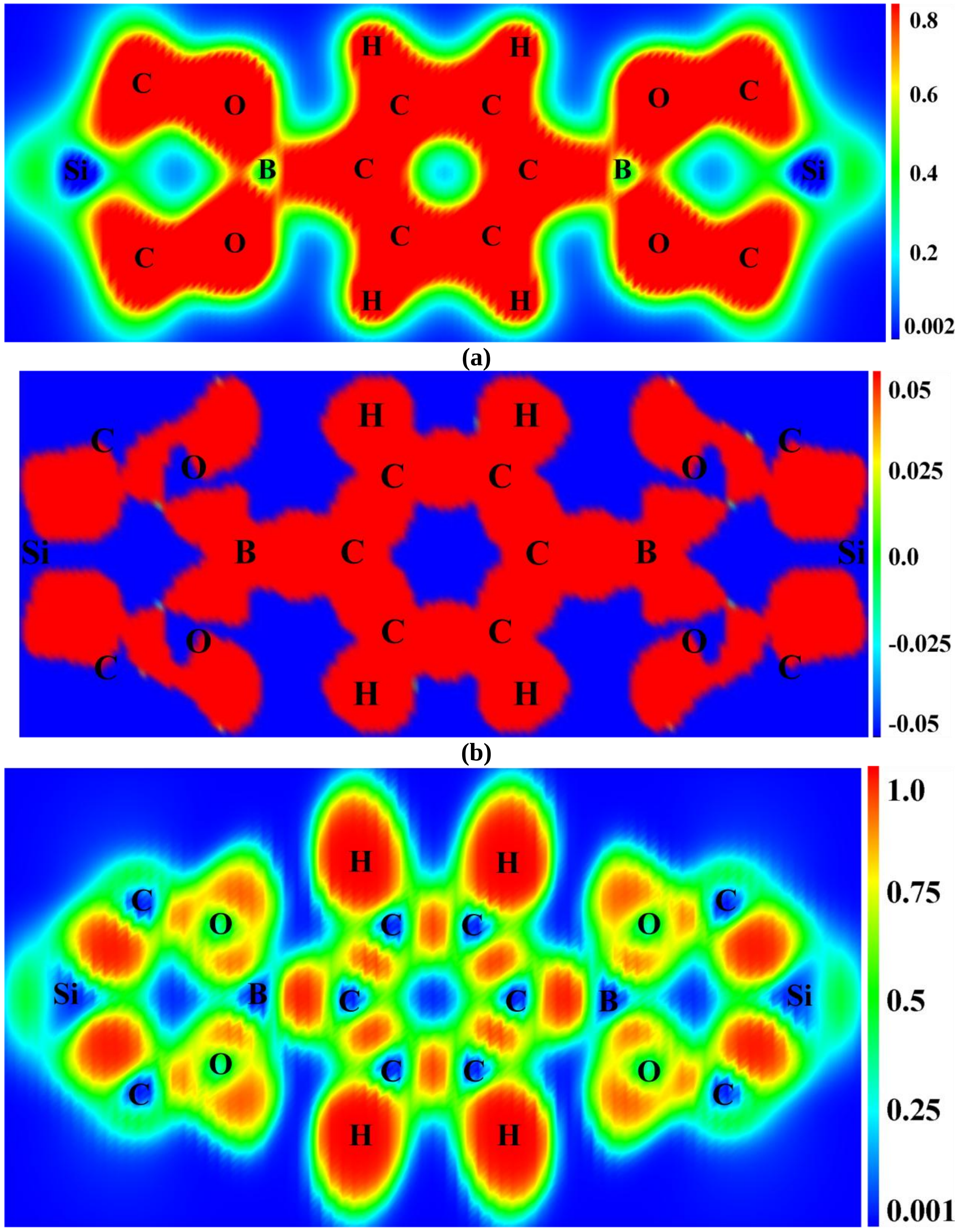
	C2	1.19	3.08	0.00	4.27	-0.27
	H	0.71	0.00	0.00	0.71	0.29
(C, Pb)	C (X)	1.10	2.53	0.00	3.63	0.37
	Pb (Y)	1.14	1.69	9.95	12.78	1.22
	O	1.76	4.82	0.00	6.58	-0.58
	B	0.58	1.49	0.00	2.07	0.93
	C1	1.16	3.10	0.00	4.25	-0.25
	C2	1.19	3.08	0.00	4.27	-0.27
	H	0.71	0.00	0.00	0.71	0.29
(Si, C)	Si (X)	0.72	1.16	0.00	1.88	2.12
	C (Y)	1.50	4.13	0.00	5.63	-1.63
	O	1.80	5.15	0.00	6.95	-0.95
	B	0.55	1.47	0.00	2.02	0.98
	C1	1.16	3.11	0.00	4.27	-0.27
	C2	1.19	3.08	0.00	4.27	-0.27
	H	0.71	0.00	0.00	0.71	0.29
(Si, Si)	Si (X)	0.83	1.26	0.00	2.09	1.91
	Si (Y)	1.39	3.57	0.00	4.97	-0.97
	O	1.80	5.13	0.00	6.93	-0.93
	B	0.56	1.46	0.00	2.02	0.98
	C1	1.16	3.10	0.00	4.26	-0.26
	C2	1.19	3.08	0.00	4.27	-0.27
	H	0.71	0.00	0.00	0.71	0.29
(Si, Ge)	Si (X)	0.83	1.24	0.00	2.07	1.93
	Ge (Y)	1.31	3.65	0.00	4.96	-0.96
	O	1.80	5.13	0.00	6.93	-0.93
	B	0.58	1.46	0.00	2.04	0.96
	C1	1.16	3.10	0.00	4.26	-0.26

	C2	1.18	3.08	0.00	4.27	-0.27
	H	0.71	0.00	0.00	0.71	0.29
(Si, Sn)	Si (X)	0.88	1.28	0.00	2.16	1.84
	Sn (Y)	1.27	3.39	0.00	4.65	-0.65
	O	1.80	5.13	0.00	6.92	-0.92
	B	0.58	1.46	0.00	2.04	0.96
	C1	1.16	3.09	0.00	4.26	-0.26
	C2	1.18	3.08	0.00	4.27	-0.27
	H	0.72	0.00	0.00	0.72	0.28
(Si, Pb)	Si (X)	0.86	1.28	0.00	2.14	1.86
	Pb (Y)	1.37	3.45	9.95	14.76	-0.76
	O	1.80	5.13	0.00	6.92	-0.92
	B	0.58	1.46	0.00	2.04	0.96
	C1	1.16	3.09	0.00	4.26	-0.26
	C2	1.18	3.08	0.00	4.27	-0.27
	H	0.72	0.00	0.00	0.72	0.28

Table S7. The electron configurations and simplified configurations of each type of atoms of each material of $(X_4Y)(O_2B\text{-}C_6H_4\text{-}BO_2)_3$ (X=C/Si; Y=C, Si, Ge, Sn, and Pb) series from atomic populations (Mulliken) with CASTEP code.

(X, Y)	electron configurations	simplified configurations[a]
(C, C)	(X)$s^{1.03}p^{2.33}$(Y)$s^{1.26}p^{2.95}$(O)$s^{1.75}p^{4.85}$(B)$s^{0.52}p^{1.46}$(C1)$s^{1.16}p^{3.11}$(C2)$s^{1.19}p^{3.09}$(H)$s^{0.70}$	(X)$sp^{2.26}$(Y)$sp^{2.34}$(O)$sp^{2.77}$(B)$sp^{2.81}$(C1)$sp^{2.68}$(C2)$sp^{2.60}$(H)$s^{0.70}$
(C, Si)	(X)$s^{1.11}p^{2.55}$(Y)$s^{1.03}p^{1.85}$(O)$s^{1.76}p^{4.83}$(B)$s^{0.54}p^{1.48}$(C1)$s^{1.16}p^{3.10}$(C2)$s^{1.19}p^{3.09}$(H)$s^{0.70}$	(X)$sp^{2.30}$(Y)$sp^{1.80}$(O)$sp^{2.74}$(B)$sp^{2.74}$(C1)$sp^{2.67}$(C2)$sp^{2.60}$(H)$s^{0.70}$
(C, Ge)	(X)$s^{1.09}p^{2.50}$(Y)$s^{1.05}p^{1.98}$(O)$s^{1.76}p^{4.83}$(B)$s^{0.56}p^{1.48}$(C1)$s^{1.16}p^{3.10}$(C2)$s^{1.18}p^{3.08}$(H)$s^{0.71}$	(X)$sp^{2.29}$(Y)$sp^{1.89}$(O)$sp^{2.74}$(B)$sp^{2.64}$(C1)$sp^{2.67}$(C2)$sp^{2.61}$(H)$s^{0.71}$
(C, Sn)	(X)$s^{1.10}p^{2.54}$(Y)$s^{0.99}p^{1.73}$(O)$s^{1.76}p^{4.83}$(B)$s^{0.58}p^{1.49}$(C1)$s^{1.16}p^{3.10}$(C2)$s^{1.19}p^{3.08}$(H)$s^{0.71}$	(X)$sp^{2.31}$(Y)$sp^{1.75}$(O)$sp^{2.74}$(B)$sp^{2.57}$(C1)$sp^{2.67}$(C2)$sp^{2.59}$(H)$s^{0.71}$
(C, Pb)	(X)$s^{1.10}p^{2.53}$(Y)$s^{1.14}p^{1.69}d^{9.95}$(O)$s^{1.76}p^{4.82}$(B)$s^{0.58}p^{1.49}$(C1)$s^{1.16}p^{3.10}$(C2)$s^{1.19}p^{3.08}$(H)$s^{0.71}$	(X)$sp^{2.30}$(Y)$sp^{1.48}d^{8.73}$(O)$sp^{2.74}$(B)$sp^{2.57}$(C1)$sp^{2.67}$(C2)$sp^{2.59}$(H)$s^{0.71}$
(Si, C)	(X)$s^{0.72}p^{1.16}$(Y)$s^{1.50}p^{4.13}$(O)$s^{1.80}p^{5.15}$(B)$s^{0.55}p^{1.47}$(C1)$s^{1.16}p^{3.11}$(C2)$s^{1.19}p^{3.08}$(H)$s^{0.71}$	(X)$sp^{1.61}$(Y)$sp^{2.75}$(O)$sp^{2.86}$(B)$sp^{2.67}$(C1)$sp^{2.68}$(C2)$sp^{2.59}$(H)$s^{0.71}$
(Si, Si)	(X)$s^{0.83}p^{1.26}$(Y)$s^{1.39}p^{3.57}$(O)$s^{1.80}p^{5.13}$(B)$s^{0.56}p^{1.46}$(C1)$s^{1.16}p^{3.10}$(C2)$s^{1.19}p^{3.08}$(H)$s^{0.71}$	(X)$sp^{1.52}$(Y)$sp^{2.57}$(O)$sp^{2.85}$(B)$sp^{2.61}$(C1)$sp^{2.67}$(C2)$sp^{2.59}$(H)$s^{0.71}$
(Si, Ge)	(X)$s^{0.83}p^{1.24}$(Y)$s^{1.31}p^{3.65}$(O)$s^{1.80}p^{5.13}$(B)$s^{0.58}p^{1.46}$(C1)$s^{1.16}p^{3.10}$(C2)$s^{1.18}p^{3.08}$(H)$s^{0.71}$	(X)$sp^{1.49}$(Y)$sp^{2.79}$(O)$sp^{2.85}$(B)$sp^{2.52}$(C1)$sp^{2.67}$(C2)$sp^{2.61}$(H)$s^{0.71}$
(Si, Sn)	(X)$s^{0.88}p^{1.28}$(Y)$s^{1.27}p^{3.39}$(O)$s^{1.80}p^{5.13}$(B)$s^{0.58}p^{1.46}$(C1)$s^{1.16}p^{3.09}$(C2)$s^{1.18}p^{3.08}$(H)$s^{0.72}$	(X)$sp^{1.45}$(Y)$sp^{2.67}$(O)$sp^{2.85}$(B)$sp^{2.52}$(C1)$sp^{2.66}$(C2)$sp^{2.61}$(H)$s^{0.72}$
(Si, Pb)	(X)$s^{0.86}p^{1.28}$(Y)$s^{1.37}p^{3.45}d^{9.95}$(O)$s^{1.80}p^{5.13}$(B)$s^{0.58}p^{1.46}$(C1)$s^{1.16}p^{3.09}$(C2)$s^{1.18}p^{3.08}$(H)$s^{0.72}$	(X)$sp^{1.49}$(Y)$sp^{2.52}d^{7.26}$(O)$sp^{2.85}$(B)$sp^{2.52}$(C1)$sp^{2.66}$(C2)$sp^{2.61}$(H)$s^{0.72}$

[a] Note that there is no *p* electrons for H atoms, so we just listed the *s* electrons in the simplified electron configurations.

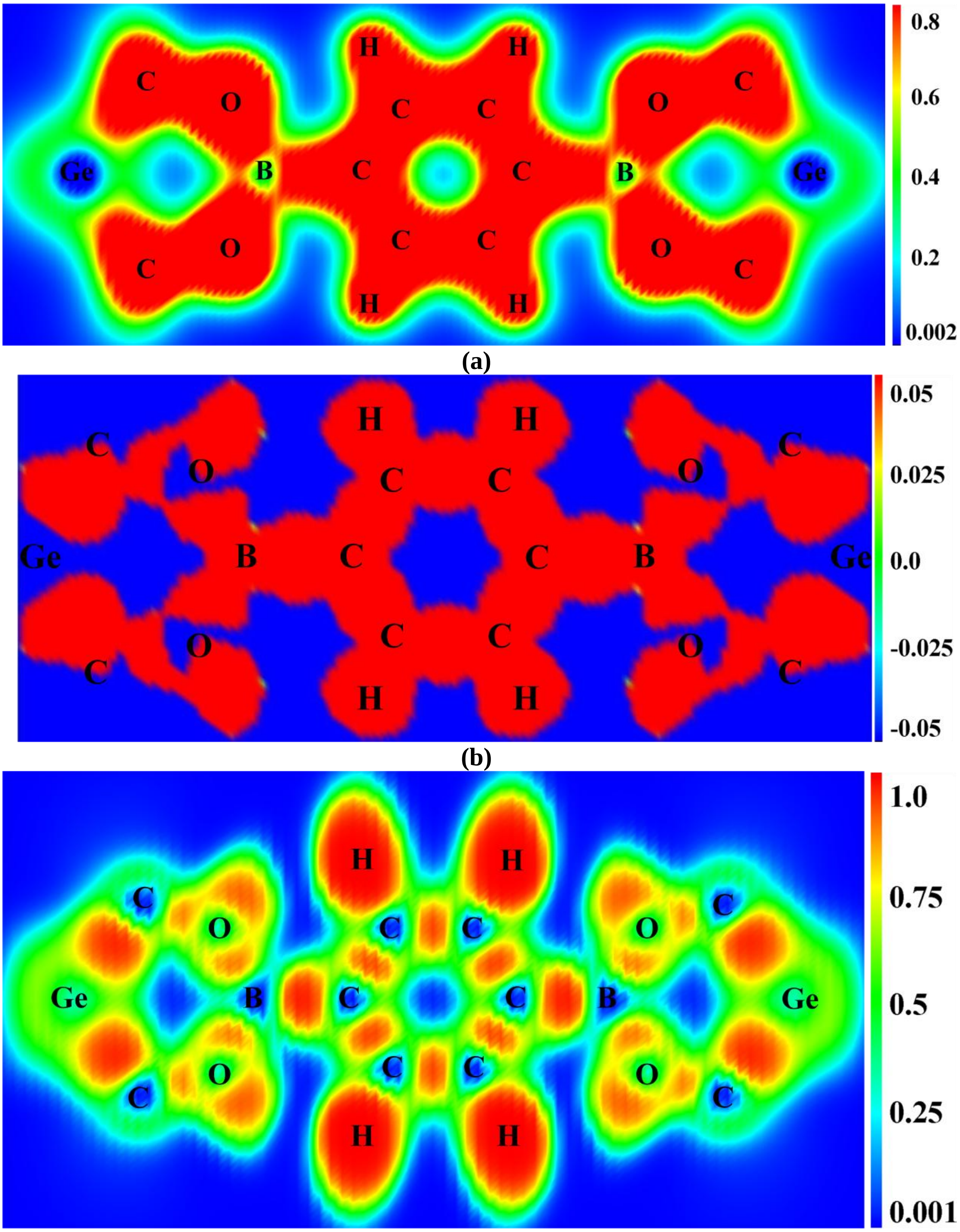


(a)

(b)

(c)

Figure S36. Calculated charge density (a) in e/Å ^{3}, charge transfer (b) in e/Å ^{3}, and electron localization function (c) plots for (C, Si) in the (110) plane.

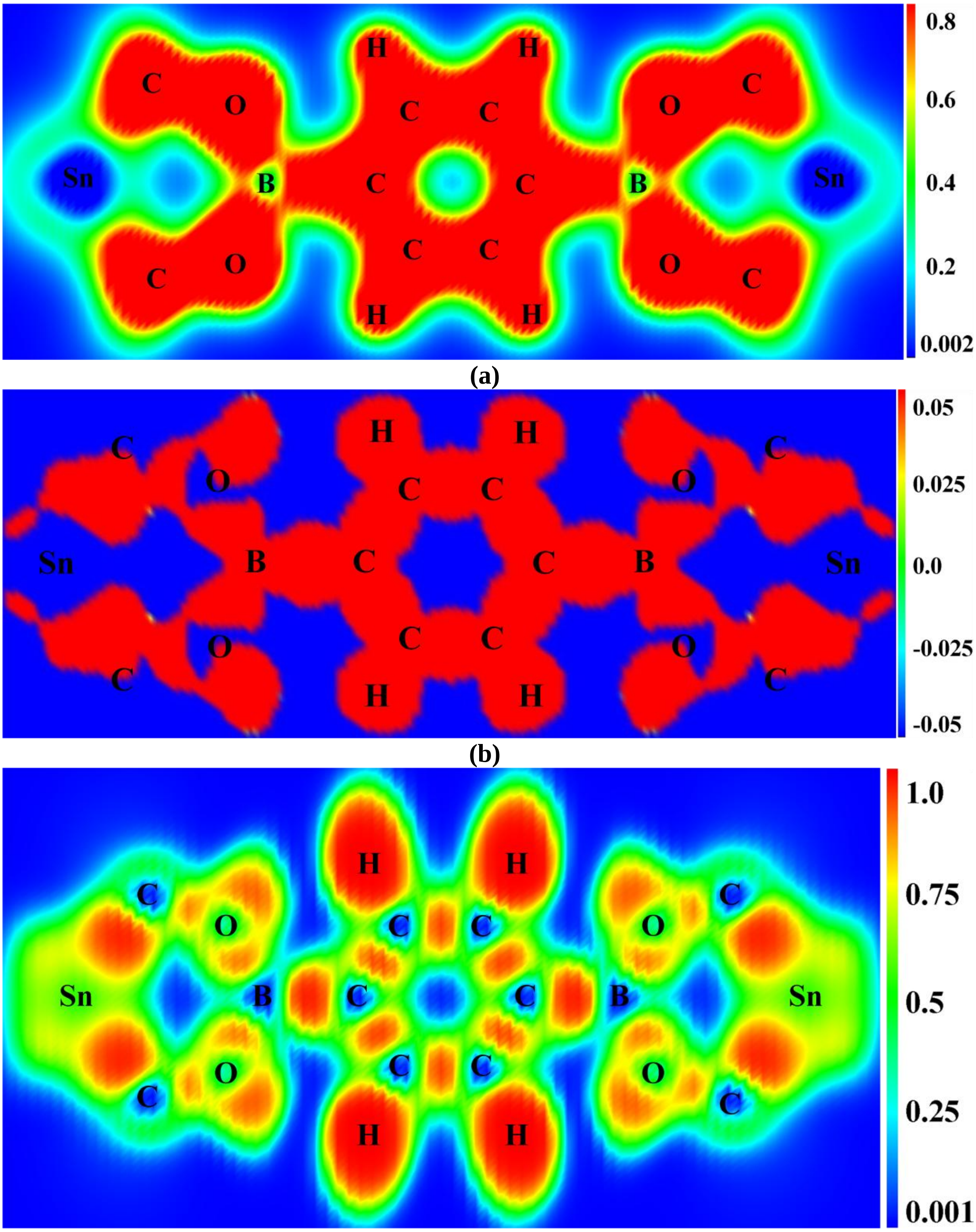


(a)

(b)

(c)

Figure S37. Calculated charge density (a) in e/Å ^{3}, charge transfer (b) in e/Å ^{3}, and electron localization function (c) plots for (C, Ge) in the (110) plane.



(a)

(b)

(c)

Figure S38. Calculated charge density (a) in e/Å ^{3}, charge transfer (b) in e/Å ^{3}, and electron localization function (c) plots for (C, Sn) in the (110) plane.

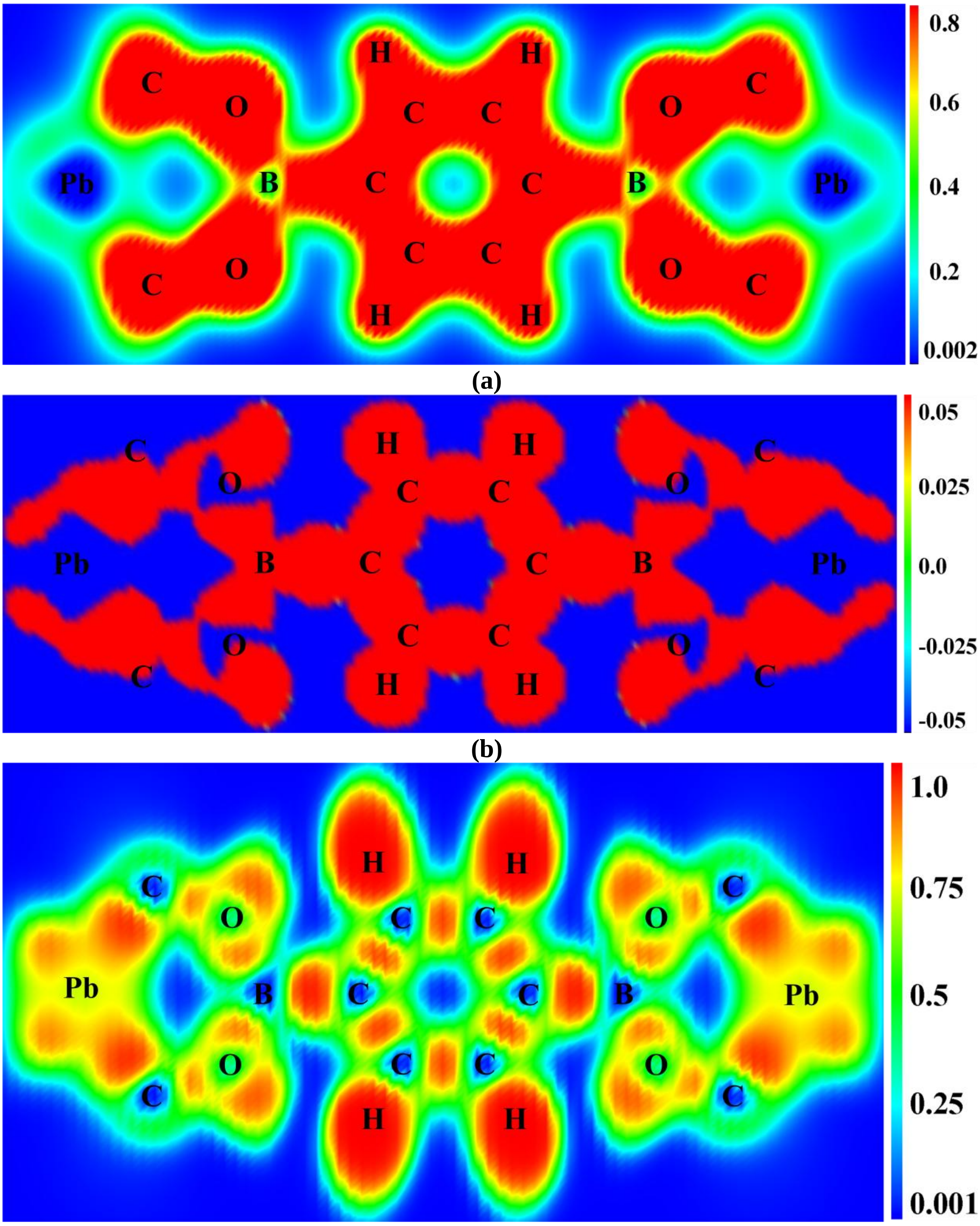


Figure S39. Calculated charge density (a) in e/Å ^{3}, charge transfer (b) in e/Å ^{3}, and electron localization function (c) plots for (C, Pb) in the (110) plane.

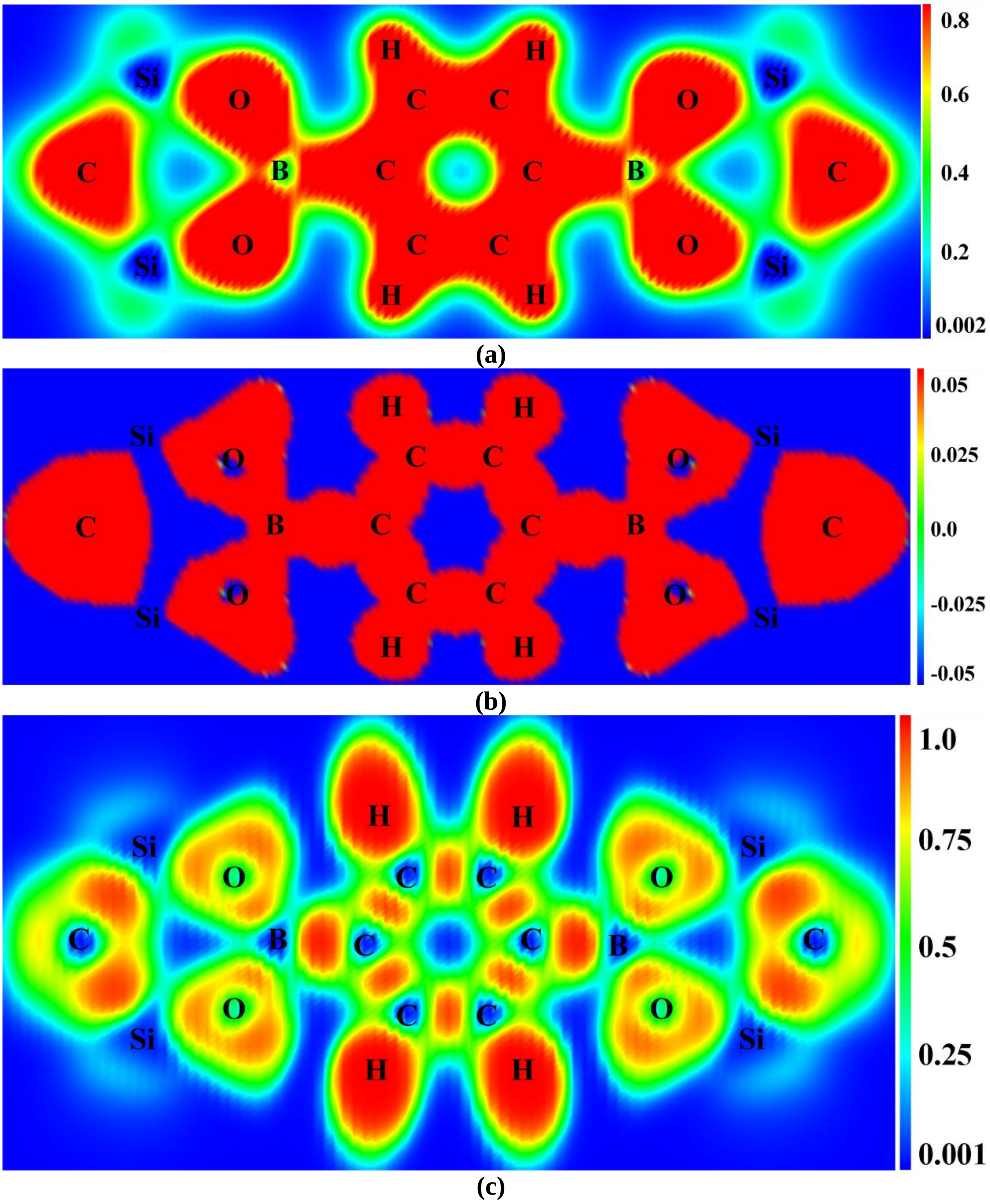
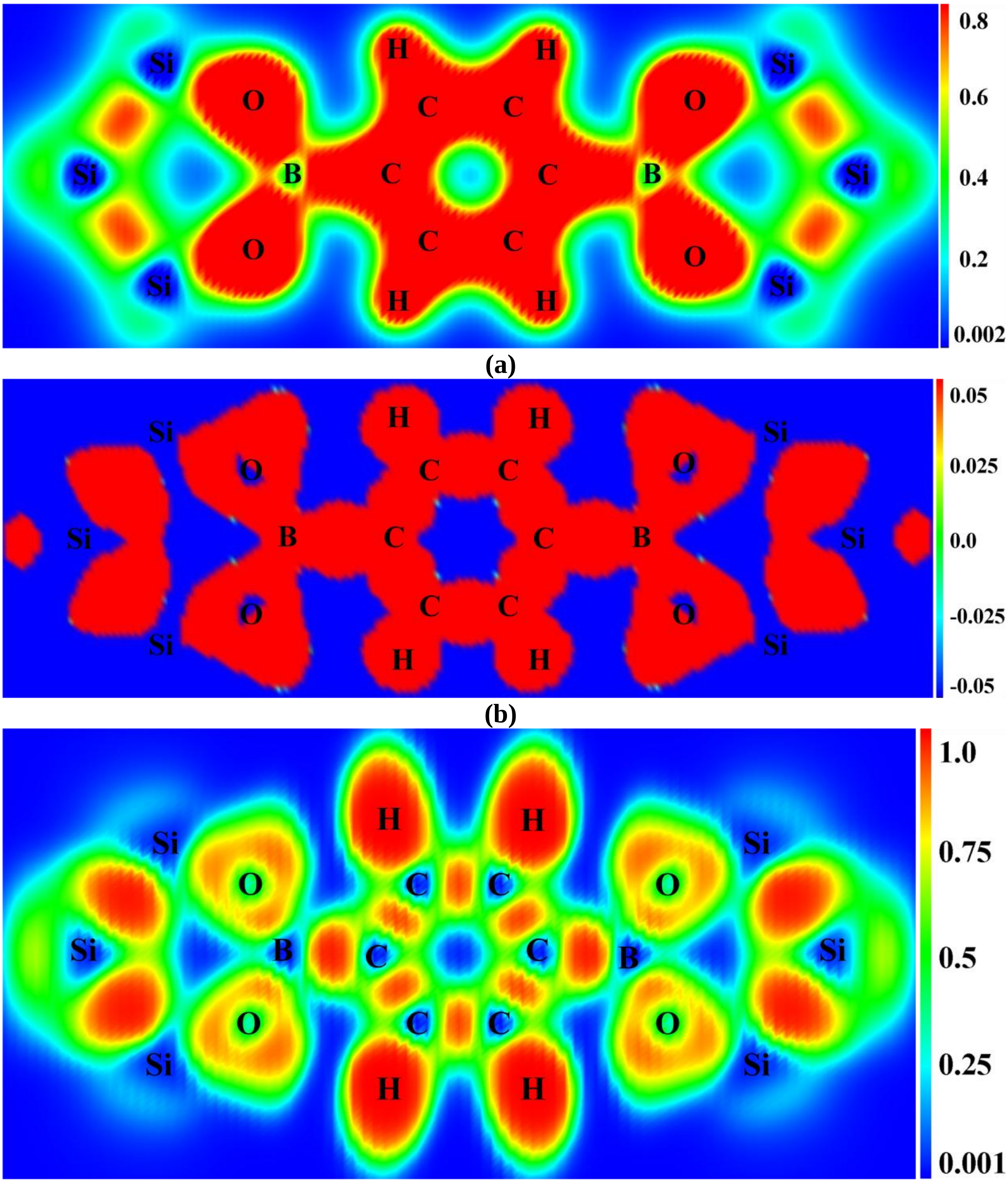


Figure S40. Calculated charge density (a) in e/Å ^{3}, charge transfer (b) in e/Å ^{3}, and electron localization function (c) plots for (Si, C) in the (110) plane.

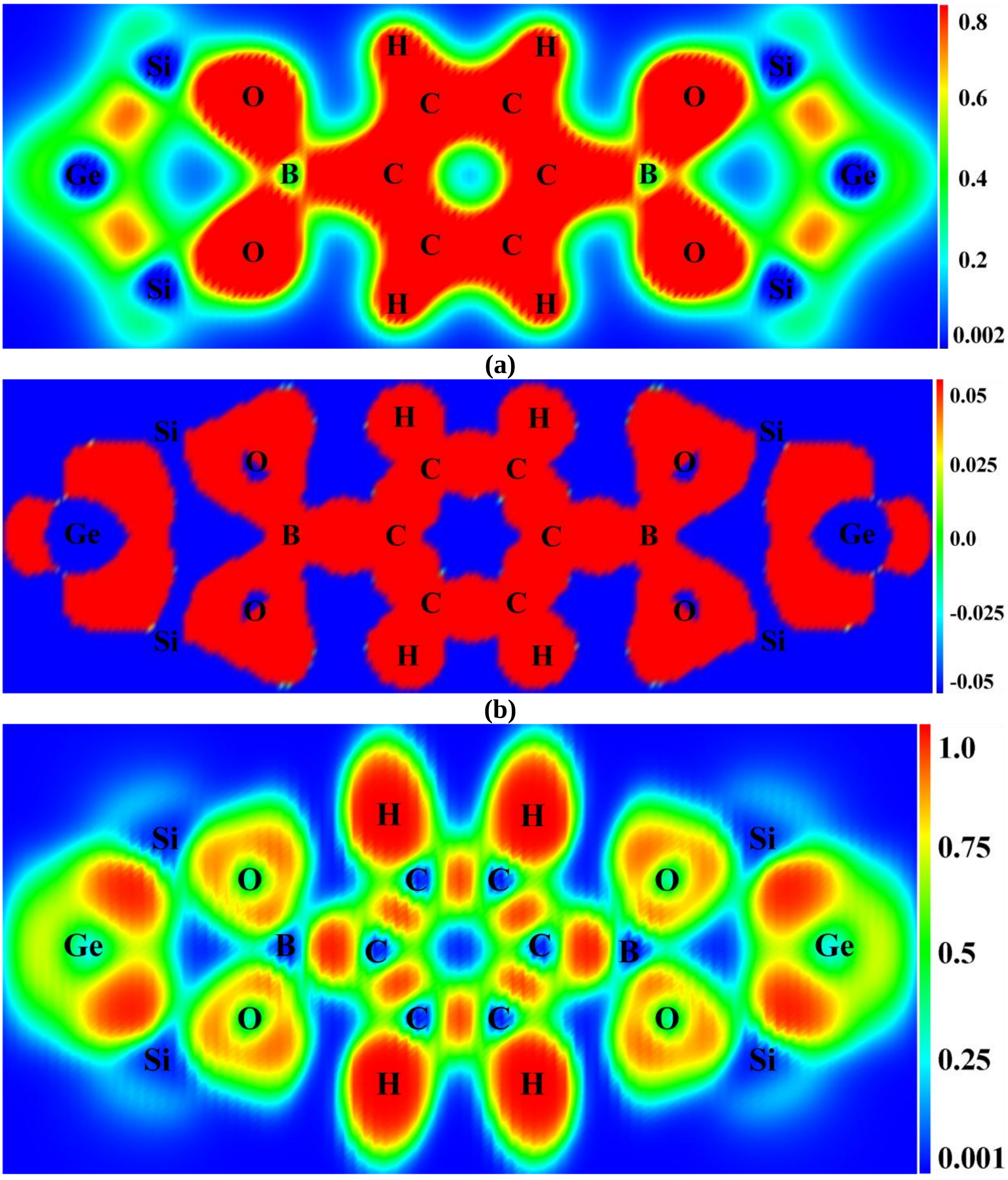


(a)

(b)

(c)

Figure S41. Calculated charge density (a) in e/Å ^{3}, charge transfer (b) in e/Å ^{3}, and electron localization function (c) plots for (Si, Si) in the (110) plane.

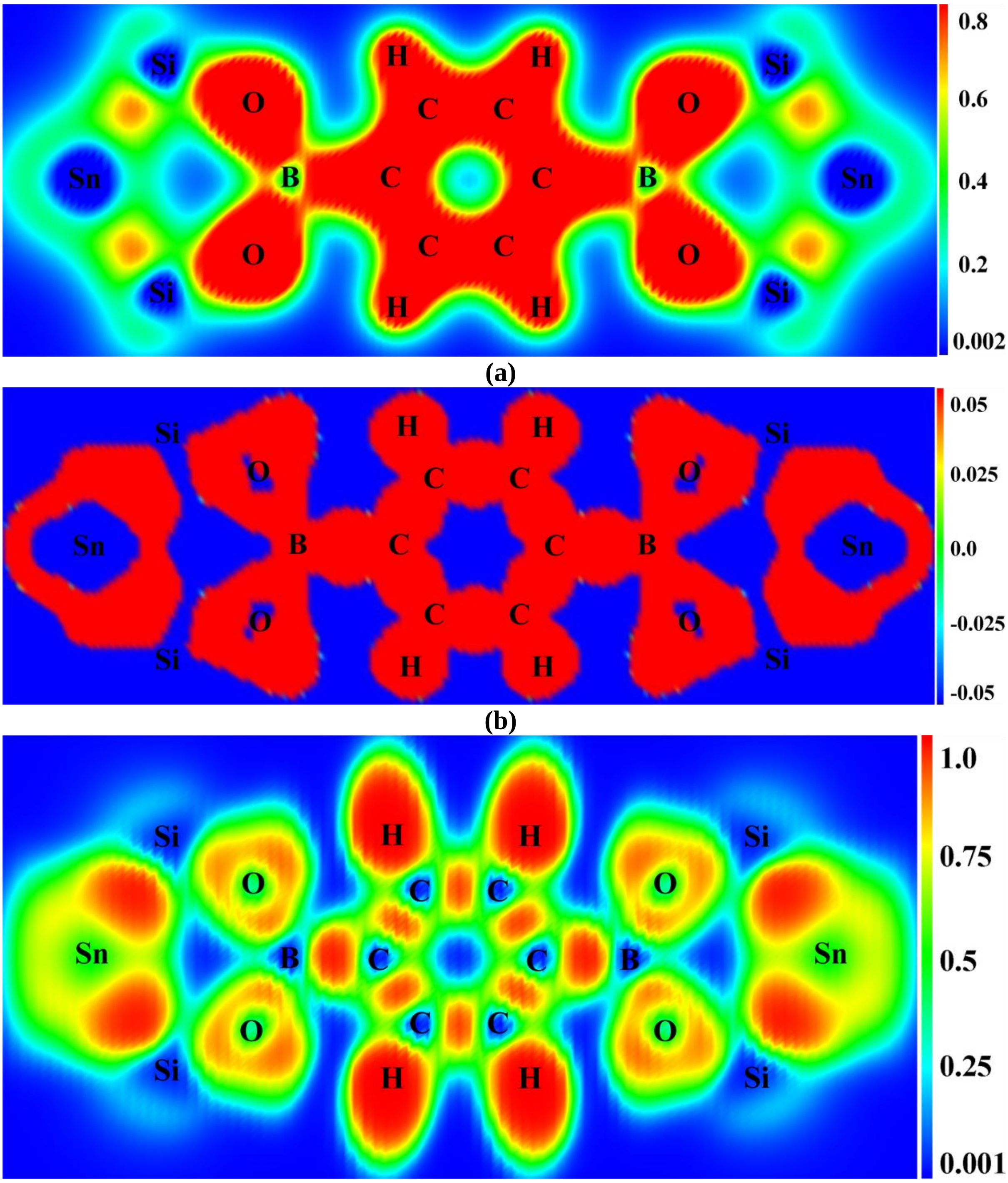


(a)

(b)

(c)

Figure S42. Calculated charge density (a) in e/Å ^{3}, charge transfer (b) in e/Å ^{3}, and electron localization function (c) plots for (Si, Ge) in the (110) plane.



(a)

(b)

(c)

Figure S43. Calculated charge density (a) in e/Å ^{3}, charge transfer (b) in e/Å ^{3}, and electron localization function (c) plots for (Si, Sn) in the (110) plane.

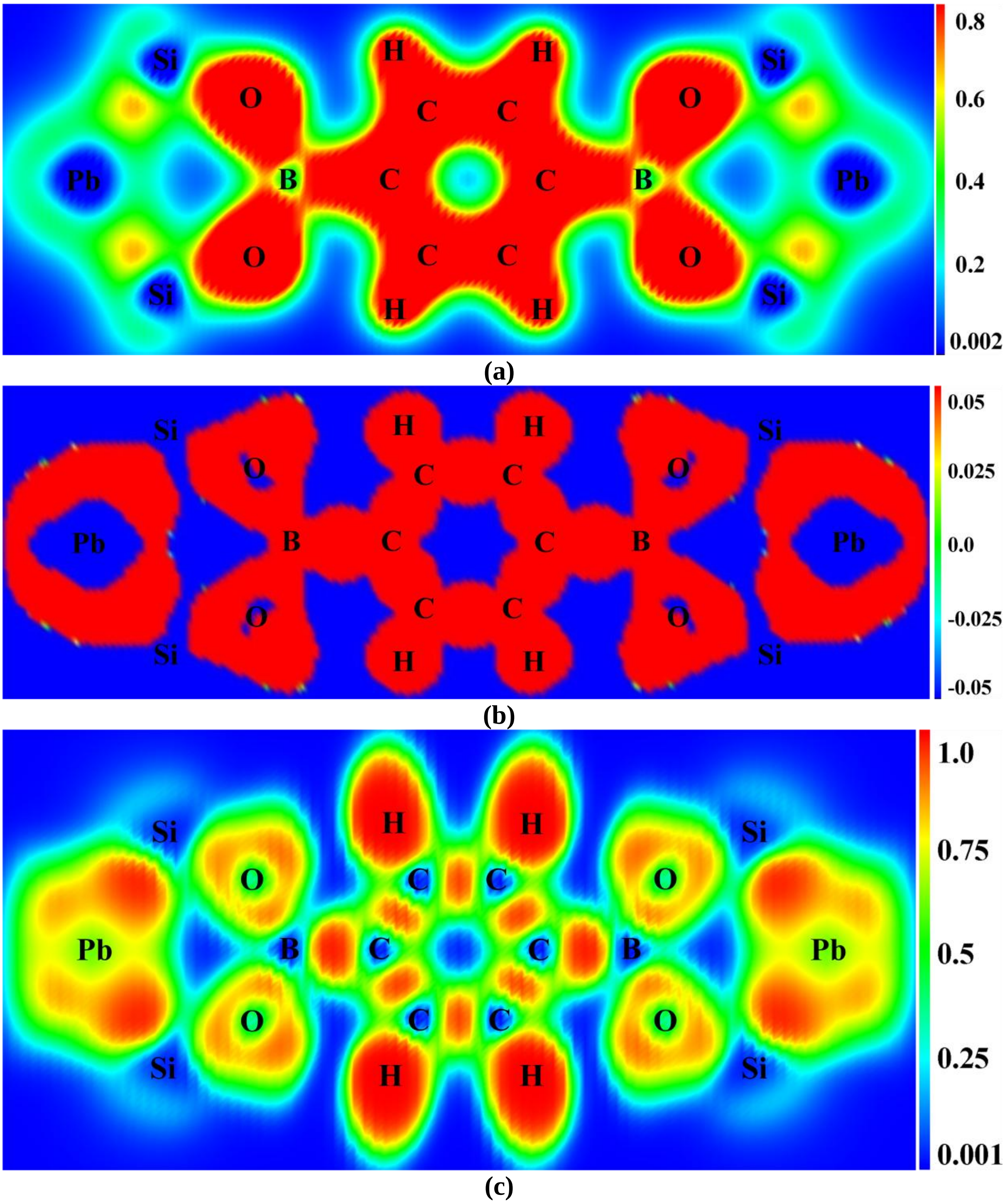


Figure S44. Calculated charge density (a) in e/Å ^{3}, charge transfer (b) in e/Å ^{3}, and electron localization function (c) plots for (Si, Pb) in the (110) plane.

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