Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

(Supplementary Information): Understanding the changes in thermoelectric properties of bournonite, $CuPbSbS_3$, with substitutions.

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Table of Contents

1 Heatmaps: Fraction of compounds that result in bournonite-type structure

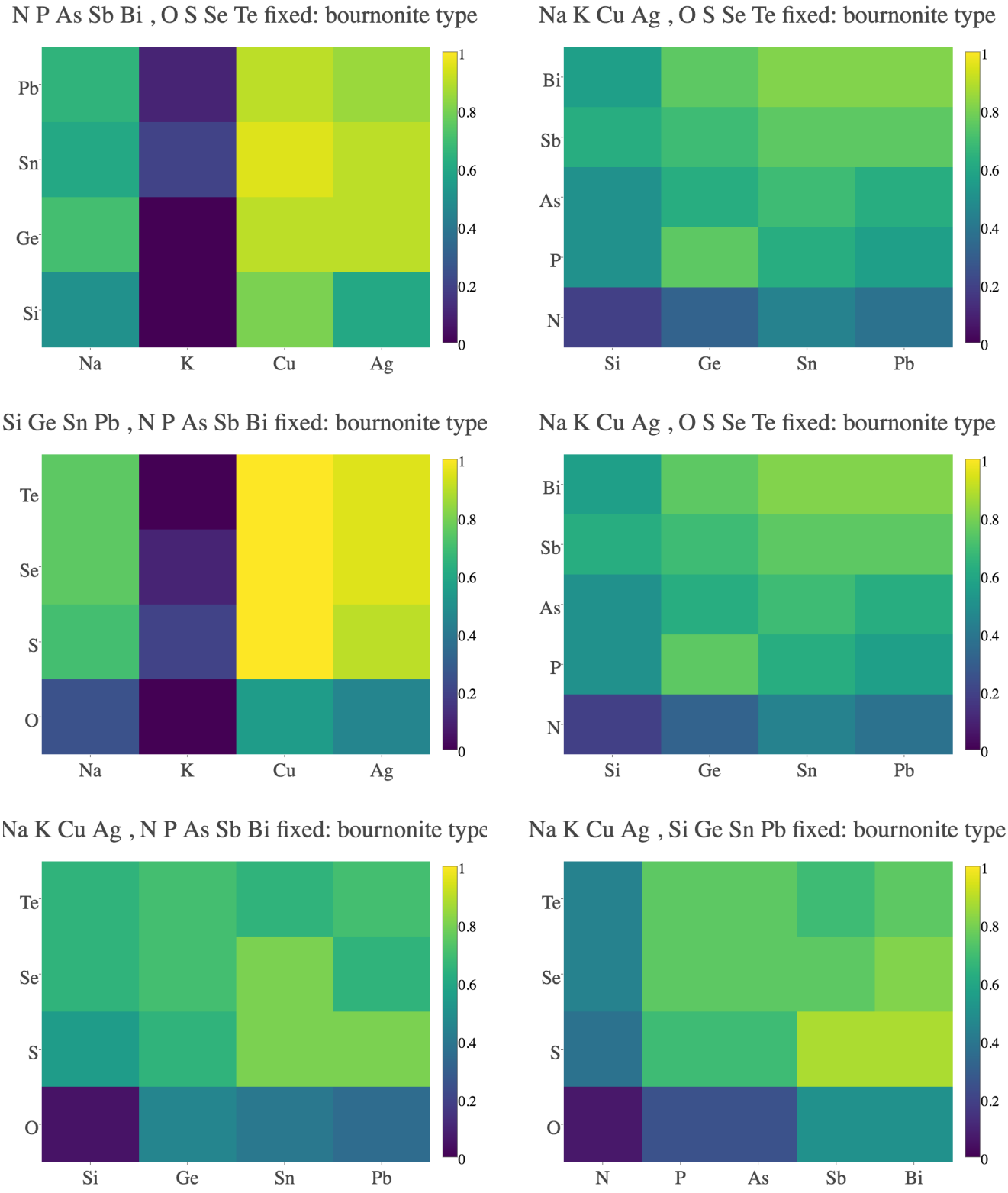


Figure S1. The fraction of compounds that relax into a bournonite-type structure (see the manuscript for definition). Note that compounds containing K almost never relaxes to a bournonite structure and those containing O rarely do so.

2 Band Structures: projected band structures and band gap statistics

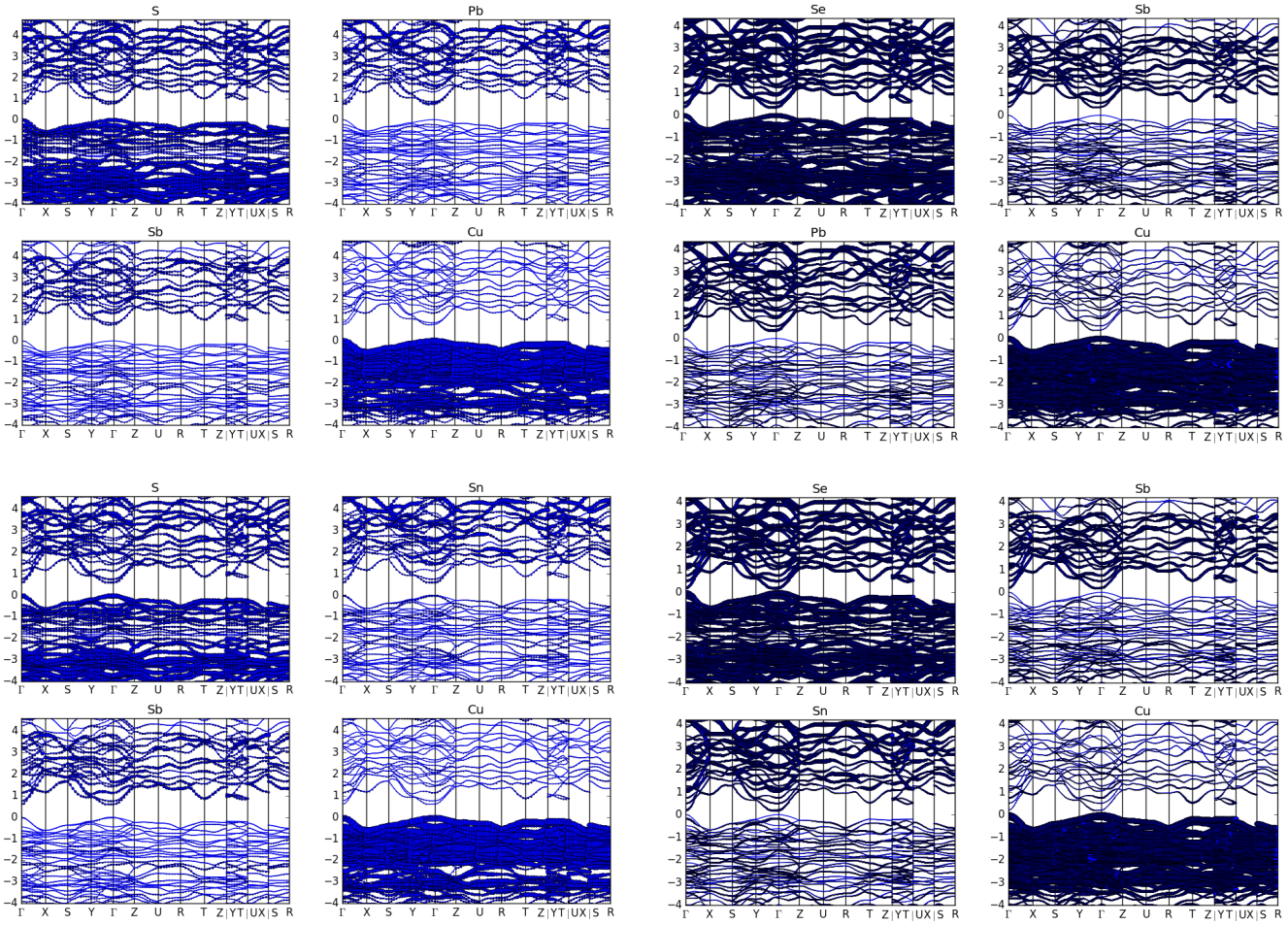


Figure S2. Comparing the band structures and their atomic projections for CuPbSbS3 (top-left), CuPbSbSe (top-right), CuSnSbS3 (bottom-left) andCuSnSbSe3 (bottom-right).

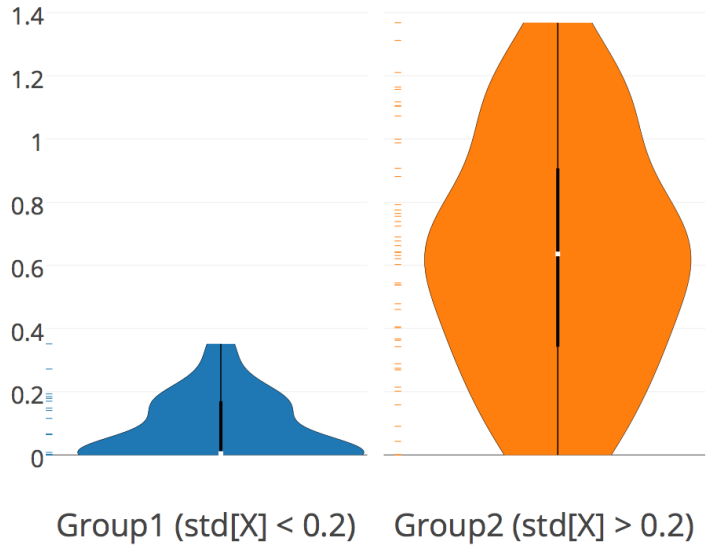
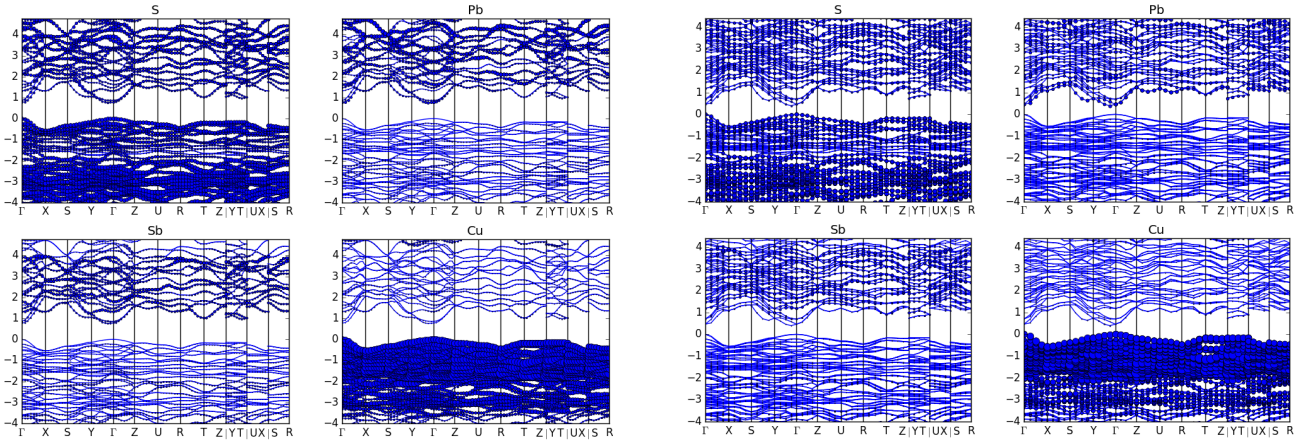


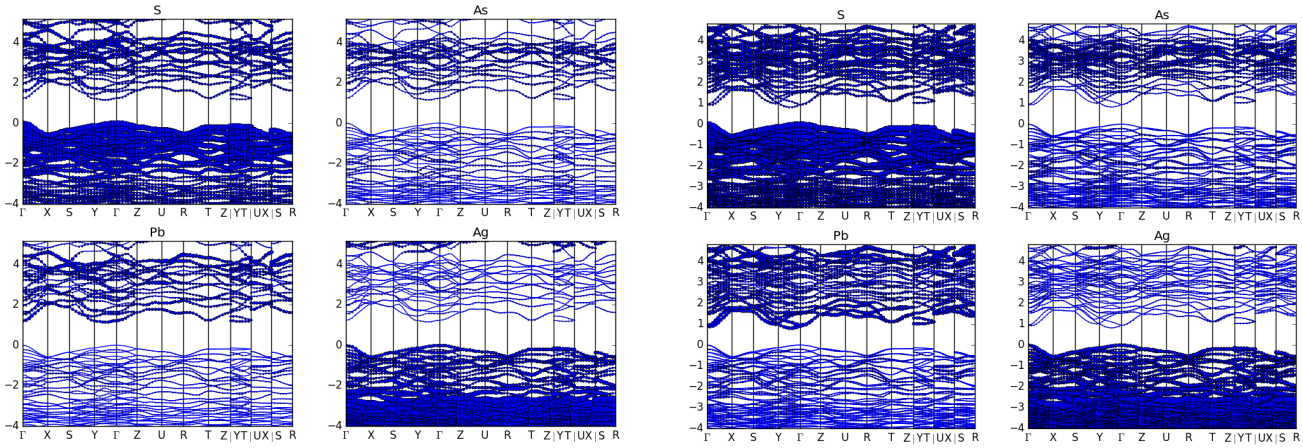
Figure S3. Distribution of calculated band gaps for elements that tend to be relatively stable in bournonite (i.e., excluding Na, K, Si, N, and O), there appear to be two broad groups of bournonite materials. Group 1 are large unit cells with relatively low electronegativity differences (>725 A^3 cells with standard deviation of electronegativity <0.2). Group 2 are smaller unit cells with medium electronegativity differences (<725 A^3 cells with standard deviation of electronegativity >0.2).

no SOC SOC

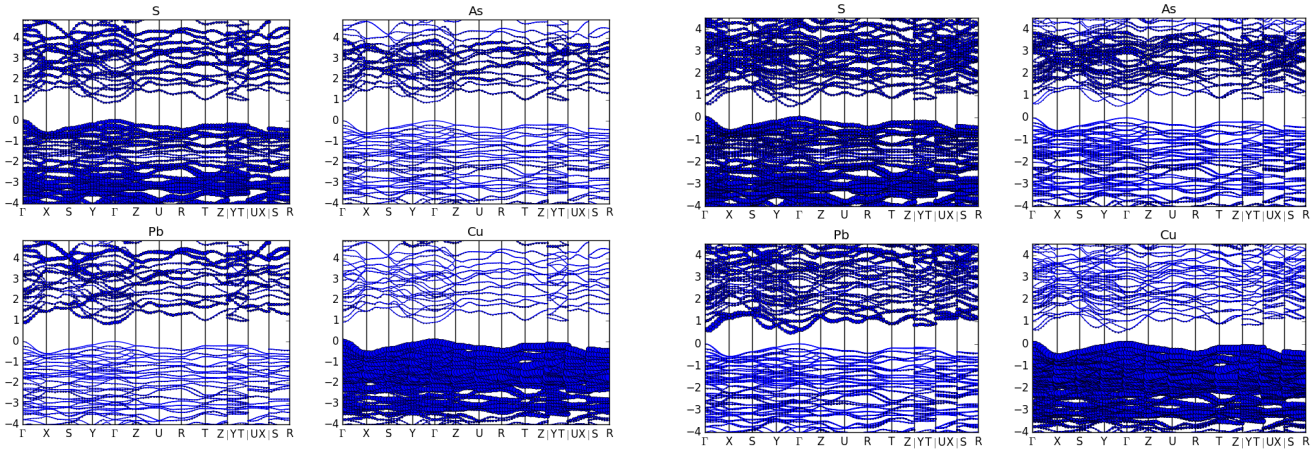
$CuPbSbS_3$



$AgPbAsS_3$



$CuPbAsS_3$



$CuSnSbS_3$

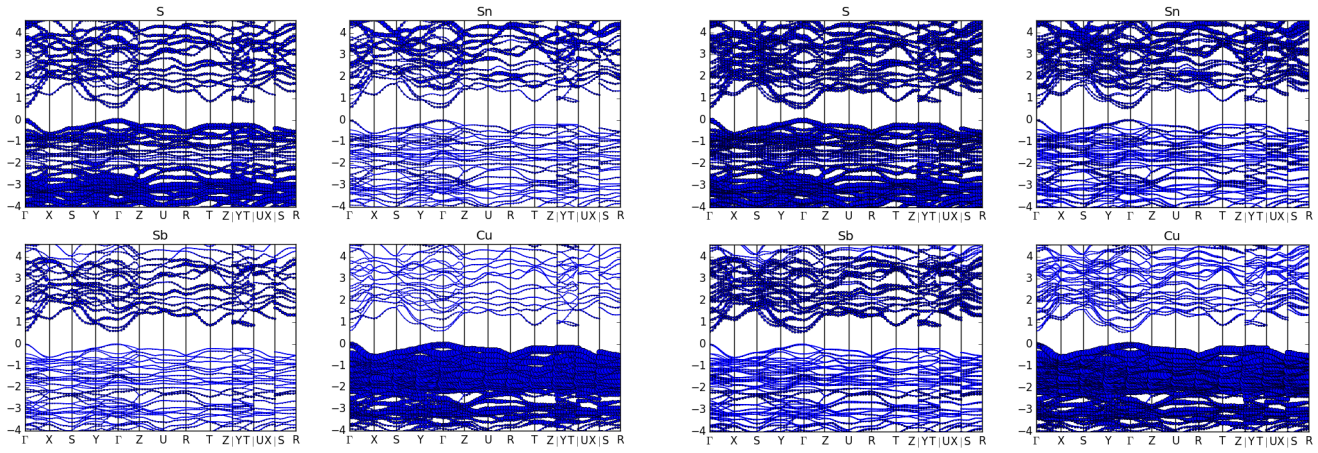


Figure S4. Comparing the band structures without (left) and with (right) spin orbit coupling (SOC) contributions. It is noteworthy that only the conduction bands hence n-type transport properties are significantly affected when SOC is included, but valence bands (and hence *p*-type power factors are largely unaffected by spin-orbit coupling.

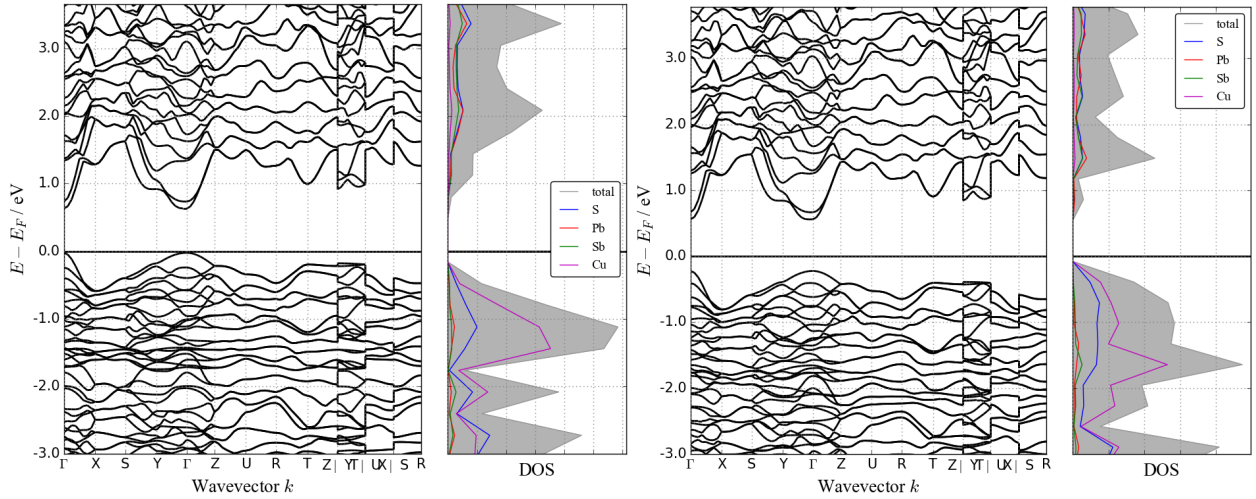
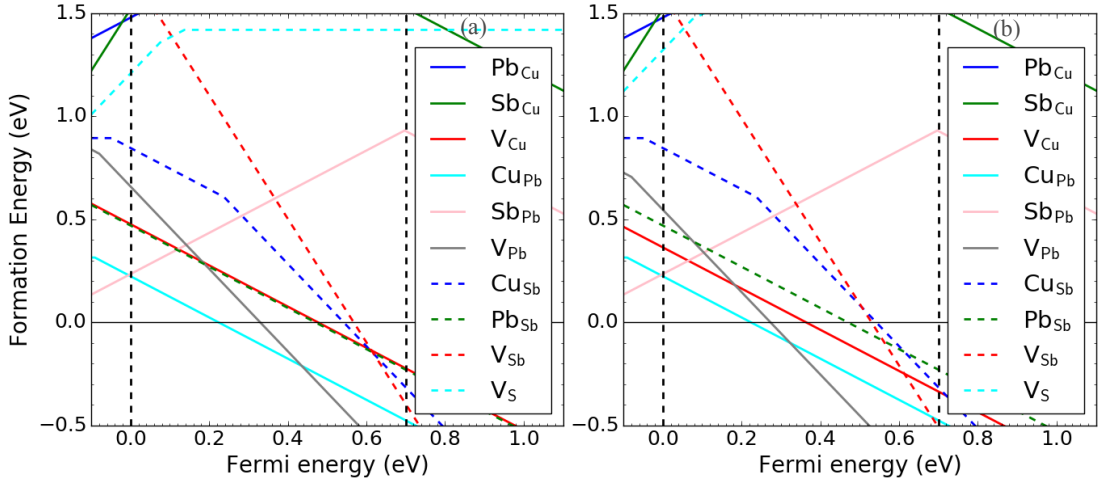


Figure S5. The band structure and atom-projected density of states of bournonite ($CuPbSbS_3$) with GGA (left) and GGA+U (right, U=3) functionals. Although the band gap increases (0.66 vs. 0.78 eV) upon the use of GGA+U, the Cu-d states remain dominant in the valence band.

3 Defects: intrinsic for $CuPbSbS_3$, $CuPbSbSe_3$, $CuSnSbSe_3$ and extrinsic for $CuPbSbS_3$



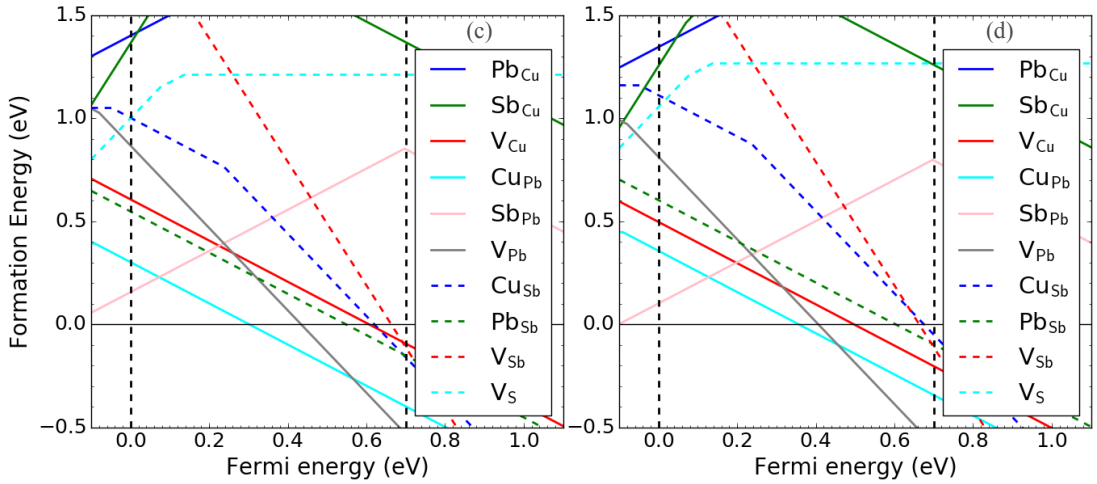


Figure S6. Formation energies of intrinsic defects in $CuPbSbS_3$ in different regions of phase diagram followed by the chemical potential in eV of each element in this region:

(a) Cu_3SbS_4-$Cu_{12}Sb_4S_{13}$-$CuSbS_2$-PbS {Pb: -4.501, Sb: -4.41, S: -4.413, Cu: -4.233}
(b) Cu_3SbS_4-$Sb_8(PbS_5)_3$-$CuSbS_2$-PbS {Pb: -4.614, Sb: -4.523, S: -4.3, Cu: -4.346}
(c) $Cu_{12}Sb_4S_{13}$-$CuSbS_2$-PbS-Sb {Pb: -4.293, Sb: -4.124, S: -4.621, Cu: -4.103}
(d) $Sb_8(PbS_5)_3$-$CuSbS_2$-PbS-Sb {Pb: -4.348, Sb: -4.124, S: -4.566, Cu: -4.213}

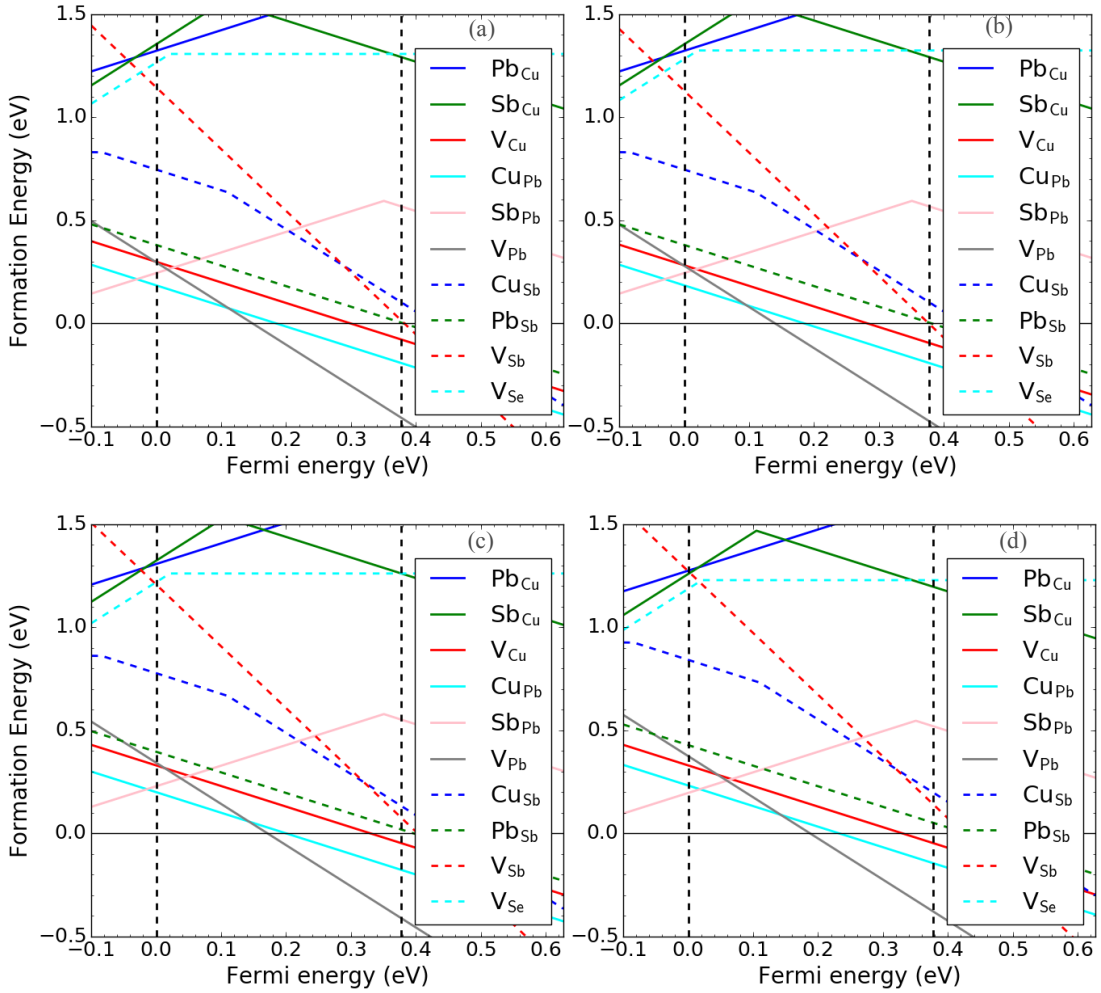


Figure S7. Formation energies of intrinsic defects in $CuPbSbSe_3$ in different regions of phase diagram followed by the chemical potential in eV of each element in this region:

(a) Cu_3SbSe_4-Cu_3Se_2-$CuSbSe_2$-PbSe {Pb: -4.554, Sb: -4.357, Cu: -4.13, Se: -3.775}

(b) Cu_3SbSe_4-$CuSbSe_2$-PbSe-Sb_2Se_3 {Pb: -4.571, Sb: -4.373, Cu: -4.147, Se: -3.758}
(c) Cu-Cu_3Se_2-$CuSbSe_2$-PbSe {Pb: -4.508, Sb: -4.295, Cu: -4.099, Se: -3.821}
(d) Cu-$CuSbSe_2$-PbSe-Sb_2Se_3 {Pb: -4.475, Sb: -4.23, Cu: -4.099, Se: -3.853}

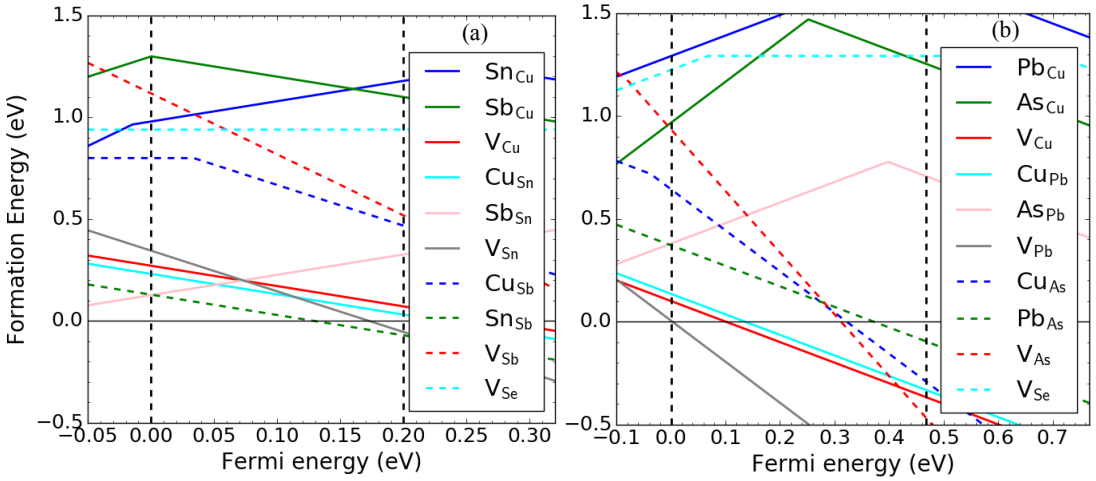
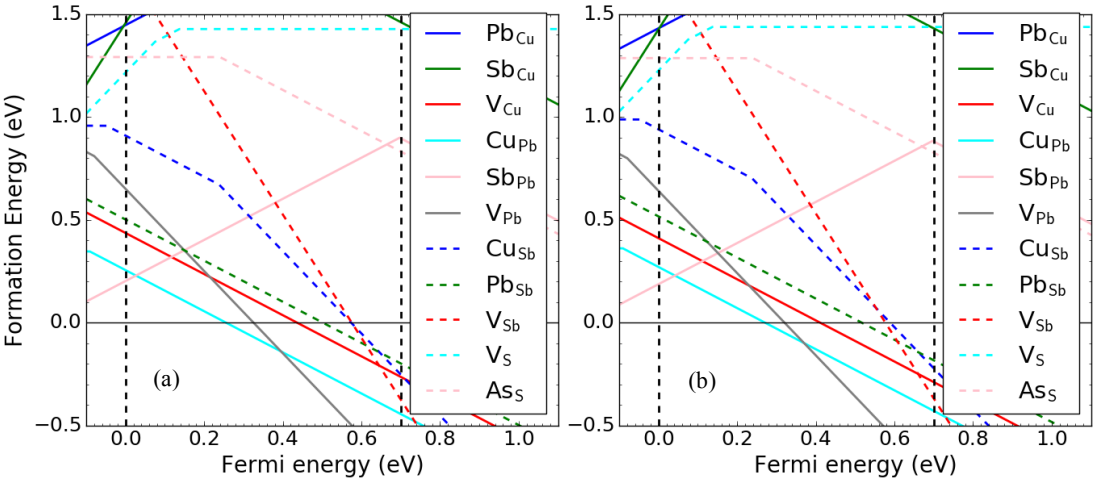
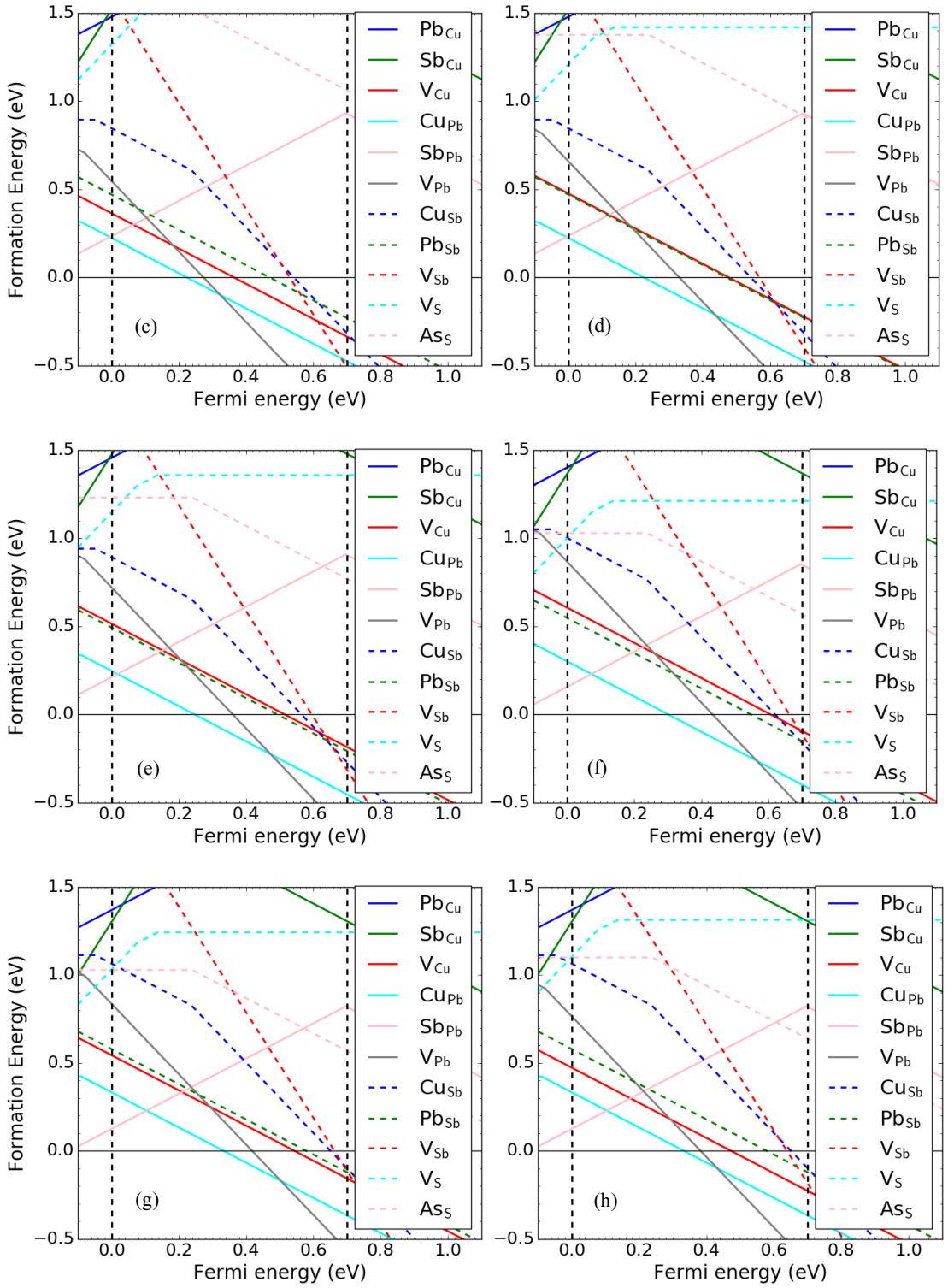


Figure S8. Formation energies of intrinsic defects in a) $CuSnSbSe_3$ and b) $CuPbAsSe_3$ with chemical potentials chosen at only one region of phase diagram. Chemical potential is in eV unit. Two dashed vertical lines are VBM and CBM respectively.

(a) $CuSnSbSe_3$ at Cu-Cu_2SnSe_3-Sb_2Se_3-SnSe region, where chemical potentials are { Cu: -4.099, Sn: -4.465, Sb: -4.16, Se: -3.9} .
(b) $CuPbAsSe_3$ at As_2Se_3-Cu_3AsSe_4-CuAsSe-PbSe region, where chemical potentials are { Cu: -4.27, Pb: -4.68, As: -4.71, Se: -3.64}




Formation Energy (eV)
Fermi energy (eV)
(c)
(d)
(e)
(f)
(g)
(h)
Pb_{Cu}
Sb_{Cu}
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V_{Pb}
Cu_{Sb}
Pb_{Sb}
V_{Sb}
V_S
As_S

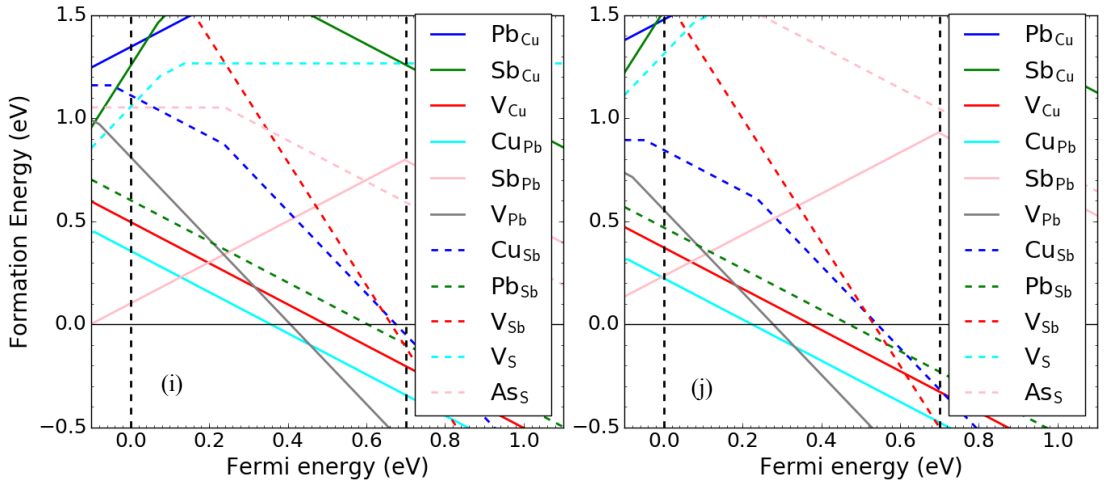


Figure S9. Formation energies of defects in $CuPbSbS_3$ including extrinsic impurity As on S in different regions of phase diagram followed by the chemical potential in eV of each element in this region:

(a) $Cu_6As_4S_9$-CuAsS-$Cu_{12}As_4S_{13}$-$CuSbS_2$-PbS {Pb: -4.51, Sb: -4.387, S: -4.404, As: -4.736, Cu: -4.273}
(b) $Cu_6As_4S_9$-$Sb_8(PbS_5)_3$-CuAsS-$CuSbS_2$-PbS {Pb: -4.52, Sb: -4.382, S: -4.394, As: -4.72, Cu: -4.299}
(c) $Cu_6As_4S_9$-$Sb_8(PbS_5)_3$-$CuSbS_2$-Cu_3SbS_4-PbS {Pb: -4.614, Sb: -4.523, S: -4.3, As: -4.861, Cu: -4.346}
(d) $Cu_{12}Sb_4S_{13}$-$Cu_{12}As_4S_{13}$-$CuSbS_2$-Cu_3SbS_4-PbS {Pb: -4.501, Sb: -4.41, S: -4.413, As: -4.829, Cu: -4.233}
(e) CuAsS-$Cu_{12}Sb_4S_{13}$-$Cu_{12}As_4S_{13}$-$CuSbS_2$-PbS {Pb: -4.44, Sb: -4.326, S: -4.474, As: -4.744, Cu: -4.195}
(f) CuAsS-$Cu_{12}Sb_4S_{13}$-$CuSbS_2$-Sb-PbS {Pb: -4.293, Sb: -4.124, S: -4.621, As: -4.689, Cu: -4.103}
(g) CuAsS-$CuSbS_2$-Sb-As-PbS {Pb: -4.324, Sb: -4.124, S: -4.59, As: -4.658, Cu: -4.165}
(h) $Sb_8(PbS_5)_3$-CuAsS-$CuSbS_2$-As-PbS {Pb: -4.395, Sb: -4.195, S: -4.519, As: -4.658, Cu: -4.236}
(i) $Sb_8(PbS_5)_3$-$CuSbS_2$-Sb-As-PbS {Pb: -4.348, Sb: -4.124, S: -4.566, As: -4.658, Cu: -4.213}
(j) $Cu_6As_4S_9$-$Cu_{12}As_4S_{13}$-$CuSbS_2$-Cu_3SbS_4-PbS {Pb: -4.605, Sb: -4.514, S: -4.309, As: -4.855, Cu: -4.337}

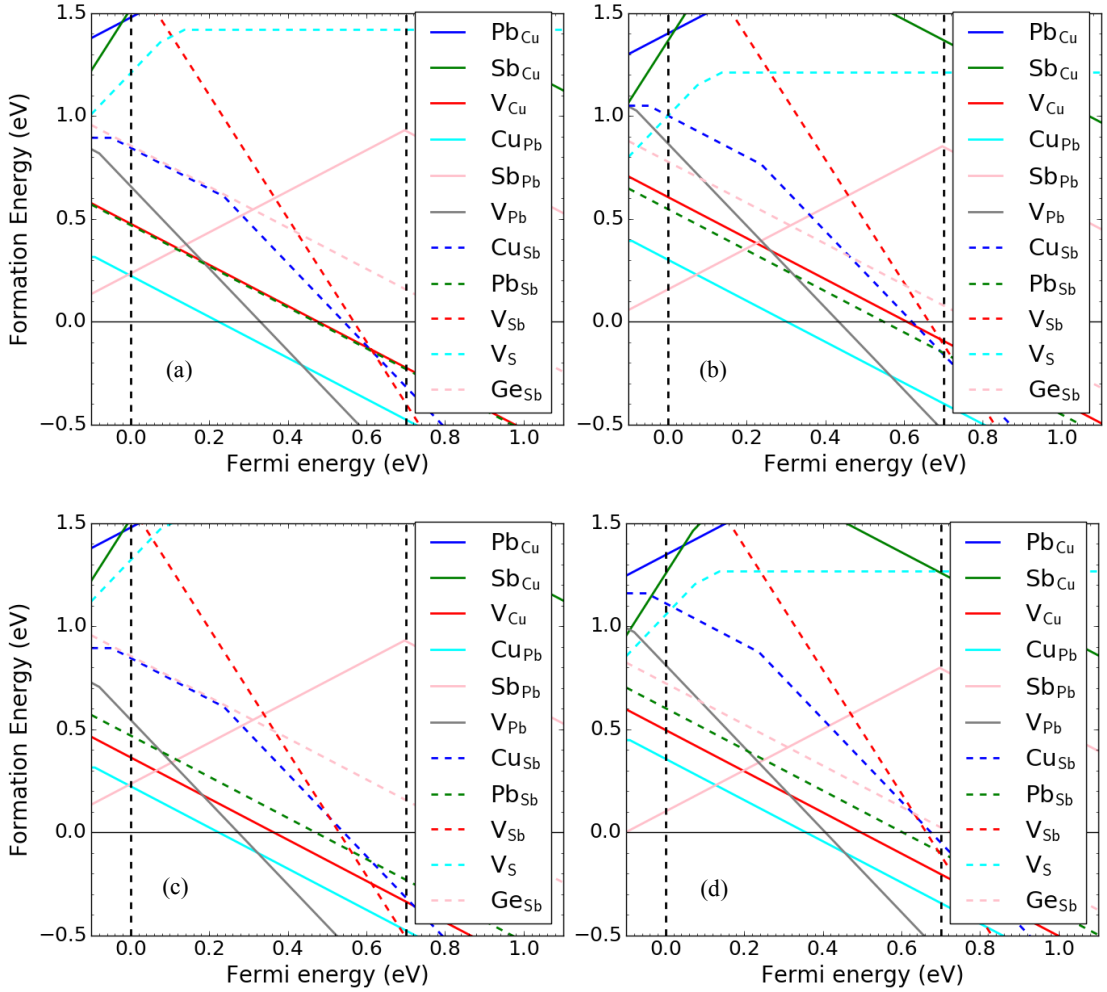


Figure S10. Formation energies of defects in $CuPbSbS_3$ including extrinsic impurity Ge on Sb in different regions of phase diagram followed by the chemical potential in eV of each element in this region:

(a) Cu_2GeS_3-$Cu_{12}Sb_4S_{13}$-$CuSbS_2$-Cu_3SbS_4-PbS {Pb: -4.501, Sb: -4.41, S: -4.413, Ge: -5.438, Cu: -4.233}
(b) Cu_2GeS_3-$Cu_{12}Sb_4S_{13}$-$CuSbS_2$-Sb-PbS {Pb: -4.293, Sb: -4.124, S: -4.621, Ge: -5.074, Cu: -4.103}
(c) $Sb_8(PbS_5)_3$-Cu_2GeS_3-$CuSbS_2$-Cu_3SbS_4-PbS {Pb: -4.614, Sb: -4.523, S: -4.3, Ge: -5.55, Cu: -4.346}
(d) $Sb_8(PbS_5)_3$-Cu_2GeS_3-$CuSbS_2$-Sb-PbS {Pb: -4.348, Sb: -4.124, S: -4.566, Ge: -5.019, Cu: -4.213}

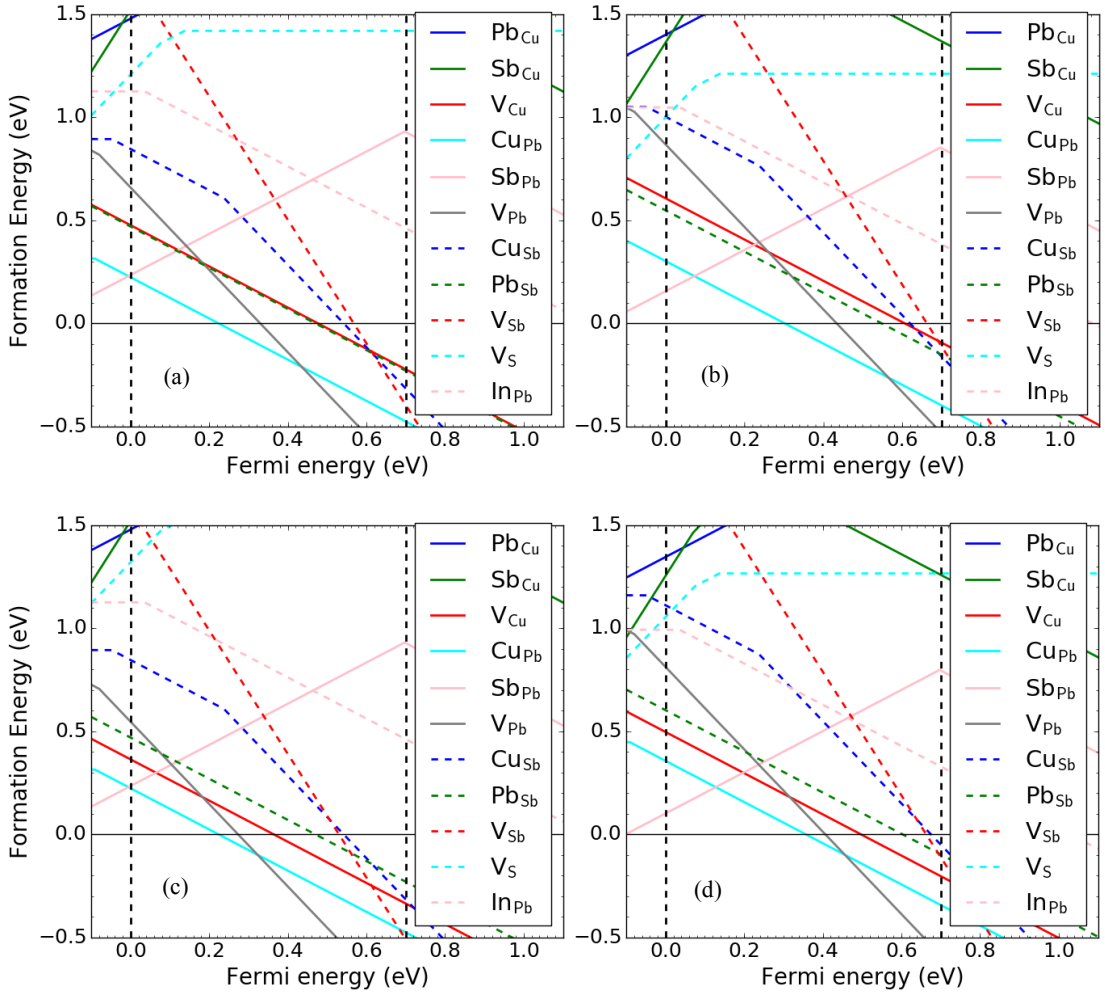
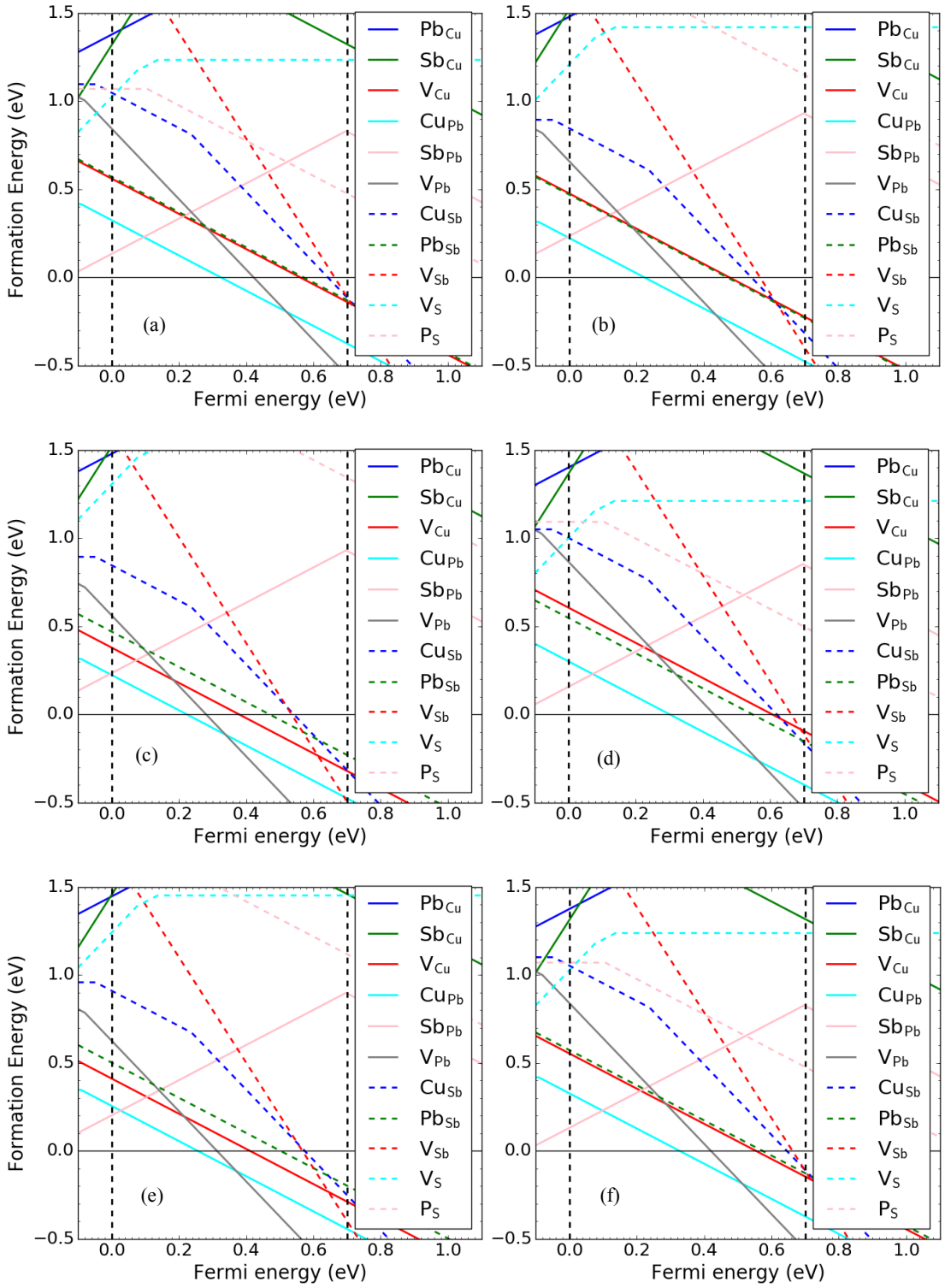


Figure S11. Formation energies of defects in $CuPbSbS_3$ including extrinsic impurity In on Pb in different regions of phase diagram followed by the chemical potential in eV of each element in this region:

(a) $InCuS_2$-$Cu_{12}Sb_4S_{13}$-$CuSbS_2$-Cu_3SbS_4-PbS {Pb: -4.501, Sb: -4.41, S: -4.413, Cu: -4.233, In: -3.983}
(b) $InCuS_2$-$Cu_{12}Sb_4S_{13}$-$CuSbS_2$-Sb-PbS {Pb: -4.293, Sb: -4.124, S: -4.621, Cu: -4.103, In: -3.696}
(c) $InCuS_2$-$Sb_8(PbS_5)_3$-$CuSbS_2$-Cu_3SbS_4-PbS {Pb: -4.614, Sb: -4.523, S: -4.3, Cu: -4.346, In: -4.095}
(d) $InCuS_2$-$Sb_8(PbS_5)_3$-$CuSbS_2$-Sb-PbS {Pb: -4.348, Sb: -4.124, S: -4.566, Cu: -4.213, In: -3.696}


Formation Energy (eV)
Fermi energy (eV)
(a)
(b)
(c)
(d)
(e)
(f)
Pb_{Cu}
Sb_{Cu}
V_{Cu}
Cu_{Pb}
Sb_{Pb}
V_{Pb}
Cu_{Sb}
Pb_{Sb}
V_{Sb}
V_S
P_S

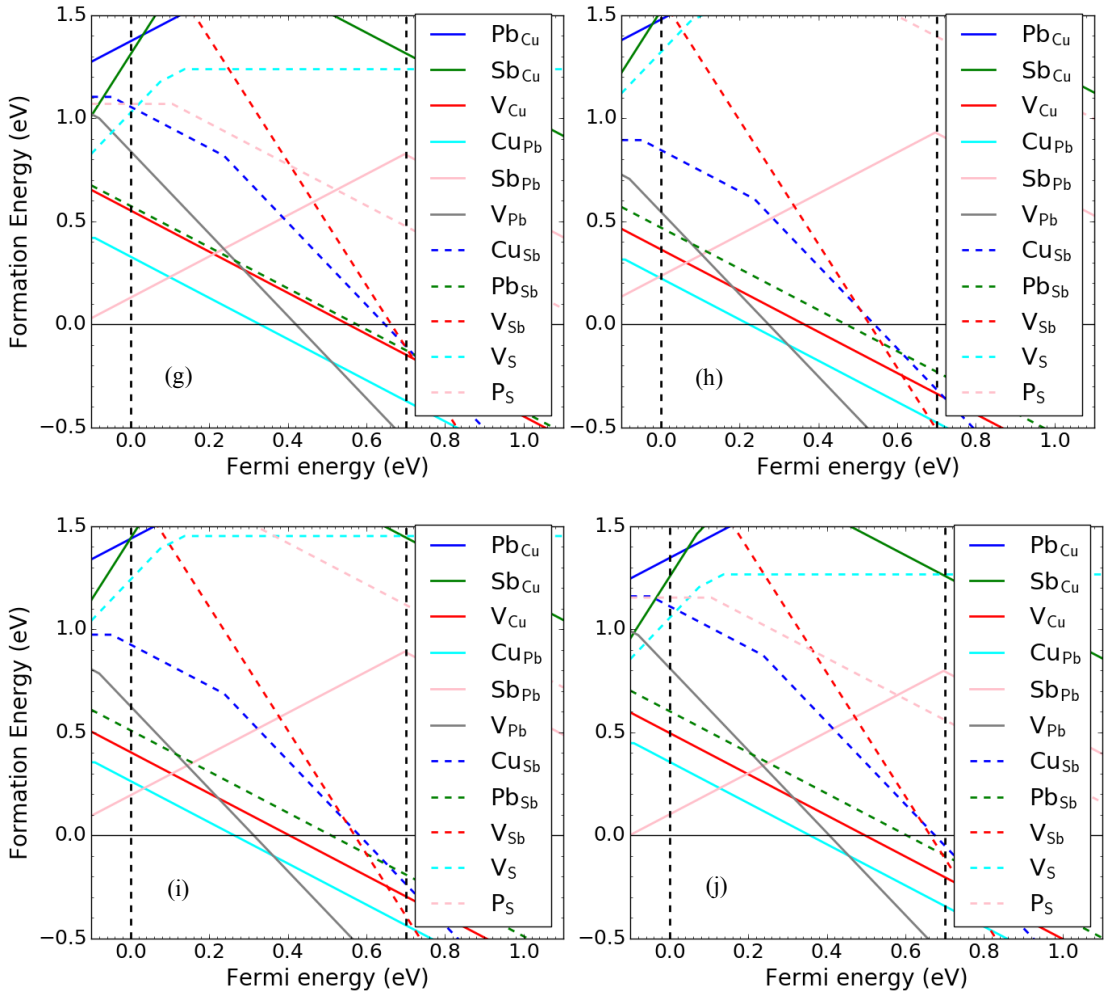


Figure S12. Formation energies of defects in $CuPbSbS_3$ including extrinsic impurity P on S in different regions of phase diagram followed by the chemical potential in eV of each element in this region:

(a) $CuSbS_2$-Cu_3PS_4-CuP_2-PbS-Sb {Pb: -4.316, Sb: -4.124, S: -4.598, Cu: -4.149, P: -5.555}
(b) $CuSbS_2$-Cu_3SbS_4-$Cu_{12}Sb_4S_{13}$-Cu_3PS_4-PbS {Pb: -4.501, Sb: -4.41, S: -4.413, Cu: -4.233, P: -6.043}
(c) $CuSbS_2$-Cu_3SbS_4-$P_2Pb_3S_8$-Cu_3PS_4-PbS {Pb: -4.598, Sb: -4.508, S: -4.315, Cu: -4.33, P: -6.141}
(d) $CuSbS_2$-$Cu_{12}Sb_4S_{13}$-Cu_3PS_4-PbS-Sb {Pb: -4.293, Sb: -4.124, S: -4.621, Cu: -4.103, P: -5.601}
(e) $CuSbS_2$-$P_2Pb_3S_8$-$PPbS_3$-Cu_3PS_4-PbS {Pb: -4.534, Sb: -4.411, S: -4.38, Cu: -4.298, P: -5.98}
(f) $CuSbS_2$-$PPbS_3$-Cu_3PS_4-CuP_2-PbS {Pb: -4.32, Sb: -4.126, S: -4.594, Cu: -4.155, P: -5.552}
(g) $CuSbS_2$-$PPbS_3$-CuP_2-PbS-Sb {Pb: -4.32, Sb: -4.124, S: -4.594, Cu: -4.157, P: -5.551}
(h) $Sb_8(PbS_5)_3$-$CuSbS_2$-Cu_3SbS_4-$P_2Pb_3S_8$-PbS {Pb: -4.614, Sb: -4.523, S: -4.3, Cu: -4.346, P: -6.179}
(i) $Sb_8(PbS_5)_3$-$CuSbS_2$-P2Pb_3S_8-$PPbS_3$-PbS {Pb: -4.534, Sb: -4.404, S: -4.38, Cu: -4.306, P: -5.98}
(j) $Sb_8(PbS_5)_3$-$CuSbS_2$-$PPbS_3$-PbS-Sb {Pb: -4.348, Sb: -4.124, S: -4.566, Cu: -4.213, P: -5.607}

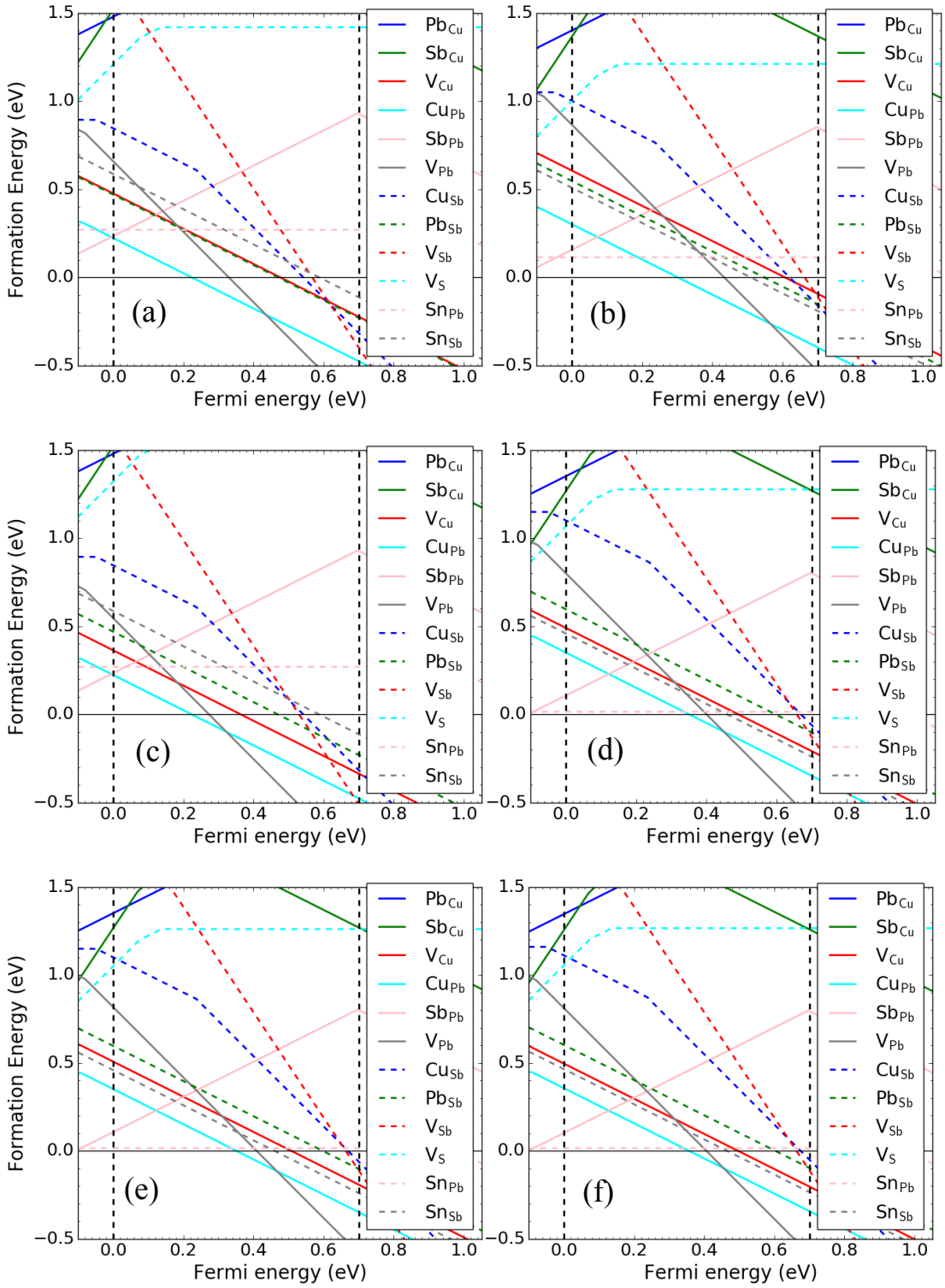
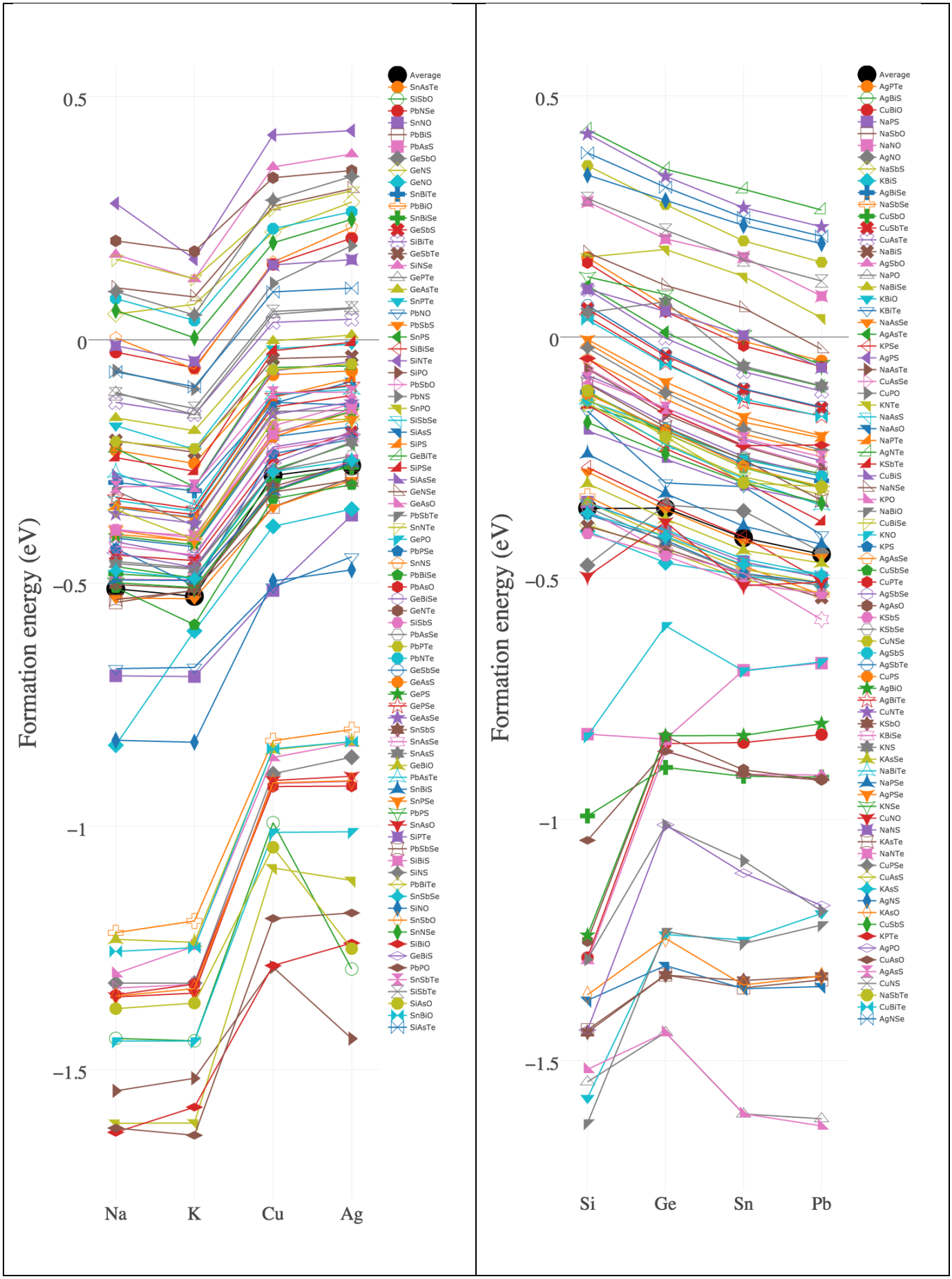
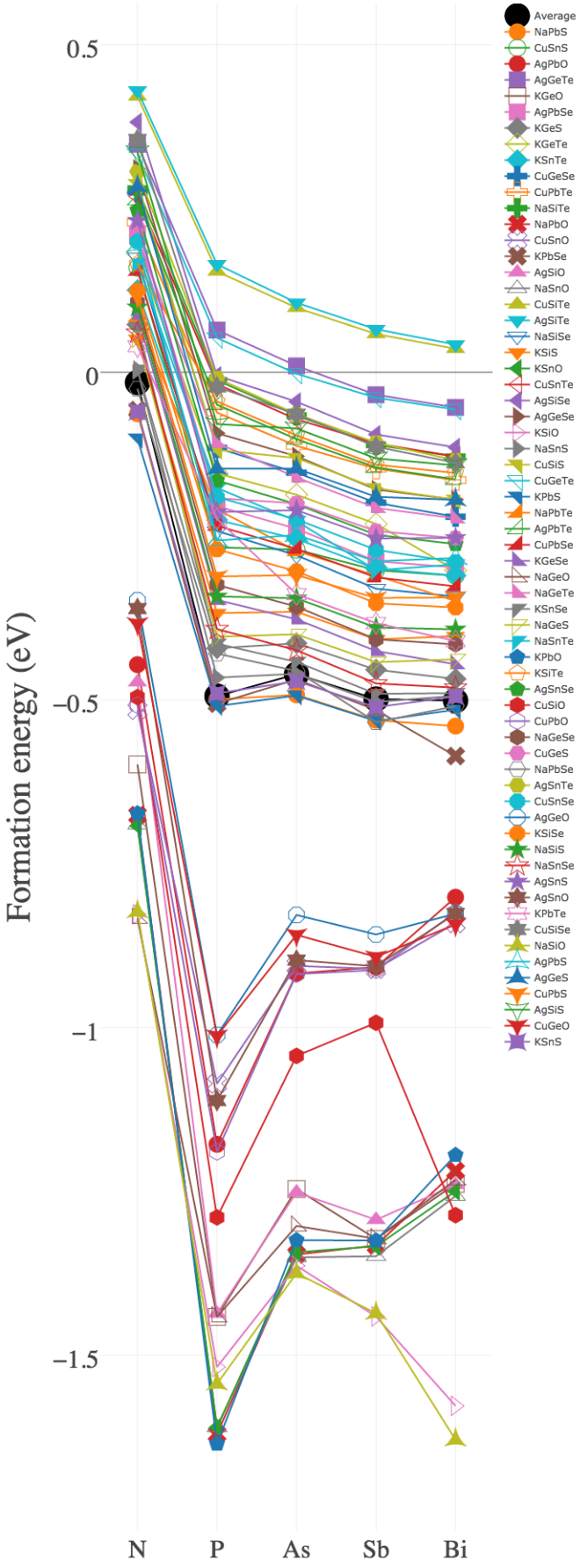


Figure S13. Formation energies of defects in CuPbSbS3 including extrinsic impurities Sn on Sb and Sn on Pb in different regions of phase diagram followed by the chemical potential in eV of each element in this region:

(a) Cu_2SnS_3-$Cu_{12}Sb_4S_{13}$-$CuSbS_2$-Cu_3SbS_4-PbS {Pb: -4.501, Sb: -4.41, S: -4.413, Sn: -4.867, Cu: -4.233}
(b) Cu_2SnS_3-$Cu_{12}Sb_4S_{13}$-$CuSbS_2$-Sb-PbS {Pb: -4.293, Sb: -4.124, S: -4.621, Sn: -4.503, Cu: -4.103}
(c) Cu_2SnS_3-$Sb_8(PbS_5)_3$-$CuSbS_2$-Cu_3SbS_4-PbS {Pb: -4.614, Sb: -4.523, S: -4.3, Sn: -4.98, Cu: -4.346}
(d) Cu_2SnS_3-$Sb_8(PbS_5)_3$-SnS-$CuSbS_2$-PbS {Pb: -4.359, Sb: -4.141, S: -4.555, Sn: -4.47, Cu: -4.218}
(e) Cu_2SnS_3-SnS-$CuSbS_2$-Sb-PbS {Pb: -4.342, Sb: -4.124, S: -4.571, Sn: -4.454, Cu: -4.202}
(f) $Sb_8(PbS_5)_3$-SnS-$CuSbS_2$-Sb-PbS {Pb: -4.348, Sb: -4.124, S: -4.566, Sn: -4.459, Cu: -4.213}

4 Intra-group changes in properties (detailed): E_{form}, E_h, E_g, *n*-PF, *p*-PF




Formation energy (eV)
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0
−0.5
−1
−1.5
N
P
As
Sb
Bi
Average
NaPbS
CuSnS
AgPbO
AgGeTe
KGeO
AgPbSe
KGeS
KGeTe
KSnTe
CuGeSe
CuPbTe
NaSiTe
NaPbO
CuSnO
KPbSe
AgSiO
NaSnO
CuSiTe
AgSiTe
NaSiSe
KSiS
KSnO
CuSnTe
AgSiSe
AgGeSe
KSiO
NaSnS
CuSiS
CuGeTe
KPbS
NaPbTe
AgPbTe
CuPbSe
KGeSe
NaGeO
NaGeTe
KSnSe
NaGeS
NaSnTe
KPbO
KSiTe
AgSnSe
CuSiO
CuPbO
NaGeSe
CuGeS
NaPbSe
AgSnTe
CuSnSe
AgGeO
KSiSe
NaSiS
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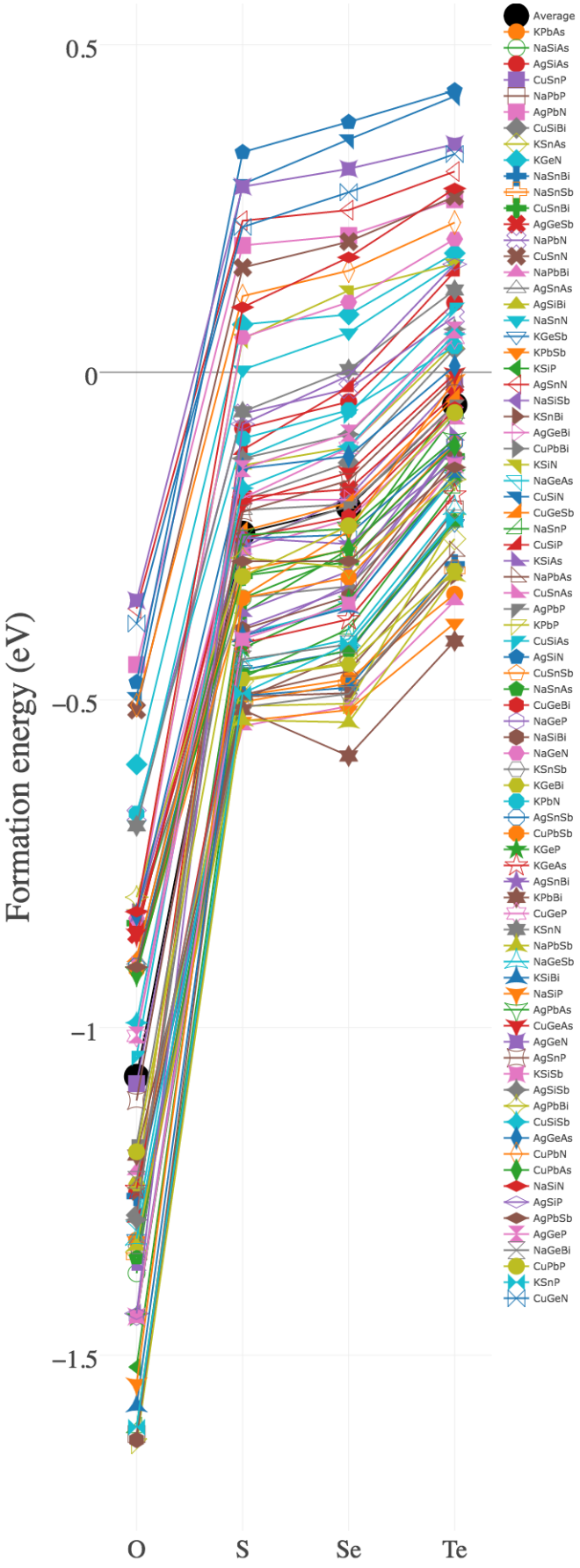
Formation energy (eV)
0.5
0
−0.5
−1
−1.5
O
S
Se
Te
Average
KPbAs
NaSiAs
AgSiAs
CuSnP
NaPbP
AgPbN
CuSiBi
KSnAs
KGeN
NaSnBi
NaSnSb
CuSnBi
AgGeSb
NaPbN
CuSnN
NaPbBi
AgSnAs
AgSiBi
NaSnN
KGeSb
KPbSb
KSiP
AgSnN
NaSiSb
KSnBi
AgGeBi
CuPbBi
KSiN
NaGeAs
CuSiN
CuGeSb
NaSnP
CuSiP
KSiAs
NaPbAs
CuSnAs
AgPbP
KPbP
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AgSiN
CuSnSb
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CuGeBi
NaGeP
NaSiBi
NaGeN
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KGeBi
KPbN
AgSnSb
CuPbSb
KGeP
KGeAs
AgSnBi
KPbBi
CuGeP
KSnN
NaPbSb
NaGeSb
KSiBi
NaSiP
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CuGeAs
AgGeN
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AgPbBi
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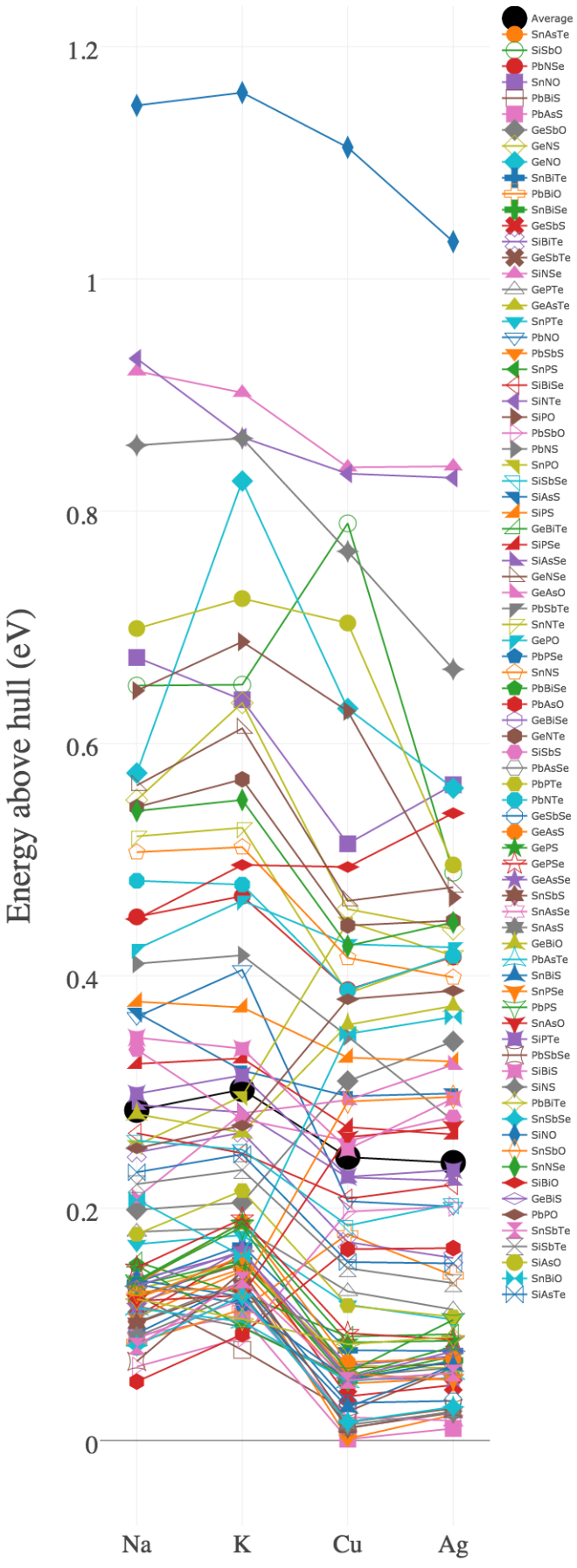
CuGeN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0.4
0.2
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K
Cu
Ag
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PbNSe
SnNO
PbBiS
PbAsS
GeSbO
GeNS
GeNO
SnBiTe
PbBiO
SnBiSe
GeSbS
SiBiTe
GeSbTe
SiNSe
GePTe
GeAsTe
SnPTe
PbNO
PbSbS
SnPS
SiBiSe
SiNTe
SiPO
PbSbO
PbNS
SnPO
SiSbSe
SiAsS
SiPS
GeBiTe
SiPSe
SiAsSe
GeNSe
GeAsO
PbSbTe
SnNTe
GePO
PbPSe
SnNS
PbBiSe
PbAsO
GeBiSe
GeNTe
SiSbS
PbAsSe
PbPTe
PbNTe
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SiBiS
SiNS
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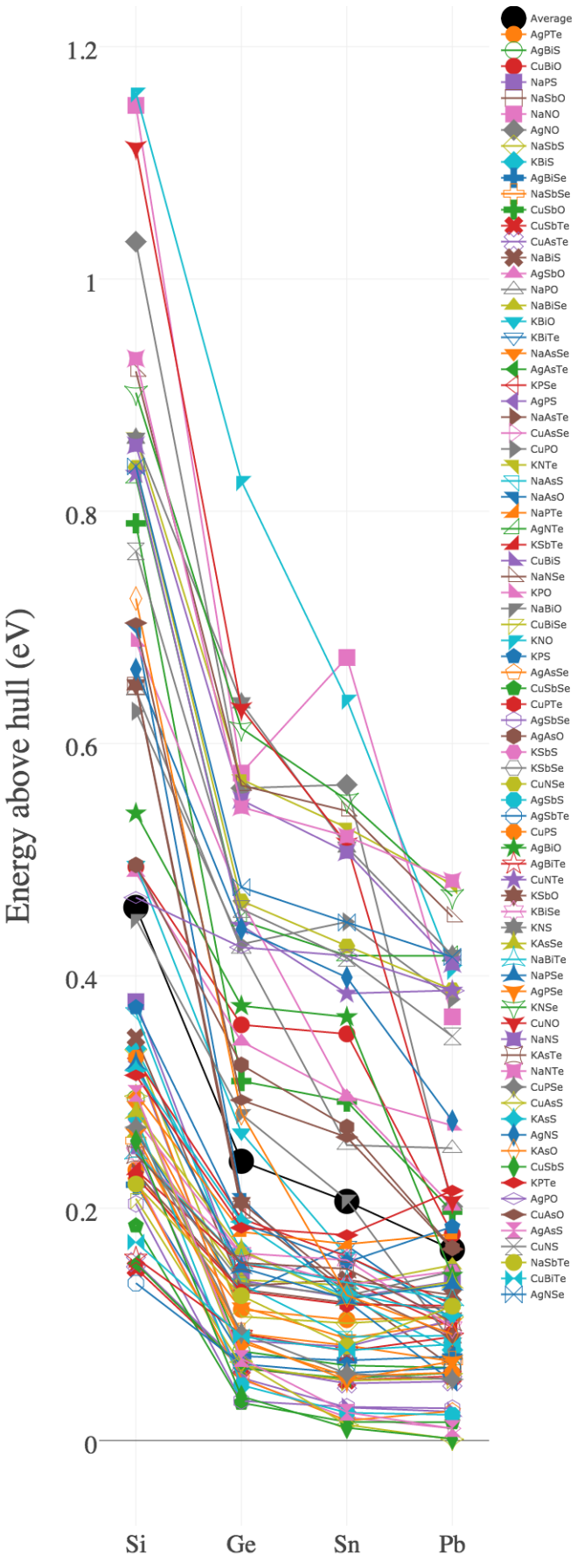
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0.8
0.6
0.4
0.2
0
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Ge
Sn
Pb
Average
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AgBiS
CuBiO
NaPS
NaSbO
NaNO
AgNO
NaSbS
KBiS
AgBiSe
NaSbSe
CuSbO
CuSbTe
CuAsTe
NaBiS
AgSbO
NaPO
NaBiSe
KBiO
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AgAsTe
KPSe
AgPS
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CuPO
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CuNSe
AgSbS
AgSbTe
CuPS
AgBiO
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KSbO
KBiSe
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KNSe
CuNO
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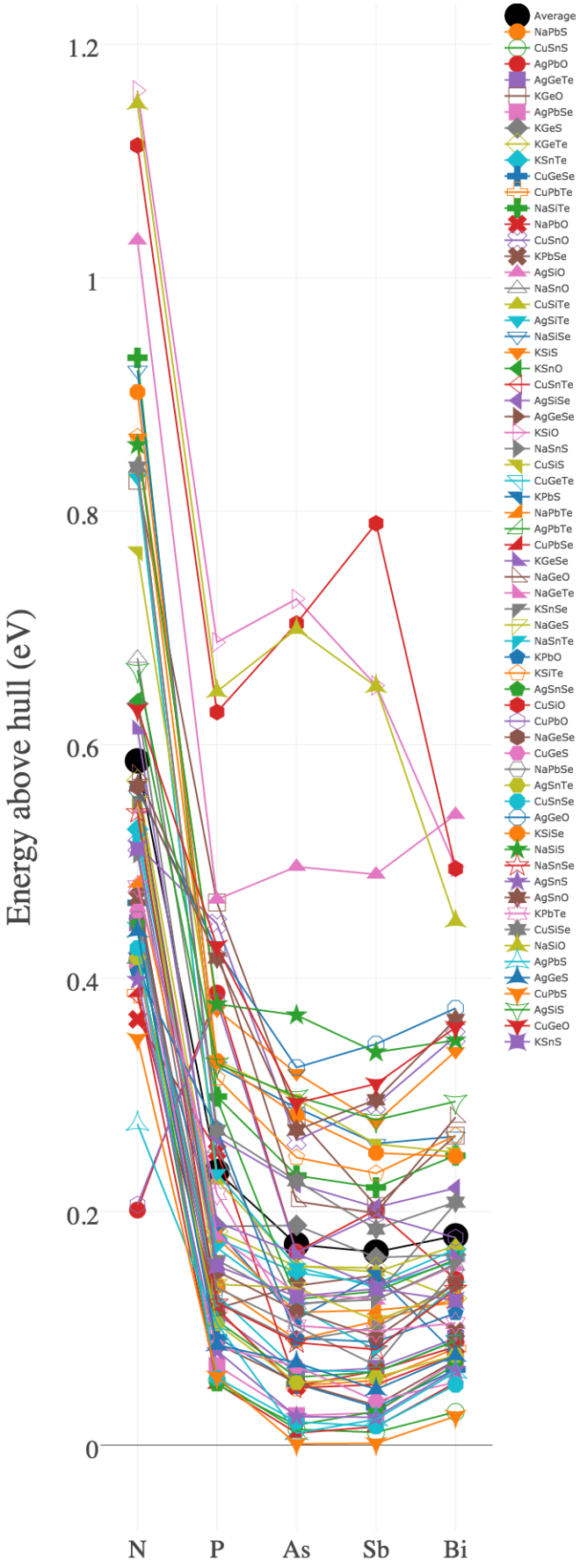
AgNSe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0.8
0.6
0.4
0.2
0
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P
As
Sb
Bi
Average
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CuSnS
AgPbO
AgGeTe
KGeO
AgPbSe
KGeS
KGeTe
KSnTe
CuGeSe
CuPbTe
NaSiTe
NaPbO
CuSnO
KPbSe
AgSiO
NaSnO
CuSiTe
AgSiTe
NaSiSe
KSiS
KSnO
CuSnTe
AgSiSe
AgGeSe
KSiO
NaSnS
CuSiS
CuGeTe
KPbS
NaPbTe
AgPbTe
CuPbSe
KGeSe
NaGeO
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KSnSe
NaGeS
NaSnTe
KPbO
KSiTe
AgSnSe
CuSiO
CuPbO
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CuGeS
NaPbSe
AgSnTe
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AgGeO
KSiSe
NaSiS
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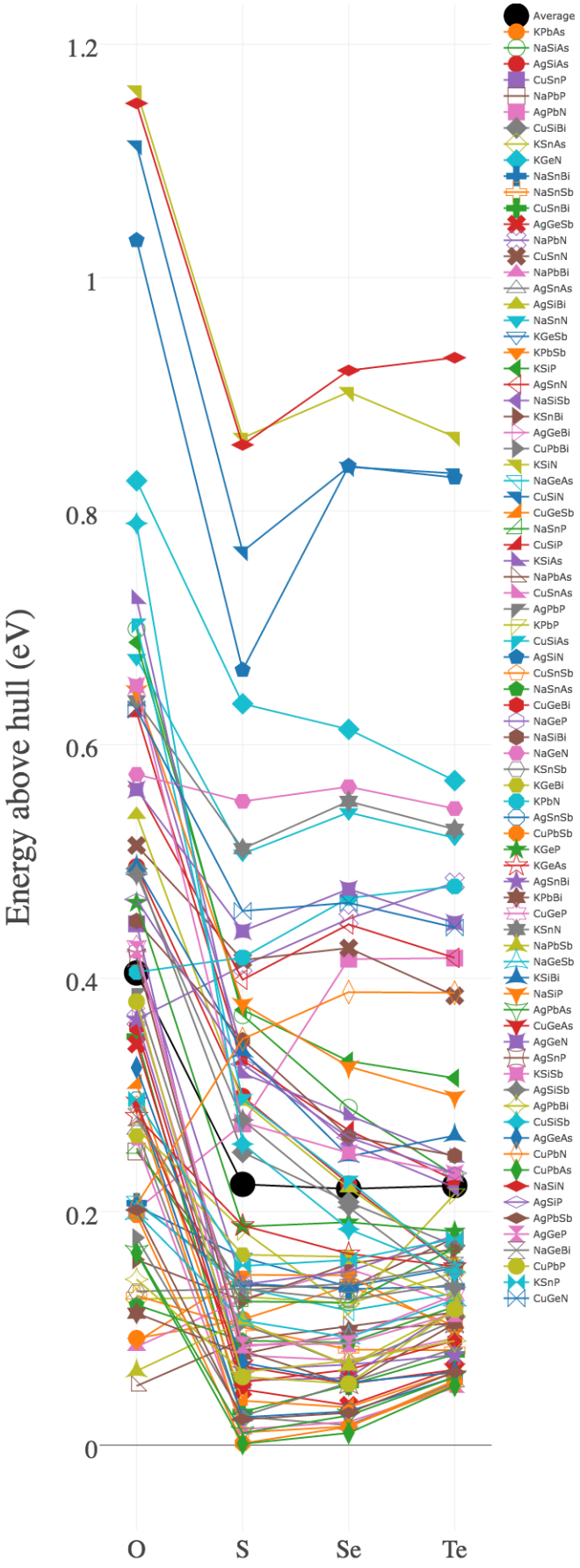
CuGeO
KSnS


Energy above hull (eV)
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0.8
0.6
0.4
0.2
0
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S
Se
Te
Average
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AgSiAs
CuSnP
NaPbP
AgPbN
CuSiBi
KSnAs
KGeN
NaSnBi
NaSnSb
CuSnBi
AgGeSb
NaPbN
CuSnN
NaPbBi
AgSnAs
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CuSiP
KSiAs
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KPbP
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AgSiN
CuSnSb
NaSnAs
CuGeBi
NaGeP
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NaGeN
KSnSb
KGeBi
KPbN
AgSnSb
CuPbSb
KGeP
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AgSnBi
KPbBi
CuGeP
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AgSiSb
AgPbBi
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CuPbP
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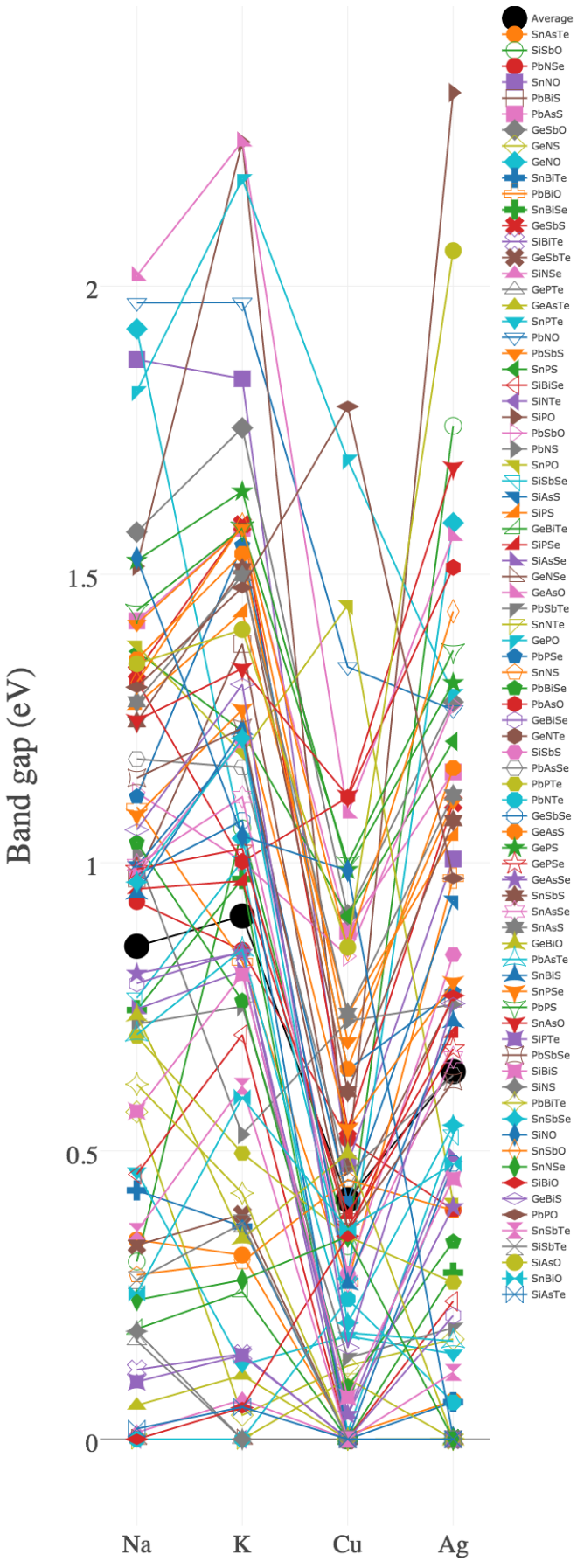
CuGeN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1
1.5
2
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K
Cu
Ag
Average
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SiSbO
PbNSe
SnNO
PbBiS
PbAsS
GeSbO
GeNS
GeNO
SnBiTe
PbBiO
SnBiSe
GeSbS
SiBiTe
GeSbTe
SiNSe
GePTe
GeAsTe
SnPTe
PbNO
PbSbS
SnPS
SiBiSe
SiNTe
SiPO
PbSbO
PbNS
SnPO
SiSbSe
SiAsS
SiPS
GeBiTe
SiPSe
SiAsSe
GeNSe
GeAsO
PbSbTe
SnNTe
GePO
PbPSe
SnNS
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PbAsO
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GeNTe
SiSbS
PbAsSe
PbPTe
PbNTe
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GePS
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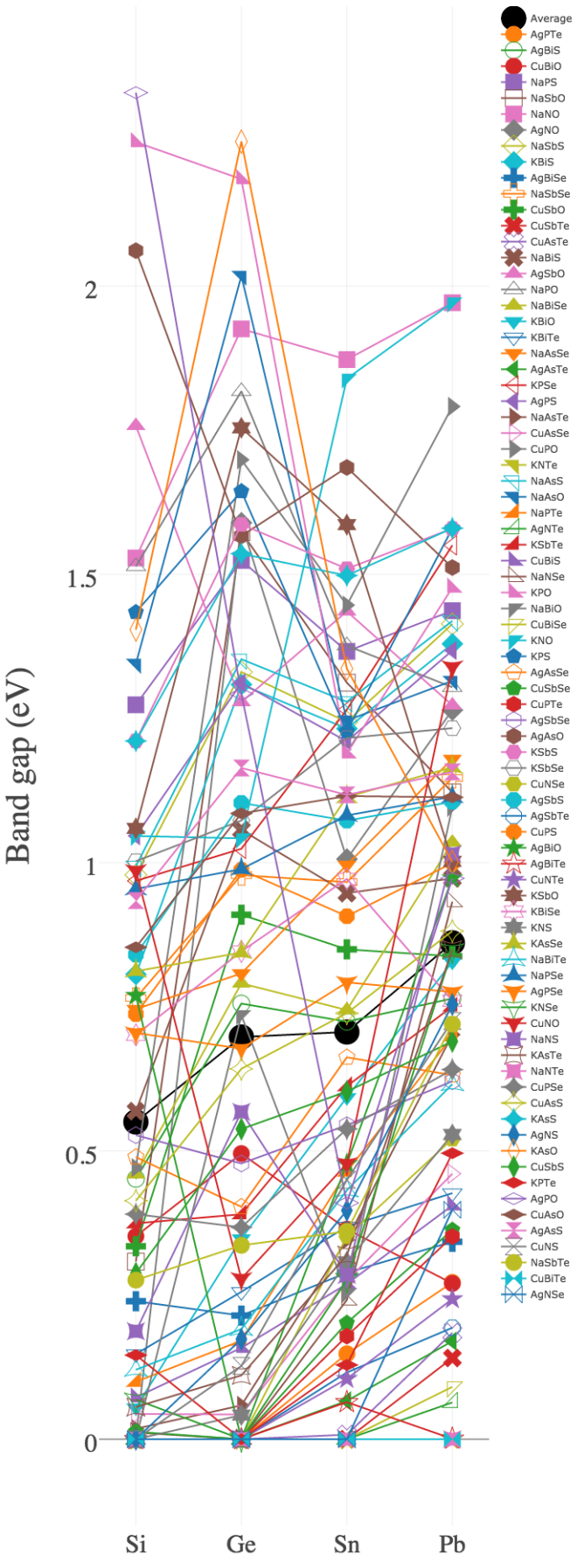
Band gap (eV)
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0.5
1
1.5
2
Si
Ge
Sn
Pb
Average
AgPTe
AgBiS
CuBiO
NaPS
NaSbO
NaNO
AgNO
NaSbS
KBiS
AgBiSe
NaSbSe
CuSbO
CuSbTe
CuAsTe
NaBiS
AgSbO
NaPO
NaBiSe
KBiO
KBiTe
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AgAsTe
KPSe
AgPS
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CuPO
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KNO
KPS
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CuPTe
AgSbSe
AgAsO
KSbS
KSbSe
CuNSe
AgSbS
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CuPS
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KNSe
CuNO
NaNS
KAsTe
NaNTe
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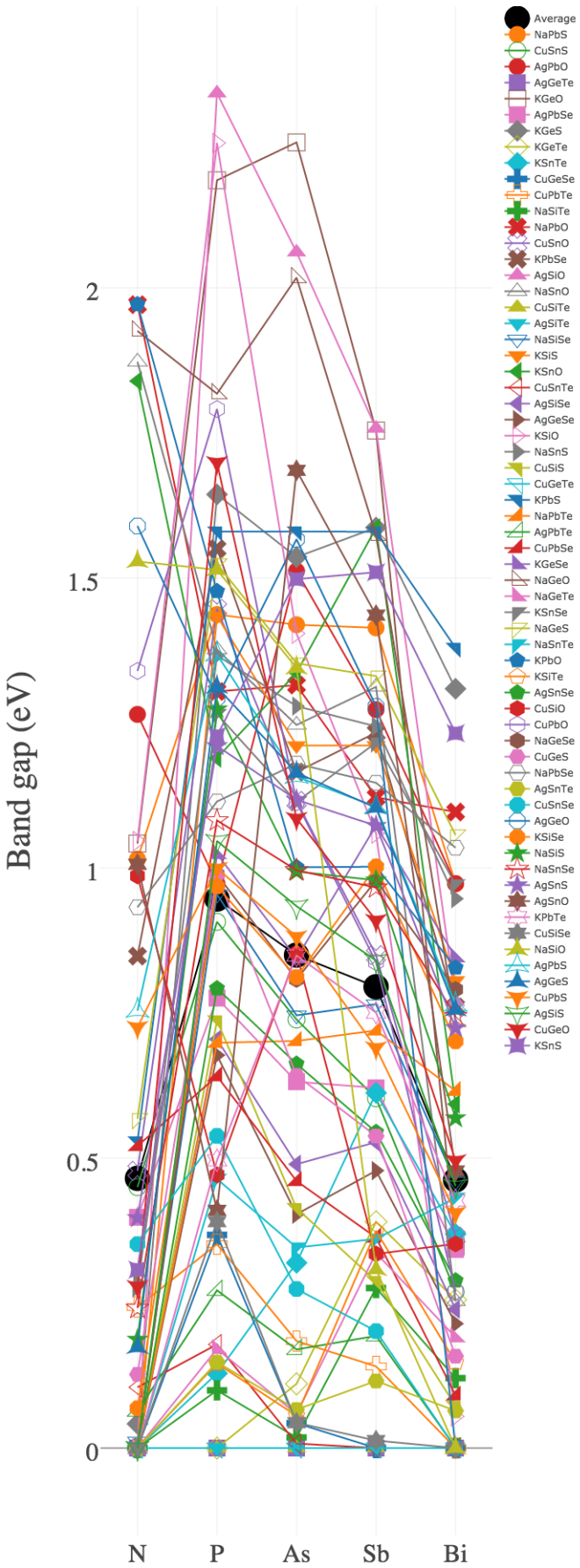
AgNSe


Band gap (eV)
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0.5
1
1.5
2
N
P
As
Sb
Bi
Average
NaPbS
CuSnS
AgPbO
AgGeTe
KGeO
AgPbSe
KGeS
KGeTe
KSnTe
CuGeSe
CuPbTe
NaSiTe
NaPbO
CuSnO
KPbSe
AgSiO
NaSnO
CuSiTe
AgSiTe
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KSiS
KSnO
CuSnTe
AgSiSe
AgGeSe
KSiO
NaSnS
CuSiS
CuGeTe
KPbS
NaPbTe
AgPbTe
CuPbSe
KGeSe
NaGeO
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NaGeS
NaSnTe
KPbO
KSiTe
AgSnSe
CuSiO
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CuGeS
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CuSnSe
AgGeO
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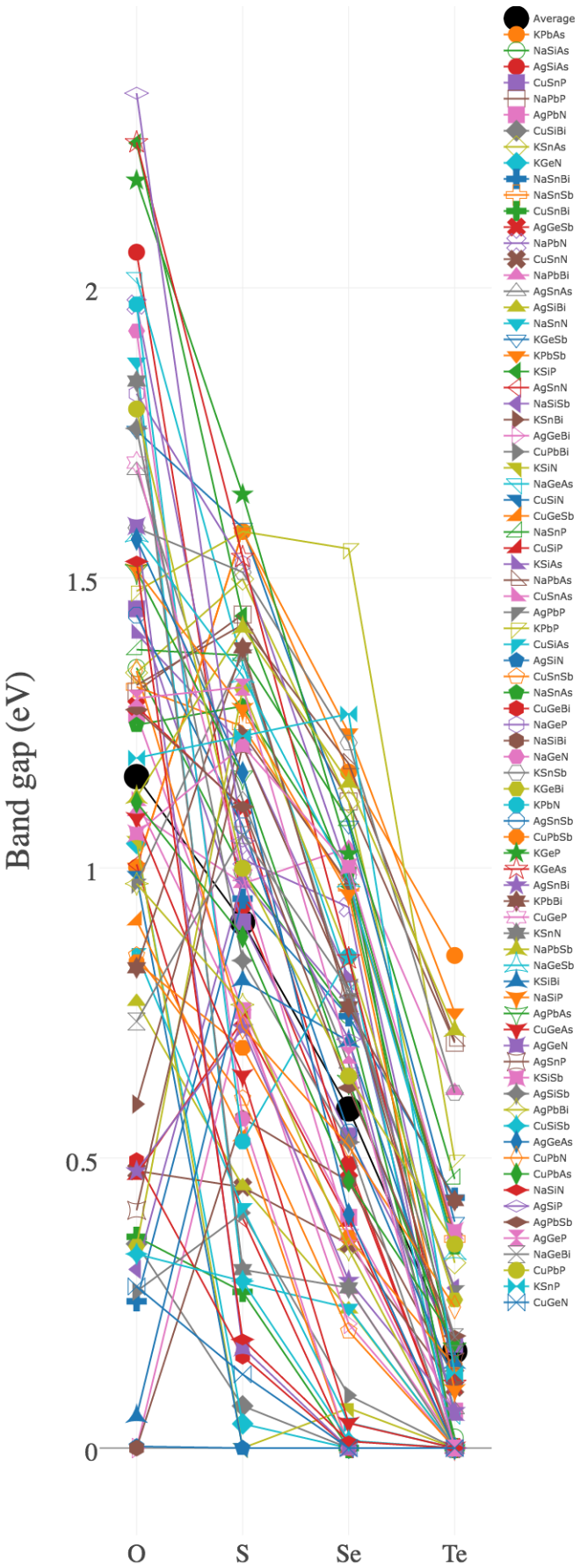
KSnS


Band gap (eV)
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0.5
1
1.5
2
O
S
Se
Te
Average
KPbAs
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AgSiAs
CuSnP
NaPbP
AgPbN
CuSiBi
KSnAs
KGeN
NaSnBi
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CuSnBi
AgGeSb
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AgSnAs
AgSiBi
NaSnN
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KPbSb
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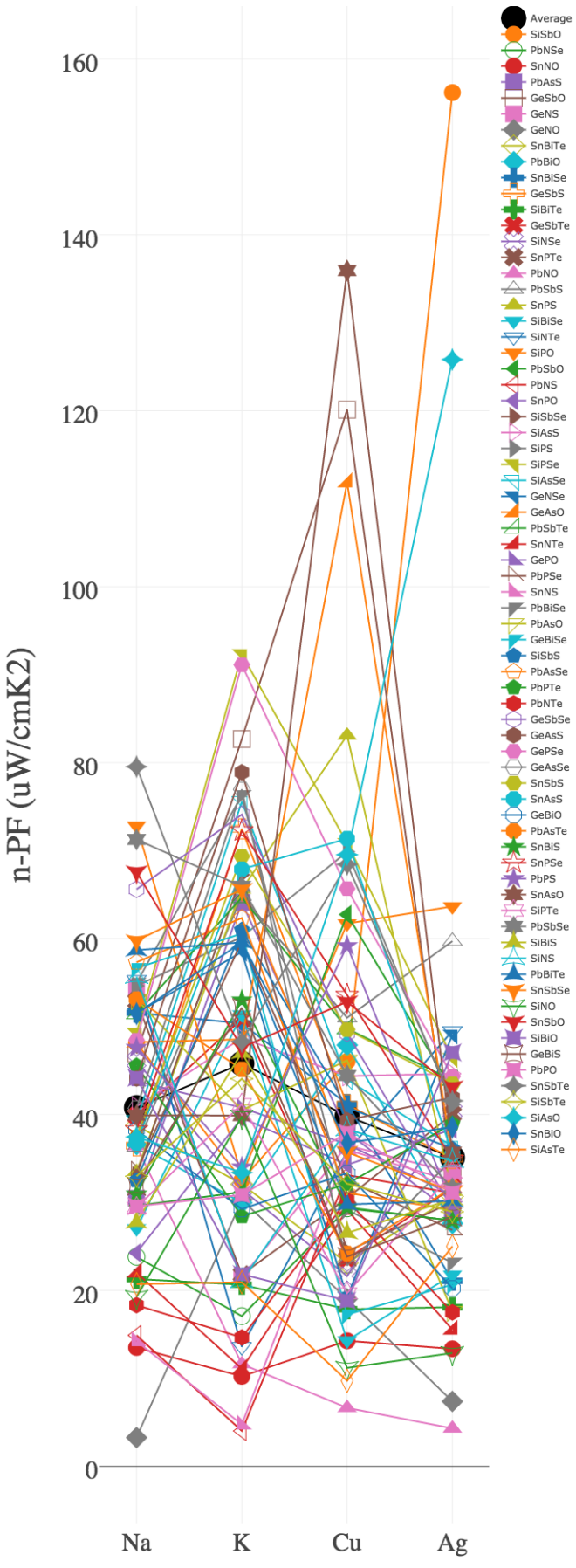
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80
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40
20
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K
Cu
Ag
Average
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PbNSe
SnNO
PbAsS
GeSbO
GeNS
GeNO
SnBiTe
PbBiO
SnBiSe
GeSbS
SiBiTe
GeSbTe
SiNSe
SnPTe
PbNO
PbSbS
SnPS
SiBiSe
SiNTe
SiPO
PbSbO
PbNS
SnPO
SiSbSe
SiAsS
SiPS
SiPSe
SiAsSe
GeNSe
GeAsO
PbSbTe
SnNTe
GePO
PbPSe
SnNS
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PbAsO
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SiSbS
PbAsSe
PbPTe
PbNTe
GeSbSe
GeAsS
GePSe
GeAsSe
SnSbS
SnAsS
GeBiO
PbAsTe
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PbSbSe
SiBiS
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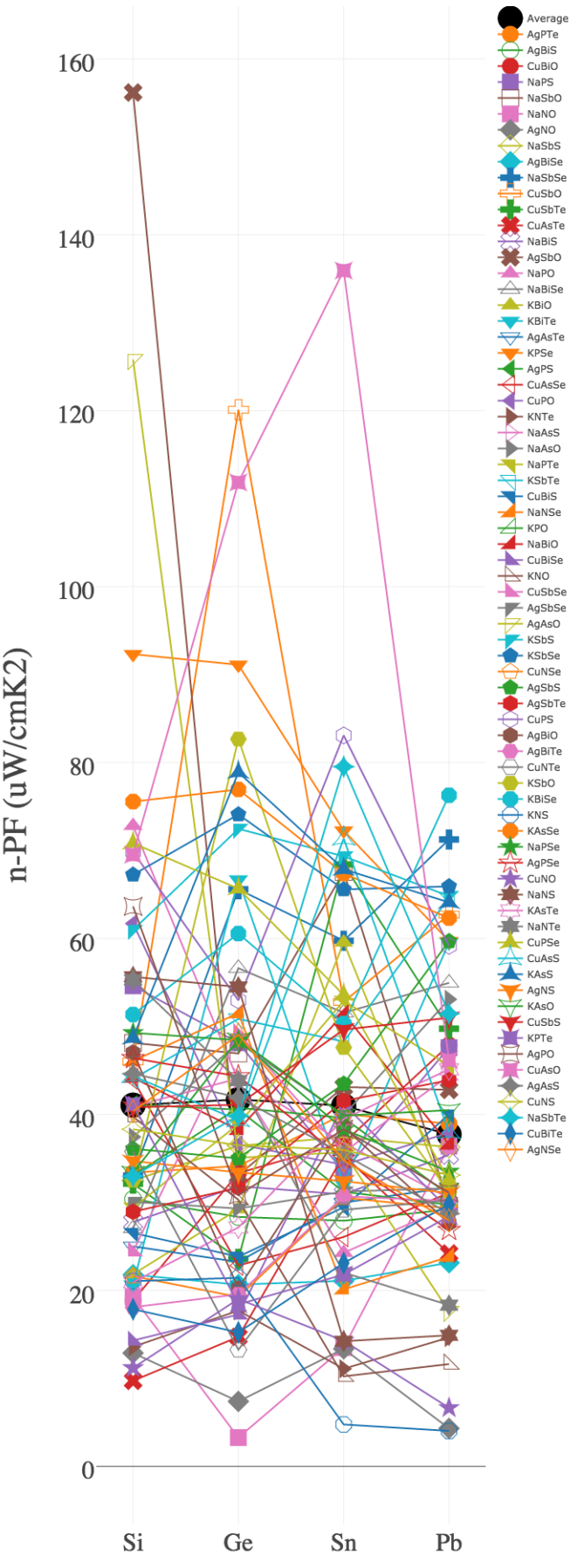
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100
80
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40
20
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Ge
Sn
Pb
Average
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CuBiO
NaPS
NaSbO
NaNO
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NaSbS
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CuSbO
CuSbTe
CuAsTe
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AgSbO
NaPO
NaBiSe
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KBiTe
AgAsTe
KPSe
AgPS
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KNTe
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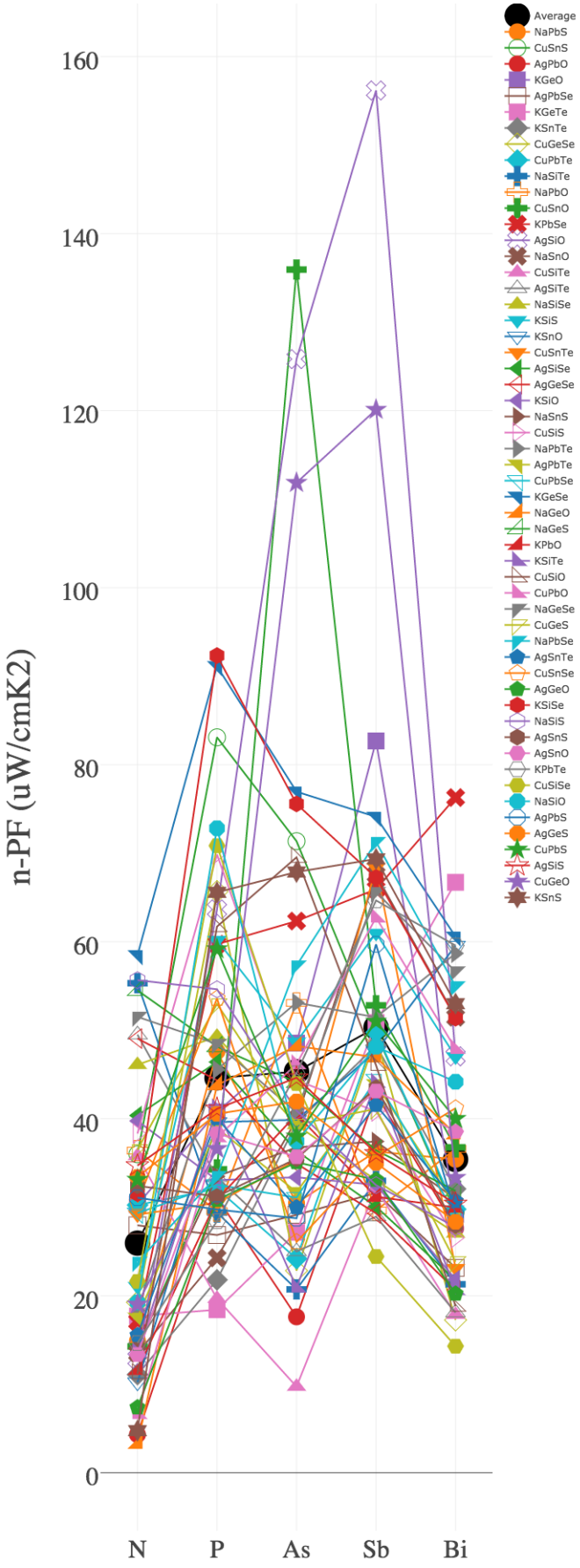
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20
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Sb
Bi
Average
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CuSnS
AgPbO
KGeO
AgPbSe
KGeTe
KSnTe
CuGeSe
CuPbTe
NaSiTe
NaPbO
CuSnO
KPbSe
AgSiO
NaSnO
CuSiTe
AgSiTe
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KSiS
KSnO
CuSnTe
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AgGeSe
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NaGeS
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CuPbO
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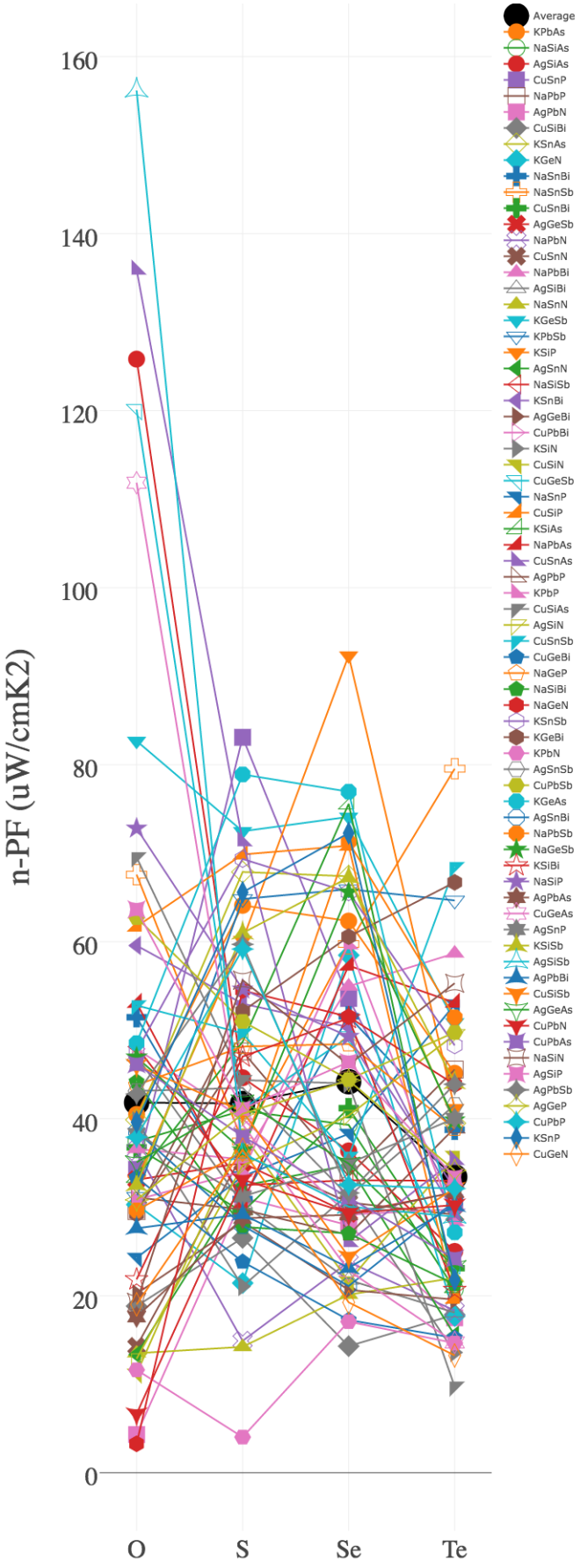
n-PF (uW/cmK2)
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120
100
80
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40
20
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S
Se
Te
Average
KPbAs
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AgSiAs
CuSnP
NaPbP
AgPbN
CuSiBi
KSnAs
KGeN
NaSnBi
NaSnSb
CuSnBi
AgGeSb
NaPbN
CuSnN
NaPbBi
AgSiBi
NaSnN
KGeSb
KPbSb
KSiP
AgSnN
NaSiSb
KSnBi
AgGeBi
CuPbBi
KSiN
CuSiN
CuGeSb
NaSnP
CuSiP
KSiAs
NaPbAs
CuSnAs
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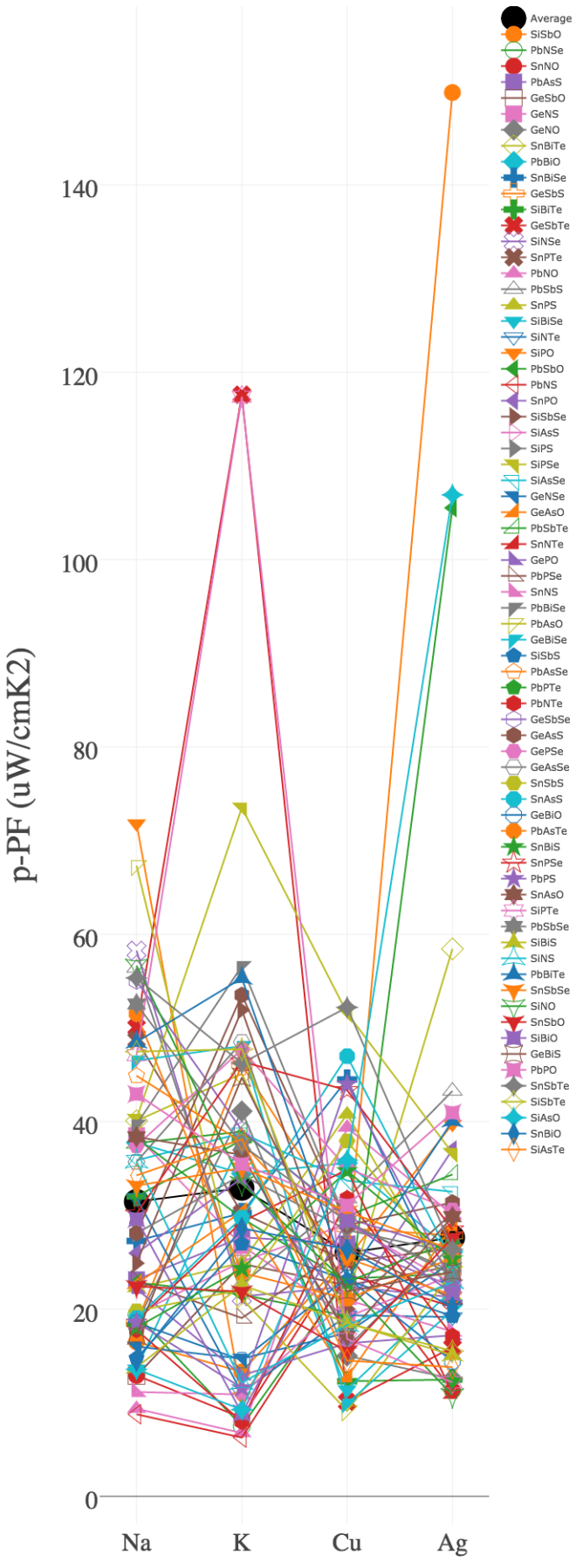
CuGeN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60
80
100
120
140
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K
Cu
Ag
Average
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PbAsS
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GeNO
SnBiTe
PbBiO
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GeSbS
SiBiTe
GeSbTe
SiNSe
SnPTe
PbNO
PbSbS
SnPS
SiBiSe
SiNTe
SiPO
PbSbO
PbNS
SnPO
SiSbSe
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SiPS
SiPSe
SiAsSe
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GeAsO
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SnNTe
GePO
PbPSe
SnNS
PbBiSe
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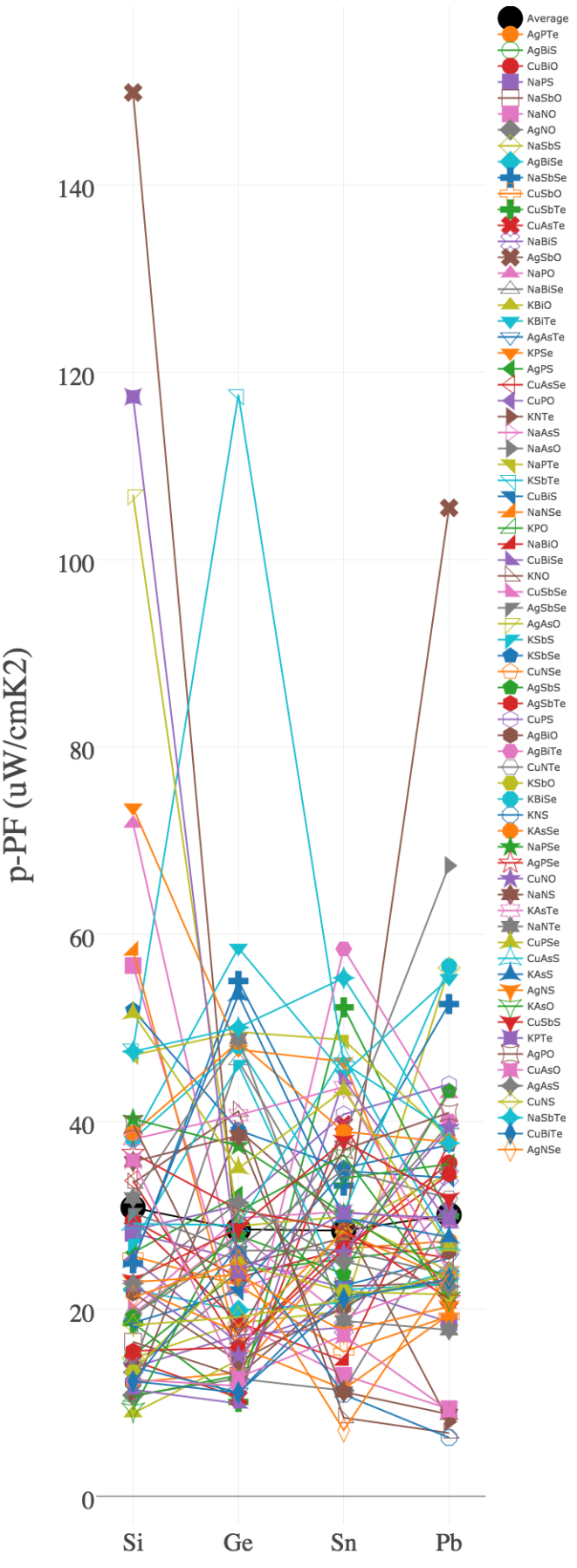
p-PF (uW/cmK2)
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40
60
80
100
120
140
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Ge
Sn
Pb
Average
AgPTe
AgBiS
CuBiO
NaPS
NaSbO
NaNO
AgNO
NaSbS
AgBiSe
NaSbSe
CuSbO
CuSbTe
CuAsTe
NaBiS
AgSbO
NaPO
NaBiSe
KBiO
KBiTe
AgAsTe
KPSe
AgPS
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CuPO
KNTe
NaAsS
NaAsO
NaPTe
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KPO
NaBiO
CuBiSe
KNO
CuSbSe
AgSbSe
AgAsO
KSbS
KSbSe
CuNSe
AgSbS
AgSbTe
CuPS
AgBiO
AgBiTe
CuNTe
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KNS
KAsSe
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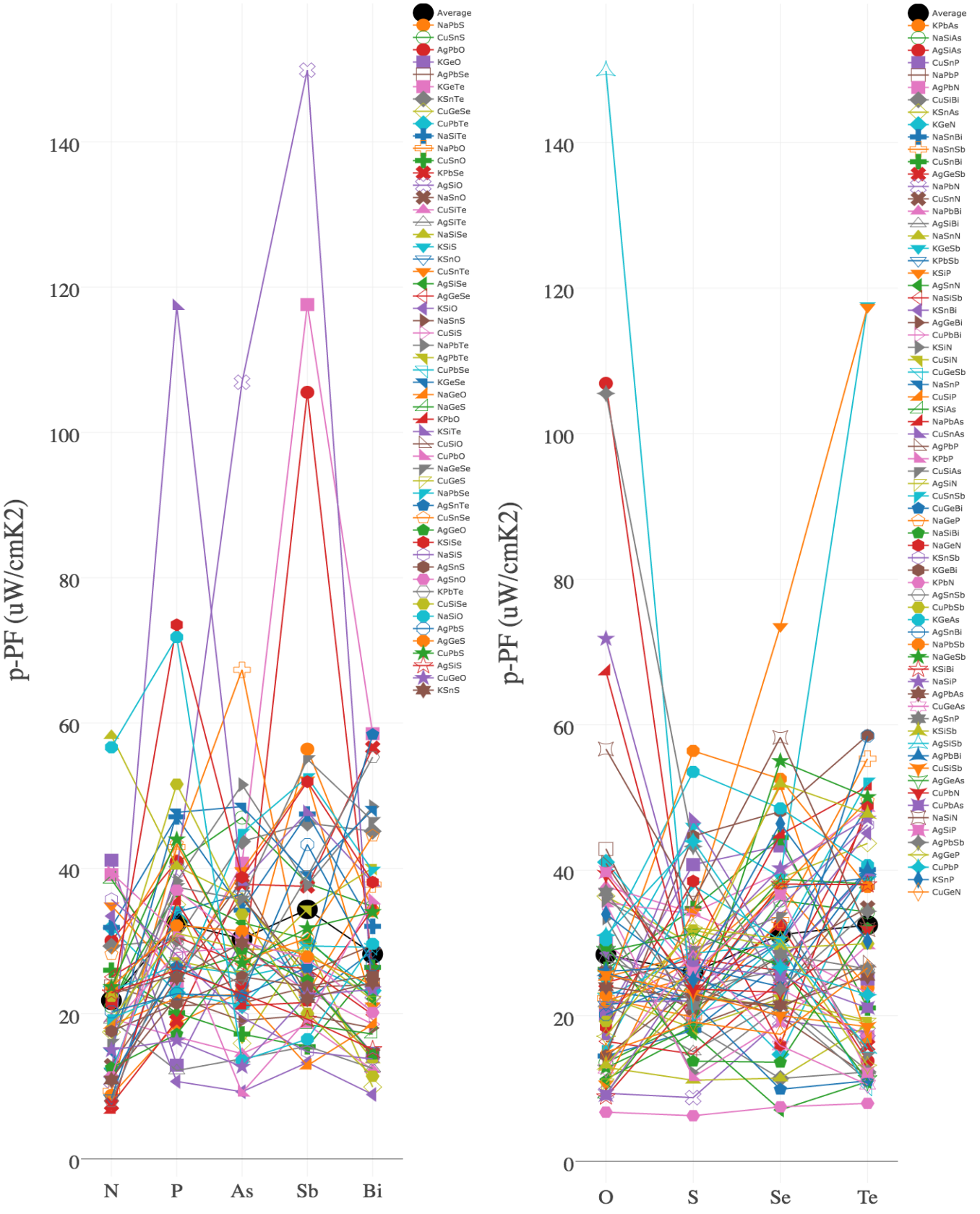
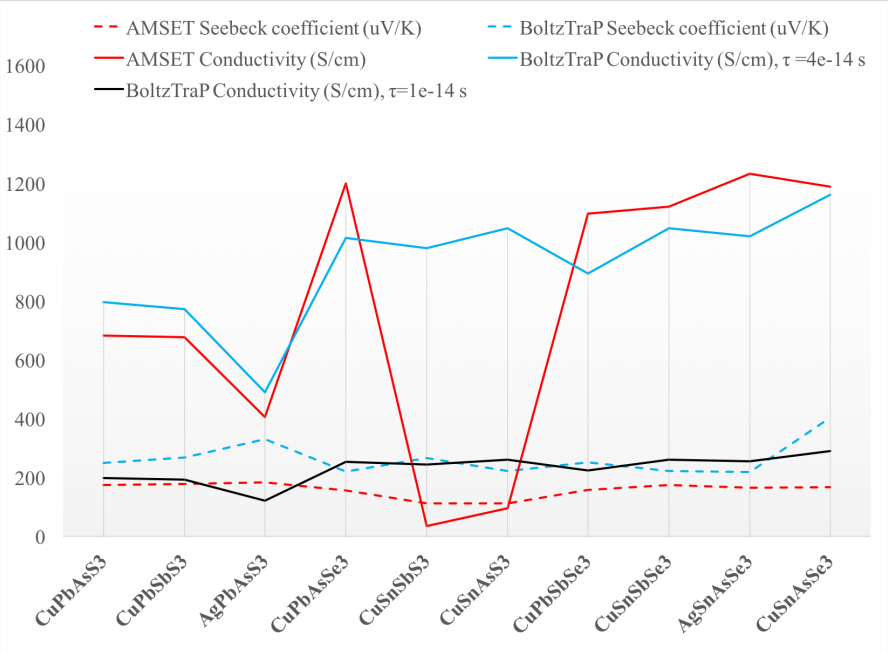


Figure S14. Detail plot of all properties across different groups of elements. Units of formation energy and E above hull are eV/atom

5 Comparison of predicted transport properties via AMSET and BoltzTraP



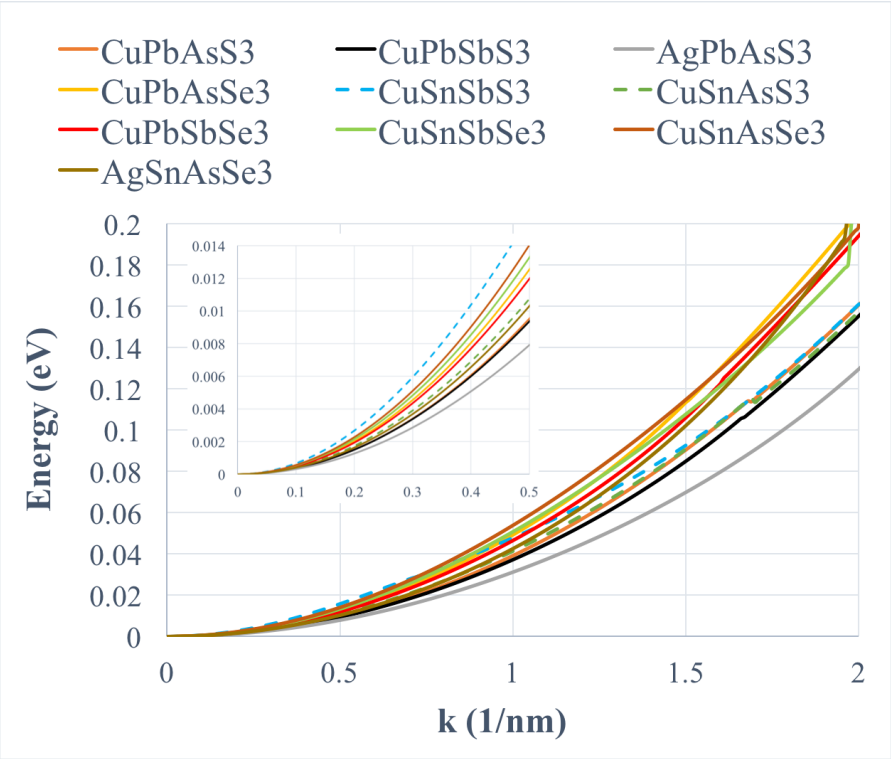


Figure S15. Comparing AMSET and BoltzTraP calculated conductivity and Seebeck coefficient that were used to calculate the power factors reported in Table 1. On top, the original calculated data (from Table 1) is presented plus the BoltzTraP conductivity if $\tau = 4.0\times10^{-14}$ s instead of 10^{-14} s which was originally assumed. Bottom plot: the fitted top valence bands in AMSET with R^2 higher than 0.99 in all the cases; the order of the calculated conductivity values have the same order as the slope of the valence bands (proportional to the group velocity) except $CuSnSbS_3$ and $CuSnAsS_3$ with very low AMSET conductivities. The reason for that is the inter-band scattering that is present in the two degenerate valence bands in these two compounds as discussed in the manuscript. The inset is a plot of the valence bands zoomed in for better illustration.

6 Heatmaps: how properties change within two groups

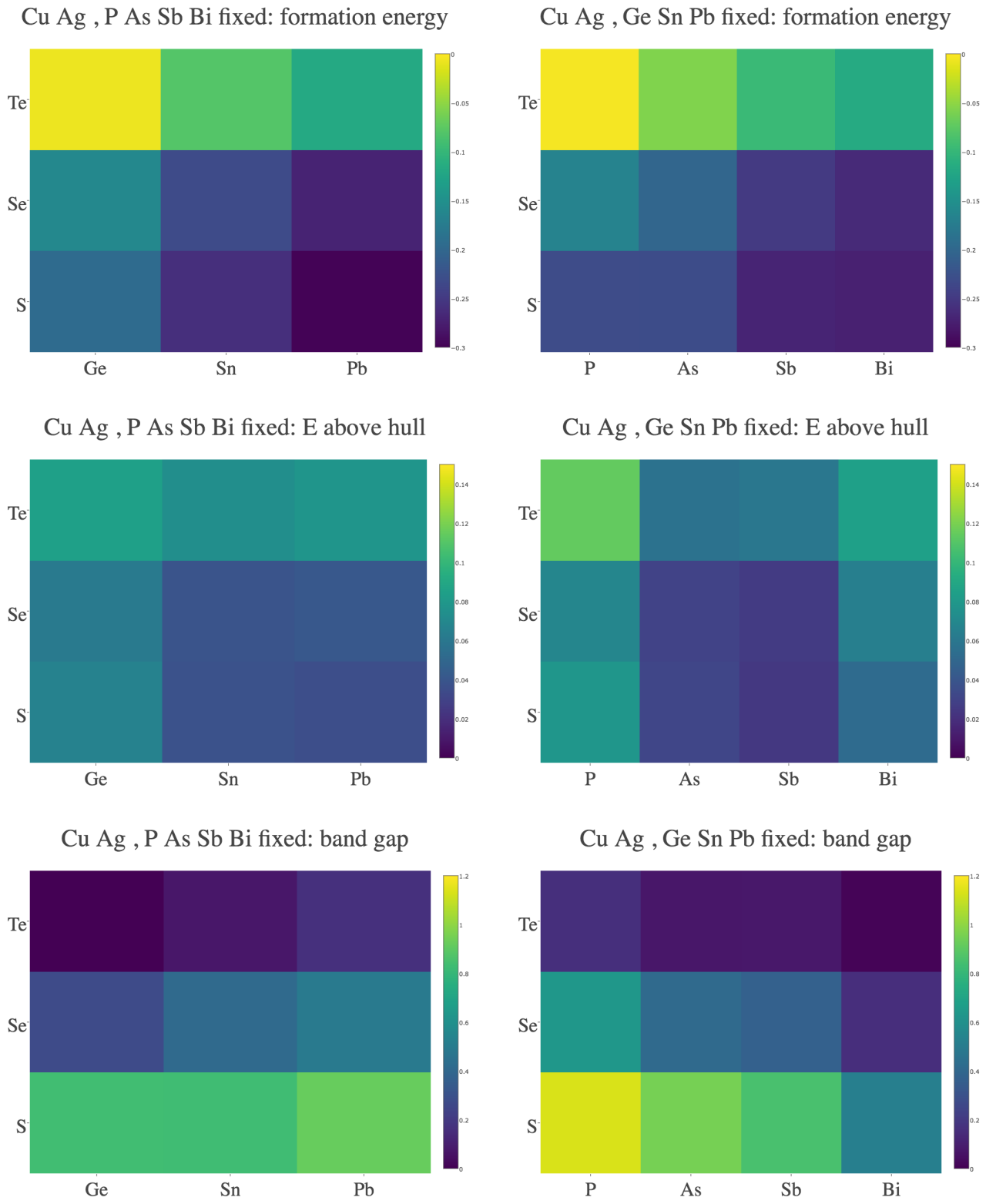


Figure S16. How average properties change with (left) *B* and *D* and (right) *C* and *D* excluding Na, K, Si, N and O.