Supplementary material for

Integrated computationally materials discovery of Silver doped Tin Sulfide as a thermoelectric material.

Chandan Bera[1)],Stephane Jacob[2)],Ingo Opahle[1)],N. S. Harsha Gunda[1)],Radoslaw Chmielowski[2)],Gilles Dennler[2)],Georg K. H. Madsen[1)]

[1)] *Department of Atomistic Modelling and Simulation, ICAMS, Ruhr-Universität Bochum, Germany*

[2)] *IMRA Europe S.A.S., 06904 Sophia Antipolis, France*

I. HIGH-THROUGHPUT CALCULATION OF TRANSPORT PROPERTIES

The electronic structure of more than 450 binary sulfides was calculated using the VASP code [1–3] within the projector augmented wave method with a cut-off energy of 350 eV. [4] The general gradient approximation (GGA) in the parametrization of Perdew, Burke and Ernzerhof [5] was used and relativistic effects were treated in a scalar relativistic approach. Fig. 1 show the band structure calculated with PBE.

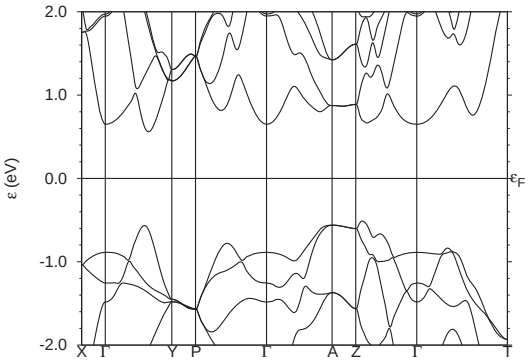

FIG. 1. Band structure of SnS calculated with the PBE-GGA

Transport calculations were carried out with the program BoltzTraP.[6] Table I shows the available transport properties along with data of alloys relevant for the calculation of the convex hulls (within $\Delta E_h < 50$ meV/atom). Data are only presented when a band gap was found in the calculation. The use of GGA will generally lead to an underestimation of the band gap. This in turn will lead to an underestimation of the high-temperature thermoelectric properties and the reported data can be viewed as a lower limit.

TABLE I: Calculated band gap E_g (in eV), distance from convex hull ΔE_h (in meV/atom), power factor with respect to relaxation time PF/τ (in $10^{14}\mu$W/cm K^2 s) and conductivity σ/τ (in 10^{16} (1/Ω m s)) at a doping level of 2×10^{19}/cm^3 for n- and p-doped material at 300 and 600 K. (†: data obtained for experimental lattice structure, otherwise for optimized structure)

alloy(structure type)	E_g	ΔE_h	PF/τ(300K)		PF/τ(600K)		σ/τ(300K)		σ/τ(600K)	
			p	n	p	n	p	n	p	n
$Ag_{0.67}S_{0.33}$(Ag2S,mP12,14)	0.6†	0	9.1†	3.2†	12.5†	6.7†	59†	113†	54†	111†
$Al_{0.40}S_{0.60}$(Al2S3,hP30,169)	2.9†	3	4.9†	10.0†	3.9†	15.3†	30†	98†	20†	88†
$Al_{0.40}S_{0.60}$(In2S3,tI80,141)	1.6†	0	7.6†	4.0†	9.7†	10.4†	51†	138†	45†	134†
$As_{0.40}S_{0.60}$(As2S3,mP20,14)	1.9†	0	5.1†	5.6†	7.1†	6.4†	48†	38†	40†	30†
$As_{0.40}S_{0.60}$(Sb2S3,oP20,62)	0.1†	33	0.7†	2.4†	0.7†	0.0†	210†	288†	862†	918†
$As_{0.44}S_{0.56}$(As4S5,mP18,11)	1.8†	2	5.0†	5.1†	4.7†	9.8†	35†	79†	22†	70†
$As_{0.50}S_{0.50}$(AsS,mS32,15)	1.7†	0	3.4†	8.1†	6.0†	7.9†	48†	46†	37†	33†
$As_{0.50}S_{0.50}$(AsS-c,mP32,14)	1.8†	20	3.4†	4.6†	3.8†	5.4†	37†	51†	22†	31†
$As_{0.57}S_{0.43}$(As4S3-a,oP28,62)	2.0†	0	4.2†	3.1†	6.1†	4.2†	39†	39†	33†	27†
$B_{0.33}S_{0.67}$(BS2,mP24,14)	2.4†	0	3.5†	4.9†	4.5†	6.3†	19†	43†	18†	29†
$B_{0.33}S_{0.67}$(BS2,mP48,14)	2.4†	7	0.6†	1.8†	0.5†	1.5†	3†	14†	2†	8†
$B_{0.40}S_{0.60}$(B2S3,mP40,14)	2.1†	0	2.0†	3.7†	2.1†	5.0†	14†	47†	10†	40†
$Bi_{0.40}S_{0.60}$(Sb2S3,oP20,62)	1.4	–	5.2	5.3	6.4	11.0	38	139	29	115
$C_{0.27}S_{0.73}$(C3S8,aP22,2)	1.6†	240	3.4†	2.5†	3.6†	2.6†	27†	23†	18†	18†
$C_{0.33}S_{0.67}$([CS2],oS12,64)	3.0†	290	6.5†	4.8†	6.4†	7.3†	23†	39†	18†	28†
$C_{0.43}S_{0.57}$(C3S4,mP56,14)	1.5†	307	2.1†	3.0†	1.5†	3.3†	12†	15†	7†	12†
$Cd_{0.50}S_{0.50}$(NaCl,cF8,225)	0.4	0	–	–	–	–	–	–	–	–
$Cd_{0.50}S_{0.50}$(NiAs,hP4,194)	0.6	42	–	–	–	–	–	–	–	–
$Cl_{0.50}S_{0.50}$(SCl,oF64,43)	2.7†	–	1.6†	2.9†	1.6†	2.6†	7†	16†	6†	11†
$Cl_{0.67}S_{0.33}$(–)	2.1†	29	0.6†	3.5†	0.4†	3.0†	2†	17†	1†	12†
$Cl_{0.67}S_{0.33}$(SCl2,oP24,19)	2.0†	36	0.4†	3.7†	0.4†	4.5†	1†	25†	1†	20†
$Cl_{0.80}S_{0.20}$(SeCl4,cP160,218)	2.3†	0	2.8†	2.8†	2.5†	3.5†	16†	44†	11†	26†

$Cu_{0.33}S_{0.67}$(CaCl2,oP6,58)	0.0	34	–	–	–	–	–	–	–	–
$Cu_{0.33}S_{0.67}$(FeS2,cP12,205)	0.0	35	–	–	–	–	–	–	–	–
$Cu_{0.33}S_{0.67}$(FeS2,oP12,29)	0.0	36	–	–	–	–	–	–	–	–
$Cu_{0.33}S_{0.67}$(FeS2,oP6,58)	0.0†	30	–	–	–	–	–	–	–	–
$Cu_{0.33}S_{0.67}$(FeSb2,oP6,34)	0.0	31	–	–	–	–	–	–	–	–
$Cu_{0.33}S_{0.67}$(HgO2,oP12,61)	0.0	36	–	–	–	–	–	–	–	–
$Cu_{0.33}S_{0.67}$(Ni(As0.4S0.6)2,aP12,1)	0.0	36	–	–	–	–	–	–	–	–
$Cu_{0.33}S_{0.67}$(PdSe2,oP12,61)	0.0	36	–	–	–	–	–	–	–	–
$Cu_{0.33}S_{0.67}$(VO2,mP12,14)	0.0	30	–	–	–	–	–	–	–	–
$Cu_{0.33}S_{0.67}$(VO2,mP6,10)	0.0	31	–	–	–	–	–	–	–	–
$Cu_{0.33}S_{0.67}$(ZrO2,oP12,29)	0.0	36	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(CuS,hP12,194)	0.0	0	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(CuS,oS24,63)	0.0†	0	–	–	–	6.9†	–	–	–	23226†
$Cu_{0.50}S_{0.50}$(FeS,oF8,22)	0.0	20	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(SiC,hP12,186)	0.0	26	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(SiC,hP16,186)	0.0	24	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(SiC,hP20,156)	0.0	27	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(SiC,hP8,186)	0.0	29	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnO,hP4,186)	0.0	35	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS,cF8,216)	0.0	18	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS,hP20,156)	0.0	23	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS,hP20,186)	0.0	23	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS,hP24,186)	0.0	22	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS,hP28,186)	0.0	22	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS,hP32,186)	0.0	21	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS,hP40,186)	0.0	20	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS-a,hP16,156)	0.0	23	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS-a,hP32,156)	0.0	21	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS-a,hP44,156)	0.0	20	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS-b,hP24,156)	0.0	22	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS-d,hP36,156)	0.0	21	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS-f,hP28,156)	0.0	27	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS-i,hP40,156)	0.0	23	–	–	–	–	–	–	–	–
$Cu_{0.50}S_{0.50}$(ZnS-l,hP48,156)	0.0	22	–	–	–	–	–	–	–	–
$Cu_{0.60}S_{0.40}$(Cu3Se2,tP10,113)	0.0	5	–	–	–	–	–	–	–	–
$Cu_{0.60}S_{0.40}$(Ni3Te2,mP10,11)	0.0	37	–	–	–	–	–	–	–	–
$Cu_{0.60}S_{0.40}$(Ta3S2,oS40,39)	0.0	0	–	–	–	–	–	–	–	–
$Cu_{0.64}S_{0.36}$(−)	0.0†	46	–	0.0†	–	0.0†	–	373†	–	418†
$Cu_{0.64}S_{0.36}$(Cu7S4,oP44,62)	0.0	6	–	–	–	–	–	–	–	–
$Cu_{0.66}S_{0.34}$(−)	0.0	–	–	–	–	–	–	–	–	–
$Cu_{0.66}S_{0.34}$(Cu31S16,mP376,14)	0.0	12	–	–	–	–	–	–	–	–
$Cu_{0.67}S_{0.33}$(Ag2S,mP12,14)	0.0	30	0.0	2.5	0.4	2.9	169	274	480	558
$Cu_{0.67}S_{0.33}$(CaF2,cF12,225)	0.0†	100	3.3†	0.8†	2.5†	0.0†	209†	212†	513†	509†
$Cu_{0.67}S_{0.33}$(Cu2S,mP144,14)	0.2†	20	4.5†	1.2†	2.0†	4.8†	56†	246†	44†	223†
$F_{0.86}S_{0.14}$(SF6,aP21,2)	6.7†	–	0.7†	3.0†	0.4†	5.0†	2†	45†	1†	41†
$F_{0.86}S_{0.14}$(SF6,cI14,229)	8.5†	–	0.7†	3.1†	0.4†	6.2†	2†	79†	1†	78†
$F_{0.86}S_{0.14}$(SF6,mS42,12)	6.7†	–	0.7†	3.0†	0.4†	5.0†	2†	46†	1†	41†
$F_{0.86}S_{0.14}$(UCl6,hP21,164)	0.5†	–	0.9†	2.5†	0.3†	2.9†	3†	33†	7†	25†
$Fe_{0.33}S_{0.67}$(FeS2,cP12,205)	0.4	8	2.8	2.5	0.8	5.6	7	128	10	122
$Fe_{0.33}S_{0.67}$(FeS2,oP12,29)	0.4	8	2.8	2.4	0.7	5.6	7	129	11	123
$Fe_{0.33}S_{0.67}$(FeS2,oP6,58)	0.8	0	8.3	5.6	9.3	10.2	41	33	29	35
$Fe_{0.33}S_{0.67}$(FeSb2,oP6,34)	0.8	0	8.3	5.6	9.3	10.2	40	33	29	35
$Fe_{0.33}S_{0.67}$(Ni(As0.4S0.6)2,aP12,1)	0.4	8	2.4	2.4	0.6	5.6	6	128	10	121
$Fe_{0.50}S_{0.50}$(PbO,tP4,129)	0.0	0	–	–	–	–	–	–	–	–
$Ga_{0.40}S_{0.60}$(Al2S3,hP30,169)	1.5†	0	4.9†	2.1†	4.0†	5.5†	34†	180†	22†	165†
$Ga_{0.50}S_{0.50}$(GaS-a,hP8,194)	1.6†	0	6.7†	9.9†	11.0†	16.2†	110†	108†	94†	109†
$Hf_{0.25}S_{0.75}$(ZrSe3,mP8,11)	1.1†	0	6.8†	5.4†	9.7†	10.7†	71†	86†	54†	85†
$Hf_{0.33}S_{0.67}$(CdI2,hP3,164)	0.8†	0	8.1†	9.9†	13.5†	16.0†	89†	100†	83†	92†
$Hf_{0.50}S_{0.50}$(NiAs,hP4,194)	0.0	0	–	–	–	–	–	–	–	–
$Hg_{0.50}S_{0.50}$(NaCl,cF8,225)	0.0	46	–	–	–	–	–	–	–	–
$Li_{0.67}S_{0.33}$(CaF2,cF12,225)	3.4†	0	8.1†	6.9†	11.1†	13.0†	50†	137†	47†	134†
$Li_{0.67}S_{0.33}$(Li2S,oP12,33)	2.9†	–	6.8†	5.6†	10.6†	10.5†	69†	123†	66†	117†
$Li_{0.67}S_{0.33}$(PbCl2,oP12,62)	3.9†	56	4.7†	6.1†	8.2†	11.9†	76†	65†	69†	64†
$Mo_{0.50}S_{0.50}$(CsCl,cP2,221)	0.0	0	–	–	–	–	–	–	–	–

$Mo_{0.50}S_{0.50}$(CuAu,tP2,123)	0.0	0	–	–	–	–	–	–	–	–
$Mo_{0.50}S_{0.50}$(NiAs,hP4,194)	0.0	29	–	–	–	–	–	–	–	–
$N_{0.33}S_{0.67}$(S2N,tP24,102)	1.4†	492	1.4†	3.0†	1.3†	4.2†	5†	30†	4†	25†
$N_{0.50}S_{0.50}$(SN,mP32,14)	2.2†	621	0.3†	3.5†	0.2†	4.0†	1†	31†	1†	21†
$N_{0.50}S_{0.50}$(SN,oP32,60)	2.1†	604	1.5†	3.6†	1.0†	3.8†	8†	24†	4†	17†
$N_{0.50}S_{0.50}$(SN-c,mP8,14)	3.0†	726	3.9†	4.6†	3.7†	5.2†	15†	21†	11†	18†
$N_{0.55}S_{0.45}$(S5N6,mS44,15)	2.2†	715	2.0†	1.7†	1.9†	1.3†	10†	7†	7†	4†
$Na_{0.29}S_{0.71}$(Na2S5,oP28,62)	1.8†	4	4.5†	5.2†	5.1†	5.9†	29†	30†	23†	25†
$Na_{0.33}S_{0.67}$(NaS2,tI48,122)	2.0†	0	2.1†	3.9†	1.9†	3.5†	9†	22†	6†	16†
$Na_{0.50}S_{0.50}$(Li2[O2]-b,hP8,194)	1.3†	0	4.9†	2.7†	7.1†	5.7†	25†	102†	26†	92†
$Na_{0.50}S_{0.50}$(Na2[O2],hP12,189)	0.9†	3	5.1†	7.9†	7.4†	16.0†	40†	139†	37†	126†
$Na_{0.67}S_{0.33}$(CaF2,cF12,225)	2.5†	0	5.8†	2.1†	7.2†	5.7†	21†	183†	19†	174†
$Na_{0.67}S_{0.33}$(Co1.75Ge,hP6,194)	2.6†	104	3.9†	2.0†	7.0†	5.6†	86†	193†	76†	187†
$Na_{0.67}S_{0.33}$(Cs2S,oP12,62)	2.7†	40	5.4†	2.1†	8.2†	5.6†	50†	194†	37†	188†
$Nb_{0.50}S_{0.50}$(NiAs,hP4,194)	0.0	0	–	–	–	–	–	–	–	–
$P_{0.29}S_{0.71}$(P2S5,aP28,2)	2.5†	0	2.6†	3.7†	2.2†	2.8†	14†	21†	9†	12†
$P_{0.31}S_{0.69}$(P4S9,cI208,206)	2.3†	2	2.1†	1.0†	1.6†	0.8†	26†	5†	12†	3†
$P_{0.31}S_{0.69}$(P4S9,mP52,14)	2.6†	0	1.1†	3.2†	0.9†	2.7†	5†	20†	3†	13†
$P_{0.36}S_{0.64}$(P4S7,mP44,14)	2.5†	0	1.5†	2.8†	1.1†	2.8†	7†	21†	4†	14†
$P_{0.40}S_{0.60}$(P2S3,mP40,14)	2.1†	10	3.5†	3.6†	4.7†	3.2†	29†	19†	26†	13†
$P_{0.44}S_{0.56}$(P4S5,mP18,11)	2.3†	18	4.8†	7.2†	4.8†	8.7†	21†	51†	16†	40†
$P_{0.44}S_{0.56}$(P4S5,mP18,4)	2.3†	4	2.7†	4.3†	2.3†	6.2†	12†	42†	8†	34†
$P_{0.50}S_{0.50}$(AsS,mS32,15)	2.0†	21	3.8†	5.2†	6.0†	4.9†	40†	26†	33†	19†
$P_{0.57}S_{0.43}$(As4S3-b,oP28,62)	2.5†	1	3.3†	4.2†	2.9†	4.8†	13†	35†	9†	26†
$P_{0.57}S_{0.43}$(P4S3,oP56,62)	2.6†	0	1.4†	2.9†	1.1†	2.6†	7†	23†	4†	13†
$Pd_{0.50}S_{0.50}$(NaCl,cF8,225)	0.0	23	–	–	–	–	–	–	–	–
$Pd_{0.50}S_{0.50}$(NiAs,hP4,194)	0.0	0	–	–	–	–	–	–	–	–
$Pt_{0.50}S_{0.50}$(NaCl,cF8,225)	0.0	46	–	–	–	–	–	–	–	–
$Rh_{0.50}S_{0.50}$(NiAs,hP4,194)	0.0	0	–	–	–	–	–	–	–	–
$Ru_{0.50}S_{0.50}$(NiAs,hP4,194)	0.0	0	–	–	–	–	–	–	–	–
$Sb_{0.40}S_{0.60}$(Sb2S3,oP20,62)	1.3†	–	5.1†	9.9†	6.5†	14.4†	43†	120†	32†	111†
$Sn_{0.33}S_{0.67}$(CdI2,hP3,164)	1.4†	0	9.7†	11.2†	13.2†	17.3†	52†	128†	45†	117†
$Sn_{0.33}S_{0.67}$(CdI2,hP6,186)	1.3†	0	8.6†	7.3†	10.5†	13.1†	41†	139†	35†	131†
$Sn_{0.40}S_{0.60}$(Sn2S3,oP20,62)	0.7†	4	5.2†	11.2†	7.6†	14.8†	71†	84†	61†	80†
$Sn_{0.50}S_{0.50}$(GeS,oP8,62)	0.8†	0	6.3†	4.8†	12.7†	14.4†	156†	271†	128†	247†
$Sn_{0.50}S_{0.50}$(NaCl,cF8,225)	0.2†	39	4.8†	6.8†	3.0†	3.6†	531†	509†	735†	723†
$Sn_{0.50}S_{0.50}$(TlI,oS8,63)	0.8†	14	8.5†	9.2†	18.7†	22.5†	328†	262†	280†	262†
$Ta_{0.50}S_{0.50}$(NiAs,hP4,194)	0.0	0	–	–	–	–	–	–	–	–
$Tc_{0.50}S_{0.50}$(NiAs,hP4,194)	0.0	0	–	–	–	–	–	–	–	–
$Ti_{0.25}S_{0.75}$(TiS3,mP8,11)	0.0†	0	0.2†	1.7†	–	0.7†	362†	366†	–	796†
$Ti_{0.33}S_{0.67}$(CdI2,hP3,164)	0.0†	0	2.3†	–	–	3.7†	2940†	–	–	3874†
$Ti_{0.33}S_{0.67}$(Ti2C,cF48,227)	0.0†	21	0.6†	1.7†	0.0†	0.3†	760†	885†	1124†	1145†
$Ti_{0.38}S_{0.62}$(V5S8,mS26,12)	0.0	0	–	–	–	–	–	–	–	–
$Ti_{0.50}S_{0.50}$(NiAs,hP4,194)	0.0	45	–	–	–	–	–	–	–	–
$Ti_{0.50}S_{0.50}$(WC,hP2,187)	0.0†	0	–	0.5†	–	–	–	3531†	–	–
$Ti_{0.67}S_{0.33}$(Ta2P,oP36,58)	0.0	0	–	–	–	–	–	–	–	–
$Ti_{0.73}S_{0.27}$(Ti8S3,mS88,12)	0.0	6	–	–	–	–	–	–	–	–
$Y_{0.50}S_{0.50}$(NaCl,cF8,225)	0.0	0	–	–	–	–	–	–	–	–
$Zn_{0.33}S_{0.67}$(FeS2,cP12,205)	0.4†	174	9.8†	2.4†	15.2†	4.8†	105†	99†	99†	77†
$Zn_{0.50}S_{0.50}$(SiC,hP12,186)	2.2†	1	5.0†	1.6†	7.3†	4.7†	48†	274†	43†	264†
$Zn_{0.50}S_{0.50}$(SiC,hP16,186)	2.1†	0	4.5†	1.3†	7.0†	3.9†	43†	279†	40†	258†
$Zn_{0.50}S_{0.50}$(SiC,hP8,186)	2.2†	1	5.5†	1.6†	8.8†	4.7†	51†	273†	50†	263†
$Zn_{0.50}S_{0.50}$(ZnO,hP4,186)	2.2†	3	5.0†	1.5†	8.5†	4.7†	49†	273†	48†	265†
$Zn_{0.50}S_{0.50}$(ZnS,cF8,216)	2.1†	0	8.6†	1.4†	13.2†	4.6†	75†	278†	72†	266†
$Zn_{0.50}S_{0.50}$(ZnS,hP20,156)	2.1†	0	4.2†	0.8†	7.0†	3.4†	40†	235†	38†	219†
$Zn_{0.50}S_{0.50}$(ZnS,hP20,186)	2.1†	0	4.4†	1.3†	7.4†	4.6†	40†	305†	39†	285†
$Zn_{0.50}S_{0.50}$(ZnS,hP24,186)	2.1†	0	4.6†	1.4†	7.4†	4.8†	41†	292†	40†	280†
$Zn_{0.50}S_{0.50}$(ZnS,hP28,186)	2.1†	0	4.1†	1.6†	6.7†	4.7†	36†	223†	35†	226†
$Zn_{0.50}S_{0.50}$(ZnS,hP32,186)	2.1†	0	4.2†	1.8†	6.8†	4.7†	36†	237†	36†	236†
$Zn_{0.50}S_{0.50}$(ZnS,hP40,186)	2.1†	0	4.2†	1.4†	6.6†	4.6†	36†	282†	36†	268†
$Zn_{0.50}S_{0.50}$(ZnS,hP68,156)	2.1†	0	2.3†	0.4†	4.2†	1.6†	31†	176†	30†	173†
$Zn_{0.50}S_{0.50}$(ZnS-a,hP16,156)	2.1†	0	5.3†	1.3†	8.5†	3.8†	49†	280†	47†	257†

$Zn_{0.50}S_{0.50}$(ZnS-a,hP32,156)	2.1†	0	4.4†	1.8†	6.6†	4.7†	37†	237†	36†	236†
$Zn_{0.50}S_{0.50}$(ZnS-a,hP44,156)	2.1†	0	3.8†	1.3†	6.0†	4.5†	33†	264†	33†	253†
$Zn_{0.50}S_{0.50}$(ZnS-a,hP52,156)	2.1†	0	3.1†	0.7†	5.0†	2.5†	31†	185†	29†	174†
$Zn_{0.50}S_{0.50}$(ZnS-a,hP64,156)	2.1†	0	2.9†	0.1†	5.1†	1.1†	30†	181†	29†	174†
$Zn_{0.50}S_{0.50}$(ZnS-b,hP24,156)	2.1†	0	4.6†	1.2†	7.1†	4.5†	40†	270†	39†	262†
$Zn_{0.50}S_{0.50}$(ZnS-d,hP36,156)	2.1†	0	4.1†	1.6†	6.4†	4.6†	36†	245†	35†	241†
$Zn_{0.50}S_{0.50}$(ZnS-d,hP56,156)	2.1†	0	2.8†	0.4†	4.8†	1.9†	30†	181†	29†	175†
$Zn_{0.50}S_{0.50}$(ZnS-f,hP28,156)	2.1†	1	3.5†	1.3†	5.9†	4.4†	35†	254†	33†	246†
$Zn_{0.50}S_{0.50}$(ZnS-i,hP40,156)	2.1†	0	3.6†	1.3†	6.1†	4.1†	36†	297†	34†	266†
$Zn_{0.50}S_{0.50}$(ZnS-l,hP48,156)	2.1†	0	3.9†	1.6†	5.9†	4.7†	35†	275†	34†	266†
$Zr_{0.25}S_{0.75}$(ZrSe3,mP8,11)	1.1†	0	6.7†	4.4†	9.5†	7.6†	62†	70†	49†	67†
$Zr_{0.33}S_{0.67}$(CdI2,hP3,164)	0.7†	0	7.6†	8.7†	11.5†	13.7†	79†	83†	75†	76†
$Zr_{0.50}S_{0.50}$(NiAs,hP4,194)	0.0	0	–	–	–	–	–	–	–	–

II. DEFECT THERMOCHEMISTRY

A. Energy correction of defect formation energy

To calculate the defect formation energy with respect the standard state of the defect $E_f(D,q) = E(D,q) - E_{bulk} + \sum_\alpha n_\alpha E_\alpha$ (Eq. (1) main text) we used the VASP code [1–3] using the projector augmented wave method[4] and the PBE GGA functional.[5]

In the supercell approach $E(D,q)$ must contain a correction for the interaction of the image charges. First of all we need to add correction term E_{corr} to align the reference potential in defect supercell with that in the bulk[8, 9]. The creation of the defect gives rise to a constant shift in the potential and the total energy of a charged defect has to be corrected by[8],

$$\Delta E_{D,q} = q[V_R(D,q) - V_R(0)], \tag{1}$$

where the term $[V_R(D,q) - V(R(0)]$ represents the difference of the potential at a reference point in the defect and host calculation.

Another issue is the treatment of periodic image charge correction. According to the Makov and Payne model[10], the charge density in a crystalline solid with a point defect can be viewed as the sum of two contributions, the periodic charge density of the underlying crystalline solid and the charge density of the aperiodic defect. This leads to a multipole correction, ΔE_{mp} of the total energy of a finite supercells with respect to the total energy of an ideal infinite cell[10],

$$\Delta E_{mp} = \frac{q^2\alpha}{2L\epsilon} + \frac{2\pi qQ}{3L^3\epsilon} + O(L^{-5}), \tag{2}$$

where α is the Madelung constant, L is the distance between defect centers, ϵ is static dielectric constant and Q is the quadrupole moment. We considered only the monopole term. ϵ is calculated for pure SnS to be $\epsilon = 14.17$, using density functional perturbation theory.[11]

B. Defect thermodynamics SnSe

Fig. 2 shows the chemical potential limits used for the calculation of defect energies in SnSe (Fig. 5 in main text)

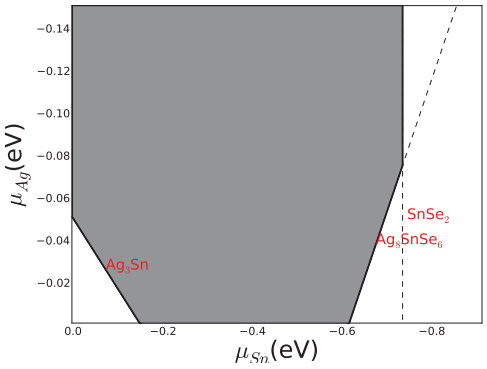

FIG. 2. Calculated chemical potential limits for Ag doping of SnSe. The shaded areas are the allowed equilibrium growth conditions.

C. Carrier concentrations

In thermodynamic equilibrium the carrier concentration of a given defect in a structure, c_d, is given by a Boltzmann distribution

$$c_d = c_0 e^{-\Delta G_f / k_B T}, \tag{3}$$

where ΔG_f is the free energy of the defect, c_0 is the concentration of possible defect sites, T is the temperature and k_B is the Boltzmann constant. We approximate ΔG_f as the formation energy of the defect, E_d when only bulk phases are involved in formation processes.

Eq. (1) in main text shows that the defect formation energy depends on the chemical potentials of the defect atoms, μ_α, and the charges, μ_e. μ_e is determined by the condition of charge neutrality. Therefore Eq. (3) can be formulated for every point defect and impurity in the material and can be solved by self consistently imposing charge neutrality[12]:

$$n_h - n_e + \sum_d q c_d = 0, \tag{4}$$

where n_h and n_e are the numbers of holes and electrons given by,

$$n_h = \int_{-\infty}^{E_{VBM}} n(\epsilon)[1 - f(\epsilon, \mu_e)]d\epsilon, \quad n_e = \int_{E_{CBM}}^{\infty} n(\epsilon) f(\epsilon, \mu_e) d\epsilon, \tag{5}$$

where E_{CBM} is the energy of conduction band minimum, $n(\epsilon)$ is the electronic density of states of the defect free crystal, and $f(\epsilon, \mu_e)$ is the Fermi distribution. $n(\epsilon)$ in Eq. (5) is the DFT density of states, calculated for pure SnS with the band gap 0.9 eV. These carrier concentrations are shown in Fig. 5 of the main text.

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