Electronic Supplementary Material (ESI) for Materials Horizons.

Electronic Supplementary Information: Computational Discovery of Promising New n-type Dopable ABX Zintl Thermoelectric Materials

Prashun Gorai,*,† Alex Ganose,‡ Alireza Faghaninia,‡ Anubhav Jain,‡ and Vladan Stevanović*,†

†*Colorado School of Mines, Golden, CO 80401*

‡*Lawrence Berkeley National Laboratory, Berkeley, CA 94720*

E-mail: pgorai@mines.edu; vstevano@mines.edu

1. Interstitial Structures in KSnSb, KSnBi, RbSnBi, NaGeP, KGeP

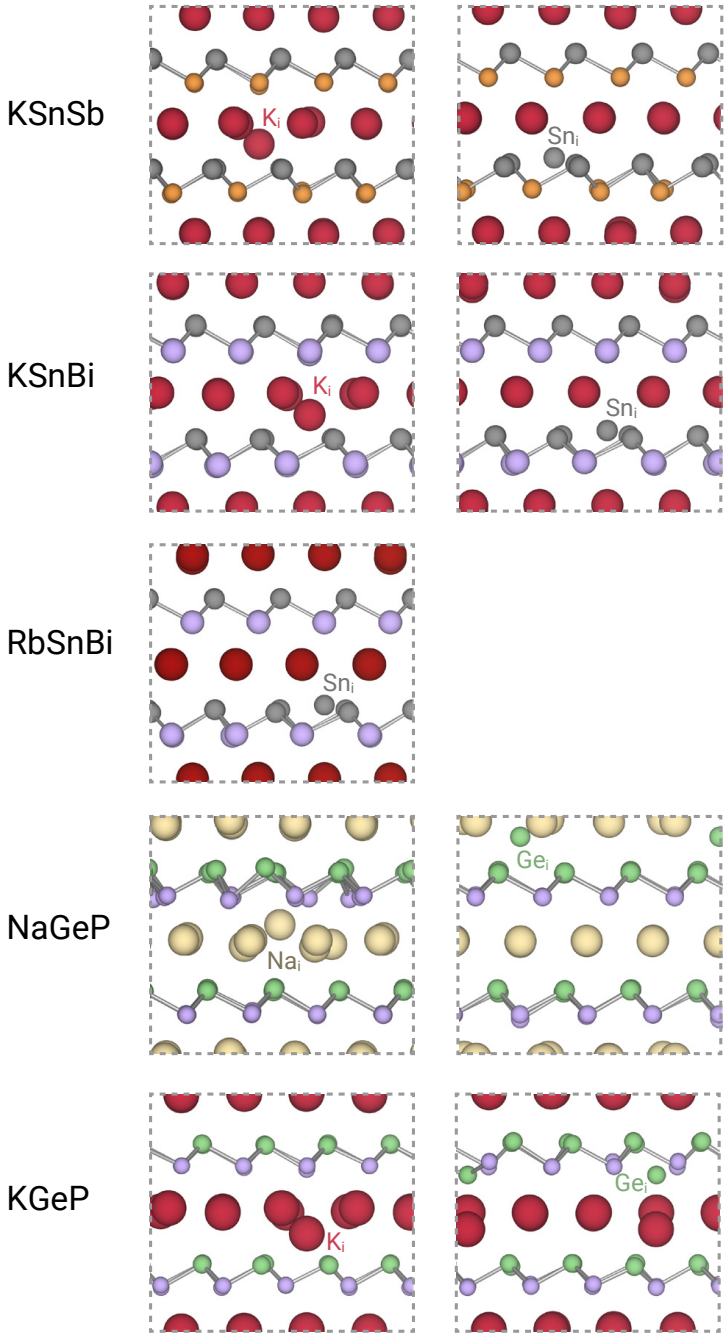

Figure S1: Structures of energetically favorable interstitials in KSnSb, KSnBi, RbSnBi, NaGeP, and KGeP determined using a Voronoi tessellation scheme (as implemented in the pylada-defects software package) and DFT total energies.

2. Fitted Elemental-Phase Reference Chemical Potentials

The fitted elemental-phase reference energies used in the defect calculations (μ_i^0 in Eq. 2):

K: -1.14 eV, Sn: -3.82 eV, Sb: -4.11 eV, Bi: -4.19 eV, Rb: -0.82 eV, Na: -1.24 eV, Ge: -4.34 eV, P: -5.17 eV

3. Structure Types Among Known ABX Zintl Phases

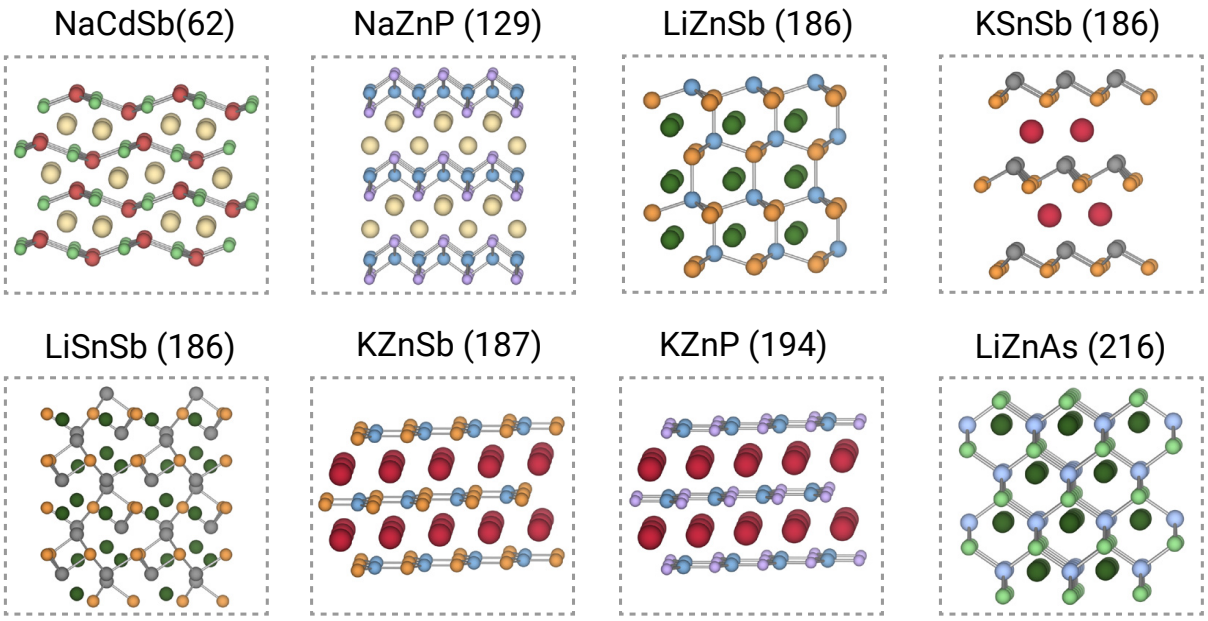

Figure S2: Unique structure types among known ABX Zintl phases. 24 known ABX compositions adopt these 8 structure types.

4. ABX Structures from ICSD Considered for Assessing Structural Stability

KSnSb (186), KZnP (194), KZnSb (187), LiSnSb (186), LiZnAs (216), LiZnSb (186), NaCdSb (62), NaZnP (129), KCN (8), KCN (9), BaCuN (15), HfRuAs (46), GeSeAs (52), BaNiN (62), CrNbN (99), LiFeP (107), LaIrP (109), MgAgSb (120), LiFeAs (129), LiMnAs (129), SrSnP (129), LiSrN (131), EuPtP (164), LiFeAs (164), LiNiN (187), YPtP (187), CrNiP (189), FeRhAs (189), TiFeP (189), LiFeAs (194), NdNiP (194), ZnCuAs (216), KCN (225), MnCoSb (225).

Numbers in parentheses denote the space group number.

5. Predicted 45 Stable ABX Zintl Phases

- 17 compounds stable in KSnSb structure type: RbSnBi, KSnBi, KGeP, NaGeAs, KPbAs, LiPbAs, NaGeP, NaPbAs, NaSnAs, RbGeAs, KGeAs, CsSnSb, RbSnSb, CsSnBi, RbSnAs, KSnP, RbPbAs.

- 28 compounds stable in other structure types: RbZnAs (LiZnSb, 186), NaBeP (LiZnSb, 186), CsCdAs (NaZnP, 129), RbCdAs (NaZnP, 129), CsCdP (NaZnP, 129), KCdP (KZnP, 194), RbZnP (KZnP, 194), RbCdSb (KZnP, 194), RbCdP (KZnP, 194), KZnBi (KZnP, 194), RbZnBi (KZnP, 194), RbZnSb (KZnP, 194), RbBeP (NaCdSb, 62), CsPbSb (NaCdSb, 62), KBeP (NaCdSb, 62), CsBeAs (NaCdSb, 62), KBeAs (NaCdSb, 62), CsPbAs (NaCdSb, 62), NaCdP (NaCdSb, 62), CsBeP (NaCdSb, 62), RbPbSb (NaCdSb, 62), CsPbBi (NaCdSb, 62), RbBeAs (NaCdSb, 62), CsZnAs (YPtP, 187), CsZnSb (YPtP, 187), CsZnP (YPtP, 187), LiCdSb (LiZnAs, 216), LiCdBi (LiZnAs, 216)

Prototype structure adopted by each of the 28 compounds is indicated in parentheses, along with their space group numbers.

6. Energy Above the Hull of 45 Stable ABX Zintl Phases

Table S1: 45 predicted stable Zintl phases. ΔE_{hull} is the energy above the convex hull (in meV/atom), and $\beta_n/\beta_{\text{PbTe}}$ is normalized n-type TE quality factor (unitless). *stable in KSnSb structure type.

Compound	ΔE_{hull}	$\beta_n/\beta_{\text{PbTe}}$
RbSnBi*	0	5.8
KSnBi*	2	4.8
KGeP*	4	4.5
NaGeAs*	0	4.0
KPbAs*	0	2.8
LiPbAs*	6	2.5
NaGeP*	0	2.4
NaPbAs*	0	2.4
NaSnAs*	0	1.7
RbGeAs*	4	0.8
KGeAs*	16	0.8
CsSnSb*	0	0.7
RbSnSb*	0	0.6
CsSnBi*	0	0.5
RbSnAs*	0	0.4
KSnP*	0	0.3
RbPbAs*	0	0.3
CsCdAs	0	0.6
KCdP	0	1.5
RbZnP	0	1.2
RbZnAs	0	1.9
NaBeP	0	1.0
RbCdAs	0	1.7
CsCdP	0	0.5
RbCdSb	0	3.4
RbCdP	0	1.6
KZnBi	0	3.9
RbZnBi	0	3.8
RbZnSb	0	1.5
RbBeP	0	1.0
CsPbSb	0	0.6
KBeP	0	0.5
CsBeAs	0	0.4
KBeAs	0	0.4
CsPbAs	0	0.3
NaCdP	0	2.6
CsBeP	0	0.4
RbPbSb	0	0.4
CsPbBi	0	0.9
RbBeAs	0	0.4
CsZnAs	0	2.0
CsZnSb	0	1.7
CsZnP	0	1.2
LiCdSb	0	2.3
LiCdBi	0	1.4

7. Electronic Structures

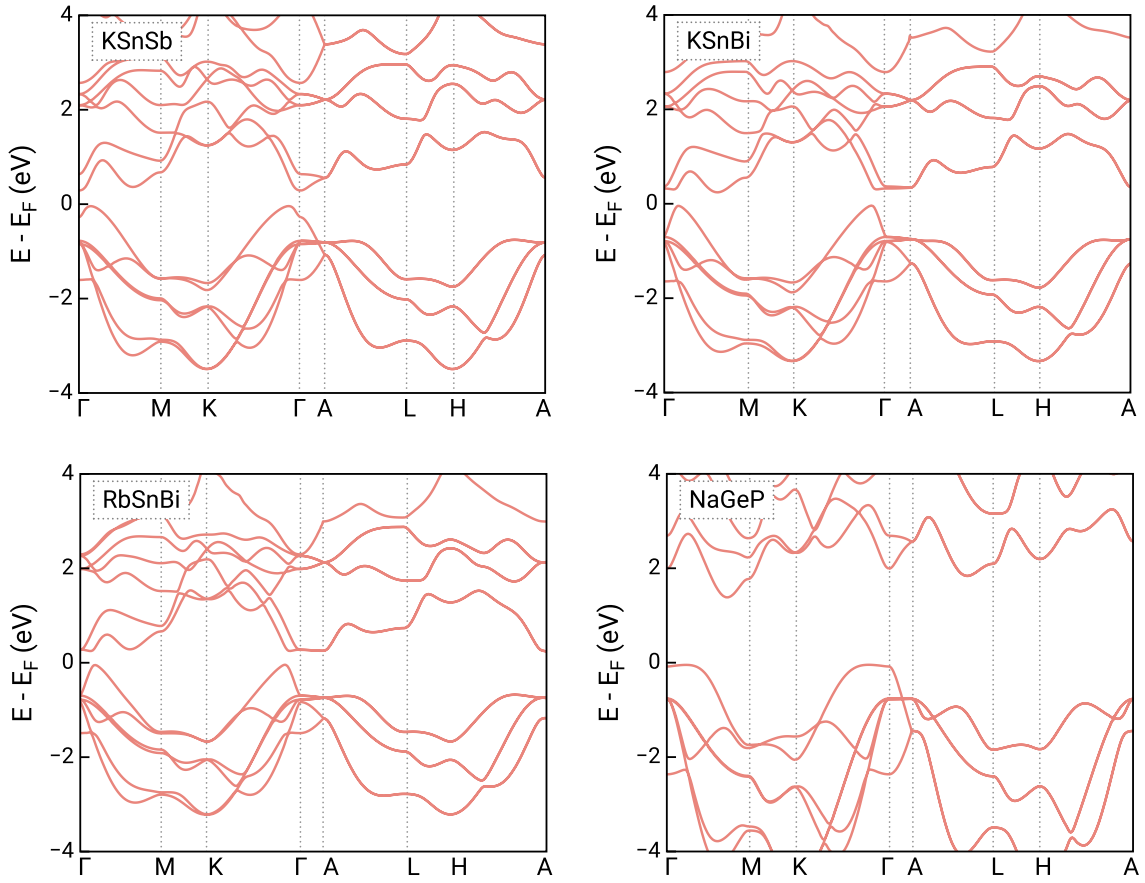

Figure S3: Electronic structures of KSnSb, KSnBi, RbSnBi, and NaGeP along the special k-point paths of the Brillouin zone of a hexagonal lattice.

8. Phonon Dispersions

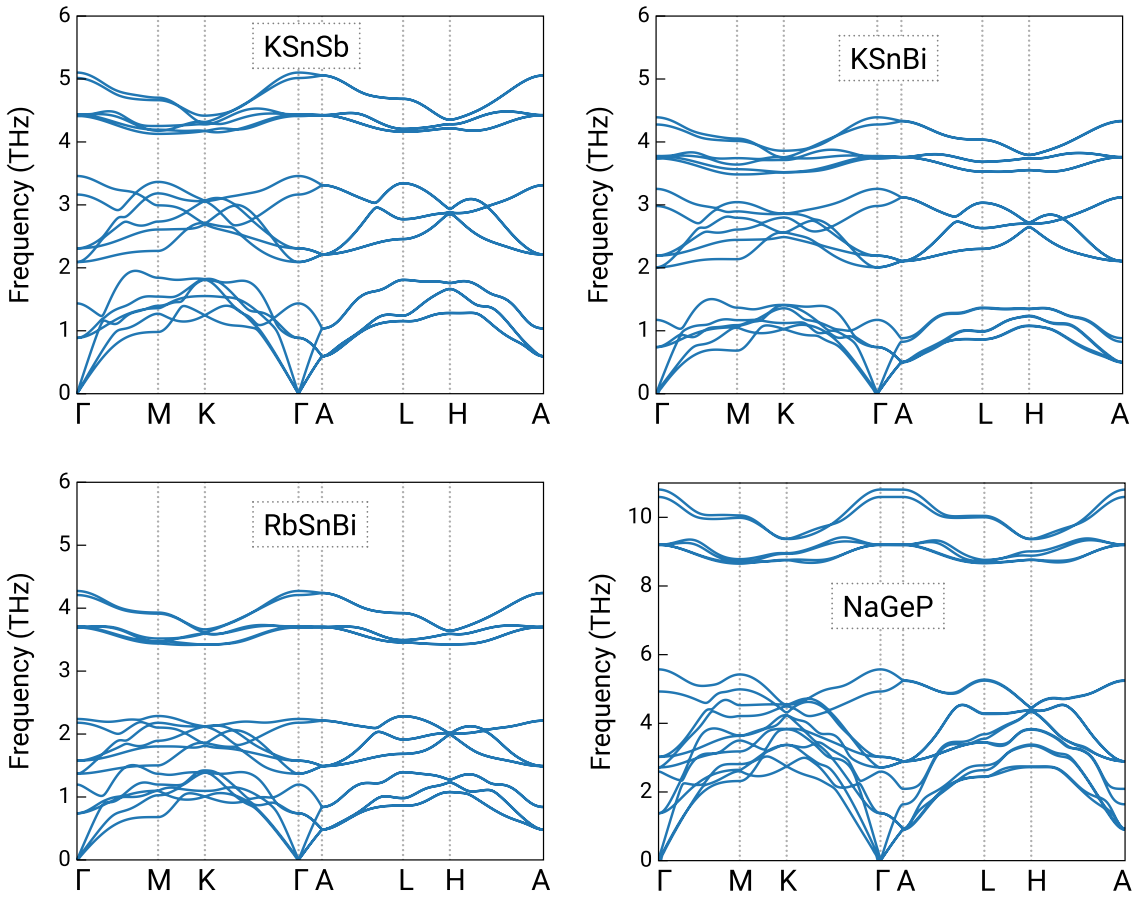

Figure S4: Phonon dispersions of KSnSb, KSnBi, RbSnBi, and NaGeP along the special k-point paths of the Brillouin zone of a hexagonal lattice. Note the different frequency (y-axis) scale for NaGeP.

9. Γ-point Frequencies of Phonon Modes

Table S2: Γ-point phonon frequencies of the 17 Zintil phases predicted to be stable in the KSnSb structure type, given in THz

	Phonon mode index																	
Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
RbSnBi	-0.01	0.00	0.00	0.75	0.75	1.19	1.39	1.39	1.60	1.60	2.22	2.24	3.68	3.68	3.70	3.70	4.17	4.21
KSnBi	0.00	0.00	0.00	0.76	0.76	1.17	2.04	2.04	2.24	2.24	3.05	3.26	3.72	3.72	3.76	3.76	4.23	4.31
KGeP	0.00	0.00	0.00	1.51	1.51	2.48	2.48	2.65	2.89	2.89	4.29	4.38	8.74	8.74	8.75	8.75	10.21	10.43
NaGeAs	-0.01	0.00	0.00	1.17	1.17	2.03	2.60	2.60	2.84	2.84	4.41	5.12	6.63	6.63	6.64	6.64	7.76	7.83
KPbAs	0.00	0.00	0.00	0.76	0.76	1.22	2.43	2.43	2.58	2.58	3.37	3.50	4.52	4.52	4.54	4.54	5.08	5.30
LiPbAs	0.00	0.00	0.00	1.20	1.20	1.76	2.80	3.10	3.10	3.23	3.23	4.07	5.72	5.95	9.06	9.06	9.11	9.11
NaGeP	-0.01	0.00	0.00	1.39	1.39	2.55	2.71	2.71	3.02	3.02	4.88	5.54	9.20	9.20	9.23	9.23	10.58	10.83
NaPbAs	0.00	-0.01	-0.01	1.26	1.26	1.13	3.58	3.58	3.60	3.61	3.61	4.06	4.36	4.36	4.61	4.61	4.87	5.28
NaSnAs	0.00	0.00	0.00	0.93	0.93	1.60	2.70	2.70	2.87	2.87	4.00	4.72	5.30	5.30	5.32	5.32	6.24	6.37
RbGeAs	-0.01	0.00	0.00	1.22	1.22	1.62	1.62	2.02	2.02	2.13	2.76	2.93	6.12	6.12	6.13	6.13	7.28	7.31
KGeAs	-0.01	0.00	0.00	1.25	1.25	2.12	2.35	2.35	2.67	2.67	3.86	4.06	6.30	6.30	6.31	6.31	7.46	7.54
CsSnSb	-0.02	-0.02	-0.01	0.88	0.88	1.26	1.26	1.47	1.52	1.52	1.94	2.05	4.25	4.25	4.26	4.26	4.71	4.73
RbSnSb	0.00	0.00	0.00	0.88	0.88	1.45	1.47	1.47	1.73	1.73	2.36	2.39	4.33	4.33	4.34	4.34	4.84	4.87
CsSnBi	-0.02	0.00	0.00	0.74	0.74	1.15	1.15	1.22	1.37	1.37	1.85	1.88	3.62	3.62	3.63	3.63	4.06	4.10
RbSnAs	0.00	0.00	0.00	0.97	0.97	1.65	1.65	1.67	1.91	1.91	2.58	2.67	5.14	5.14	5.14	5.14	5.86	5.96
KSnP	0.00	0.00	0.00	1.10	1.10	1.98	2.45	2.45	2.68	2.68	3.88	4.10	7.50	7.50	7.51	7.51	8.69	9.01
RbPbAs	0.00	0.00	0.00	0.73	0.73	1.23	1.71	1.71	1.87	1.87	2.48	2.51	4.41	4.41	4.43	4.43	4.95	5.09