Doping remains a bottleneck in discovering novel functional materials for applications such as thermoelectrics (TE) and photovoltaics. The current computational approach to materials discovery is to identify candidates by predicting the functional properties of a pool of known materials, and hope that the candidates can be appropriately doped. What if we could "design" new materials that have the desired functionalities and doping properties? In this work, we use an approach, wherein we perform chemical replacements in a prototype structure, to realize doping by design. We hypothesize that the doping characteristics and functional performance of the prototype structure are translated to the new compounds created by chemical replacements. Discovery of new n-type Zintl phases is desirable for TE; however, n-type Zintl phases are a rarity. We demonstrate our doping design strategy by discovering 7 new, previously-unreported ABX$_4$ Zintl phases that adopt the prototypical KGaSb$_4$ structure. Among the new phases, we computationally confirm that NaAlSb$_4$, NaGaSb$_4$, and CsInSb$_4$ are n-type dopable and potentially exhibit high n-type TE performance, even exceeding that of KGaSb$_4$. Our structure prototyping approach offers a promising route to discover new materials with designed doping and functional properties.
Doping by Design

Plausible chemical substitutions

Prototype with desired doping characteristics

New materials with "designed" doping properties
Doping by Design: Finding New n-type Dopable ABX$_4$ Zintl Phases for Thermoelectrics

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Doping remains a bottleneck in discovering novel functional materials for applications such as thermoelectrics (TE) and photovoltaics. The current computational approach to materials discovery is to identify candidates by predicting the functional properties of a pool of known materials, and hope that the candidates can be appropriately doped. What if we could “design” new materials that have the desired functionalities and doping properties? In this work, we use an approach, wherein we perform chemical replacements in a prototype structure, to realize doping by design. We hypothesize that the doping characteristics and functional performance of the prototype structure are translated to the new compounds created by chemical replacements. Discovery of new n-type Zintl phases is desirable for TE; however, n-type Zintl phases are a rarity. We demonstrate our doping design strategy by discovering 7 new, previously-unreported ABX$_4$ Zintl phases that adopt the prototypical KGaSb$_4$ structure. Among the new phases, we computationally confirm that NaAlSb$_4$, NaGaSb$_4$ and CsInSb$_4$ are n-type dopable and potentially exhibit high n-type TE performance, even exceeding that of KGaSb$_4$. Our structure prototyping approach offers a promising route to discover new materials with designed doping and functional properties.

1 Introduction

Doping has been an enduring and pervasive challenge in the discovery of new functional materials for thermoelectrics,$^{1,2}$ transparent conductors,$^{3,4}$ photovoltaics,$^{5,6}$ etc. There are several challenges in doping materials: (1) cannot be sufficiently doped with either electrons (n-type) or holes (p-type) i.e., material is an insulator, or (2) cannot be doped with the desired carrier type (doping asymmetry), or (3) cannot be doped to the desired carrier concentration needed for the specific application. For instance, wide band gap oxides such as SiO$_2$ and Al$_2$O$_3$ are insulators that cannot be doped either n- or p-type. Some materials suffer from doping asymmetry, wurtzite ZnO being one of the prominent examples. While n-type doping of ZnO is achieved by Al doping, p-type doping remains elusive.$^7$ Doping asymmetry has practical implications. ZnSb is predicted to be a promising n-type TE material; however, it has been shown theoretically$^9$ and experimentally$^{10}$ that n-type doping cannot be achieved. The low formation energy of acceptor Zn vacancies lead to degenerate p-type doping behavior of ZnSb.$^9$

Within intermetallic compounds, there exists a subset known as Zintl phases that generally exhibit doping asymmetry. To date, most well-known Zintl phases with moderate carrier concentrations are native p-type due to self-doping. However, only a few n-type ones have been reported in experiments.$^{11-14}$ The inherent features of Zintl phases, such as small band gaps, dispersive electronic bands, and complex structures, make them suitable as TE materials. Zintl phases such as Yb$_{14}$MnSb$_{11},$ CaZn$_2$Sb$_2$ and Ca$_3$Al$_2$Sb$_6$$^{17}$ are among the TE materials with best performance in mid- to high-temperature regime. The experimental data in Figure 1 demonstrates the well-known doping asymmetry in Zintl phases. The maximum electronegativity difference is a measure of the bonding ionicity between the cation-anion framework. The p-type Zintl phases, denoted by blue markers, outnumber the n-type phases (red markers).

Computational predictions indicate that Zintl phases when doped n-type have comparable or better TE performance than their p-type versions.$^{11}$ However, the discovery of new n-type Zintl phases so far has been driven by chemical intuition and serendipity. The recent discoveries of new n-type Zintl phases, including KAlSb$_4$, KGaSb$_4$, RbGaSb$_4$, CsGaSb$_4$, and Ba$_3$Cd$_2$P$_4$, seem to suggest that (1) there are Zintl phases that may overcome the doping asymmetry, and (2) the chemical and structural phase space of n-type Zintl phases is largely underexplored. One plausible route for finding new n-type dopable Zintl phases with high TE performance is by chemical replacements in structure prototype (CRISP).$^{15}$ Computational efforts in the past have utilized chemical substitution in known compounds to search for undiscovered phases.$^{20,21}$ In the last decade, various routes have been explored to search for as-yet-unknown materials for functional applications.$^{22-25}$ These studies served the general purpose of discovering new compounds rather than new compounds with designed functionalities.

In this work, we show that chemical substitutions in appropriately chosen prototype structures is a viable route to discover new compounds with designed doping properties. Selecting an appropriate prototype structure is one of the key aspects of this approach. The prototype should possess the same functionality (e.g. high TE performance) and doping (e.g. n-type dopable) characteristics that we desire to “transfer” to the new compounds.

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created by chemical substitutions. We demonstrate this approach to discover new ABX₄ Zintl phases (A = Na, K, Rb, Cs; B = Al, Ga, In; X = As, Sb, Bi) that adopt the KGaSb₁₄ prototype structure (Figure 2), predicted to have high TE performance and are n-type dopable. KGaSb₁₄ serves as an appropriate prototype for two reasons: (1) it has good n-type TE performance, with $zT \sim 1$, and (2) can be doped n-type to $>10^{19}$ cm$^{-3}$ electron concentrations.¹² Out of the 36 plausible Zintl phases, only 2 are reported in the Inorganic Crystal Structure Database (ICSD)²⁶ and four of them have been recently discovered,¹³ indicating that the phase space of KGaSb₁₄ type Zintl phases is under-explored. Importantly, the 6 known ABX₄ phases are all n-type dopable.¹²,¹³ Using first-principles calculations, we theoretically evaluate the thermodynamic and dynamic stability of the 36 ABX₄ Zintl phases and predict that 13 of them should be stable, including the 6 known phases (KGaSb₁₄, KAlSb₁₄, CsGaSb₁₄, CsAlSb₁₄, RbGaSb₁₄, RbAlSb₁₄) and 7 new phases. Of the 7 undiscovered phases, we choose the top 3 candidates (NaAlSb₁₄, NaGaSb₁₄, and CsInSb₁₄) that are predicted to have the highest n-type TE performance; first-principles defect calculations reveal that they are all n-type dopable.

2 Methods

The computational workflow is summarized in Figure 3. We create hypothetical Zintl phases by chemical replacements in the prototype KGaSb₁₄ structure and relax them with DFT. Next, we calculate their electronic structures and theoretical TE performance. Subsequently, we assess the thermodynamic and dynamic stability of those structures with predicted high n-type TE performance. Finally, we assess the n-type dopability of the top candidates using first-principles defect calculations.

2.1 Chemical Replacements in Prototype Structure

Chemical substitutions are performed in the prototype structure KGaSb₁₄ to create hypothetical ABX₄ compounds. With consideration to nominal oxidation states and electronegativity, we choose alkali elements Na, K, Cs, and Rb for the A site, group 13 elements (Al, Ga, In) for the B site, and pnictides (As, Sb, Bi) for the X site. The orthorhombic crystal structure of KGaSb₁₄ (Pnma) consists of an anionic framework formed by GaSb tetrahedra linked by Sb–Sb covalent bonds. K atoms occupy the channels formed by the anionic framework (Figure 2). The small electronegativity difference between Ga and Sb ($\Delta \chi_{Ga-Sb} = 0.24$ on Pauling scale) gives rise to the covalent nature of the anionic frameworks, while the high electropositivity of K ($\Delta \chi_{K-Sb} = 1.23$) leads to ionic bonding with the anionic frameworks i.e., electron transfer from K to the anionic framework.

2.2 Structure Relaxation and Electronic Structure

The hypothetical structures generated using chemical substitutions are relaxed with density functional theory (DFT) using the plane-wave VASP code.²⁷ The Perdew-Burke-Ernzerhof (PBE) exchange correlation functional²⁸ is used within the generalized gradient approximation (GGA). The core and valence electrons are treated with the projector-augmented wave (PAW) method.²⁹ The hypothetical structures are relaxed with a plane-wave en-

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Fig. 1 Binary and ternary Zintl phases from the ICSD represented by the number of atoms in the primitive cell and the maximum electronegativity difference (on the Pauling scale) between the constituent elements. The color scheme denotes the experimentally measured charge carrier concentrations of 46 Zintl phases, with blue denoting p-type (hole) and red n-type (electron). KGaSb₁₄ and CsSb₁₄ can be doped both n- and p-type; only n-type is shown for clarity. n-type is not shown because carrier concentration has not been measured yet.¹⁵ Data adapted from Ref. 18, with permission from the Royal Society of Chemistry.

Fig. 2 Crystal structure of KGaSb₁₄, a Zintl phase with an anionic framework composed of [GaSbₓ]₄ tetrahedra linked by homoatomic Sb–Sb bonds. K atoms occupy the channels formed by the anionic framework. We perform chemical replacements in the prototypical KGaSb₁₄ structure, where K is replaced with Na, K, Rb, Cs, Ga with Al, Ga, In, and Sb with As, Sb, Bi. Sb has four unique Wyckoff sites, labelled 1 through 4.
Fig. 3 Schematic computational workflow of chemical replacements in structure prototype approach. Here, $E_g$ is the band gap and $\beta$ is the predicted thermoelectric quality factor, a measure of thermoelectric performance. Specifically, the $n$-type $\beta$ is considered.

energy cutoff of 340 eV and a Monkhorst-Pack $k$-point sampling. The space groups of the relaxed structures are then determined to check whether they retain the prototype structure. Electronic structures are calculated on a dense $k$-mesh with a fixed number of $k$-points. The $k$-point grid is determined according to the equation: $N_{\text{atoms}} \times N_{\text{kpts}} \approx 8000$, where $N_{\text{atoms}}$ is the number of atoms in the primitive cell and $N_{\text{kpts}}$ is the number of $k$ points. Structures with zero DFT-calculated band gaps are not considered in the subsequent steps. Therefore, hypothetical compounds that retain the prototype structure and have non-zero band gaps are considered for further analysis.

2.3 Thermoelectric Performance Assessment

The quality factor ($\beta$) provides a measure of the potential for thermoelectric performance of a material. We have previously developed semi-empirical models to computationally evaluate $\beta$ (see Ref. 30 for details). The quality factor is expressed in terms of the electronic and lattice thermal transport parameters as:

$$\beta \propto \frac{\mu_0 m^{*}_{\text{DOS}}}{\kappa_L} \frac{3/2}{T^{5/2}}$$

where $\mu_0$ is the intrinsic charge carrier mobility at 300 K, $m^{*}_{\text{DOS}}$ the density-of-states (DOS) effective mass, and $\kappa_L$ the lattice thermal conductivity at 300 K. Semi-empirical models of $\mu_0$ and $\kappa_L$ allow computational assessment of the quality factor with first-principles calculations. To determine $\mu_0$ and $\kappa_L$ from the semi-empirical models, band degeneracy ($N_\nu$), DOS effective mass ($m^{*}_{\text{DOS}}$) and bulk modulus ($B$) need to be determined. The parabolic band approximation is used to extract $m^{*}_{\text{DOS}}$ within a 100 meV energy window away from the band edge positions. With $m^{*}_{\text{DOS}}$ and $N_\nu$, the band effective mass ($m^{*}_n$) can be determined within the parabolic and isotropic band approximation: $m^{*}_n = m^{*}_{\text{DOS}} N_\nu^{-2/3}$. Bulk modulus $B$ is obtained by fitting the Birch-Murnaghan equation of state. $\kappa_L$ is calculated using a semi-empirical model based on the modified Debye-Callaway model; the model inputs are bulk modulus ($B$), density, volume per atom, average atomic mass, average coordination number, and the number of atoms in the primitive cell. Besides $B$, the other model parameters are directly accessible from the structure.

2.4 Stability Assessment

Compositional Stability: Stability against chemical decomposition into competing phases can be assessed with convex hull analysis. The energies of ABX₄ compositions as well as different binary and ternary competing phases are calculated. Materials on the convex hull are stable. The energy above the convex hull (AE_{null}) is an indicator of the compositional stability of the ABX₄ phase. If the ABX₄ phase lies on the hull or within 20 meV/atom from the hull, it is deemed to be compositionally stable. The competing phases are searched within the ICSD. The total energies of the competing phases are calculated by relaxing the structures with the same methodology as described in Section 2.2. The formation enthalpies are calculated from the total energies and reference chemical potentials of the elemental phases. The reference chemical potentials are obtained by fitting to a set of experimentally measured formation enthalpies, similar to the procedure described in Ref. 33, which has been shown to provide accurate predictions for formation enthalpies. See supplementary material for the fitted reference chemical potentials.

Structural Stability: The aim of the structural stability analysis is to find if the lowest-energy (most favorable) structure for a given ABX₄ composition is the prototype structure. Plausible structures are selected from the ICSD that can accommodate 1-1-4 ternary stoichiometries. In order to identify plausible 1-1-4 stoichiometry structures, we impose further the following constraints: cations on A and B sites with compatible oxidation states (1+ for A, 3+ for B). To assess structural stability, each ABX₄ composition is fully relaxed in all plausible structures chosen from ICSD, including in the prototype KGaSb₄ structure. Structure relaxation is performed as described in Section 2.2. The most favorable structure is the lowest-energy structure; if the prototype KGaSb₄ structure is the lowest-energy structure, then the ABX₄ composition is deemed structurally stable.

Dynamic Stability: For ABX₄ Zintl phases that are found to be compositionally and structurally stable, we test their dynamic stability w.r.t. $\Gamma$-point phonons using density functional perturbation theory (DFPT), as implemented in VASP. The structures are relaxed with a plane-wave energy cutoff of 520 eV with an energy convergence criterion of $10^{-8}$ eV. The Brillouin zone is sampled using a $\Gamma$-centered $4 \times 4 \times 2$ Monkhorst-Pack $k$-point grid. Structures with no imaginary frequencies at $\Gamma$ point are considered dynamically stable. We also calculate the full phonon dispersion for
three stable ABX₄ phases using the supercell finite-displacement method implemented in the Phonopy package, with VASP as the force calculator. The self-consistent calculations in VASP are performed with the same plane-wave energy cutoff and k-point grid as the DFPT calculation, with an energy convergence criterion of of 10⁻⁸ eV.

### 2.5 Defect energetics

To understand the defect chemistry of ABX₄ Zintl phases, we employ the standard supercell approach to calculate the defect formation energies of native point defects. The defect formation energy (ΔHₐ,q) is calculated from the total energies as follows:

\[
\Delta H_{D,q} = E_{D,q} - E_{\text{host}} + \sum_{i} n_{i} \mu_{i} + qE_{\text{F}} + E_{\text{corr}}
\]

where ΔHₐ,q represents the formation energy of a defect D in charge state q; Eₐ,q and Eₜₜ are the total energies of the supercell with and without the defects, respectively, Eₚ is the Fermi energy which varies from the valence band maximum (VBM) to the conduction band minimum (CBM), Eₐₚ is the term that accounts for the finite-size corrections within the supercell approach, μᵢ is the chemical potential of elemental species i added (nᵢ < 0) or removed (nᵢ > 0) from the host supercell to form defects. The elemental chemical potential μᵢ is expressed as μᵢ = μᵢ⁰ + Δμᵢ, where μᵢ⁰ is the reference elemental potential (see Section 2.4) and Δμᵢ the deviation from the reference elemental phase. The bounds on Δμᵢ are set by the thermodynamic stability condition, with Δμᵢ = 0 corresponding to i-rich conditions and a large negative value of Δμᵢ represents i-poor growth conditions.

First-principles defect calculations are performed using the GGA-PBE exchange correlation functional. The Brillouin zone of the 192-atom supercells is sampled using a Γ-centered 2 × 2 × 2 k-grid. The atomic positions in the defect supercells are fully relaxed to obtain the total energies. The following corrections to the defect formation energies are included in Eₐₚ as described in Ref. 36: (1) image charge correction for charged defects, (2) potential alignment correction for charged defects, (3) band-filling corrections for shallow defects, and (4) band gap correction. The static dielectric constant (electronic + ionic), which is needed for calculating the image charge correction, is evaluated using DFPT. To correct the band gap under-estimation in GGA-PBE, we employ state-of-art GW quasiparticle energy calculations to compute the band edge shifts relative to the DFT band edge positions. A computational framework for automation of point defect calculations, pylada-defects, is utilized in this work for creating the defect supercells and analysis of the results, including calculation of finite-size corrections.

The formation energies for the native point defects (vacancy, anti-site defect, interstitial) are calculated in charge states q = -3, -2, -1, 0, +1, +2, and +3. All unique Wyckoff positions in the crystal structures (Figure 2) are considered in the calculations for vacancies and anti-site defects. The likely interstitial sites are determined by a Voronoi tessellation scheme, as implemented in pylada-defects. In each structure, we consider up to 20-25 possible interstitial sites and then determine the lowest-energy site based on total energies of the relaxed supercells. The free carrier concentrations at specific temperatures are calculated self-consistently by solving the charge-neutrality conditions.

### 3 Results and Discussion

Figure 4(a) presents the summary of the computational search of new ABX₄ Zintl phases in the prototypical KGaSb₄ structure. Out of the 36 phases considered in this study, only 6 are known/reported, indicating that the chemical phase space of ABX₄ compound is under-explored. From electronic structure calculations, we find that 25 out of 36 ABX₄ phases (in the assumed KGaSb₄ structure) have non-zero DFT band gap (Figure 4a). Furthermore, 22 out of 25 have n-type β larger than that of PbTe, a well-known thermoelectric material. Of the remaining 22 compositions, we find that 13 of them are stable - compositionally (within 20 meV/atom from the convex hull), structurally (most favorable in KGaSb₄ structure), and dynamically (no imag-
The existence of the 6 known experimentally synthesized phases, CsInSb phases (NaAlSb and CsGaSb), and NaGaSb phases (KAlSb and NaAlSb under Na-rich growth condition, CsAlSb, RbInSb, and NaGaSb, respectively), lends credence to our stability predictions. Among the 13 stable phases, 8 of them lie on the hull while the remaining 5 are above the hull but within 20 meV/atom (Table 1). These predicted stable compounds comprise of 2 arsenides and 11 antimonides. We find that all the bismuthides are thermodynamically unstable, which is consistent with synthesis attempts in Ref. 13. Our convex hull analysis shows that the primary competing phases, which restrict the compositional stability of the ABX$_3$ phases, are ternary A$_2$B$_2$X$_3$ phases. For instance, Na$_3$InSb$_3$ and NaSb competes with NaAlSb under Na-rich growth condition.

For establishing structural stability, we consider 34 plausible structures from the ICSD using the criteria explained in the Methods (Section 2.4). The full list of the 34 structures are provided in the Supplementary Information. We perform the structural stability analysis on all 13 compositionally stable phases and find that all of them are structurally stable in the prototype KGaSb$_4$ structure. Furthermore, we find that all 13 phases are dynamically stable at Γ-point (see Supplementary Information).

To further confirm the dynamic stability, we calculated the full-path phonon dispersions of the 3 newly predicted phases - NaAlSb$_4$, NaGaSb$_4$ and CsInSb$_4$ (see in Figure 5). See Section 3.3 for the reasons why we choose these three candidate materials. The absence of imaginary phonon modes in the phonon bandstructure further confirms the dynamic stability of NaAlSb$_4$, NaGaSb$_4$ and CsInSb$_4$. As expected, the low-energy modes are dominated by contributions from the heavy element Sb. The phonon dispersions (Figure 5) feature low-energy optical modes (<1 THz) that appear to hybridize with the acoustic modes. It has been shown that such acoustic-optical hybridization can lead to increased scattering of the primary heat-carrier acoustic modes, resulting in low lattice thermal conductivities. 39

3.2 Electronic Structure of $ABX_3$ Phases

Figure 6 presents the electronic band structures of NaAlSb$_4$, NaGaSb$_4$, and CsInSb$_4$. The band structures are plotted along the special k-point paths of the orthorhombic Brillouin zone. The band gap underestimation in DFT is adjusted by applying band edge shifts calculated with GW quasi-particle energy calculations (see Section 2.5). NaAlSb$_4$, NaGaSb$_4$, and CsInSb$_4$ are all small band gap semiconductors (<1 eV), which is typical of Zintl phases. CsInSb$_4$ has a larger band gap compared to NaAlSb$_4$ and NaGaSb$_4$ owing to the larger electronegativity difference between Cs and In. In all three phases, there exist conduction band (CB) valleys at Γ and at Z. NaAlSb$_4$ and NaGaSb$_4$ have additional CB valleys along Γ-Y ($\Gamma_6 = 2$) and Γ-Z ($\Gamma_8 = 2$) that also lie within the 100 meV energy window from the CBM shown by the red shaded region in Figure 6. In NaAlSb$_4$ and NaGaSb$_4$, the CBM lie along Γ-Z while in CsInSb$_4$, the CBM is located at Γ. The electronic structure of other $ABX_3$ phases is available in Supplementary Information.

When band valleys (or pockets) do not lie at special k-points, it increases band degeneracy due to symmetry. Consequently, NaAlSb$_4$ and NaGaSb$_4$ have high conduction band degeneracies of 6 and 7, respectively. High band degeneracy coupled with low band effective mass enhances charge transport properties for

![Fig. 5 Phonon dispersions of (a) NaAlSb$_4$, (b) NaGaSb$_4$, and (c) CsInSb$_4$ along the special k-point paths of the Brillouin zone of an orthorhombic lattice.](image-url)
thermoelectrics, including high carrier mobility (low band effective mass) and high thermopower (high DOS effective mass).

### 3.3 Predicted Thermoelectric Performance

Figure 7 presents the predicted \( n \)-type thermoelectric performance of the 13 stable ABX\(_4\) phases; the 7 newly predicted ABX\(_4\) phases are labeled. The computed intrinsic electron mobility (\( \mu_e \)) is plotted as a function of the lattice thermal conductivity (\( \kappa_L \)), with the color scheme representing the CB degeneracy (\( N_{\text{CB}} \)) in Figure 7(a) and the DOS effective mass (\( m_{\text{DOS,CB}} \)) in Figure 7(b). The size of the markers scales with \( n \)-type \( \beta \). The \( \beta \) for \( n \)-type PbTe is shown for reference in Figure 7(a). In general, we find that the 13 ABX\(_4\) phases exhibit low \( \kappa_L \) (<1.5 W/mK) and high \( \mu_e \) (75 to 150 cm\(^2\)/Vs), which indicates that ABX\(_4\) Zintl phases are promising \( n \)-type materials for thermoelectrics.

The predicted transport properties and TE performance assessment are summarized in Table 1, sorted in the descending order of their \( n \)-type \( \beta \) values. All 13 compounds in Table 1 have relatively high \( n \)-type TE performance - larger \( \beta \) than PbTe, when optimally doped. NaGaSb\(_4\) and NaAlSb\(_4\) stand out as the most promising candidates with the highest normalized \( \beta/\beta_{\text{PbTe}} \) of 4.8 and 4.5, respectively. The high predicted \( n \)-type TE performance of NaGaSb\(_4\) and NaAlSb\(_4\) can be primarily attributed to their high conduction band degeneracy of 7 and 6, respectively, which is larger than that of other ABX\(_4\) phases (\( N_{\text{CB}} = 2 \)). Coupled with moderately low CB effective mass (0.072 for NaAlSb\(_4\) and 0.090 for NaGaSb\(_4\)), the high band degeneracy leads to high DOS effective mass, as shown in Figure 7(b). The full assessment of transport properties and TE performance of the 13 ABX\(_4\) phases is available in the Supplementary Information. The data will be also made available on our thermoelectrics-focused open-access database, TEDesignLab (www.tedesignlab.org).

### 3.4 Defect Chemistry of ABX\(_4\) Zintl Phases

Although \( \beta \) serves to screen candidate TE materials, the successful prediction relies on a key assumption - the material must be optimally doped with electrons or holes, depending on \( n \)- or \( p \)-type TE. Materials with high \( \beta \) may be insulators or suffer from doping asymmetry. In such cases, the predicted TE performance cannot be realized. Therefore, we perform first-principles defect
Fig. 7 Calculated \( n \)-type quality factor (\( \beta \)) plotted as a function of the computed room-temperature electron mobility and lattice thermal conductivity. The marker size scales with the value of \( \beta \). For reference, the marker size corresponding to the \( \beta \) value of PbTe (15) is shown as a legend. The color scheme in (a) denotes the conduction band degeneracy \( (N_{\beta,\text{CB}}) \) while in (b) the conduction band density-of-states (DOS) effective mass \( (m'_{\text{DOS, CB}}) \). The 7 newly predicted stable \( \text{ABX}_4 \) Zintl phases are labeled.

calculations to assess the dopability of the newly predicted candidate \( \text{ABX}_4 \) phases.

For defect calculations, we select the top three candidate materials (\( \text{NaAlSb}_4 \), \( \text{NaGaSb}_4 \), \( \text{CsInSb}_4 \)) from Table 1 and assess their \( n \)-type dopability. These three candidate materials are composed of relatively earth-abundant and non-toxic elements. We assess the \( n \)-type dopability at the most alkali-rich condition within the phase stability region because the formation of the dominant electron-compensating, acceptor alkali vacancies is suppressed under those conditions. The acceptor cation vacancies, colloquially referred to as “killer defects”, compensate electron doping by extrinsic dopants. The existence of cation vacancies with low formation energy is the primary cause of self \( p \)-type doping or difficulty in \( n \)-type doping in Zintl phases.\(^{18}\) As such, Zintl phases where cation vacancies have high formation energies are considered \( n \)-type dopable. While \( n \)-type dopable Zintl phases are rare, we show here that our targeted search has enabled us to “design” as-yet-unknown Zintl phases with the desired doping characteristics as well as thermoelectric performance.

The calculated formation energies of native point defects (vacancies, anti-site defects and interstitials) in \( \text{NaAlSb}_4 \), \( \text{NaGaSb}_4 \) and \( \text{CsInSb}_4 \) under alkali-rich conditions are shown in Figure 8. The \( n \)-type dopability can be quantitatively assessed by \( \Delta E_{\text{don}} \) - which is the energy “window” at CBM formed by the lowest-energy acceptor defects. If \( \Delta E_{\text{don}} \) is large, then there is a better chance for \( n \)-type doping because of the limited electron compensation by the acceptor defects. The \( \Delta E_{\text{don}} \) for \( \text{NaAlSb}_4 \), \( \text{NaGaSb}_4 \) and \( \text{CsInSb}_4 \) are large and positive - 0.34 eV, 0.30 eV and 0.47 eV under alkali-poor growth condition, respectively. In contrast, \( \Delta E_{\text{don}} \) in well-known Zintl phases are typically negative.

For example, \( \Delta E_{\text{don}} \) for \( \text{Ca}_5\text{Al}_2\text{Sb}_6 \) is -0.1 eV.\(^{18}\)

**\( \text{NaAlSb}_4 \):** The formation energies (\( \Delta H_{\text{D},q} \)) of native point defects under Na-rich growth condition are shown in Figure 8(a). The lowest-energy acceptor defects are sodium vacancies \( \text{V}_{\text{Na}} \) and donors are anti-site defects \( \text{Sb}_{\text{Al}} \) and Na interstitials \( \text{V}_{\text{Na}} \). The equilibrium Fermi energy is usually in the vicinity of the intersection between the lowest-energy defects. In this case, the equilibrium Fermi energy lies around the mid-gap (marked by the dotted line in Figure 8). The predicted hole concentrations for undoped \( \text{NaAlSb}_4 \) is \( 6.5 \times 10^{17} \) cm\(^{-3} \) at 800 K. However, what is more important is the high formation energy of acceptor Na vacancies, which creates a large \( n \)-type dopability window \( \Delta E_{\text{don}} \) of 0.34 eV. Therefore, \( \text{NaAlSb}_4 \) is \( n \)-type dopable with high predicted \( n \)-type TE performance.

**\( \text{NaGaSb}_4 \):** The native defect energetics of \( \text{NaGaSb}_4 \) are similar to that of \( \text{NaAlSb}_4 \) (Figure 8b). The predominant native defects are \( \text{Sb}_{\text{Ga}} \), \( \text{Na} \) and \( \text{V}_{\text{Na}} \). The relatively high \( \Delta H_{\text{D},q} \) for \( \text{V}_{\text{Na}} \) creates a \( n \)-type dopability window of 0.30 eV. The smaller \( \Delta E_{\text{don}} \) can be attributed to the slightly wider band gap of \( \text{NaGaSb}_4 \) (0.374 eV) compared to \( \text{NaAlSb}_4 \) (0.357 eV). The equilibrium Fermi energy in undoped \( \text{NaGaSb}_4 \) under Na-rich conditions is closer to the valence band maximum, with an estimated free hole concentration of \( 9.4 \times 10^{17} \) cm\(^{-3} \) at 800 K synthesis temperature.

**\( \text{CsInSb}_4 \):** \( \text{CsInSb}_4 \) has a wider band gap (0.794 eV) than \( \text{NaAlSb}_4 \) and \( \text{NaGaSb}_4 \) due to the higher electronegativity difference between Cs and In. The native defect energetics of \( \text{CsInSb}_4 \) at Cs-rich growth condition are shown in Figure 8(c). The alkali vacancies \( \text{V}_{\text{Cs}} \) have even higher formation energy than \( \text{V}_{\text{Na}} \) in \( \text{NaAlSb}_4 \) and \( \text{NaGaSb}_4 \). Consequently, the \( n \)-type dopability window (\( \Delta E_{\text{don}} \)) of 0.47 eV is quite large. Thus, \( \text{CsInSb}_4 \) is likely more \( n \)-type dopable than \( \text{NaAlSb}_4 \) or \( \text{NaGaSb}_4 \). In contrast with \( \text{NaAlSb}_4 \) and \( \text{NaGaSb}_4 \), \( p \)-type dopability of \( \text{CsInSb}_4 \) is limited by the low energy donor \( \text{Sb}_{\text{Al}} \) anti-site defects under Cs-rich growth conditions. Undoped \( \text{CsInSb}_4 \) is predicted to be lightly \( p \)-type with free hole concentration of \( 1.9 \times 10^{17} \) cm\(^{-3} \), assuming synthesis at 800 K.
In summary, we find the three newly predicted ABX₄ Zintl phases, namely, NaAlSb₄, NaGaSb₄, and CsInSb₄, to be n-type dopable. Among these three candidates, CsInSb₄ has the largest n-type dopability window of 0.47 eV followed by NaAlSb₄ (0.34 eV) and NaGaSb₄ (0.30 eV). Further work will explore possible extrinsic donor dopants to achieve optimal n-type doping that maximize the thermoelectric performance. In a prior study⁰, we found Ba to be an effective n-type dopant for KGaSb₄, with free electron concentrations exceeding 1×10¹⁹ cm⁻³. This suggests that it may be possible to find suitable n-type dopants for the candidate phases, NaAlSb₄, NaGaSb₄, and CsInSb₄. The demonstration of n-type dopability of the new ABX₄ Zintl phases, constructed by chemical replacements, provides further confidence in the “doping by design” strategy undertaken in this study.

4 Conclusions

In this work, we utilize a new route to “design” materials with desired doping and functional characteristics. We hypothesize that the doping properties and functional performance of the prototype structure are translated to the new compounds created by chemical replacements, and we demonstrate this design strategy by discovering new n-type dopable ABX₄ Zintl phases. We perform first-principles calculations to explore 36 hypothetical ABX₄ Zintl phases in the KGaSb₄ structure, where A = Na, K, Cs, Rb, B = Al, Ga, In, and X = Sb, As, Bi, and assess their stability and n-type TE performance. We find 13 stable ABX₄ phases, including 6 known and 7 as-yet-unreported ABX₄ phases. Among the newly discovered phases, we consider the top candidates (NaAlSb₄, NaGaSb₄, CsInSb₄) with highest predicted n-type TE performance, and show that they are n-type dopable. The “doping by design” strategy demonstrated in this work offers an exciting route to discover new compounds with desired doping and functional performance and can be extended to discover new materials with applications beyond thermoelectrics.

Acknowledgements

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References

Electronic Supplementary Information:

Doping by Design: Finding New n-type ABX$_4$ Zintl Phases for Thermoelectrics

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1. Fitted Elemental-Phase Reference Chemical Potentials

The fitted elemental-phase reference energies used in calculating the phase stability region ($\mu^0_i$ in Eq. 2):

- Li: -1.74 eV
- Na: -1.24 eV
- K: -1.14 eV
- Rb: -0.82 eV
- Cs: -0.96 eV
- Al: -3.55 eV
- Ga: -3.12 eV
- In: -2.62 eV
- As: -4.59 eV
- Sb: -4.11 eV
- Bi: -4.19 eV

2. ABX$_4$ Structures from ICSD Considered for Assessing Structural Stability

RbAlF$_4$ (123), KAI$_4$ (123), CuGaCl$_4$ (112), CuGaI$_4$ (82), CuAuSe$_4$ (11), CuAlCl$_4$ (112), CuAlBr$_4$ (112), AgAuTe$_4$ (13), RbFeF$_4$ (127), NaMnF$_4$ (14), CsCrF$_4$ (189), RbFeF$_4$ (18), KAI$_4$ (11), KFeF$_4$ (63), RbMnF$_4$ (14), RbFeF$_4$ (57), CsFeF$_4$ (129), TlAI$_4$ (15), TlAI$_4$ (140), LiMnO$_4$ (63), NaTiF$_4$ (60), KAuI$_4$ (14), KAuCl$_4$ (14), RbAlF$_4$ (59), LiAuF$_4$ (13), LiAuF$_4$ (15), CsAuF$_4$ (71), CsMnF$_4$ (85), AlInI$_4$ (11), TlMnF$_4$ (15), KTlF$_4$ (144), KScF$_4$ (12), KFeF$_4$ (31), CsReBr$_4$ (61).

Numbers in parentheses denote the space group number.

3. Γ-point Frequencies of Phonon Modes

Table S1: Γ-point phonon frequencies of the 13 Zintl phases predicted to be stable in the KGaSb$_4$ structure type, given in THz. Only the 10 lowest frequency modes are shown, including the three acoustic modes.

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<th>6</th>
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4. Electronic Structures of Stable ABX₄ Zintl Phases

![Graph](image)

Figure S1: Electronic structures (GGA-PBE) of KGaAs₄, KInSb₄, NaGaAs₄, and RbInSb₄ along the special k-point paths of the Brillouin zone.
5. Predicted Thermoelectric Performance

Table S2: Computed electronic structure and transport parameters, and thermoelectric performance of 13 ABX$_4$ Zintl phases that are predicted to be stable in the KGaSb$_4$ structure. $\beta$ is referenced to $\beta$ of PbTe (15 for both $p$- and $n$-type). $\beta_p$ and $\beta_n$ are $p$- and $n$-type thermoelectric quality factor, $E_g$ is DFT band gap, $B$ is bulk modulus, $m^*_{\text{DOS,VB}}$ and $m^*_{\text{DOS,CB}}$ are density-of-states effective masses of valence and conduction bands, $N_{b,\text{VB}}$ and $N_{b,\text{CB}}$ are valence and conduction band degeneracies, $\mu_p$ and $\mu_n$ are room-temperature hole and electron mobilities, and $\kappa_L$ is room-temperature lattice thermal conductivity.

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<th>Phases</th>
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<th>$\beta_n$/$\beta_{\text{PbTe}}$</th>
<th>$E_g$ (eV)</th>
<th>$B$ (GPa)</th>
<th>$m^*_{\text{DOS,VB}}$ (m$_e$)</th>
<th>$m^*_{\text{DOS,CB}}$ (m$_e$)</th>
<th>$N_{b,\text{VB}}$</th>
<th>$N_{b,\text{CB}}$</th>
<th>$\mu_p$ (cm$^2$/Vs)</th>
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<th>$\kappa_L$ (W/mK)</th>
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