A Simple Chemical Guide for Finding Novel n-type Zintl Pnictide Thermoelectric Materials

Average Oxidation State of Pnictide Anion

-3
-2
-1

Known Zintl thermoelectric materials

- n-type
- p-type

Likely n-type dopable Zintl phases

Easy to calculate from stoichiometry
A Simple Chemical Guide for Finding Novel n-type Dopable Zintl Pnictide Thermoelectric Materials†

Prashun Gorai,†a Anuj Goyal,†a Eric S. Toberer,b and Vladan Stevanović†a

Computations have predicted good thermoelectric performance for a number of Zintl phases when doped n-type. Combined with the successful experimental realization of n-type KGaSb4, KAlSb4, and Mg2Sb2 with \( zT \geq 1 \), this has fueled efforts to discover novel n-type dopable Zintl phases. However, a majority of Zintl phases exhibit strong proclivity toward p-type doping and prior successes in finding n-type dopable Zintls were largely serendipitous. Herein we use modern first-principles defect calculations to study trends in the dopability of Zintl pnictides and find that the average oxidation state of the anion is a useful chemical guide to identify novel n-type dopable phases. Specifically, we observe that Zintl pnictides with average oxidation of the anion near -1 are n-type dopable. The trend is mainly a consequence of the high formation energy of native acceptor defects (e.g. cation vacancies) and the resulting absence of charge (electron) compensation. Using the oxidation state guide in conjunction with a descriptor of thermoelectric performance, we conduct a large-scale materials search and identify promising candidates that are n-type dopable.

keywords: thermoelectrics, Zintls, doping, materials discovery, transport properties

1 Introduction

Zintl phases are composed of electropositive cations (alkali, alkaline, or rare-earth elements) that are ionically bonded to a polyanionic framework,1 as shown for KGaSb4 in Figure 1. Zintl phases continue to intrigue chemists because of their unique characteristics, including dispersive bands, small band gaps,2 and weakly bound cations.3 Together, these yield materials with excellent charge transport and poor phonon transport. These attributes make Zintl phases particularly suitable for thermoelectric applications.4-15 Indeed, they are among the best thermoelectric materials, with demonstrated thermoelectric figure of merit \( zT > 1 \) for p-type Yb4MnSb14,14 Ca6Zn4+xSbx,15 Ca6.3Yb3.5Mg2Bi2,16 and Ba8Ga16Ge30.17 While Zintl phases, in general, span a diverse range of chemistries, many Zintl thermoelectric materials are pnictides, i.e., compounds containing group 15 anions such as As, Sb, and Bi. It is for this reason that we focus on Zintl pnictides in this study.

It is not surprising that Zintl pnictides exhibit good thermoelectric performance for p-type doping because the majority of them are, as grown, natively p-type due to self-doping. Examples of p-type Zintl pnictides include the “14-1-11” phases16 (e.g. Yb14MgBi11), “1-2-2” phases19 (e.g. SrZn2Sb2), “5-2-6” phases12 (e.g. Ca4Al2Sb6), “16-11” phases20 (e.g. Ca16Bi11) etc. Hence, efforts to improve their thermoelectric performance have focused mainly on optimizing hole conductivity through extrinsic doping. Few attempts have been made to dope Zintl pnictides n-type; it is only recently that n-type doping has been experimentally demon-

† Electronic Supplementary Information (ESI) available

aMetallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401. bPhysics, Colorado School of Mines, Golden, CO 80401. †E-mail: pgorai@mines.edu, vstevano@mines.edu

† Electronic Supplementary Information (ESI) available

strated in a handful of Zintl phases. The most prominent example is n-type Mg2Sb2 with a maximal achieved \( zT \) in excess of 1.5,21,22 followed by n-type KAlSb423 and KGaSb424 with \( zT \approx 1 \), which was achieved without optimization of the transport properties. However, the discovery of these n-type dopable Zintl pnictides was largely serendipitous and driven mainly by chemical intuition. An accurate and quantitative understanding of the dopability Zintl pnictides is still lacking. Interestingly, the potential for good thermoelectric performance of Zintl pnictides, if doped n-type, was first suggested in computational searches23,25 and subsequently, validated through experiments.23-25

The observed strong proclivity of Zintl pnictides toward p-type conductivity is generally due to the facile formation of native ac-

Image 335x291 to 510x431

Fig. 1 Crystal structure of a Zintl phase, KGaSb4, with an anionic framework composed of GaSb4 tetrahedra linked by Sb-Sb bonds and the interstices filled with electropositive K cations.
ceptor defects, typically cation vacancies – they act as “killer” defects by charge compensating electrons from native and extrinsic donors. The facile formation of cation vacancies is plausibly a consequence of the weak chemical bonding of the cations to the anionic framework. Conversely, cation vacancies likely have high formation energies in n-type dopable Zintl pnictides, which prevents electron compensation.

In this work, we use modern defect theory and first-principles defect calculations to investigate the dopability and the existence of design principles for n-type doping of Zintl pnictides. These design principles could be used in conjunction with descriptors of thermoelectric performance to advance the computational search for novel Zintl thermoelectric materials. We identify a simple, yet effective, chemical guide that correlates with the n-type dopability of Zintl pnictides. Specifically, we observe that Zints with average oxidation state of the anion (pnictogen) near -1 are n-type dopable. This observation follows from the analysis of the chemical composition of n-type dopable Zintl pnictides, as determined from our defect calculations. Interestingly, we find that in Zintl pnictides with average pnictide oxidation state near -1, the formation of cation vacancies is suppressed, which makes them n-type dopable. The relatively high formation energy of the cation vacancies in these Zintl pnictides is likely due to their cation-poor chemical compositions such that formation of cation vacancies is energetically unfavorable. In contrast, known p-type dopable Zintl phases have cation-rich compositions, where cation vacancies form readily. We utilize our chemical guide in combination with a previously developed descriptor of thermoelectric performance in a large-scale materials search and identify novel n-type dopable Zintl pnictides that are promising for thermoelectric applications. Furthermore, we confirm the n-type dopability of three candidate materials through direct defect calculations.

2 Results and Discussion

The dopability of a semiconductor, which is quantified as the achievable carrier type(s) and concentrations, depends on several factors, including the native defect energetics and the existence of dopants with sufficient solubility and desired electronic properties. Here, we focus on native defects under various growth conditions and how they allow or prevent the desired doping.

2.1 Role of Native Defects in Dopability

With the advent of first-principles computations, the formation energetics of point defects can be reliably calculated with standard methods such as the supercell approach. The defect formation energy is calculated as:

$$\Delta H_{D,q} = (E_{D,q} - E_H) + qE_F + \sum_{i} n_i \mu_i + E_{corr}$$

where $E_{D,q}$ and $E_H$ are the total energies of the supercell containing defect $D$ in charge state $q$ and the defect-free host supercell, respectively. $E_F$ is the Fermi energy and $E_{corr}$ comprises all the finite-size corrections that are applied within the supercell approach. The dependence of the formation energy on the phase stability and growth conditions is captured by the term $\sum_{i} n_i \mu_i$.

The chemical potential of element $i$ is denoted by $\mu_i$ and $n_i$ is the number of atoms of element $i$ added ($n_i<0$) or removed ($n_i>0$) from the supercell. Conventionally, the elemental chemical potential $\mu_i$ is expressed relative to the reference elemental phase as $\mu_i = \mu_i^0 + \Delta \mu_i$, where $\mu_i^0$ is the reference chemical potential under standard conditions and $\Delta \mu_i$ is the deviation from the reference chemical potential. $\Delta \mu_i = 0$ corresponds to $i$-rich growth conditions while large negative values of $\Delta \mu_i$ correspond to $i$-poor growth conditions. The bounds on $\Delta \mu_i$ for a given material are set by the region of phase stability. Further computational details are provided in the Methods section.

Computed defect energetics are typically presented in the form of a “defect diagram” – formation energies ($\Delta H_{D,q}$) of defects plotted as functions of Fermi energy ($E_F$) (see following sections for several examples). For each defect, the trace corresponding to the charge state with lowest $\Delta H_{D,q}$ at a given Fermi energy is drawn. The slope of the trace is the charge state of the defect because of the linear dependence in Eq. 1. Defects with positive and negative slopes are donors and acceptors, respectively, while those with zero slope are charge neutral. As described above, the defect energetics also depends on the growth conditions, which is quantified by the $\Delta \mu$ of each of the elements present in the compound. Therefore, a different “defect diagram” exists for each unique growth conditions.

Under a given growth condition, the equilibrium $E_F$ and the corresponding free carrier concentration is determined by solving the condition of charge neutrality. The concentration of donor and acceptor defects are determined using a Boltzmann distribution, such that $N_{D,q} = N_{B}e^{-\Delta H_{D,q}/k_B T}$, where $N_{D,q}$ is the defect concentration, $N_{B}$ is the concentration of lattice sites where the defect can be formed, $k_B$ is the Boltzmann constant, and $T$ is the temperature. Here, $\Delta H_{D,q}$ is a function of $E_F$ (“defect diagram”). The concentrations of donors and holes at a given $T$ are also functions of $E_F$. To establish charge neutrality, the total positive charges should equal the negative charges. In this equation, at a given temperature, the Fermi energy is the only free parameter. Solving the charge neutrality condition self-consistently yields the equilibrium $E_F$; the corresponding free carrier concentration can then be determined straightforwardly. In computing the carrier concentration, typically, the synthesis temperature is used because it is assumed that the defect concentrations at higher temperatures are “frozen-in” (quenched). A change in the defect concentrations require significant atomic rearrangement, which is likely to be kinetically limited at low temperatures.

The dopability of a material is often limited by their native defects. For instance, when acceptor defects with low formation energy (high concentration) are present, the material can be only doped p-type; in such cases, n-type doping may lead to low free electron concentration or it may not be possible altogether. Such acceptor defects are colloquially termed electron “killers” because they limit n-type doping.

2.2 Defect Chemistry of p-type Zintl Pnictides

Many well-known Zintl phases, such as CaAl$_2$Sb$_6$ and CaZn$_2$Sb$_2$, are examples of materials where cation vacancies act as “killer”...
defects to limit n-type doping. Conversely, the absence of acceptor defects with low formation energy presents an opportunity for n-type doping. Analogous arguments can be drawn for the role of native donor defects in p-type dopability. As discussed earlier, defect energetics and therefore, dopability, is also a function of the growth conditions expressed in terms of the chemical potentials of the constituent elements. A material may also be both n- and p-type dopable under all growth conditions or n-type dopable under certain growth conditions while p-type under another growth condition. KGaSb, a recently discovered Zintl thermoelectric material, is an example of the former while PbTe and Mg$_3$Sb$_2$ are examples of the latter. More specifically, Mg$_3$Sb$_2$ is doped p-type when grown under Mg-poor conditions and n-type under Mg-rich conditions.

The pervasiveness of electron “killer” defects in Zintl pnictides has been extensively documented and characterized through both experiments and theory. A Zintl pnictide that is notorious for being degenerately p-type under all growth conditions is LiZnSb. In 2006, Madsen performed one of the first high-throughput computational searches for identifying thermoelectric materials – LiZnSb emerged as a promising n-type candidate. However, the computational search, like other computational searches that followed, was agnostic of material dopability. Subsequent experimental efforts to dope LiZnSb n-type were futile; even lowering the hole concentration to below $10^{20}$ cm$^{-3}$ proved daunting. In the absence of detailed defect characterization or calculated formation energetics, it was speculated that facile formation of one of the cation vacancies (V$_{Li}$ or V$_{Zn}$) resulted in degenerate hole doping.

To quantitatively understand the role of native defects in the p-type behavior of LiZnSb, we performed first-principles calculations – the computed defect energetics are presented in the form of a “defect diagram” in Figure 2(a). It is evident that acceptor Li vacancies (V$_{Li}$) have low formation energy even at the most Li-rich conditions allowed by the phase stability (equilibrium with Li$_3$Sb) with $\Delta H_{F,a} = -0.98$ eV. The formation energy of V$_{Li}$ is noticeably small such that the equilibrium Fermi energy at 873 K lies inside the valence band and the free hole concentrations are in the degenerate limit ($6 \times 10^{39}$ cm$^{-3}$). The corresponding V$_{Li}$ concentration is ~4% of the Li site concentration, which is consistent with the observed significant off-stoichiometry in LiZnSb.

The defect energetics presented in Figure 2(a) correspond to growth under relatively Li-rich conditions – this is intentional because the formation energy of V$_{Li}$ is highest under the most Li-rich conditions and provides the lower bound for the hole concentration. From another perspective, the Li-rich conditions offer the best scenario to gauge opportunities for n-type doping of LiZnSb. Given the facile formation of the “killer” defect V$_{Li}$, it is not possible to n-type dope LiZnSb, at least under equilibrium growth conditions.

To further our understanding of defect-limited dopability of Zintl pnictide phases, we consider the well-known Ca$_3$M$_2$Sb$_3$ family (M = Al, Ga, In) of p-type thermoelectric materials. The
structure contains 1-D chains of corner-sharing MSb$_4$ tetrahedra that are linked by Sb-Sb bonds and interspersed with Ca cations. Specifically, we calculated the native defect energetics of Ca$_3$Al$_2$Sb$_6$. Under both Ca-rich (Figure 2b) and Ca-poor conditions, we find that the acceptor-type Ca vacancies (V$_{\text{Ca}}$) are the lowest-energy defects and Ca$_3$Al$_2$Sb$_6$ is natively $p$-type, consistent with experiments. The high formation energy of the lowest-energy donor V$_{\text{Sb}}$ should facilitate extrinsic $p$-type doping. Indeed, Ca$_3$Al$_2$Sb$_6$ is known to be degenerately $p$-type doped with Na. Additionally, it is known from experiments that M-site substitutions do not noticeably influence the hole concentrations, which further corroborates that Al vacancies, in fact, are not the predominant defects. As in the case of LiZnSb, the “killer” cation vacancies limit $n$-type doping of Ca$_3$Al$_2$Sb$_6$. However, the formation energy of Ca vacancies at Ca-rich conditions is not as low as Li vacancies in LiZnSb.

Finally, we examine the native defect chemistry of CdSb, the lesser-known cousin of ZnSb – a material that has been widely investigated for thermoelectrics. CdSb possess the same orthorhombic structure as ZnSb and features the characteristic Sb-Sb covalent bonds (Figure 2c). As in the previous two examples, the cation vacancies (V$_{\text{Cd}}$) are the lowest-energy defects (Figure 2c) such that CdSb is natively $p$-type under Cd-rich as well as Cd-poor growth conditions. The defect chemistry of CdSb is similar to that of ZnSb, where the presence of large concentrations of Zn vacancies lead to degenerate hole doping. In summary, the doping asymmetry of many Zintl pnictides that are only $p$-type doped (Figure 4) is attributed to the low formation energy of cation vacancies that act as electron “killers” and hinder $n$-type doping.

### 2.3 Defect Chemistry of Known $n$-type Dopable ZintlS

Given the general scarcity of $n$-type ZintlS, not much is known about their defect chemistry. Also, how the defect chemistry of $n$-type dopable ZintlS differ from the persistently $p$-type ZintlS (Section 2.2) remains to be understood. In this section, we present the computed defect energetics of two Zintl pnictides that are known to be $n$-type dopable: (1) KGaSb$_4$, which has been experimentally confirmed to be extrinsically dopable $n$-type with Ba, and (2) CdAs$_2$, an $n$-type Zintl with low electron concentrations in self-doped samples. The calculated defect diagrams along with the crystal structures are shown in Figure 3.

KGaSb$_4$ possess a tunnel-like structure formed by the anionic framework of GaSb$_4$ tetrahedra that are linked by Sb-Sb bonds (Figure 3a). The cation (K) occupies the large interstitial voids created by the tunnel structure. We have previously demonstrated through theory and experiments that $n$-type KGaSb$_4$ can be realized via Ba doping resulting in electron concentrations of $\sim 10^{19}$ cm$^{-3}$. At first glance, the defect energetics of KGaSb$_4$ (Figure 3a) has one striking difference compared to the $p$-type ZintlS discussed in Section 2.2 – the formation energy of all the defects is significantly higher in KGaSb$_4$, which has important implica-

---

Fig. 3 Formation energies of native defects ($\Delta H_{\text{D},q}$) as functions of Fermi energy ($E_F$) for (a) KGaSb$_4$, and (b) CdAs$_2$ under K-rich, and Cd-rich growth conditions, respectively. The corresponding crystal structures are shown above. $E_F$ is referenced to the valence band maximum. The upper limit of $E_F$ shown is the conduction band minimum such that $E_F$ values range from 0 to the band gap. Multiple lines of the same color represent the same defect type at different Wyckoff sites. $\Delta H_{\text{D},q}$ of some defects, particularly interstitials, are outside the energy window shown. In these materials, the formation energies of cation vacancies are relatively higher compared to the Zintl phases in Figure 2, which facilitates extrinsic $n$-type doping.
tions for dopability. The lowest energy acceptor, as in p-type Zintl pnictides, is the cation vacancy (V\text{K}). However, the formation energy of acceptor V\text{K} is fairly high such that their concentrations will be low, which will not hinder extrinsic n-type doping. The formation energy of V\text{K} is the highest under K-rich conditions (Figure 3a) offering the best opportunity to extrinsically n-type dope KGaSb\text{4}. Another interesting observation from Figure 3(a) is that the lowest-energy native donor, the antisite Sb\text{Ga}, also has a relatively high formation energy. This implies KGaSb\text{4} should also allow extrinsic p-type doping. Indeed, we have previously confirmed that KGaSb\text{4} is p-type doped with Zn,\textsuperscript{24} albeit the hole concentrations are lower than electron concentrations in n-type samples, consistent with the differences in formation energy of V\text{K} and Sb\text{Ga} at the CBM and VBM, respectively. The lower hole concentrations in p-type samples can be attributed to the lower formation energy of Sb\text{Ga} compared to V\text{K} – some hole compensation by donor Sb\text{Ga} likely occurs when doped with Zn. Therefore, the defect calculations reveal that n-type doping of KGaSb\text{4} is enabled by the high formation energy of the otherwise “killer” acceptor cation vacancies.

Figure 3(b) shows the formation energies of the native defects in the binary Zintl phase, Cd\text{As}_2, under assumed Cd-rich growth conditions. The defect chemistry of Cd\text{As}_2 is qualitatively similar to KGaSb\text{4} in that the cation vacancies (V\text{Cd}) have relatively high formation energies. In fact, the formation energy of V\text{Cd} at the conduction band minimum (CBM) is even higher than that of V\text{K} in KGaSb\text{4}. As a result, extrinsic n-type doping of Cd\text{As}_2 grown under metal-rich conditions is very promising. Under Cd-rich conditions (Figure 3b), Cd\text{As}_2 is predicted to be natively p-type with low free electron concentration of \(2 \times 10^{17}\) cm\(^{-3}\) (\(T = 873\) K). Available experimental reports confirm that self-doped Cd\text{As}_2 is indeed an n-type material with \(\sim 10^{17}\) cm\(^{-3}\) free electron concentration.\textsuperscript{27} It is also possible to realize p-type Cd\text{As}_2 via extrinsic doping because the formation energies of compensating donors, V\text{As}, and antisite As\text{Cd} at the valence band maximum (VBM) under Cd-poor growth conditions are also relatively high.

In summary, we find that (1) the cation vacancies are one of the lowest-energy native acceptor defects, (2) the formation energies of cation vacancies are high, and (2) the Zintl phases may also be p-type dopable, making them good candidate materials for fabricating both n- and p-type legs of a thermoelectric device. Interestingly, we observe that the chemical compositions of KGaSb\text{4} and Cd\text{As}_2 are cation-poor; in contrast, the chemical compositions of known p-type Zintl pnictides are generally cation-rich (e.g. Ca\text{Al}_2Sb\text{6}). As a consequence, we find that the average oxidation state of the pnictide (Sb, As) is -1 in KGaSb\text{4} and Cd\text{As}_2, which are both n-type dopable. In comparison, the average pnictide oxidation state in known p-type Zintl phases is further from -1. For instance, -3 and -2 in LiZnSb and CdSb, respectively. To further build upon this observed correlation between n-type dopability and average pnictide oxidation state, we surveyed the experimental literature of Zintl pnictides, which is discussed next.

<table>
<thead>
<tr>
<th>avg. oxidation state of Pn</th>
<th>[charge carrier]</th>
<th>[electron]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The literature data in Figure 4 presents the experimentally measured charge carrier (electrons, holes) concentrations of 40 Zintl pnictides as a function of the average oxidation state of the pnictide (Pn) anion. The average oxidation state of Pn is calculated by assuming the formal oxidation state of the cations and dividing the total positive valence with the number of Pn atoms. For example, in Ca\text{Zn}_6Sb\text{14}, the formal oxidation states of Ca and Zn are 2+, such that the total positive valence is 9×2+4×2 = 26, and therefore, average oxidation state of Pn is \(-26/9 = -2.89\). Similarly, in KGaSb\text{4}, the average oxidation state of Pn is -(1+3)/4 = -1.

The literature data in Figure 4 is intriguing in that it presents a rather useful demarcation between Zintl pnictides with experimentally-verified n-type dopability (measured electron concentrations) and those for which data on n-type doping is not available. We find that all Zintl compounds with -1 average oxidation state of the pnictide (e.g. As, Sb, Bi) are n-type dopable, while those with average oxidation state less than -1 show privity for p-type doping. Therefore, the average oxidation state of the anion, which can be straightforwardly determined from the stoichiometry, seems to be a simple predictor of n-type dopability of Zintl pnictides and as such, could potentially be used as a chemical guide for rapidly identifying n-type dopable Zintl. Mg\text{Sb}_2, with -3 average oxidation state of Sb, is the only outlier that has been successfully doped n-type by growing the material under Mg-rich conditions.\textsuperscript{63} Considering Mg\text{Sb}_2 as a Zintl phase, which has been debated,\textsuperscript{64} the data in Figure 4 indicate that while it may be possible to find n-type dopable Zintl pnictides that disobey the oxidation state guide, the likelihood increases as the average pnictide oxidation state approaches -1.

We know from existing experimental studies that there are a few Zintl pnictides that do not suffer from the p-type doping
asymmetry (Figure 4). These include CoSb$_3$, KGaSb$_4$, KAlSb$_4$, and Mg$_3$Sb$_2$ that have been doped both $p$- and $n$-type.$^{21,24,31,44}$ ZnAs$_2$ and CdAs$_2$ are reported only as $n$-type$^{37}$ with lower electron concentrations of $\sim 10^{17}$ cm$^{-3}$. We observe that the known $n$-type dopable Zintl pnictides, with the exception of Mg$_3$Sb$_2$, all share a simple common feature – the average oxidation state of the pnictide ($Pn$) in these materials are small negative values (Figure 4). Specifically, the $Pn$ average oxidation state is near -1 in $n$-type dopable Zintls whereas in most other Zintl phases, the oxidation states range from -2 to -3.

A few preliminary observations that emerge from Figure 4 are: (1) the average $Pn$ oxidation state seems to suggest that the likelihood of finding $n$-type dopable Zintl pnictides increases for metal-poor chemistries, which offers a simple chemical guide to discover $n$-type dopable Zintl phases, (2) the chemical guide needs to be further tested because the empirical data for $n$-type Zintls is comparatively sparse, and (3) given that $n$-type Mg$_3$Sb$_2$ has been realized, it is plausible to discover $n$-type Zintls even when the $Pn$ average oxidation state is not close to -1. Regarding Mg$_3$Sb$_2$, it appears from the data in Figure 4 that the likelihood of discovering $n$-type dopable Zintls is higher when the $Pn$ average oxidation state is near -1. Additionally, there is an ongoing debate on whether Mg$_3$Sb$_2$ can be considered a Zintl phase.$^{64}$

It is not immediately obvious how the $Pn$ average oxidation state is related to the $n$-type dopability of Zintl pnictides. The high formation energy of "killer" cation vacancies is what makes certain Zintl pnictides $n$-type dopable. According to Eq. 1, the formation energy of cation vacancies ($V_{\text{cation}}$) depends on the energy difference between the defect and host supercells ($E_{D,q} - E_H$) and the chemical potential of the cation ($\mu_{\text{cation}}$). The Fermi energy ($E_F$) is treated as a free parameter. It is not straightforward to deconvolute the energetic contributions of $E_{D,q} - E_H$ and $\mu_{\text{cation}}$ to $V_{\text{cation}}$ formation energy (Eq. 1) for a wide range of chemistries; however, a plausible explanation for the relation between the average oxidation state and $n$-type dopability can be gleaned from the stoichiometry of the Zintl phases.

Zintl pnictides with $Pn$ average oxidation state near -1 have uniquely cation-poor chemical compositions; in contrast, $p$-type Zintl pnictides are cation-rich. For example, in KGaSb$_4$ and CdAs$_2$, the metal-to-pnictide ratio is 0.5 while in LiZnSb, Ca$_3$Al$_2$Sb$_6$, and CdSb the ratios are 2, 1.2, and 1, respectively. These $n$-type dopable Zintl pnictides already have cation-poor compositions and formation of cation vacancies would further deplete their cation content, which is likely associated with a stiff energetic cost. As a result, the formation energy of "killer" cation vacancies in cation-poor Zintl pnictides is energetically unfavorable, which creates opportunities for $n$-type doping of these phases. An analogous example of this effect in non-Zintl chemistries is observed in SnO and SnO$_2$ – the former has a relatively cation-rich composition compared to the latter. While formation of Sn vacancies ($V_{\text{Sn}}$) in SnO is facile,$^{65,66}$ the formation of $V_{\text{Sn}}$ in SnO$_2$ is unfavorable.$^{67,68}$

Based on the curated experimental data (Figure 4), and first-principles defect calculations presented in Sections 2.2, and 2.3, the proposed chemical guide appears promising for rapid identification of $n$-type dopable Zintl pnictides. In the next section

---

![Zintl pnictides in ICSD](image)

**Fig. 5** 900 Zintl phases identified from the ICSD denoted by the number of atoms in the primitive cell and the maximum electronegativity difference between the constituent elements. Well-known Zintl phases (e.g. ZnSb, Ca$_3$Al$_2$Sb$_6$, CaZn$_2$Sb$_2$, KSnSb) are correctly identified. Red markers denote those Zintl phases where the pnictide average oxidation state is near -1 – based on our proposed chemical guide, these Zintl compounds are predicted to be dopable $n$-type. Complete list of 900 Zintls phases is documented in the ESI.

(Section 2.5), we perform a large-scale search to identify Zintl pnictides that are predicted to exhibit good $n$-type thermoelectric performance, and expected to be $n$-type dopable based on their $Pn$ average oxidation state. For three identified candidate materials, we confirm their $n$-type dopability through first-principles defect calculations, providing further confidence to this approach. To truly demonstrate the usefulness of the approach, we call upon the experimentalists to: (1) synthesize and characterize the promising Zintl pnictides identified in Section 2.5, and (2) perform targeted synthesis of new, undiscovered Zintl phases that satisfy the oxidation state guide. To realize the latter, one may consider chemical substitutions in known Zintl phases with $Pn$ average oxidation state near -1.

### 2.5 Search for $n$-type Dopable Zintl Pnictides with Promising Thermoelectric Performance

Traditionally, computational searches for novel thermoelectric materials using descriptor-based approaches have either overlooked material dopability altogether$^{26,34}$ or assessed the dopability of the identified candidates post-search through first-principles defect calculations or experimental doping studies.$^{24,69}$ While dopability can be reliably assessed with first-principles defect calculations, their practical implementation is
still computationally expensive such that it cannot be performed for a large set of candidate materials. In this work, the proposed chemical guide for identifying n-type dopable Zintl pnictides presents a unique opportunity to assess material dopability prior to gauging their thermoelectric performance – this is enabled by the simplicity of the chemical guide. With the chemical guide, it is possible to rapidly search vast chemical spaces, which would not be possible even with computationally-tractable descriptors of thermoelectric performance such as $\beta$. 

With the goal of accelerating the discovery of n-type Zintl thermoelectric materials, we performed a broad search within ~40,000 stoichiometric and ordered structures reported in the Inorganic Crystal Structure Database (ICSD) to identify candidate n-type dopable Zintl pnictides that are predicted to exhibit good thermoelectric performance. The search was a three-step process involving: (1) automated search of Zintl pnictide structures, (2) identification of Zintl pnictides that are predicted to be dopable n-type according to the chemical guide, and (3) assessment of the thermoelectric performance of the n-type dopable Zintl pnictides to identify promising candidates.

The methodology for automated search of Zintl pnictide structures is presented in the Methods section. Using the $Pn$-$Pn$ bond as a structural search criteria, we identified 185 binary (78 arsenides, 73 antimonides, 34 bismuthides), and 160 ternary (50 arsenides, 84 antimonides, 26 bismuthides) compounds. The automated search correctly identifies well-known Zintl compounds such as ZnSb, Mo$_3$Sb$_7$, Ca$_3$Al$_2$Sb$_6$, Yb$_2$MnSb$_4$, and that have been widely studied as thermoelectric materials. In addition, we identified 555 ternary polar intermetallics, which can be classified as Zintls. Well-known phases such as CaZn$_2$Sb$_2$ and KSnSb are correctly identified. The 900 identified Zintl phases are shown in Figure 5, represented by the number of atoms in the primitive cell and the maximum of the electronegativity (Pauling) differences between pairwise combinations of the constituent elements.

Among the 900 structures, we identified 67 compounds where the pnictide (As, Sb, Bi) average oxidation state is -1 or higher (red markers in Figure 5) – according to our chemical guide, these Zintl phases are likely n-type dopable. For compounds containing cations that assume multiple oxidation states, especially those containing transition metals, the highest oxidation state of the metal was used to determine the average oxidation state of the pnictide. This identification of potentially n-type dopable candidate materials was designed to be conservative. It is notable that these potentially n-type dopable Zintl phases cluster on the right side of Figure 5 corresponding to larger values of maximum electronegativity difference. From a materials design perspective, the chemical guideline to realize Zintl phases with pnictide average oxidation state of -1 or higher seems to require that the cation be highly electropositive.

Of the 67 Zintl phases, 43 have finite DFT-calculated band gap, for which we computationally assessed their potential for thermoelectric performance using our previously-developed descriptor $\beta$ (see Refs. 26 and 71 for details). The larger the value of $\beta$, the better the predicted thermoelectric performance. The value of $\beta$ for the assumed n-type doped materials, expressed relative to the n-type $\beta$ of PbTe, is presented in Table 1 for the candidate Zintl phases with relative $\beta_n/\beta_{\text{PbTe}}$ of 0.5 and greater. Also, other computed properties such as band gap ($E_g^\text{b}$), conduction band density of states effective mass ($m^*_{\text{DOS,CB}}$), and modeled lattice thermal conductivity ($k_\text{L}$) and intrinsic electron mobility ($\mu_i$) in cm$^2$/Vs. $\beta_n$ is expressed relative to the $\beta$ of n-type PbTe.

<table>
<thead>
<tr>
<th>compound</th>
<th>$N$</th>
<th>$m^*_{\text{DOS,CB}}$</th>
<th>$k_\text{L}$</th>
<th>$\mu_i$</th>
<th>$\beta_n/\beta_{\text{PbTe}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnAs$_2$</td>
<td>24</td>
<td>0.04</td>
<td>6.0</td>
<td>2209</td>
<td>1.9</td>
</tr>
<tr>
<td>NaSb</td>
<td>16</td>
<td>0.42</td>
<td>1.1</td>
<td>36</td>
<td>1.7</td>
</tr>
<tr>
<td>KGaSb$_4$</td>
<td>24</td>
<td>0.12</td>
<td>1.0</td>
<td>120</td>
<td>1.5</td>
</tr>
<tr>
<td>NaAs</td>
<td>16</td>
<td>0.50</td>
<td>1.4</td>
<td>34</td>
<td>1.5</td>
</tr>
<tr>
<td>KAlSb$_3$</td>
<td>24</td>
<td>0.14</td>
<td>1.1</td>
<td>103</td>
<td>1.4</td>
</tr>
<tr>
<td>CdAs$_2$</td>
<td>6</td>
<td>0.08</td>
<td>6.3</td>
<td>738</td>
<td>1.3</td>
</tr>
<tr>
<td>KSn</td>
<td>16</td>
<td>0.60</td>
<td>0.9</td>
<td>15</td>
<td>1.2</td>
</tr>
<tr>
<td>Li$_3$As$_7$</td>
<td>160</td>
<td>3.72</td>
<td>1.1</td>
<td>2</td>
<td>1.2</td>
</tr>
<tr>
<td>Cs$_4$ZnAs$_14$</td>
<td>304</td>
<td>4.85</td>
<td>0.7</td>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>Ba$<em>3$As$</em>{14}$</td>
<td>34</td>
<td>3.81</td>
<td>1.0</td>
<td>2</td>
<td>0.6</td>
</tr>
<tr>
<td>KSnSb</td>
<td>6</td>
<td>0.11</td>
<td>1.0</td>
<td>60</td>
<td>0.6</td>
</tr>
<tr>
<td>Cs$_5$Sb$_7$</td>
<td>160</td>
<td>4.34</td>
<td>0.5</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>CsBi</td>
<td>32</td>
<td>0.66</td>
<td>0.7</td>
<td>6</td>
<td>0.6</td>
</tr>
<tr>
<td>KBi</td>
<td>32</td>
<td>1.10</td>
<td>0.6</td>
<td>3</td>
<td>0.6</td>
</tr>
<tr>
<td>RbSb$_2$</td>
<td>6</td>
<td>0.14</td>
<td>0.7</td>
<td>35</td>
<td>0.5</td>
</tr>
<tr>
<td>KBa$_2$As$_5$</td>
<td>16</td>
<td>0.89</td>
<td>1.2</td>
<td>8</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 1 Candidate n-type Zintl pnictides predicted to exhibit high thermoelectric performance with relative $\beta_n/\beta_{\text{PbTe}}$ of 0.5 and greater. Properties: number of atoms in the primitive cell ($N$), conduction band density of states effective mass ($m^*_{\text{DOS,CB}}$) in units of electronic mass ($m_e$), lattice thermal conductivity ($k_\text{L}$) in W/mK, and intrinsic electron mobility ($\mu_i$) in cm$^2$/Vs. $\beta_n$ is expressed relative to the $\beta$ of n-type PbTe.

Most notable among the candidate materials are KGaSb$_4$ and KAlSb$_4$ that we have previously demonstrated to be n-type dopable Zintl with thermoelectric figure of merit $zT$ approaching ~1, without aggressive optimization. Specifically, we have demonstrated that Ba-doped KGaSb$_4$ is n-type (as well as p-type via Zn doping). In addition, first-principles defect calculations of candidate materials KGaSb$_4$ (Figure 3a), CdAs$_2$ (Figure 3b), and KSn (Figure 3c) confirm that these materials are dopable n-type. As with other well-known Zintl thermoelectric materials, most Zintl phases in Table 1 exhibit low lattice thermal conductivities. To further confirm the validity of the proposed chemical guide, we performed defect calculations for three candidate materials from Table 1, which are discussed next.

ZnAs$_2$: Based on the value of $\beta_n$ presented in Table 1, n-type ZnAs$_2$ is predicted to exhibit superior thermoelectric performance, mainly arising from its high electron mobility. The formation energetics of the native defects in ZnAs$_2$ grown under Zn-rich conditions, shown in Figure 6a, suggest that the material is dopable n-type. As expected, zinc vacancies are the lowest-energy acceptors but their formation energies are significantly high – larger than 1 eV for Fermi energy at the CBM. Also, the formation energy of the lowest-energy antisite donors, Zn$_{As}$/As$_{Zn}$, are high even under Zn-rich/As-poor growth conditions. The high

\[ \text{Table 1 Candidate n-type Zintl pnictides predicted to exhibit high thermoelectric performance with relative } \beta_n/\beta_{\text{PbTe}} \text{ of 0.5 and greater.} \]

\[ \text{Properties: number of atoms in the primitive cell (} N \text{), conduction band density of states effective mass (} m^*_{\text{DOS,CB}} \text{) in units of electronic mass (} m_e \text{), lattice thermal conductivity (} k_L \text{) in W/mK, and intrinsic electron mobility (} \mu_i \text{) in cm}^2/\text{Vs. } \beta_n \text{ is expressed relative to the } \beta \text{ of n-type PbTe.} \]

\[ \text{Table 1 Candidate n-type Zintl pnictides predicted to exhibit high thermoelectric performance with relative } \beta_n/\beta_{\text{PbTe}} \text{ of 0.5 and greater.} \]

\[ \text{Properties: number of atoms in the primitive cell (} N \text{), conduction band density of states effective mass (} m^*_{\text{DOS,CB}} \text{) in units of electronic mass (} m_e \text{), lattice thermal conductivity (} k_L \text{) in W/mK, and intrinsic electron mobility (} \mu_i \text{) in cm}^2/\text{Vs. } \beta_n \text{ is expressed relative to the } \beta \text{ of n-type PbTe.} \]
formation energy of native donor and acceptor defects mean that ZnAs is intrinsic when not extrinsically doped. The very high formation energy of the “electron killer” cation vacancies presents the opportunity for extrinsic n-type doping of the material.

**KSB**: The Zintl phase KSB has a LiAs structure type composed of corrugated ...Sb-Sb-Sb... chains interspersed with K (Figure 6b). Besides its crystal structure, phase competition with K and Ba in the interstices (Figure 6c). We find that while formation energy of V_K at the CBM is still high enough to not cause significant electron compensation when doped with a suitable extrinsic donor. Additionally, we find that the anion vacancy (V_As) due to its negative-U behavior acts as an amphoteric defect i.e. a donor or an acceptor depending on the Fermi energy. The formation energetics are such that the anion vacancy is also one of the lowest-energy acceptor defects (for E_F closer to the conduction band) but its formation energy is about the same as the cation vacancy. Therefore, KSB is an n-type dopable Zintl, which further validates the chemical guide.

**KBA_2As_5**: Beyond KAlSb_4 and KGaSb_4, two other ternary Zintl phases feature in Table 1 – Cs_4ZnAs_14 and KBA_2As_5. Since Cs_4ZnAs_14 has a large unit cell with 304 atoms, first-principles defect calculations are computationally intractable. Therefore, we chose to calculate the formation energetics of native defects in KBA_2As_5, which are presented in Figure 6(c). The crystal structure of KBA_2As_5 is characterized by the ...As-As-As... backbone with K and Ba in the interstices (Figure 6c). We find that while the defect chemistry of KBA_2As_5 is unlike other Zintl phases with 1 pn average oxidation state (KGaSb_4, CdAs_5, ZnAs_2, KSB), it is still an n-type material, consistent with our predictions. Instead of the expected cation vacancy (V_K), the lowest-energy acceptors in KBA_2As_5 under K-rich conditions are V_As, vacancies and K_Fa antisites. Nevertheless, KBA_2As_5 is natively self-doped n-type with predicted free electron concentrations ranging from ~10^18 cm^-3 at 600K to ~10^19 cm^-3 at 1000K (Figure S1). The particularly low formation energy of the antosite Ba_K is responsible for the n-type self-doping in KBA_2As_5.

Through these three additional examples (ZnAs_2, KSB, KBA_2As_5), we have further demonstrated that our proposed chemical guide for identifying n-type dopable Zintl phases is reliable. Also, the chemical guide is particularly useful to rapidly assess the dopability of Zintl phases with large unit cells, such as Cs_4ZnAs_14, where direct first-principles defect calculations are impractical.

## 3 Conclusions

In this work, we propose a simple chemical guide for finding novel n-type Zintl thermoelectric materials. We find that Zintl pnictides
with average oxidation state of the pnictide near -1 are likely n-type dopable. Combined with descriptors of thermoelectric performance, the simple chemical guide offers exciting opportunities for synthetic chemists to realize new Zintl pnictides for thermoelectrics with designed doping characteristics. More generally, through this work, we demonstrate that it may be possible to describe the dopability of specific material classes with relatively simple compositional and structural descriptors.

Methods

Calculation of Defect Energetics

First-principles defect calculations are performed with density functional theory (DFT) in the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE), utilizing the projector augmented wave (PAW) formalism as implemented in the VASP software package. Defect energetics are calculated using the standard supercell approach. The total energies of defect supercells are calculated with a plane-wave energy cutoff of 340 eV and a Γ-centered Monkhorst pack k-point grid to sample the Brillouin zone. The defect supercells are relaxed following the procedure used in Refs. and 63. Typically, DFT-calculated total energies (0K) of elemental phases are used as reference elemental chemical potentials ($\mu_0$), which can lead to erroneous formation enthalpies. Inspired by the FERE approach, the reference chemical potentials in this work are obtained by fitting to a set of measured formation enthalpies.

The underestimation of band gap in DFT-GGA is remedied by applying band edge shifts as determined from GW quasi-particle energy calculations, following the procedure previously employed in Refs. and 63. The following corrections are included in $E_{corr}$, following the state-of-the-art methodology described in Ref.: (1) image charge correction for charged defects, (2) potential alignment correction for charged defects, (3) band filling correction for shallow defects, and (4) band gap correction for shallow acceptors/donors. The calculation setup and analyses are performed using a software package, pylada-defects, that we have developed to automate point defect calculations.

For a given material, the defect formation energies of all vacancies, antisites, and interstitials are calculated in charge states $q = -3$, -2, -1, 0, 1, 2, and 3. In most materials considered in this study, the formation energy of interstitials is relatively high; in some cases, interstitial formation energies are larger than the plotted energy window. Vacancies and antisite defects derived from all unique Wyckoff positions in the crystal structure are included in the calculations. The most likely interstitial sites are automatically identified via a Voronoi tessellation scheme as implemented in pylada-defects.

Automated Identification of Zintl Pnictides from ICSD

To search for Zintl pnictides in the Inorganic Crystal Structure Database (ICSD), we developed an algorithmic procedure to automatically identify such structures. Given that all the Zintl pnictides in Figure 4 are arsenides, antimonides, and bismuthides, we limited our search to all structures that contain $Pn = As$, Sb, or Bi, but not N or P. Mixed anion compounds containing $Pn$ and one or more of the following anions: O, S, Se, Te, F, Cl, Br, and I, were not considered in this search. The presence of covalent $Pn – Pn$ bonds in the structure is a characteristic feature of many Zintls, including several shown in Figure 4 such as $ZnSb$, $KGaSb_4$, and $Yb_{14}MnBi_{11}$. We identified structures comprising binary, ternary, and quaternary chemistries that contain at least one $Pn$-$Pn$ bond.

Certain polar intermetallic compounds, which lack $Pn$-$Pn$ bonds, can also be classified as Zintl phases because their structures can be rationalized using the Zintl-Klemm concept. Within thermoelectrics, the “1-2-2” (e.g. CaZn$_2$Sb$_2$, Mg$_2$Sb$_2$) and “1-1-1” (e.g. KZnS) polar intermetallic are considered Zintl phases (Figure 5). We considered $Pn$-based ternary polar intermetallics with $A,B,C$ stoichiometry, where $A$ is an electropositive cation, $B$ is a less-electropositive cation that is part of the “anionic framework”, and $C$ is a pnictogen (As, Sb, or Bi). The automated search uses the following criteria to identify these structures: (1) at least one bond exists between $B$-$C$, (2) $\mu_C - \mu_A < 0.7$, and (3) $\chi_C - \chi_A > 1.0$, where $\chi$ is the electronegativity on the Pauling scale. This search scheme correctly identifies the well-known “1-1-1” and “1-2-2” phases, as shown in Figure 5. In these Zintl phases, the $Pn$ oxidation state is 3-. For the purposes of identifying n-type dopable Zintl phases, we are specifically interested in compounds where the $Pn$ average oxidation state is -1 or higher, a feature lacking in these Zintl phases.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

We acknowledge support from NSF DMR program, grant no. 1729594. Part of this work was performed at the California Institute of Technology/Jet Propulsion Laboratory under contract with the National Aeronautics and Space Administration (NASA). This work is supported by the NASA Science Mission Directorate’s Radioisotope Power Systems program. We thank G. Jeffrey Snyder (Northwestern University) for the insightful discussions and feedback. The research was performed using computational resources sponsored by the Department of Energy’s Office of Energy Efficiency and Renewable Energy and located at the National Renewable Energy Laboratory.

References

4. S. Bobev, J. D. Thompson, J. L. Sarrao, M. M. Olmstead, H. Hope and S. M. Kauzlarich, Probing the Limits of the Zintl Concept: Structure and Bonding in Rare-Earth and Alkaline-


63. P. Gorai, B. Ortiz, E. S. Toberer and V. Stevanovic, Investiga-
tion of $n$-type Doping Strategies for Mg$_3$Sb$_2$, J. Mater. Chem. A, 2018, 6, 13806.

64 J. Zhang, L. Song, K. Tolborg and B. B. Iversen, Chemical bonding origin of the unexpected isotropic physical properties in thermoelectric Mg$_3$Sb$_2$ and related materials, Nat. Comm., 2018, 9, 4716.


Supplementary Information


Prashun Gorai,*† Anuj Goyal,† Eric S. Toberer,‡ and Vladan Stevanović*†

†Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401, USA.
‡Physics, Colorado School of Mines, Golden, Colorado 80401, USA.

E-mail: pgorai@mines.edu; vstevano@mines.edu
Predicted Thermoelectric Performance of \(n\)-type Dopable Zintl Phases

Table S1: Computed parameters used in determining the descriptor of thermoelectric performance \(\beta\). The following are tabulated: compound, Inorganic Crystal Structure Database (ICSD) identification number, \(\beta_p\) and \(\beta_n\) for valence (\(p\)-type) and conduction (\(n\)-type) band transport, lattice thermal conductivity (\(\kappa_L\)) in Wm\(^{-1}\)K\(^{-1}\), bulk modulus (\(B\)) in GPa, valence band density-of-states effective mass (\(m^*_{DOS,VB}\)) and conduction band density-of-states effective mass (\(m^*_{DOS,CB}\)) in the units of \(m_e\), and valence band (\(N_{b,VB}\)) and conduction band (\(N_{b,CB}\)) degeneracy.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ICSD</th>
<th>(\beta_p)</th>
<th>(\beta_n)</th>
<th>(\kappa_L)</th>
<th>(B)</th>
<th>(m^*_{DOS,VB})</th>
<th>(m^*_{DOS,CB})</th>
<th>(N_{b,VB})</th>
<th>(N_{b,CB})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnAs(_2)</td>
<td>002021</td>
<td>6.63</td>
<td>29.46</td>
<td>5.98</td>
<td>86</td>
<td>0.531</td>
<td>0.044</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>NaSb</td>
<td>026473</td>
<td>26.80</td>
<td>26.60</td>
<td>1.06</td>
<td>20</td>
<td>1.061</td>
<td>0.417</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>KGaSb(_4)</td>
<td>300158</td>
<td>5.04</td>
<td>23.03</td>
<td>1.03</td>
<td>21</td>
<td>0.303</td>
<td>0.121</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>NaAs</td>
<td>182159</td>
<td>5.99</td>
<td>22.67</td>
<td>1.41</td>
<td>25</td>
<td>4.571</td>
<td>0.497</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Na(_2)As(_2)</td>
<td>421420</td>
<td>5.97</td>
<td>22.37</td>
<td>1.42</td>
<td>25</td>
<td>4.556</td>
<td>0.504</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>KAiSb(_4)</td>
<td>300157</td>
<td>5.29</td>
<td>20.79</td>
<td>1.08</td>
<td>21</td>
<td>0.261</td>
<td>0.135</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>CdAs(_2)</td>
<td>020518</td>
<td>5.26</td>
<td>19.25</td>
<td>6.30</td>
<td>49</td>
<td>0.717</td>
<td>0.083</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>K(_3)Sb</td>
<td>056529</td>
<td>4.35</td>
<td>18.37</td>
<td>0.87</td>
<td>14</td>
<td>3.220</td>
<td>0.592</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Li(_3)As(_7)</td>
<td>409657</td>
<td>8.64</td>
<td>17.99</td>
<td>1.08</td>
<td>14</td>
<td>1.489</td>
<td>3.717</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>Cs(<em>3)ZnAs(</em>{14})</td>
<td>423082</td>
<td>11.93</td>
<td>14.69</td>
<td>0.67</td>
<td>7</td>
<td>4.299</td>
<td>4.849</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>Ba(<em>3)As(</em>{14})</td>
<td>001404</td>
<td>4.86</td>
<td>9.38</td>
<td>1.01</td>
<td>18</td>
<td>3.462</td>
<td>3.805</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>K(_2)Sb</td>
<td>080945</td>
<td>4.91</td>
<td>8.95</td>
<td>0.95</td>
<td>19</td>
<td>1.685</td>
<td>0.114</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Cs(_3)Sb(_7)</td>
<td>092473</td>
<td>8.71</td>
<td>8.93</td>
<td>0.53</td>
<td>6</td>
<td>4.526</td>
<td>4.341</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>CsBi</td>
<td>055067</td>
<td>6.35</td>
<td>8.77</td>
<td>0.66</td>
<td>14</td>
<td>1.121</td>
<td>0.655</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>KBi</td>
<td>055065</td>
<td>8.98</td>
<td>8.72</td>
<td>0.63</td>
<td>10</td>
<td>3.461</td>
<td>1.102</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>RbSb(_2)</td>
<td>419402</td>
<td>2.97</td>
<td>7.98</td>
<td>0.73</td>
<td>15</td>
<td>0.718</td>
<td>0.138</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>KBa(_2)As(_5)</td>
<td>414140</td>
<td>15.21</td>
<td>7.86</td>
<td>1.21</td>
<td>28</td>
<td>0.760</td>
<td>0.886</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>LiAs</td>
<td>026472</td>
<td>26.73</td>
<td>7.53</td>
<td>1.82</td>
<td>34</td>
<td>0.672</td>
<td>0.654</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>CsAs</td>
<td>412595</td>
<td>12.86</td>
<td>7.51</td>
<td>0.76</td>
<td>12</td>
<td>1.863</td>
<td>2.713</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>K(<em>3)As(</em>{11})</td>
<td>036591</td>
<td>4.38</td>
<td>6.26</td>
<td>0.82</td>
<td>10</td>
<td>9.826</td>
<td>3.538</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Rb(_3)As(_7)</td>
<td>412597</td>
<td>5.07</td>
<td>5.62</td>
<td>0.76</td>
<td>9</td>
<td>3.126</td>
<td>2.631</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Compound</td>
<td>ICSD</td>
<td>$\beta_p$</td>
<td>$\beta_n$</td>
<td>$\kappa_L$</td>
<td>$B$</td>
<td>$m_{\text{DOS,V}}$</td>
<td>$m_{\text{DOS,CB}}$</td>
<td>$N_{\text{VB}}$</td>
<td>$N_{\text{CB}}$</td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
<td>-----------</td>
<td>-----------</td>
<td>------------</td>
<td>-----</td>
<td>----------------</td>
<td>----------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>RbBi</td>
<td>055066</td>
<td>13.89</td>
<td>5.56</td>
<td>0.58</td>
<td>10</td>
<td>2.741</td>
<td>0.972</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>CsSb</td>
<td>412154</td>
<td>5.39</td>
<td>5.13</td>
<td>0.64</td>
<td>10</td>
<td>0.910</td>
<td>0.989</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>NaAs</td>
<td>610971</td>
<td>5.29</td>
<td>5.10</td>
<td>1.38</td>
<td>23</td>
<td>0.989</td>
<td>0.209</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Cs$_3$As$_7$</td>
<td>412598</td>
<td>3.28</td>
<td>5.07</td>
<td>0.67</td>
<td>8</td>
<td>6.523</td>
<td>1.613</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Rb$_4$As$_6$</td>
<td>409381</td>
<td>2.64</td>
<td>4.87</td>
<td>0.76</td>
<td>12</td>
<td>0.602</td>
<td>1.094</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>RbSb</td>
<td>014030</td>
<td>4.05</td>
<td>3.92</td>
<td>0.71</td>
<td>11</td>
<td>1.467</td>
<td>0.307</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>MgAs$_4$</td>
<td>001079</td>
<td>26.18</td>
<td>3.68</td>
<td>2.39</td>
<td>43</td>
<td>0.680</td>
<td>2.110</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>RbAs</td>
<td>412594</td>
<td>3.42</td>
<td>3.60</td>
<td>0.88</td>
<td>14</td>
<td>1.889</td>
<td>0.344</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>CsSb</td>
<td>014031</td>
<td>2.67</td>
<td>3.49</td>
<td>0.55</td>
<td>8</td>
<td>2.729</td>
<td>0.345</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>BaAs$_2$</td>
<td>414139</td>
<td>7.11</td>
<td>3.41</td>
<td>1.21</td>
<td>30</td>
<td>3.035</td>
<td>0.798</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>KAs</td>
<td>409653</td>
<td>1.44</td>
<td>3.27</td>
<td>1.10</td>
<td>16</td>
<td>1.393</td>
<td>0.353</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Na$_3$As$_7$</td>
<td>409658</td>
<td>6.56</td>
<td>3.26</td>
<td>0.99</td>
<td>12</td>
<td>5.560</td>
<td>1.375</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Cs$<em>4$As$</em>{11}$</td>
<td>412873</td>
<td>1.36</td>
<td>3.16</td>
<td>0.65</td>
<td>8</td>
<td>5.371</td>
<td>3.383</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Rb$<em>3$As$</em>{11}$</td>
<td>412872</td>
<td>5.93</td>
<td>2.90</td>
<td>0.73</td>
<td>8</td>
<td>8.448</td>
<td>3.854</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>Cs$_5$Sb$_8$</td>
<td>412155</td>
<td>19.15</td>
<td>2.63</td>
<td>0.68</td>
<td>11</td>
<td>2.070</td>
<td>3.040</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>K$_3$As$_7$</td>
<td>412596</td>
<td>7.02</td>
<td>2.53</td>
<td>0.83</td>
<td>9</td>
<td>3.787</td>
<td>1.597</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Rb$_3$As$_7$</td>
<td>409652</td>
<td>4.10</td>
<td>2.39</td>
<td>0.72</td>
<td>8</td>
<td>3.763</td>
<td>1.842</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>NaCs$_2$As$_8$</td>
<td>423080</td>
<td>1.26</td>
<td>2.23</td>
<td>0.77</td>
<td>11</td>
<td>1.548</td>
<td>0.600</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cs$_4$As$_6$</td>
<td>409382</td>
<td>2.57</td>
<td>2.15</td>
<td>0.64</td>
<td>11</td>
<td>0.660</td>
<td>0.891</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Rb$_4$Sb$_6$Sn</td>
<td>300212</td>
<td>5.32</td>
<td>1.45</td>
<td>0.65</td>
<td>9</td>
<td>5.817</td>
<td>1.183</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>CdCs$<em>4$As$</em>{14}$</td>
<td>423081</td>
<td>1.94</td>
<td>1.38</td>
<td>0.49</td>
<td>4</td>
<td>4.720</td>
<td>3.253</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>
KBa$_2$As$_5$: Native Defect Energetics and Predicted Free Electron Concentration

(a) KBa$_2$As$_5$

(b) Predicted free electron concentrations in self-doped KBa$_2$As$_5$ ranges from $\sim 10^{18}$ cm$^{-3}$ at 600K to $\sim 10^{19}$ cm$^{-3}$ at 1000K.

Figure S1: Crystal structure, defect energetics, and carrier concentrations: (a) Formation energetics of native defects in KBa$_2$As$_5$ reveal that under K-rich growth conditions, the antisite donor Ba$_K$ self dopes KBa$_2$As$_5$ $n$-type. (b) Predicted free electron concentrations in self-doped KBa$_2$As$_5$ ranges from $\sim 10^{18}$ cm$^{-3}$ at 600K to $\sim 10^{19}$ cm$^{-3}$ at 1000K.
List of Zintl Pnictides in ICSD

Numbers in parenthesis are the ICSD numbers.

As₃Rh (034052), As₁₁Cs₃ (412873), As₃Ca₄ (252055), AsCa (026263), As₂Ru (000994), As₂Na (182161), AsIn (043973), AsIn (156105), As₇Cs₃ (412598), As₄Cu₃ (041169), As₂Fe (065168), As₃Co (009188), AsRb (412594), As₇Rb₃ (409652), As₇Rb₃ (412597), As₁₃K₃ (036591), AsSb (042576), As₂Mo (016820), As₂Zn (002021), As₂Ge (610061), As₈Sr (041831), As₈Sr (611440), As₂Nb (018143), As₂Nb (081218), As₃Ca (086400), As₃Ba (086402), As₇Na₃ (409658), As₄Sr₃ (100110), AsGa (043951), AsGa (043950), As₂Si (611405), As₂Si (024801), As₂Ni (076940), As₂Ni (034851), As₂Ni (042569), As₂Sr₂ (083353), As₂Cr (043898), As₂Cu (610303), AsZn (427612), As₂Cd (016037), As₂Cd (020518), As₂Ti (611500), AsCd (000432), As₃Sr₄ (402110), As₁₄Ba₃ (001404), As₂Pt (056021), AsSr (026264), As₂V (611574), As₂Zr (168665), As₇K₃ (412566), As₂W (611576), As₂Na₂ (421420), As₂Ta (044069), As₂Ta (107966), As₂Ca₂ (043876), As₆Cs₄ (409382), As₆ (412595), AsLi (026472), As₂Pd (043101), As₃Mo₂ (043814), As₃W₂ (043185), As₁₁Rb₃ (412872), AsNa (610971), AsNa (182159), As₂Hf (610636), As₂Co (610039), As₂Co (610034), As₆Rb₄ (409381), As₄Mg (001079), As₂Ba (414139), As₂Rh (611271), As₂La (280294), As₂La (610769), AsLa (098427), As₃V₅ (611571), AsK (409653), As₄Na₅ (182165), As₇Li₃ (409657), Sb₂Ti (651676), RhSb₂ (659978), Ag₃Sb (064716), AlSb (107877), RuSb₂ (042608), K₃Sb₂ (080945), Sb₂Sr (052307), Sb₂Zr (042878), In₅Sb₃ (640434), CdSb (620395), LaSb₂ (641892), Cs₃Sb₇ (092473), K₅Sb₉ (056529), Ba₅Sb₄ (280022), Ba₅Sb₄ (052693), AsSb (042576), Sb₄Zr₅ (189947), Sb₁₄Zn₁₃ (159092), NiSb₂ (646409), Li₂Sb (100020), CoSb₂ (076120), CoSb₂ (063553), BaSb₂ (409517), Mo₃Sb₇ (173974), Mo₃Sb₇ (164763), Cs₅Sb₈ (412155), HfSb₂ (066780), HfSb₂ (638876), AnSb₃ (043504), CsSb (041431), CsSb (421514), LaSb (044806), NbSb₂ (645350), Ca₄₁Sb₁₀ (000433), RhSb₃ (044716), R₃Sb₄ (280591), Sb₁₈Zr₁₁ (280817), CaSb₂ (000862), R₃Sb (014030), Hf₅Sb₉ (413979), SbZn (043825), R₃Sb₂ (419402), K₅Sb₄ (056530), Sb₂Y (651733), Sb₂Ta (052311), Sb₂Ta (651600), AuSb₂ (612288), PdSb₂ (043102), Sb₃Sr₂ (032033), Sb₁₀Sr₁₁ (659275), CrSb₂ (046201), CrSb₂ (088903), Cs₄Sb₂ (092474), Cd₁₃Sb₁₀ (260098), Ba₁₁Sb₁₀ (413518), SbSn (154085), Sb₂V (052331), Ba₂Sb₃ (061089), Cd₆Sb₅ (420110), PhSb (648506), Sb₁₅Zn₈₄ (418213), PtSb₂ (057470), NaSb (206473), BaSb₃ (040000), FeSb₂ (151397), FeSb₂ (186639), GaSb (103952), GaSb (041982), InSb (659364), InSb (655298), InSb (010021), InSb (156996), Sb₇Zn₈ (238947), Bi₁₀Sr₁₁ (659276), Ba₁₁Bi₁₀ (051797), BiH₂ (168286), Bi₃ (055067), BiNa (058816), Bi₃Hf (616683), Bi₂Tl (058864), BaBi₃ (058634), BiRb (055066), Bi₂K (055068), Bi₂K (058794), Bi₁₄Rh₄ (245517), Bi₁₄Rh₃ (195777), BiNi (058820), Bi₂Zr (042880), Bi₃Sr (058858), Bi₄Rh (058854), Bi₂Rh (617009), BiLi (616780), BiSn (058857), BiSn (160382), Bi₁₀Ca₁₁ (000434), Bi₂Ca (659277), Bi₂Rb (150969), Bi₂Rb (055069), Bi₂Cs (058771), Bi₂Cs (055070), Ba₂Bi₃ (170218), BiK (055065), Bi₃Sr₂ (106329), Bi₂Pt (077111), Bi₂Pt (150886), Au₂Bi (052284), Bi₂Ca₃ (240017), As₂GaK₂ (300142),
Contd...

Numbers in parenthesis are the ICSD numbers.

As₄Cd₂Ge (042132), AsPb₂Zr₅ (604204), As₃In₂K₂ (300198), As₂K₂Pt (610762), As₂Cs₂Pd (069647), AsSb₃Zr₅ (611352), As₆Ca₅Ga₂ (000027), As₃LaPd₂ (192474), As₂Pd₃Sr (047170), As₆Cs₇In₃ (411989), As₆BaPt₄ (062519), As₆In₄K₄ (071244), As₉K₂Pd (032009), As₇Rb₄Zn₇ (237457), As₁₂LaRu₄ (610778), Al₂₃As₃Na₂ (300193), As₂K₂Ni (300120), As₂BaPt (405112), As₁₄CdCs₄ (423081), As₂BaPd (405110), As₂CuY (412550), As₂BaCu₇ (236307), As₂Pt₃Ru (107529), As₃Ga₂Na₂ (300194), As₁₈Ca₂₁Zn₄ (429152), As₂BaPd₂ (061196), As₂BaPd₄ (036377), As₂BaPd₂ (190705), AsSn₃Zr₅ (656301), As₃Ba₂Cd₂ (420833), As₂Cu₂Sr (610366), As₃Sr₂Zn₂ (262413), As₁₄Cs₇Zn (423082), As₂CaPd₂ (604341), As₁₂Fe₄La (168584), As₂CaNi₂ (023004), As₃Ga₂K₂ (300195), As₃Pt₄Sr (062518), As₃LaSi (039160), As₇LaSi (068205), As₂CaRu₂ (609914), As₄Ba₃Cd₂ (424761), As₅Ga₉Ru₂ (300143), As₁₁₁₄Ga (071176), As₇Cs₂Na (423080), AgAs₂La (420609), As₅Ba₂K (414140), As₅Ba₃Li₄ (280027), As₄Ba₃Zn₂ (424760), Ca₅In₂Sb₆ (036467), Cs₂PtSb₂ (658700), Sb₄Sn₃Sr (165617), AlCa₁₄Sb₁₁ (033266), AnSb₁₁Tl (391381), CaMnSb₂ (052705), BaPdSb₂ (405111), LaPdSb₂ (658217), In₄K₄Sb₆ (071245), Mn₁₂Rb₇Sb₁₂ (237459), Ba₃Cd₂Sb₄ (173685), CrLaSb₃ (083907), LaRu₄Sb₁₂ (641783), La₃Sb₅Ti (080907), Ni₂Sb₃Sr (644642), Hf₃NiSb₇ (195051), GaK²Sb₂ (053579), Fe₃Sb₁₂Sr (658739), HfLa₃Sb₅ (083906), MnSb₁₁Sr₁₄ (075939), Cd₃Sb₁₂Sr₁₁ (418887), Ca₁₁₁₄In₉ (042371), In₉K₂Sb₃ (300197), NiSb₇Zr₃ (260035), BaMnSb₂ (100024), AlK₃Sb₄ (300157), Mn₂Sb₂Sr (643539), Cd₃Sb₇Tl₂ (076500), AgSb₂Y (190094), Ba₁₁Cd₆Sb₁₂ (418886), Ga₂K₂Sb₃ (300196), Hf₃PdSb₇ (195052), FeLaSb₂ (657985), Al₂₃Na₇Sb₅ (048168), Ba₃LiSb₄ (428114), Ba₃Li₄Sb₄ (615946), Al₂Sb₆Sr₅ (062304), Ca₁₀Mg₂Sb₂ (171162), Rb₄Sb₄Sn (300121), In₅K₁₀Sb₉ (056323), InSb₁₁Sr₁₁ (240900), Al₂Ca₅Sb₆ (183853), Al₂Ca₅Sb₆ (060146), SbSn₃Tl (097545), Na₉Sb₄Tl (096942), AgLaSb₂ (095222), CoLaSb₃ (419540), GaRb₂Sb₂ (300135), Pd₂Sb₂Sr (061195), Mn₄Sb₁₈Sr₂₁ (290280), BaCdSb₂ (052683), Ba₅In₂Sb₆ (062305), Ca₁₂Mn₄Sb₁₈ (281257), Ca₂₁Mn₄Sb₁₈ (416972), Pb₃SbZr₅ (604080), CoLaSb₂ (657990), LaSb₁₁ (658208), BaPd₂Sb₂ (061197), La₃Sb₅Zr (083905), In₂Na₂Sb₃ (300192), Li₄Sb₄S₃ (025307), Ca₁₄MnSb₁₁ (059710), PdSb₇Zr₃ (426314), Sb₂SrZn (010001), Ca₂₁Sb₁₈Zn₄ (429153), BaRu₁₄Sb₁₂ (616049), CaS₃Ga₂Sb₆ (036466), CuSb₂Y (153572), LaNiSb₃ (249473), Cs₂PdSb₂ (658702), AuLaSb₂ (082589), Cs₂In₂Sb₃ (056387), BaFe₄Sb₁₂ (658735), GaK₁₂Sb₂ (300202), CuLaSb₂ (658225), Ru₄Sb₁₂Sr (042962), In₂Sb₂Sr₅ (036468), In₉Rb₂Sb₃ (083663), Ba₂Cd₂Sb₃ (420834), GaK₁₂Sb₂ (300158), Al₂K₂Sb₃ (052627), Ba₃Cd₄Sb₁₈ (173283), Al₂Na₂Sb₃ (052628), Ba₂Sb₂Sn₃ (085259), Bi₁₈Ca₂₁Mn₄ (416520), Bi₂Cs₂Pd (658703), Bi₁₃MnS₀₄ (106328), BaBi₂Mn (615787), BaBi₂Zn (058638), Bi₂MnSr (100025), Ba₁₁Bi₁₄Cd₆ (240338), Bi₂Cs₂Ni (658704), Bi₁₁Ca₁₄Mn (106319), Bi₂GaLa (165559), Bi₂CaMn (010454), Bi₂Cs₂Pt (658701), Bi₁₈Cd₄Sr₀₂₁ (173284), Bi₂LaLi (415728), Bi₅K₆Zn (238106), Bi₃La₃Mg (415727), Bi₂SrZn (041924), BaBi₂Cd (058635),
Contd...

Numbers in parenthesis are the ICSD numbers.

Bi$_5$La$_3$Sc (416609), Bi$_2$CdSr (058764), Ba$_3$Bi$_4$Li$_4$ (428115), Bi$_4$In$_2$Sr$_5$ (415576), Bi$_5$La$_3$Mn (173362), Ba$_{14}$Bi$_{11}$Mn (106304), AuBi$_3$La (238704), Bi$_4$Ca$_3$Pd$_4$ (412563), As$_2$BaRu$_2$ (609861), As$_6$Sn$_2$Sr$_5$ (262646), As$_2$CdSr$_2$ (422940), As$_3$CoHf$_5$ (085884), As$_2$Co$_2$La (610073), As$_2$GaK$_2$ (300142), As$_4$Ga$_3$K$_3$ (040206), As$_4$NbRb$_7$ (380111), As$_2$Cs$_3$Ga (300115), As$_4$Ba$_4$Ti (380115), As$_7$Mg$_6$Ni$_{16}$ (078834), AsFeNa (163143), AsFeNa (187137), AsFeNa (187136), AsHfNb (424124), AsMgPt$_5$ (610830), As$_4$MgRh$_6$ (089611), As$_5$K$_6$Sn$_3$ (071009), As$_2$LaRu$_2$ (602111), AsLiZn (074504), As$_2$HgK$_4$ (402573), AlAs$_3$Ca$_3$ (606012), As$_3$CsZn$_4$ (262030), Al$_4$As$_3$K$_{12}$ (300121), As$_3$In$_2$K$_2$ (300198), As$_2$CdK$_4$ (300190), AsBeNa (100091), AsPdSr (404723), AsFeLi (246338), AsFeLi (042331), AsFeLi (166457), AsFeLi (187131), AsFeLi (187133), AsFeLi (168206), As$_2$K$_2$Pt (610762), As$_3$GaNa$_6$ (300276), As$_3$Ca$_3$Ga (060126), As$_2$BRb$_3$ (402802), Al$_2$As$_4$Sr$_3$ (423787), Ag$_4$As$_2$Sr (424309), As$_4$Rb$_2$Zn$_5$ (250688), As$_{2}$BC$_{3}$S$_{3}$ (300122), AsCaPt (060828), As$_2$HfNi$_4$ (610561), AsCu$_2$K$_2$ (043936), As$_2$KRh$_2$ (031474), As$_2$Cu$_4$K (059207), As$_3$Na$_5$Sn (650658), As$_2$BaCu$_4$ (089628), As$_5$La$_4$Mn$_2$ (429102), As$_2$CsRh$_2$ (610296), AsMnNa (026461), As$_4$Cs$_3$In$_3$ (280723), As$_3$Ba$_3$In (402338), As$_2$Cd$_2$Sr (023249), As$_2$CsFe$_2$ (074877), AsKMN (060745), As$_2$SrZn$_2$ (023248), As$_2$Cs$_2$Pd (069647), As$_2$Ru$_2$Sr (165118), As$_4$Ca$_5$Ga$_2$ (000027), As$_2$BK$_3$ (300105), As$_2$CaCo$_2$ (609899), Al$_2$As$_3$K$_3$ (060950), As$_6$K$_{10}$Sn$_2$ (409486), As$_2$Ba$_2$Cd (422941), As$_2$Cu$_3$K$_3$ (032015), As$_2$BaCo$_2$ (609848), As$_2$Co$_2$Sr (610122), As$_2$LaPd$_2$ (192474), As$_2$Ga$_2$Sr (422527), As$_2$Pd$_2$Sr (047170), As$_2$BaCu$_6$ (079256), As$_2$BaCr$_2$ (609849), As$_2$Ba$_{14}$Sr$_7$ (251516), AsCaCu (049741), As$_6$BaCo$_{10}$ (092463), As$_2$Ni$_2$Y (611100), As$_4$Ga$_2$Sr$_3$ (423785), As$_6$Ce$_7$In$_3$ (411989), Al$_3$As$_3$Ba$_3$ (425292), As$_2$Rb$_2$Sr (417001), As$_2$Rb$_2$Sr (417002), AsCdK (609693), As$_4$Ge$_2$Sr$_3$ (016454), As$_2$BaPt$_4$ (062519), As$_2$CuRu$_2$ (610297), As$_6$Ca$_5$Sn$_2$ (061037), As$_4$In$_4$K$_4$ (071244), As$_2$CuK$_5$ (040699), As$_2$Pt$_2$Sr (418156), As$_2$Pt$_2$Sr (181396), As$_3$Ni$_3$Zr$_2$ (611109), AsCdNa (609968), AsCdNa (009571), AsCoHf (406953), As$_3$Ba$_3$Si$_2$ (041183), As$_3$Cd$_4$Na (262035), AsAuCa (404725), As$_2$Sn$_3$Sr$_{14}$ (195752), As$_2$K$_2$Pd (032009), As$_3$In$_3$K$_3$ (300199), As$_3$Cd$_4$Rb (262037), As$_3$Hf$_2$Ni$_3$ (610649), AlAs$_2$Cs$_3$ (300113), Al$_2$As$_4$Ba$_3$ (423779), As$_7$Rb$_4$Zn$_7$ (237457), As$_6$Ge$_2$Na$_{10}$ (300187), As$_4$Ca$_3$In$_2$ (601336), As$_2$LaRu$_4$ (610778), AsKSn (040815), Al$_2$As$_3$Na$_2$ (300193), As$_2$In$_3$Na$_3$ (300139), AsCoLi (107932), As$_2$K$_2$Ni (300120), As$_2$BeK$_4$ (300111), As$_2$Fe$_2$K (031473), AsPtY (044047), As$_3$BaPt (405112), AgAsK$_2$ (001154), As$_2$BaZn$_2$ (012146), As$_2$BaZn$_2$ (417000), As$_2$LaRh$_2$ (610777), As$_2$Na$_2$Sn$_4$ (073307), As$_2$Rb$_2$Sn$_2$ (071223), As$_3$NaZn$_4$ (262036), As$_3$BaCu$_8$ (066017), As$_4$BaNi$_2$ (164196), As$_2$BaNi$_2$ (609856), As$_2$Fe$_2$Sr (163208), As$_2$Fe$_2$Sr (610527), As$_3$Cs$_3$Si$_3$ (065716), As$_2$BaPd (405110), As$_6$Na$_{10}$Si$_2$ (300188), As$_7$Co$_{12}$Mg$_2$ (094408), As$_2$CuY (412550), As$_2$BaCu$_2$ (236307), AsAuBa (420341), As$_4$Cd$_3$Rb$_2$ (290262), As$_3$Rb$_3$Si (300191), As$_2$PtRb$_2$ (107529), As$_2$BaRh$_2$ (416983), As$_3$Cr$_3$Rb$_2$ (195012), As$_2$SiSr$_4$ (611409), As$_2$Cu$_4$Sr (089626),
Numbers in parenthesis are the ICSD numbers.

As$_3$Ga$_2$Na$_2$ (300194), As$_2$Cs$_2$Sn (071226), As$_{18}$Ca$_{21}$Zn$_4$ (429152), AsLaPd (056974), As$_2$BaGa$_2$ (380478), As$_2$BaPd$_2$ (061196), As$_2$BaPd$_2$ (036377), As$_2$BaPd$_2$ (190705), As$_3$Cs$_5$Ge (065718), As$_4$K$_7$Ta (380110), As$_7$Ca$_2$Ni$_{12}$ (609008), As$_3$CaFe$_5$ (427443), AsLaRh (095191), As$_4$Ca$_3$Ge$_2$ (016455), As$_4$Ba$_2$Cd$_2$ (420833), As$_2$Cu$_2$Sr (610366), AsAn$_2$ (023254), As$_6$Ba$_3$Sn$_4$ (411652), As$_2$NaSn$_2$ (082366), As$_4$Ba$_4$Ge (026408), As$_3$LaZn$_3$ (261981), As$_7$K$_2$Ni$_{12}$ (300138), As$_3$Sr$_2$Zn$_2$ (262413), AsHfRu (610654), AsHfRu (610655), As-PdZr (092440), As$_2$CaCu$_4$ (032619), As$_2$GeK$_2$ (071222), As$_{16}$Cs$_4$Zn (423082), AsBaPt (059192), As$_2$Ni$_4$Sc (611064), As$_3$Ba$_4$Si (026467), AsKZn (043985), AsKZn (010459), As$_2$CaPd$_2$ (604341), As$_2$K$_2$Si (040426), As$_{12}$Fe$_4$La (168584), AsMnRb (089596), AsRuZr (035593), Ag$_2$As$_2$K$_3$ (032016), As$_3$CaFe$_4$ (260320), As-NaN$_5$ (160956), As$_6$Cs$_9$N$_3$ (281086), As$_3$Cs$_8$In (300145), As$_2$K$_3$Zn (409919), As$_2$Sn$_2$Sr (082371), As$_2$Sn$_2$Sr (611428), As$_2$MgSi (182367), As$_3$RbZn$_4$ (262038), AsCuNa$_2$ (043937), Al$_2$As$_4$Ca$_3$ (060161), As$_2$BaFe$_2$ (180480), As$_2$BaFe$_2$ (166020), AgAsCa (010017), As$_3$Cd$_4$K (262032), As$_4$Rh$_6$Sr (089613), As$_2$Be$_2$Mg (609872), As$_4$Si$_2$Sr$_3$ (016453), As$_2$CaNi$_2$ (032004), As$_3$Ga$_2$K$_2$ (300195), As$_2$CaGa$_2$ (422526), AsLaCu (041705), AsLiMn (060739), AsLiMn (192816), As$_3$Ni$_5$Sr (033915), As$_2$Co$_2$K (601072), As$_2$Ni$_4$Zr (611111), As$_5$BaNi$_9$ (033919), As$_6$Pt$_4$Sr (062518), As$_2$NiZr$_2$ (068141), As$_2$CaMn$_2$ (609096), As$_4$Sr$_4$Ti (380113), As$_8$Na$_{10}$Sn$_2$ (040559), As$_3$LaSi (039160), As$_3$LaSi (068205), As$_2$Sn$_2$Sr$_3$ (428136), As$_1$Sn$_2$Sr$_3$ (428135), As$_4$K$_7$Nb (380109), As$_3$Cd$_4$Cs (262029), As$_2$CaRu$_2$ (609914), As$_2$Ni$_2$Sr (611078), As$_2$Ba$_2$Zn (421423), AsCaPd (072349), As$_2$Ba$_2$Ge (035151), As$_4$Ba$_3$Cd$_2$ (424761), As$_4$CaRh$_6$ (089612), As$_2$CaFe$_2$ (192310), As$_2$CaFe$_2$ (160017), As$_2$CaCd$_2$ (609896), As$_2$Mn$_2$Sr (049020), AgAsBa (008278), As$_4$Ba$_4$Sn$_2$ (030702), As$_2$BaMn$_2$ (041794), As$_2$GaRb$_2$ (300143), As$_1$Ca$_4$Ga (071176), As$_2$Fe$_2$Rb (167329), AgAsSr (049742), AlAs$_2$Na$_3$ (063149), As$_3$LaNi$_5$ (414080), AsBaPd (404724), AgAsMg (655132), As$_2$Cs$_2$Si (071225), As$_2$Rb$_2$Si (060617), AgAsLa (420609), AsBeLi (609869), As$_4$Ca$_3$Si$_2$ (016456), AgAsNa$_2$ (049007), As$_2$CaZn$_2$ (609920), As$_8$Mg$_4$Rh$_7$ (094391), As$_2$BaCd$_2$ (030917), AsCuLi$_2$ (043938), AsTiZr (186253), As$_4$K$_2$Zn$_5$ (250687), As$_2$Ca$_2$Cd (422579), As$_2$Ca$_2$Cd (422578), As$_3$K$_5$Pb$_3$ (055419), As$_7$Ni$_{12}$Y$_2$ (611099), As$_1$GeSr$_4$ (610619), As$_3$Ba$_2$In$_5$ (161775), As$_4$Na$_9$Ti (073310), AsC$_8$Mn (040573), As$_2$Cr$_2$Sr (610273), As$_2$GeMg (182368), AsHgK (010458), AsPtSr (059187), As$_2$LaNi$_2$ (068147), As$_2$LaNi$_2$ (610772), As$_2$AuK$_5$ (040698), As$_2$BaGe$_2$ (026417), As$_2$Be$_2$Ca (609867), AsCuMg (610335), AsCuMg (412296), As$_3$Ba$_3$Zn$_2$ (424760), AsCuSr (107943), K$_8$Sb$_4$Sn (044679), Ca$_5$In$_2$Sb$_6$ (036467), Cs$_2$GaSb$_2$ (300156), Cs$_2$PtSb$_2$ (658700), LaNiSb (079979), Au$_2$BaSb$_2$ (416298), Sb$_8$Sn$_3$Sr (165617), MnSb$_2$Sr$_2$ (165582), Ca$_2$CdSb$_2$ (173172), AlCa$_{14}$Sb$_{11}$ (033266), Cu$_3$Sb$_4$Y$_3$ (658636), CaMnSb$_2$ (052705), BaPdSb$_2$ (405111), MgNi$_2$Sb (104841), LaPdSb$_2$ (658217), In$_4$K$_4$Sb$_6$ (071245), Mn$_{12}$Rb$_7$Sb$_{12}$ (237459), Sb$_2$SrZn$_2$ (012152), Ba$_3$Cd$_2$Sb$_4$ (173685), BaRu$_2$Sb$_2$ (188980),
Contd...

Numbers in parenthesis are the ICSD numbers.

BaPtSb (059186), Na5Sb3Sn (076495), CaPtSb (060830), CrLaSb3 (083907), LaRu4Sb12 (641783), KMnSb (085951), La3Sb2Ti (080907), Au3K3Sb2 (078977), BcNaSb (100092), CsMnSb (627028), BaPt2Sb2 (195017), Ni2Sb2Sr (646442), Hf3NiSb2 (195051), Cu4NaSb2 (059206), GaK2Sb2 (053579), Fe4Sb12Sr (658733), CaMn2Sb2 (163778), CuMgSb (077364), CuMgSb (412294), MnSb11Sr14 (075939), Cd6Sb12Sr11 (418887), AuLaSb (251686), LiSbZn (042064), InNa3Sb2 (300140), Ca11InSb9 (042371), Ca2Pd3Sb4 (416139), CdGaSb (012159), Au3Sb4Y3 (009597), CuHf2Sb3 (093243), LiSbSn (603169), Li2PtSb (044895), MgNiSb (044925), In2K2Sb3 (300197), GaHf2Sb3 (189076), LaPd2Sb2 (189724), Ba7Ga4Sb9 (060583), HgKsSb (056201), NiSb7Zr3 (260035), BaMnSb2 (100024), Fe4NaSb12 (246577), Na8Sb4Sn (655768), CuSb2Zr2 (195058), LaSbSc (427126), CuSb2Zr4 (427673), KSnSb (040816), AlKsSb4 (300157), AlCs6Sb3 (300128), MnSb2Sr (643539), AgSb2Y (190094), AlCa3Sb3 (036363), MgPdSb (044825), Ba11Cd6Sb12 (418886), GaK2Sb3 (300196), LiMnSb (642150), Mn-NaSb (060735), Hf5PdSb7 (195052), FeLaSb2 (657985), Fe4LaSb12 (053490), Al2Na7Sb5 (048168), Cu2Sb2Sr (041923), CaCuSb (042137), RuSbZr (107126), Al2Sb6Sr5 (062304), CoSbZr (108317), Rb4Sb6Sb (300212), BaSb2Zn2 (032020), In5K10Sb9 (056323), InSb2Sr11 (240900), NiSbY (105331), Al2Ca5Sb6 (183853), Al2Ca5Sb6 (060146), NiSbZr (408195), Hf5PdSb3 (195060), Ni2SbZr (162585), Ni2SbZr (076703), K5Sb4Sn (656024), Ga3Na2Sb3 (063617), CaCd4Sb2 (012151), Au3Rh2Sb2 (078978), Na6Sb4Tl (096942), CuLiSb (053300), Au3La3Sb4 (612105), CoLaSb3 (419540), AuLi2Sb (058529), Ni3Sb4Zr3 (087995), CuK2Sb (053298), Li3SbZn (001243), BaCd2Sb2 (032021), NiSb9Zr5 (195053), GaRb2Sb2 (300135), Cs6GaSb3 (300216), Pd2Sb2Sr (061194), Pd2Sb2Sr (061195), Cd5K11Sb2 (425646), Mn3Sb18Sr21 (280280), BaCdSb2 (052683), Ba6In2Sb6 (062305), AgLi2Sb (052589), Ca11Mn4Sb18 (281257), Ca21Mn4Sb18 (416972), LaPdSb (641676), Ba6In4Sb6 (195087), CoLaSb2 (657990), LaNiSb2 (658208), KSnZn (044680), KSnZn (012161), BaPd2Sb2 (061197), BaPd2Sb2 (604350), La2NiSb (427930), Cu3La3Sb4 (658637), HfRuSb (107125), CaSb2Zn2 (012150), In2Na2Sb3 (300192), AuLiSb (107996), Ca11MnSb11 (059710), PdSb7Zr3 (426314), Sb2SrZn (010001), Ca21Sb18Zn4 (429153), AgBaSb (056981), CoHfSb (108294), NaSbZn (160957), NaSbZn (012154), PdSbZr (092441), BaRu4Sb12 (616049), Ru2Sb2Sr (188979), AgCaSb (056982), PtSbSr (059185), Ca5Ga2Sb6 (036666), CuK2Sb2 (032032), CuSb2Y (153572), AlRb5Sb3 (300217), PdSb3Zr2 (426315), K10Sb6Sn2 (057401), Rb2Sb4Zn5 (290263), LaNiSb3 (249473), MgPtSb (044826), Cs2PdSb2 (658702), AlBa3Sb3 (032728), AuLaSb2 (082589), Cs2In3Sb3 (056387), BaFe2Sb12 (658735), Mn2Sb2Sr (416094), GaKsSb2 (300202), K6Sb4Tl2 (093048), CuLaSb2 (658225), CuSbSr (053339), HfNi2Sb (638718), BaMn2Sb2 (032019), Li2PdSb (044816), BaCu2Sb2 (236308), Ba3GaSb3 (060124), MnRbSb (643395), BaGaSb2 (280662), BaCuSb (057020), Ca5Sb9Zn4 (052787),
Contd...

Numbers in parenthesis are the ICSD numbers.

AgNa$_2$Sb (010010), Ru$_4$Sb$_{12}$Sr (042962), AuCaSb (052662), In$_2$Sb$_6$Sr$_5$ (036468), AgK$_2$Sb (001155), CdK$_3$Sb (620064), GaSb$_3$Sr$_3$ (065055), Cd$_2$Sb$_2$Sr (012153), Sb$_9$V$_4$Zr$_2$ (408565), PtSbY (649578), AuNa$_2$Sb (023255), In$_2$Rb$_2$Sb$_3$ (083663), Ba$_2$Cd$_2$Sb$_3$ (420834), MgSb$_2$Si (237071), AgMgSb (187150), AgMgSb (187151), Ag-MgSb (187149), CaFe$_4$Sb$_{12}$ (248622), GaK$_3$Sb$_4$ (300158), Al$_2$K$_2$Sr (042627), AlSb$_3$Sr$_3$ (052652), Cu$_4$K$_3$Sb$_2$ (602179), Ba$_2$Sb$_2$Zn (421425), AuK$_2$Sb (380340), CsFe$_2$Sb$_2$ (658698), BeLiSb (616318), Ba$_{21}$Cd$_2$Sb$_{18}$ (173283), Ag$_4$Sb$_2$Sr (424311), Al$_2$Na$_2$Sb$_3$ (052628), Ba$_2$Sb$_6$Sn$_3$ (082529), Bi$_{18}$Ca$_{21}$Mn$_4$ (416520), Bi$_2$Cs$_2$Pd (658703), Bi$_{11}$Mn$_3$Sr$_{14}$ (106328), Bi$_2$CaMn$_2$ (041791), BaBi$_2$Mn (615787), BiPd$_4$Y (616964), Bi$_2$K$_4$Zn (192439), Ba$_2$Bi$_4$Cd$_3$ (416446), BaBi$_2$Zn (058638), BiMnNa (060736), BiCuMg (058774), Bi$_4$La$_3$Pt$_3$ (616774), BiMgNi (076253), AgBiCa (416283), AgBiCa (659377), BiPd$_2$Y (058842), BiK$_2$Sn (107616), Bi$_2$MnSr (100025), Bi$_9$Ca$_9$Mn$_4$ (008157), Al$_2$Bi$_6$Ca$_5$ (036364), Bi$_{12}$Cs$_{14}$In$_8$ (410420), Bi$_6$K$_{10}$Sn$_2$ (300261), AgBiLi$_2$ (057350), AuBiNa$_2$ (261790), AuBiCa (248679), AuBiCa (248676), Ba$_{11}$Bi$_{14}$Cd$_8$ (240338), Bi$_2$Cs$_2$Ni (658704), Bi$_{11}$Ca$_{14}$Mn (106319), Bi$_9$Ca$_9$Zn$_4$ (008158), BaBiCu (106303), Bi$_9$Ca$_9$Cd$_4$ (058760), BiNiY (058826), BiCsMn (616575), BiCaCu (057018), Bi$_2$GaLa (155559), Bi$_2$CaMn (010454), AuBiLi$_2$ (261785), AuBiLi$_2$ (058400), Ba$_2$Bi$_2$Zn (421424), Bi$_2$Cs$_2$Pt (658701), Bi$_{18}$Cd$_{4}$Sr$_{21}$ (173284), BiMnRb (616824), Bi$_6$In$_3$Na$_9$ (413312), AgBaBi (056978), AuBiK$_2$ (380341), BiK$_3$Mn (601586), Bi$_5$K$_4$Zn (238106), Bi$_9$Cd$_4$Sr$_9$ (058763), Bi$_2$Sr$_2$Zn (041924), BiCuSr (058777), BaBi$_2$Cd (058635), Bi$_2$Pd$_2$Sr (416300), Bi$_2$Pd$_2$Sr (604338), Bi$_9$In$_9$K$_{11}$ (413314), Ba$_2$Bi$_3$In$_4$ (054853), Bi$_5$La$_3$Sc (416609), Bi$_2$CdSr (058764), Bi$_2$LaNi$_2$ (616770), Bi$_6$In$_2$Sr$_5$ (415576), Bi$_6$La$_3$Mn (173362), Ag-BiSr (057019), Bi$_4$Cu$_3$La$_3$ (167250), AgBiK$_2$ (001156), BiMg$_3$Si$_{32}$ (291431), Ba$_{14}$Bi$_{11}$Mn (106304), BiLaPt (248481), BaBi$_2$Pd$_2$ (416299), AuBi$_2$L$_a$ (238704), Bi$_8$Ca$_3$Pd$_4$ (412563),