High-throughput exploration of alloying as design strategy for thermoelectrics.

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We explore a material design strategy to optimize the thermoelectric power factor. The approach is based on screening the band structure changes upon a controlled volume change. The methodology is applied to the binary silicides and germanides. We first confirm the effect in antifluorite Mg$_2$Si and Mg$_4$Ge where an increased power factor by alloying with Mg$_2$Sn is experimentally established. Within a high-throughput formalism we identify six previously unreported binaries that exhibit an improvement in their transport properties with volume. Among these, hexagonal MoSi$_2$ and orthorhombic Ca$_2$Si and Ca$_2$Ge have the highest increment in $zT$ with volume. We then perform super-cell calculations on special quasi-random structures to investigate the possibility of obtaining thermodynamically stable alloy systems which would produce the necessary volume changes. We find that for Ca$_2$Si and Ca$_2$Ge the solid solutions with the isostructural Ca$_2$Sn readily forms even at low temperatures.

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Despite their importance, the discovery of new materials are often based on trial and error. High-throughput (HT) computational screening is an important step towards identifying materials with desired properties in a more systematic way. Thermoelectric (TE) materials are attractive for such computational searches because continuous development of computational methodology means that all parts of the TE figure of merit, $zT$ can in principle be calculated from first principles. In practice computational HT searches for new TE materials have focused on parts of the $zT$ lattice computational HT searches for new TE materials that could be experimentally realized.

Beyond screening known compounds, there still exists great challenges designing new materials with specific properties. This is especially the case for electronic structure dependent properties, which have highly non-trivial dependencies on the atomic structure. For TE materials one strategy for designing new alloys with optimized properties is by a controlled volume change. We label this procedure volumetric band-structure alignment (VBA). The idea is illustrated in Fig. 1 where the energy dependence of two bands vary differently upon a change of volume. Thereby a scenario can occur when the band edges are aligned, as schematically illustrated in the mid-panel of Fig. 1. How this optimizes the TE power factor, $PF = S^2\sigma$, can be understood by considering the generalized transport coefficients,

$$L^{(n)} = q^2 \int \sigma(\varepsilon)(\varepsilon - \mu)^{\alpha} \left( -\frac{\partial f}{\partial \varepsilon} \right) d\varepsilon,$$

where $f$ is the Fermi-distribution and $\sigma(\varepsilon)$ the transport distribution. The Seebeck and electric conductivity are given as $S = L^{(1)}/qTL^{(0)}$ and $\sigma = L^{(0)}$, respectively. For two channels (labelled $'$ and $''$) conducting in parallel, $L^{(n)}$ is given as the sum of the contributions from each channel, so that the PF is,

$$S^2\sigma = \frac{1}{q^2T^2} \frac{(L^{(1)}') + (L^{(1)})''^2}{L^{(0)'} + L^{(0)''}}.$$

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{Schematic illustration of volumetric band alignment for a $n$-type material. VBM stands for the Valence Band Minimum.}
\end{figure}

Without loss of generality we can write $L^{(1)'} = \alpha_1L^{(1)}$ and $L^{(0)''} = \alpha_0L^{(0)}. \ \text{Thereby it is clear that the PF will be increased if,}$

$$(1 + \alpha_1)^2 > 1 + \alpha_0.$$

$L^{(1)}$ and thereby $S$ will be significant when the chemical potential is located within the relatively narrow energy window defined by $\partial f/\partial \varepsilon$ of a band edge. Aligning band edges with similar effective masses within $\partial f/\partial \varepsilon$, will satisfy Eq. (3) and lead to an increased PF when compared to the largest of the individual contributions. Such bandstructure characteristics are found in several materials with complex carrier pocket shapes which results in enhanced TE properties.
VBA has been successfully applied to optimize the PF in the n−doped Mg$_2$Si$_{1-x}$Sn$_x$ (and Mg$_2$Ge$_{1-x}$Sn$_x$) and in p−doped PbTe$_{1-x}$Se$_x$ alloys.[21][22] In both the cases the volume was controlled by alloying. Consider as an example the alloy composition MX$_{1-x}$X'$_x$. According to Vegard’s law, the volume of the resulting alloy system, will be directly proportional to the fraction of the new composition added, i.e. $x$. The volume will also be influenced by the thermal expansion, and this together with alloying offers the possibility to control the peak temperature of TE performance.[23]

The question whether it is possible to optimize the band structure by VBA for a given compound, is very difficult to answer from intuition alone. It depends on the detailed band structure and how the different bands react to a volume change. The effect of VBA can be strongly affected by changes to the band gap and doping level. Furthermore, it can be very difficult to predict whether a given compound can be alloyed or not. E.g. while a solid solution of Si and Sn in Mg$_2$Si$_{1-x}$Sn$_x$ can form even at low temperatures,[24][25] it is well known that Sn is hardly soluble in diamond-Si.

The idea behind the present work is to explore a HT computational strategy to identify systems where VBA can be applied. The approach is based on screening the volumetric effect on the band structure and calculate ab-initio thermodynamics to assess the possibility of alloying. It is shown that systems allowing VBA are quite rare and that the procedure leads to a very strong screening of potential candidates. We focus on the electronic part of the $zT$. However, alloying will also be advantageous in terms of reducing the thermal conductivity either by lowering mass-disorder scattering or by using natural solubility limits to nano-structure the material.[26]

We will explore binary alloys of the group 14 elements. Silicon is the second most abundant element on the earth’s crust[27] making such systems quite attractive. Stable alloys and solid solutions with optimized electronic structures and transport properties have been realized with many binary silicides plus the corresponding germanides and stannides compounds.[21] While Ge and Sn are not as abundant and cheap as Si, they are certainly not rare elements either.[28] Other crucial advantages that these M-Si/Ge/Sn alloy systems enjoy, is the ease with which they can be doped. Indeed silicide group compounds exhibit a high density of mobile charge carriers upon doping of up to $n = 10^{20} - 10^{21}$ cm$^{-3}$. Furthermore, they often have high melting points making them attractive stable candidates for high-T TE.[31]

I. METHODS

A. High-throughput scheme

Our HT scheme is illustrated in Fig. 2. We consider binary M-X systems, where M is a metal taken to be a 3d, 4d or 5d Transition Metals (TM) or 2s, 3s and 4s Alkali (A) or Alkaline Earth (AE) metals and X is Si, Ge or Sn. The first step of our work is to identify the stable structures in the constituent binary system. The phase stability is evaluated within a high throughput formalism based on our previous works.[29] For each metal silicide (or germanide) combination, the crystal structures were relaxed and the formation energy was calculated. The candidate structures were generated by extracting the known structures from the Pearson’s database,[30] and appropriate substitution of the known structures with similar atoms (in same group of Periodic Table). Furthermore, we have also incorporated the silicides structures from our previous work[32] and consequent substitution of similar atoms.

In total, we have investigated 3150 different compounds. For a given M-X binary system, we select the structures that have the difference in formation energies from the corresponding convex hull, $\Delta E_f$, lower than 50 meV/atom. The $\Delta E_f < 50$ meV/atom tolerance has statistically been shown to contain 80% of the experimentally known compounds in the TM-Si system[33] and narrows the original number to 522 thermodynamically stable compounds, Fig. 2.

Thereafter, the self-consistent calculations for these selected structures were performed using the (L)APW+lo method[34] implemented within the WIEN2k code.[35] These were followed by bandstructure calculations on a finer k-mesh of 64×10$^2$ k-points in the full BZ. All calculations in this work are reported for Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential. Subsequently, the electronic transport properties were evaluated using the BoltzTrap code.[36] The code evaluates the Seebeck coefficient on an absolute scale and electrical conductivity in terms of the carrier relaxation time $\tau$ using the rigid band approximation. To evaluate the potential for TE energy conversion we utilize a modified

FIG. 2: Flowchart of the HT procedure employed to investigate the candidates for volumetric band engineering. The criterion for good thermoelectrics, i.e. $zT > 0.4$, within our scheme is checked at $T = 600$ K and $n = 2 \times 10^{20}$ cm$^{-3}$ with $zT$ evaluated from Eq. (4).
given material, if calculated equilibrium volume respectively. Thus, for any dependence of the descriptor, i.e. $zT$, of $zT$ and we identify in the $\pm$ criteria of 29.

It can be viewed as a descriptor for identifying potential high TE performance under the assumption of a low thermal conductivity, a long electron life time and the possibility of reaching the optimal doping. Setting a criteria of $zT > 0.4$ [evaluated using Eq. (4)] at $T = 600$ K and $2 \times 10^{20}$ cm$^{-3}$ reduces the number of potential candidates to 29.

The procedure was then repeated at unit-cell volumes in the $\pm7\%$ range of the equilibrium volume. The volume dependence of the descriptor, i.e. $zT(V)$, is evaluated and we identify $zT_{\text{opt}}$ and $zT_0$ which are the magnitude of $zT$ at the volume which maximizes $zT(V)$ and at the calculated equilibrium volume respectively. Thus, for any given material, if $\frac{zT(V_{\text{opt}})}{zT(V_0)} > 1.1$, it will be of interest for the purpose of this work. As can be seen in Fig. 2 this lowers the number of candidate structures to only eight.

The final step is to consider whether the volume change by alloying is thermodynamically feasible. Consider a mixture of $1 - x$ mole fractions of the binary $AB_n$ and $x$ mole fractions of the binary $AC_n$ producing the alloy $AB_n-xC_x$. The excess energy which is required to obtain the alloy; also referred to as the mixing energy, is

$$
\Delta E_{\text{mix}}(x; AB_n, AC_n) = \frac{\Delta E_f(AB_n-xC_x) + x\Delta E_f(AC_n) + (n-x)\Delta E_f(AB_n)}{n}
$$

where $\Delta E_f$ are the formation energies per atom for the given compounds. We have calculated the mixing energies from Eq. (5), by taking Special Quasi-random Structure (SQS) alloy distributions for different values of $x$ using the ATAT code. For solids, since at ambient pressures, $P\Delta_{\text{mix}}V$ term is negligible, the enthalpy of mixing can be approximated as $\Delta H_{\text{mix}} = \Delta E_{\text{mix}}$. Thus the mixing Gibbs free energy is,

$$
\Delta G_{\text{mix}}(x) = \Delta E_{\text{mix}}(x) + \frac{RT}{n+1}[x\ln x + (1-x)\ln(1-x)]
$$

where, the last term accounts for entropy of mixing. For each of the alloys, the minimum temperatures, at which the entropy gain in alloy formation compensates the energy cost of mixing, can be obtained by minimizing Eq. (6). We will report $T_m$, which is the maximum temperature of the boundary of corresponding miscibility. As will be discussed later, this in the end limits the number of potential candidates to only four.

B. Identifying Mg$_2$X as a promising candidate.

In the following we will introduce the HT scheme by example, using the Mg$_2$Si/Ge/Sn system, which is well known for its potential VBA. In the top panel of Fig. 3 the temperature dependance of the enhancement of the TE properties upon volume optimization, i.e. $PF(V_{\text{opt}}) - PF(V_0)$ and $S(V_{\text{opt}}) - S(V_0)$ for the antifluorite structure of Mg$_2$Si (Fig. 3a) and Mg$_2$Ge (Fig. 3b) are shown at a doping of $n = 2 \times 10^{20}$ cm$^{-3}$. In the bottom panel Fig. 3d, the bandstructures for Mg$_2$Si at

![Fig. 3: Volumetric Band Alignment in Mg$_2$X](image-url)
equilibrium volume and the optimized volume are plotted. Likewise, Fig. 3c illustrates the bandstructures at equilibrium volume. The insert shows the miscibility gap calculated by minimizing Eq. (6).

In Fig. 3c and Fig. 3d, we observe that for the p–type behavior the change in PF with volume is negligible for all T. On the other hand, for n-type behavior, the PF shows a pronounced increase at the optimized volume for both the compounds, that further enhances with T. Moreover S also exhibits an increase. Note that for n–doping, the higher the negative value of $S(V_{\text{opt}}) - S(V_0)$, the more is the desired enhancement of the thermopower and $zT$. Also, it is well known that Mg$_2$Si exhibits a persistent n–type conductivity under any kind of crystal growth conditions. When we analyze the variation in the conduction bands (CB) of the compounds with volume (Fig. 3a and Fig. 3b), the large increment in the PFs for n–doped Mg$_2$Si and Mg$_2$Ge becomes quite apparent. At the X point in the BZ near the conduction band minimum (CBM), the first and second CBs directly coincide at $V_{\text{opt}}$ for Mg$_2$Si and are only a few meV apart for Mg$_2$Ge (see insets). Therefore, even at low dopings, the charge carriers (electrons) residing in both the bands will contribute to enhance the PF and Seebeck coefficient, as opposed to the contributions coming from electrons in only a single band, at equilibrium volume.

For Mg$_2$Si, at a doping of $n = 2 \times 10^{20}$ cm$^{-3}$ and $T = 600$ K, the highest increment in $zT$ is observed at volume increase of 2% from the equilibrium volume, Table I. According to Vegard’s law this corresponds roughly to alloying Mg$_2$Si with 10% Mg$_2$Sn. This value will also be dependent on the carrier concentration and temperature at which the transport properties are calculated. The important rule is if a large VBA effect is observed at a small volume change that in principle can be attained by alloying. The second crucial criterion is whether the alloying is thermodynamically feasible. The energy of formation vs volume for Mg$_2$X$_{1-x}$Y$_x$ solid solution is depicted in Fig. 4. Here X is Si or Ge while Y is Ge or Sn. It can be seen that the excess mixing energy required for the formation of stable alloys is small in magnitude. As a result the optimal Sn content can be reached at moderate growth temperature, Fig. 4 inserts. $\Delta E_{\text{mix}}$ and $\Delta E_{\text{opt}}$ are in good agreement with previous DFT calculations, especially considering that we employ a somewhat different computational approach using SQS based supercells and linear interpolation between the calculated points when minimizing Eq. (6). We also find a good agreement with CALPHAD and experimental results for this system.

Thus in the particular cases of antifluorite Mg$_2$Si and Mg$_2$Ge, the VBA can be conveniently achieved through alloying. While Mg$_2$Si$_{1-x}$Ge$_x$ alloy thermodynamically exists as a solid solution even at low temperatures, for Mg$_2$Si$_{1-x}$Sn$_x$ and Mg$_2$Ge$_{1-x}$Sn$_x$ alloys the desired volume increment can be achieved at the expense of only a small magnitude of mixing energy.

### II. RESULTS AND DISCUSSION

#### A. Electronic screening

Based on the descriptors discussed above other candidates for VBA effect will now be identified. The top and bottom panels in Fig. 5 depicts $zT_{\text{opt}}$ vs $zT_0$ respectively for all silicides and germanides, at a doping of $n = 2 \times 10^{20}$ cm$^{-3}$ and $T = 600$ K. Each data point in Fig. 5 represents a particular compound.

Thus Fig. 5 contains three vital descriptors to identify candidates for VBA, (i) the magnitude of $zT_0$, which indicates if a particular candidate is a good TE material, (ii) the value $\frac{zT_{\text{opt}}}{zT_0}$, which helps us to identify the promising candidates exhibiting the volumetric enhancement of their TE properties, (iii) the magnitude of the distance from the corresponding convex hull of the possi-

| Compound | $zT_{\text{opt}}$ | $zT_{\text{opt}}/zT_0$ | $\Delta E_h$ | $\Delta E_{\text{mix}}$ | Doping | $V_{\text{opt}}$ |
|----------|-----------------|-----------------|-------------|---------------------|-------|-------------|
| Mg$_2$Si | 1.07            | 1.33            | 0[0]       | n                   | 2.0   |             |
| Mg$_2$Ge | 1.17            | 2.19            | 0[0]       | n                   | 5.0   |             |
| Ca$_2$Si | 0.80            | 1.33            | 0[0]       | n                   | 5.0   |             |
| Ca$_2$Ge | 0.81            | 1.25            | 0[0]       | n                   | 2.5   |             |
| Ca$_2$Ge$_2$ | 0.96         | 1.47            | 37.4[17.9] | p                   | 6.1   |             |
| β−MoSi$_2$ | 0.77          | 1.75            | 27.3[180.8]| n                   | 3.0   |             |
| α−Fe$_2$Ge$_3$ | 0.47        | 1.19            | 0.1[22.5]  | n                   | 3.0   |             |
| t−Fe$_2$Ge$_3$ | 0.54         | 1.38            | 0[22.8]    | n                   | 3.0   |             |
ble alloying choices, which would produce the necessary volumetric change upon alloying (according to Vegard’s law).

A summary of the promising silicide and germanide structures that exhibit a large VBA effect are shown in Table I, with the corresponding value of $zT_{\text{opt}}$, $zT_{\text{opt}}/zT_0$ and $\Delta E_h$ [$(E_{\text{mix}}^\text{Sn})$]. Eight such compounds were identified to exhibit encouraging VBA effects upon using the magnitude of $zT_{\text{opt}}/zT_0$ and $\Delta E_h$ as descriptors.

In general, with increasing doping we observe that more number of candidates show the VBA effect. This is due to a large value of $zT$ itself that is improved upon doping. However the best candidates, as listed in Table I, exhibiting VBA remained unchanged. Apart from Mg$_2$Si and Mg$_2$Ge, discussed previously, orthorhombic Ca$_2$Si and Ca$_2$Ge, hexagonal Ca$_9$Ge$_5$ and hexagonal MoSi$_2$ show encouraging results.

Note that in Fig. 5 there are compounds that show very little to no VBA effect but exhibit large $zT_0$. Indeed, despite our semi-emperical determination of $zT$, we correctly predict most of these binaries with large values of $zT_0$, that are already established as encouraging TE materials. Compounds which exhibit $zT_0$ in excess of 1.0, at $n = 2 \times 10^{20}$ carriers per cm$^{-3}$, are the orthorhombic and tetragonal structures of Ru$_2$Ge$_3$, cubic RuSi (at low temperatures) and tetragonal NaGe and NaSi. Furthermore, the following compounds have $zT_0$ between 0.5 and 1.0 (not listed in Fig. 5): hexagonal CrSi$_2$, Mn$_4$Si$_7$, FeSi$_2$, ReSi$_1.75$, and CoSi.

### B. Feasibility in alloying

We will now explore the possibility of forming thermodynamically stable alloys among the candidates for VBA, identified based on the descriptors discussed so far. These alloys are summarized in Table II together with proportion of alloying component $x_{\text{alloy}}$ required to produce the highest optimized PFs in the candidates. Note that the optimal VBA for most candidates are achieved at $x \leq 0.30$.

In the previous section we have established that Ca$_2$Si and Ca$_2$Ge are attractive candidates for VBA effect based on the descriptors which characterize their transport properties. In Fig. 6 we illustrate the energy of formation of orthorhombic Ca$_2$X$_{1-x}$Y$_x$ solid solutions as a function of volume. We observe that for $x = 0.25$.

### Table II: Alloy thermodynamics of the candidates. $x_{\text{alloy}}$ is the amount of alloying component, calculated using Vegard’s law, required to obtain the volume change for the VBA effect. $\Delta E_{\text{mix}}(x = 0.25)$ is the mixing energy required to form the alloy (at $x = 0.25$). $T_m$ is the maximum temperature of the boundary of the miscibility gap and $x(T = 800 \text{ K})$ is the amount of alloying component which can be accommodated at $T = 800 \text{ K}$ in the alloy.

| Alloys                  | $x_{\text{alloy}}$ | $\Delta E_{\text{mix}}(x = 0.25)$ (kJ/mol·atom) | $T_m$ (K) | $x(T = 800 \text{ K})$ |
|-------------------------|---------------------|-----------------------------------------------|------------|------------------------|
| Mg$_2$Si$_{1-x}$Sn$_x$  | 0.09                | 1.997                                         | 1281       | 0.171                  |
| Mg$_2$Ge$_{1-x}$Sn$_x$  | 0.26                | 1.595                                         | 1023       | 0.138                  |
| Ca$_2$Si$_{1-x}$Sn$_x$  | 0.30                | 0.013                                         | 78         | all                    |
| Ca$_2$Ge$_{1-x}$Sn$_x$  | 0.18                | 0.015                                         | 97         | all                    |
| Ca$_9$Ge$_{5-x}$Sn$_x$  | 0.28                | 4.495                                         | > 5000     | 0.019                  |
| β-MoSi$_{2-x}$Sn$_x$    | 0.07                | 30.980                                        | > 5000     | 0.008                  |
| o-Fe$_2$Ge$_{1-x}$Sn$_x$| 0.10                | 32.746                                        | > 5000     | 0.004                  |
| t-Fe$_2$Ge$_{3-x}$Sn$_x$| 0.10                | 29.681                                        | > 5000     | 0.005                  |

![Fig. 5: $zT_{\text{opt}}$ vs $zT_0$ for all silicides (top) and germanides (bottom) at doping $n = 2 \times 10^{20}$ cm$^{-3}$ and $T = 600$ K. Furthermore, the scatter points are colored based on the distance from the convex hull, $\Delta E_{\text{Sn}}$ of the corresponding Sn compound with the same structure as the host binary. For example, in the case of the Ca$_9$Ge$_5$ compound, $\Delta E_{\text{Sn}}$ of the corresponding iso-structural Ca$_9$Sn$_5$ is used for the color code, and so on. The candidates that exhibit VBA, $zT_{\text{opt}}/zT_0 > 1.1$, or have a large value of $zT_0$ are labelled. Also, if a compound crystallizes in more than one phase, the corresponding structure is also indicated with a prefix o- for orthorhombic, t- for tetragonal and af- for anti-fluorite phase.](image)
The shortest crystallographic axis, an unitcell contains 12 atoms, i.e. Ca\textsubscript{12} supercell. Here the blue balls are Ca atoms, the grey balls are Sn distance within the unitcell. In Table. II the energy difference between the ordered and disordered alloy is reported as \( \Delta E \). The energy difference is very low and the alloying necessary to obtain the desired volume increment should be readily achieved through Ca\textsubscript{2}Si\textsubscript{1-x}Sn\textsubscript{x} and Ca\textsubscript{2}Ge\textsubscript{1-x}Sn\textsubscript{x} alloys. Thus Ca\textsubscript{2}Si and Ca\textsubscript{2}Ge compounds are confirmed to exhibit the VBA effect and the required volume change can also be conveniently achieved through alloying. Interestingly, Ca\textsubscript{2}Sn has been previously proposed\textsuperscript{23} as a thermoelectric material.

Unfortunately for all the other alloys, we obtained the mixing energy \( \Delta E \) to be very large (see Table. II). Therefore for Ca\textsubscript{9}Ge\textsubscript{5}, \( \beta \)-MoSi\textsubscript{2}, \( \alpha \)-Fe\textsubscript{2}Ge\textsubscript{3} and \( \tau \)-Fe\textsubscript{2}Ge\textsubscript{3}, the optimal VBA volume cannot be expected to be attained by the simple alloy choices listed in Table. II.

Interestingly, we observe that for all four alloys having a large \( \Delta E \) (\( x = 0.25 \)) in Table II the corresponding pure compounds are found above the convex hull, Table II. E.g. in the case of \( \beta \)-MoSi\textsubscript{2} we had obtained that \( \beta \)-MoSn\textsubscript{2} is far from the convex hull (i.e. \( \approx 180 \) meV/atom). This could indicate that \( \Delta E \) can serve as a minimal requirement for the possibility of forming a stable alloy system. Such a descriptor could help to avoid the computationally more expensive SQS supercell calculations.

C. Origin of high \( zT(V_{\text{opt}}) \) in encouraging structures

In the following, we shall investigate the role played by the electronic structure on VBA effect for the candidates. The main focus will be put on Ca\textsubscript{2}Si and Ca\textsubscript{2}Ge where it has been shown that the necessary volume expansion should be achieved by alloying. We will furthermore discuss \( \beta \)-MoSi\textsubscript{2} and Ca\textsubscript{9}Ge\textsubscript{5}. For these candidates, while the optimal VBA volume can not be attained by alloying, we point out that even a small volume increase generated from either alloying or thermal expansion could improve their transport properties through the VBA effect.

1. Orthorhombic Ca\textsubscript{2}Si and Ca\textsubscript{2}Ge

Both Ca\textsubscript{2}X compounds show a large volumetric enhancement in their TE properties. The top panel in Fig. 8 illustrate the temperature dependence of the difference in \( PF \) and \( S \) between \( V_{\text{opt}} \) and \( V_0 \), for Ca\textsubscript{2}Si in Fig. 8a and Ca\textsubscript{2}Ge in Fig. 8b. Likewise, the bottom panel shows the bandstructures of the two compounds (Fig. 8c for Ca\textsubscript{2}Si and Fig. 8d for Ca\textsubscript{2}Ge), at the two volumes.

The \( p \)-type behavior for both the compounds show a negligible amount of increase in \( PF \) and \( S \) at \( V_{\text{opt}} \). Accordingly, the VBM, around the vicinity of \( \Gamma \) point, is relatively unchanged. The situation is different for the CBM which has contributions coming from the \( \Gamma \) and \( T \) points at \( V_0 \). Due to this we have \( zT_0 \) for Ca\textsubscript{2}Si = 0.60 and \( zT_0 \) for Ca\textsubscript{2}Ge = 0.64, at \( T = 600 \) K and \( n = 2 \times 10^{20} \) cm\textsuperscript{–3}. At optimal volume, n-type Ca\textsubscript{2}Si and Ca\textsubscript{2}Ge show an increase in their TE properties to \( zT_0 \) = 0.80 and \( zT_0 \) = 0.81. From the bandstructures of Ca\textsubscript{2}Si in Fig. 8c, one can understand this volumetric enhancement. There is a lowering of the CBM at the \( T \) and
2. Hexagonal Ca$_2$Ge

![Diagram of hexagonal Ca$_2$Ge structure]

We shall now discuss the hexagonal structure of Ca$_2$Ge, which also exhibits an increase in its TE properties with volume change. In the same fashion as the data presented in the previous sections, Fig. 10a shows the temperature dependence of the change in $PF$ and $S$ at the two volumes, $V_{\text{opt}}$ and $V_0$. The bottom panel shows the bandstructure at the two volumes. The situation for Ca$_2$Ge is quite interesting. Upon an increase in volume, there is an opening of the bandgap at the $\Gamma$ point in its BZ. This metal to semiconductor transition with volume change is the sole reason behind the enhancement of $PF$ and $S$ at $V_{\text{opt}}$, graphed in Fig. 10b. Interestingly, a very high $\Delta T_{\text{opt}} S_{\text{Ca}_2\text{Ge}} = 0.96$ and $zT_{\text{opt}}/zT_0 = 1.47$ (at $T = 600$ K and $n = 2 \times 10^{20}$ cm$^{-3}$) was observed.

3. Hexagonal MoSi$_2$

Molybdenum di-silicide, MoSi$_2$, exists as $\alpha$–MoSi$_2$, having a tetragonal body-centered packing with a space group of $I4/mmm$ and as $\beta$–MoSi$_2$ that has a hexagonal closed packing arrangement with space group $P6_3$22. Both the structures are composed of Mo and Si layers in which Mo atoms are surrounded by 6 Si atoms. Both the allotropes of MoSi$_2$ exhibit properties such as high melting points, low resistivity and high mechanical strength. While $\beta$–MoSi$_2$ is found to be 27.3 meV/atom above the convex hull, it can be conveniently synthesized from Mo and Si powders using spark plasma sintering techniques, thus confirming the $\Delta E_h <$
is steadily reduced at temperatures above 350 K due to the small band gap. Please note that the results for all the candidates in Table I are presented at \( T = 600 \) K.

The explanation for the observed magnification in \( PF \) and \( S \) with volume, can be pinned down to the lowering in energy of the first CB, along multiple directions in its BZ observed in Fig. 11b. These changes in the bandstructure not only causes an increased DOS of carriers around the CBM, but also an increased number of electron pockets. The Fermi surface demonstrating the electronic contributions at \( V_{\text{opt}} \) under doped scenario is shown in Fig. 12. Both the above discussed factors improve \( PF \) and \( S \) for \( n \)-doped MoSi\(_2\) with volume enlargement. Consequently at a doping of \( n = 2 \times 10^{20} \) cm\(^{-3}\), we obtain the observe the largest VBA effect in this work of \( zT_{\text{opt}}^{\beta\text{MoSi}_2} = 1.07 \) and \( zT_{\text{opt}}/zT_0 = 3.84 \) (at \( T = 450 \) K) for \( n \) doping scenario. The same values at \( T = 600 \) K are tabulated in Table II.

III. CONCLUSION

In this paper a computational HT-scheme to identify compounds where the thermoelectric properties can be optimized by alloying is presented.

We confirm that Mg\(_2\)Si and Mg\(_2\)Ge exhibit large enhancement of their thermoelectric properties with volume. We report for the first time that Ca\(_2\)Si and Ca\(_2\)Ge, hexagonal MoSi\(_2\) and Ca\(_9\)Ge\(_5\) could exhibit increased thermoelectric properties due to a volumetric band alignment. In the cases of Ca\(_2\)Si and Ca\(_2\)Ge the solid-solutions with Sn can be obtained at the expense of a negligible amount of mixing energy and therefore the volume changes can be obtained by alloying. Among the remaining candidates, the volume increase for the VBA effect is thermodynamically difficult to achieve by alloying. However, we have obtained that \( \beta \)-MoSi\(_2\) exhibits a significant increase in its thermoelectric properties due VBA, by the virtue of favorable changes to its bandstructure with volume. Thus, in this case even a small volume change due to alloying or thermal expansion may enhance its thermoelectric properties. Finally, we have established that \( \Delta F^{\text{eh}} \) can be a reliable descriptor to provide initial information on the stability of the corresponding alloys.

We have focused on systems where the electronic PF can be optimized with controlled volume changes. Alloying will also decrease the lattice part of the thermal conductivity, which will further improve the thermoelectric performance of the candidates.

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