1 Introduction

Thermoelectric (TE) devices can directly convert between electrical and thermal energies for cooling or heating or to recover waste heat. These materials have traditionally had an important role in energy conversion, especially portable refrigeration devices, and power generation especially for space crafts.1–3 They are increasingly seen as having the potential to make important contributions to energy technology more generally.4–5 Furthermore, there has been a connection with topological insulators and the possibility of important contributions to energy technology more generally.3–5 They are increasingly seen as having the potential to make important contributions to energy technology more generally.4–5 Furthermore, there has been a connection with topological insulators and the possibility of important contributions to energy technology more generally.3–5

Efficiency plays a central role in energy technology. In the case of TE, this is limited by a figure of merit $ZT = \sigma S^2 T / k$, where $\sigma$ is the electrical conductivity, $S$ is the thermopower, $k$ is the thermal conductivity, and $T$ is the absolute temperature. A good TE material should have excellent electrical transport properties, measured by the TE power factor ($PF = S^2 \sigma$) and also a low thermal conductivity $k$.

Caillat et al. found a high $ZT$ of 1.3 at 970 K in p-type $\beta$-Zn$_x$Sb$_{1-x}$ in 1997.16 The high performance combined with the relatively inexpensive, environmentally acceptable composition stimulated considerable interest. Four compounds in the narrow range of 50–60 atomic% of Zn were reported in the binary Zn–Sb phase diagram: ZnSb is a stoichiometric compound with a well characterised crystal structure (CdSb-type)7 and stable up to 822 K. Zn$_x$Sb$_{1-x}$ displays temperature dependent polymorphism, with a $\beta$–$\alpha$ transition at approximately 250 K.16,19 Two phases of Zn$_x$Sb$_{1-x}$ have been reported, $\alpha$ and $\beta$.20,21 Zn$_2$Sb$_3$ is metastable and has been reported without any crystal structure solution.22 Interestingly, the experimental values and temperature dependences of $S$ and $\sigma$ are very similar for ZnSb, $\beta$-Zn$_x$Sb$_{1-x}$ and $\beta$-Zn$_2$Sb$_3$. What makes the $\beta$-phase special is the exceptionally low thermal conductivity, which is as low as that expected for glass-like materials. The presence of the interstitial Zn atoms in the $\beta$-phase crystal structures is the key to the low lattice thermal conductivity.20,23 There have been several studies of electrical and transport properties for $\beta$-Zn$_x$Sb$_{1-x}$, $\alpha$-Zn$_x$Sb$_{1-x}$, Zn$_2$Sb$_3$, and ZnSb,24–32 including first principles studies of the electronic structures of these binaries26,30–32 and the related Zintl phases SrZn$_2$Sb$_2$ and YbZn$_2$Sb$_2$. However, the other phases have not been studied in similar detail. Here we report detailed first-principles calculations to establish the electronic structures of Zn–Sb binary system compounds, elucidate the structures and bonding, and to assess their thermoelectric potential.

2 Computational methodology

Full structure optimizations were performed using the projector augmented wave (PAW)33 method with generalized approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) as implemented in the VASP code.34 Following a series of test calculations a plane-wave cutoff of 360 eV and k-point meshes of spacing $2\pi \times 0.03$ Å$^{-1}$ or better were adopted. In all of the calculations the convergence limit was set to $1 \times 10^{-4}$ eV Å$^{-1}$ for the force and $1 \times 10^{-5}$ eV Å$^{-1}$ for the energy. Standard GGA methods underestimate the band gaps due to the presence of artificial self-interaction and the absence of the derivative discontinuity.
in the exchange–correlation potential.\textsuperscript{35,36} We used the modified Becke Johnson (MBJ) potential to obtain more accurate bandgaps and optical properties. This potential generally improves the accuracy of the gap values relative to experiments. For example, the band gaps calculated using MBJ potential for ZnSb and $\beta$-Zn$_3$Sb$_2$ (0.60 and 0.77 eV, respectively) are much closer to experimental values (0.61 and 0.8 eV\textsuperscript{38,39}) than PBE values (0.15 and 0.4 eV).

This is important for predicting the thermoelectric properties, as the thermopower in particular can be strongly reduced by spurious bipolar effects from underestimated band gaps. However, the MBJ potential does not have a corresponding energy functional and therefore cannot be used to predict the structures. Therefore we use the PBE functional, which is designed to produce reliable total energies and structures, but not band gaps, to obtain crystal structures, and then do calculations with the MBJ potential to obtain band structures and transport properties. We did not include the spin–orbit coupling (SOC) effect in transport calculations since it shows a negligible effect on the electronic structures of the studied system. The values of the gaps are given in Table 1 along with calculated transport coefficients at 400 K. The available experimental and calculated data are listed for comparison. The transport coefficients are discussed for each compound in the sections below.

In order to demonstrate the validity of using the MBJ potential, we calculate the optical spectra shown in Fig. 1. The onset of absorption is at 0.85 eV. The experimental onset of strong absorption transition is at approximately 1.05 eV. We find noticeable anisotropy in the optical absorption, very close to the onset. It shows significantly stronger absorption for polarization along $c$, in accord with the experiment.\textsuperscript{38} We predict that this anisotropy switches at higher energy so that the strongest absorption is for polarization along $a$ in the range 2–4 eV.

The transport calculations were done using the BoltzTraP program.\textsuperscript{40} We used approximately 5000 $k$-points in the irreducible Brillouin Zone, with the constant relaxation time approximation. The necessary crystal structure and eigenenergies were obtained from VASP results by using MBJ potential. This approach uses a rigid band approximation. This is generally valid for semiconductors that have good conductivity when doped, as is the case for the Zn–Sb phases (note that strong band distortion upon doping is indicative of strong electronic scattering by dopants). It is also consistent with spectroscopic measurements for some of these phases in relation to prior density functional calculations.\textsuperscript{30–32} Going beyond the rigid band approximation would require knowledge of the specific doping elements and defects that occur in actual samples.

Previous studies on the phase diagram of the zinc-antimony system have reported compound Zn$_3$Sb$_2$.\textsuperscript{41,42} But it is metastable and crystals amorphize over time, which impedes its structure and property characterization. We performed a crystal structure prediction for Zn$_3$Sb$_2$ via global minimization of free energy surfaces as implemented in the CALYPSO code, which searches for the stable structures of the given compounds. Using particle swarm optimization (PSO) the most stable structures based on the chemical composition can be found. Importantly, this approach is unbiased by already known structures.\textsuperscript{43,44} In this sense it differs from approaches such as those used in most materials genome projects, for example, the materials project,\textsuperscript{45} where known structures and structure types are generally relied upon. The advantage of the PSO approach is that it can find structures that were previously unknown, while on the other hand it requires calculations for many structures during the global optimization. Structure searching was performed at zero pressure with simulation cells consisting of 1–4 formula units (f.u.). This global optimization

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Compound & $E_g$ (direct) & $E_g$ (indirect) & $S$ (400 K, 10$^{20}$ cm$^{-2}$) & $\sigma S^2/\tau$ (400 K, 10$^{20}$ cm$^{-2}$) \\
\hline
ZnSb & 0.60 & 0.88 & 98 & 7.3 \\
 & 0.61 (Exp.)\textsuperscript{30} & 0.56 (Cal.)\textsuperscript{31} & 90 (Cal.)\textsuperscript{30} & 135 (Cal.)\textsuperscript{31} \\
$\alpha$-Zn$_3$Sb$_2$ & 0.68 & 0.77 & 205 & 14.5 \\
 & 0.77 & & 161 & \\
$\beta$-Zn$_3$Sb$_2$ & 0.83 (Exp.)\textsuperscript{29} & 0.81 & 110 (Cal.)\textsuperscript{29} & 15.9 \\
 & 0.83 (Cal.)\textsuperscript{30} & & 180 (Cal.)\textsuperscript{29} & \\
$\alpha$-Zn$_3$Sb$_2$ & 0.71 & 0.76 & 164 & 7.5 \\
 & & & 142 (Cal.)\textsuperscript{29} & \\
$\beta$-Zn$_3$Sb$_2$ & 0.61 & 0.61 & 129 & 8.1 \\
ZnSb$_2$ & 0.06 & 0.1 & 109 & 6.9 \\
\hline
\end{tabular}
\caption{Calculated indirect and direct bandgaps $E_g$ (in eV), as well as thermopowers $S$ (in $\mu$V K$^{-1}$) and power factor divided by scattering time $\sigma S^2/\tau$ (in 10$^{10}$ W K$^{-2}$ ms) at a temperature of 400 K and a carrier concentration of 10$^{20}$ cm$^{-3}$. The available experimental (Exp.) and calculated (Cal.) results are listed for comparison, for $S$, the data for comparison are: ZnSb at a carrier concentration of 0.75 x 10$^{20}$ cm$^{-3}$ at a temperature of 400 K from ref. 29, and 1 x 10$^{20}$ cm$^{-3}$ at 600 K from ref. 31; $\alpha$-Zn$_3$Sb$_2$ at 4.9 x 10$^{20}$ cm$^{-3}$ at 400 K from ref. 29, and 0.75 x 10$^{20}$ cm$^{-3}$ at 400 K from ref. 26; $\beta$-Zn$_3$Sb$_2$ at 4.7 x 10$^{20}$ cm$^{-3}$ at 400 K from ref. 29.}
\end{table}
involved density functional relaxations of approximately 1500 distinct structures to find the ground state. The most stable predicted structure was then further optimized using VASP as described above. This calculation adds the structure and energy of ZnSb₂ to the phase diagram.

3 Structure and phase diagram

We consider all Zn–Sb binary materials for which structures have been reported and ZnSb₂ with a predicted structure. Orthorhombic ZnSb (space group Pbam) was reported in 1948. It may be regarded as an arrangement of Zn centered, vertex and corner sharing Sb₄ tetrahedra (quasitetrahedral close-packing), as shown in Fig. 2a. The formal valence state of Sb is −2, and it has the appearance of a classical Zintl phase with Sb present as (Sb₂)⁴⁻ dimers. The ZnSb₄ tetrahedra are linked by Sb–Sb bonds. We note that such Sb–Sb dumbbells have been implicated in the low thermal conductivity of the ZnSb₂ phase.

The low temperature α-phase and high temperature β-phase of ZnSb₂ were considered in this work. The unit cell of β-Zn₅Sb₁₀ is rhombohedral (space group R₃c) and contains three distinct atomic positions (36 Zn, 18 Sb₁, and 12 Sb₂ amounting to a Zn₃.6Sb₃ stoichiometry). The atoms on the Sb₁ site are free Sb³⁻ while those on the Sb₂ site form (Sb₂)⁴⁻ dimers, according to the Zintl-Klemm concept. The problem posed by apparent deviation from the nominal composition was solved by Snyder et al. They found a high degree of disorder in the Zn substructure of β-Zn₅Sb₁₀, and in particular interstitial Zn atoms distributed on three partially occupied general sites in space group R3C (36f). Additionally, the regular framework position (also 36f) displayed a considerable occupational deficiency with only 0.89–0.9 of the sites filled. Based on this, the framework of β-Zn₅Sb₁₀ for our calculations was constructed in the following way: first, a rhombohedral primitive cell was built with full occupancy of Zn₁, Sb₁ and Sb₂ sites resulting in the Zn₁₂Sb₁₀ stoichiometry. Then we removed two Zn atoms from the main site (Zn₁) and inserted three different Zn interstitials in the Zn₂, Zn₃ and Zn₄ sites, respectively, while maximizing the distance between interstitial atoms to minimize the total energy. We considered all the possible configurations and chose the lowest total energy. The final structure is shown in Fig. 2d. Below about 250 K β-Zn₅Sb₁₀ transforms into α-Zn₅Sb₁₀, which surprisingly has a completely ordered structure with a crystallographic composition of Zn₁₅Sb₁₀ for fully occupied sites. The structure of α-Zn₅Sb₁₀ is triclinic, but is often described with a C-centred cell (i.e. C1). Here, the interstitial Zn atoms are located on two fully occupied sites, and the main Zn site is also fully occupied (Fig. 2c). α-Zn₅Sb₁₀ is a new metastable compound whose synthesis was reported in 2015. It crystallizes in a noncentrosymmetric orthorhombic space group Pmn2₁. Twenty-four Zn atoms are distributed over 6 fully occupied crystallographic sites, while the remaining 8 Zn atoms are distributed over 4 sites with partial occupancies. It contains 10 (Sb₂)⁴⁻ dumbbells and 8 isolated Sb⁷⁻ anions, which is similar to Zn₁₅Sb₁₀. Each Zn atom is surrounded by distorted tetrahedra with sharing of common edges. The distances of the reported Zn7–Zn8 and Zn9–Zn10 sites are in the range of 1.2–1.4 Å. This indicates that only one of two possible Zn atoms is present. Thus, we use one Zn8 atom to replace the nearest Zn7 atom, similarly for Zn9 and Zn10. The final crystal structure with the lowest total energy is shown in Fig. 2f. The α-Zn₅Sb₁₀ phase was reported as Zn₁₅Sb₁₀ (with δ = 0.068) with a space group Pm. It has an ordered structure with an ideal stoichiometry of Zn₅Sb₁₀ and few Zn defects in it. We adopt its ideal full occupancy structure in our calculation (Fig. 2e).

We performed variable-cell prediction simulations using the PSO methodology for Zn₅Sb₁₀ at 0 GPa. The lowest energy structure was chosen, as shown in Fig. 2b. Its crystal structure is tetragonal (space group P421m, Z = 2), with lattice parameters a = 7.090 Å and c = 4.777 Å. Sb occupies the 4e (1.134, 0.634, 0.738) sites, while Zn atoms are at the 4c sites (1.134, 0.634, 0.738) and 2d sites (0, 0, 0.5). All Sb in this structure are isolated Sb³⁻ anions, with no bonds between Sb atoms. We note that this structure differs from the hexagonal and cubic structures of Mg₅Sb₂ and Ca₅Sb₂. Each Sb atom is exclusively surrounded by six Zn atoms (at distances between 2.65 and 2.82 Å, similar to the known structures for β-Zn₅Sb₁₀ 2.7–2.8 Å, for α-Zn₅Sb₁₀ 2.67–2.75 Å, for β-Zn₅Sb₁₀ 2.64–2.87 Å, and 2.56–2.92 Å for the α-Zn₅Sb₁₀ phase). Each ZnSb₄...
tetrahedron shares a common Sb atom with another five tetrahedra. It is perhaps surprising that Zn₄Sb₃ has a different structure than hexagonal Mg₃Sb₂. However, we note that the electronegativity of Zn is significantly higher than Mg, which suggests chemical differences. We carefully checked the result by performing all-electron calculations for Zn₄Sb₃ in the fully relaxed Mg₃Sb₂ structure and our predicted tetragonal ground state structure. These calculations were done using the general potential linearized augmented plane-wave (LAPW) method as implemented in the WIEN2k code. We used highly converged basis sets based on the accurate LAPW augmentation, plus local orbitals to treat semicore states. We added additional local orbitals to improve the accuracy for the Zn d state. Spin–local orbitals were included in these calculations. We find that our predicted tetragonal structure is lower in energy by 0.25 eV per formula unit. This means that the tetragonal structure is strongly preferred over the Mg₃Sb₂ structure for Zn₄Sb₃.

We calculated the formation energy with respect to the elements for six configurations. As plotted in Fig. 3, the formation enthalpies of all the configurations are negative. In order to analyze phase stability at 0 K, we constructed the convex hull of formation enthalpy, as illustrated by the solid lines in Fig. 3. Here we included the SOC effect. ZnSb is the most stable system with a formation energy of approximately 27 meV per atom. The data shown for the interstitial structures are for the lowest formation energy structure out of all those that we built. A structure whose formation enthalpy lies above the convex hull, which can be considered as a global stability line, is metastable or unstable. The formation enthalpies of Zn₄Sb₃, Zn₈Sb₇ and Zn₃Sb₂ are above the convex hull, which can be considered as a global stability line, is metastable or unstable. The formation enthalpies of Zn₄Sb₃, Zn₈Sb₇ and Zn₃Sb₂ are above the convex hull. As expected, the interstitial frameworks of β-phases are less stable than those of the ordered α-phases, but they still have a negative energy of formation (4.5 meV per atom for β-Zn₄Sb₃, 6 meV per atom for β-Zn₃Sb₂). Surprisingly the α-phase is unstable with respect to the decomposition into ZnSb and Zn. The predicted structure of Zn₃Sb₂ has a little lower formation enthalpy (8 meV per atom). Without the SOC the formation energies are a little lower. But this does not change the stability situation for the Zn–Sb binary system.

4 Electronic and transport properties

The calculated band structures and total and projected density of states (DOS) obtained with MBJ potential are shown in Fig. 4–9a. The Fermi levels are set to the top of the valence band. The results show that the MBJ method performs consistently better than PBE-GGA and produces band gaps that are in excellent agreement with the experimental values. This is in accord with prior results for other non-d-electron semiconductors. All the band structures shown are indirect band gap except Zn₄Sb₃. The PDOS show that the valence bands are formed from Zn p, Sb s, and Sb p hybridized states. The conduction band is characterized mainly by s-electrons of zinc which are hybridized with 5p-electrons of antimony. The total density of states show a similar shape and magnitude of the valence band edges of Zn₄Sb₃ and Zn₈Sb₇, which suggests a similar hole carrier effective mass and similar electronic properties. It is remarkable that in spite of the different Zn–Sb ratios and crystal structures, all these compounds show similar electronic structures. This is an example of the robustness of the Zintl concept for the Zn–Sb system, specifically the balance between the Zn:Sb and the Sb₃/2(Sb₂)₁/2 ratios.

Here we focus on the p-type, since experimentally all these compounds form as the p-type. We performed calculations of the thermopower as a function of temperature and the p-type
doping level with Boltzmann theory in the CSTA with rigid bands. We also show $S^2/\tau$ as a function of carrier concentration at different temperatures. This is the power factor divided by the scattering time, $\tau$, which is an undetermined parameter that can depend on both doping and temperature. Generally $\tau$ decreases with both temperature and carrier concentration, though the carrier concentration dependence is often weaker than the $\tau$ dependence. The validity of these approaches can be established by studying the agreement between theoretical results and experimental data shown in Fig. 4–6 and 8 and is discussed further in the text.

**ZnSb**

The valence bands are nearly parabolic at the band edge. We show the thermopower of ZnSb at carrier concentrations...
transport properties. The doping level at 300–700 K corresponding to the peak $\sigma S^2/\tau$ lies in the range of $1 \times 10^{20}$ to $4 \times 10^{20}$ cm$^{-3}$ for both $\alpha$ and $\beta$ phases (Fig. 7 and 8c). It was found that the thermopower values of the disordered $\beta$ phase and the ordered $\alpha$-phase of Zn$_8$Sb$_7$ and Zn$_4$Sb$_3$ were very similar. Hence, the key to the outstanding thermoelectric properties of the $\beta$-phase lies in the exceptionally low thermal conductivity, which is as low as that for glass-like materials combined with its favorable electronic properties.

Zn$_3$Sb$_2$

A narrow band gap of 0.06 eV separates the valence states to the conduction states. The electronic structure of Zn$_3$Sb$_2$ exhibits the charge carrier pockets with light bands near the VBM and CBM, which leads to low thermopower. As predicted the light band at the edge of bands indeed leads to a low thermopower for Zn$_3$Sb$_2$ (Fig. 9b). The very small gap suggests that this phase will not be a good thermoelectric at least at room temperature and above. This is also seen in the thermopower, which shows strong bipolar effects.

5 Conclusions

The $\beta$-phases of Zn$_8$Sb$_7$ and Zn$_4$Sb$_3$ have complex crystal structures. These structures challenge crystallography because of the presence of site disorder for the Zn atoms. In this work, we have proposed structural models of $\beta$-phases, which are close to experimental studies. All binary Zn/Sb compounds are narrow-gap semiconductors. We have analysed the phase stability, electronic structure, optical property of ZnSb and transport properties by means of first principles density functional theory and Boltzmann transport calculations. Additionally, we have searched for the Zn$_3$Sb$_2$ structure using the PSO method. This yields a structure different from the hexagonal structure of Mg$_3$Sb$_2$, reflecting the different chemistries of Zn and Mg. In terms of the formation energy, this phase is comparable to Zn$_8$Sb$_7$ and Zn$_4$Sb$_3$. In thermodynamic stability analysis, they are all metastable phases.

A similar shape and magnitude of the total density of states in the valence band edge of Zn$_8$Sb$_7$ and Zn$_4$Sb$_3$ lead to similar thermopower values. The thermopower data and transport properties from our calculations show that Zn$_3$Sb$_2$ should not be a good candidate for thermoelectric materials at room temperature and above. The existing experimental results show the best performance for $\beta$-Zn$_3$Sb$_2$. This material has a reasonable band gap, shows multiple valence bands sufficiently near the band edge to influence the thermoelectric behavior and importantly has a low thermal conductivity characteristic of the $\beta$-phases. However, our results also show that there is still room for improvement in $ZT$ of the $\beta$ phases by optimization of carrier concentration. A comparison of the compounds in terms of the balance between $\sigma/\tau$ and $S$ at 400 K and a carrier concentration of $10^{19}$ cm$^{-3}$ as well as the doping dependence of $S$ is given in Fig. 10.
Finally it is interesting to note that although some gaps are small, all the compounds are semiconducting. This is a reflection of the Zintl concept in those phases, especially the balance between the Zn:Sb and Sb$^{3-}$:2(Sb$_2$)$^{4-}$ ratios reflecting stabilization or destabilization of (Sb$_2$)$^{4-}$ polyanions according to the amount of charge available from the Zn$^{2+}$ cations. We note that several of these phases are underdoped for thermoelectric performance. The flexibility of these compounds in terms of carrier compensation via the Sb$^{3-}$:2(Sb$_2$)$^{4-}$ ratio poses a challenge for achieving the optimum doping level. The solution to this problem may lead to significantly better ZT in the Zn–Sb phases.

Acknowledgements

The authors acknowledge funding support from the Recruitment Program of Global Youth Experts in China and special funds for talent development in Jilin Province. Part of calculations was performed in the high performance computing center of Jilin University. Work of D. J. S is supported by S3TEC an Energy Frontier Research Center funded by the Department of Energy, Office of Science, Basic Energy Sciences under award DE-SC0001299/DE-FG02-09ER46577.

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