Predicted Electronic and Thermodynamic Properties of a Newly Discovered Zn$_8$Sb$_7$ Phase

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ABSTRACT: A new binary compound, Zn$_8$Sb$_7$, has recently been prepared in nanoparticulate form via solution synthesis. No such phase is known in the bulk phase diagram; instead, one would expect phase separation to the good thermoelectric semiconductors ZnSb and Zn$_4$Sb$_3$. Here, density functional calculations are employed to determine the free energies of formation, including effects from vibrations and configurational disorder, of the relevant phases, yielding insight into the phase stability of Zn$_8$Sb$_7$. Band structure calculations predict Zn$_8$Sb$_7$, much like ZnSb and Zn$_4$Sb$_3$, to be an intermetallic semiconductor with similar thermoelectric properties. If sufficient entropy or surface energy exists to stabilize the bulk material, it would be stable in a limited temperature window at high temperature.

INTRODUCTION

Intermetallic compounds are fascinating due to the diversity of their crystal structures and resulting properties. For thermoelectric applications, ZnSb and Zn$_4$Sb$_3$ are two intermetallic compounds which exhibit good thermoelectric efficiencies. In particular, Zn$_4$Sb$_3$ has a thermoelectric figure of merit ($zT$) in excess of unity$^{1,2}$ due to its low thermal conductivity, which arises in part due to its complex, defect-ridden structure. Both of these materials have band gaps at or near the Fermi level which can be rationalized from valence charge counting.$^3$

Recently, a new binary Zn–Sb phase between ZnSb and Zn$_4$Sb$_3$, was discovered and characterized at room temperature by Birkel et al.$^4$ Binary nanoparticles were synthesized in solution through the controlled reaction of elemental Zn and Sb nanoparticles. The small particle size of the reactants ensures minimum diffusion paths, low activation barriers, and low reaction temperatures, thereby eliminating solid—solid diffusion as the rate-limiting step as found in conventional bulk-scale solid-state synthesis.$^4$ In the present work, the authors denote this new phase as Zn$_8$Sb$_7$, based on the idealized crystal structure, rather than Zn$_{11.4}$Sb$_3$ (with $\delta = 0.068$) as used in ref 4.

Determination of the Zn$_8$Sb$_7$ structure was a tour de force of automated electron diffraction tomography (ADT) combined with precession electron diffraction (PED) on individual nanoparticle grains. This work yielded the structure in Figure 1, shown along the [001] and [100] directions in the distorted hexagonal cell (PT). Much like Zn$_4$Sb$_3$, Zn$_8$Sb$_7$ contains both Sb$_2^{4-}$ dimers and isolated Sb$_3^{-}$; however, the long-range atomic arrangement is completely distinct.

The Zn$_8$Sb$_7$ phase enters into an interesting region of the binary phase diagram$^5$ between ZnSb and Zn$_4$Sb$_3$. Since the three phases are so close in composition, the competition for thermodynamic stability will be fierce. Below $\sim 250 \text{ K}$, Zn$_8$Sb$_7$ transforms to a variant (the $\alpha$ or $\alpha'$ phase) where the interstitial atoms form an ordered arrangement.$^{5,6}$ The disordered $\beta$ phase is stable from $\sim 250 \text{ K}$ (to 700 K), while no compounds have been characterized in the bulk at compositions between Zn$_8$Sb$_7$ and ZnSb. Several phase diagrams have been reported that include a phase between Zn$_4$Sb$_3$ and ZnSb stable only at high temperature,$^{5,8,9}$ sometimes denoted as $\gamma'$, but no crystal structures have been determined for these high-temperature phases.

Ab initio calculations have considered various interstitial configurations of Zn$_8$Sb$_7$ at 0 K and found that they should decompose to ZnSb and Zn when considering the enthalpy of formation alone.$^{10–13}$ Additional theoretical work has recently shown Zn$_8$Sb$_7$ to be entropically stabilized due to the high configurational disorder with the three interstitial Zn sites and the effects of lattice vibrations.$^{14}$ The narrow stable composition range is near Zn$_{3.89}$Sb$_3$, as inferred from Hall carrier measurements and valence charge counting,$^{2,14}$ which is off from the valence-balanced composition of Zn$_{6.9}$Sb$_3$. We will continue to use the conventional Zn$_8$Sb$_7$ terminology.

In this work, we explore the electronic and thermodynamic properties of a theoretical bulk Zn$_8$Sb$_7$ phase. Electronic structure calculations probe the band structure and valence band edge character of Zn$_8$Sb$_7$ to compare with known bulk thermoelectrics ZnSb and Zn$_4$Sb$_3$. Since the formation of Zn$_8$Sb$_7$ is not readily observed in practice, a thermodynamic investigation determines if the phase might be thermodynamically stable or metastable with respect to competing Zn–Sb phases. A thorough thermodynamic treatment considers the bonding enthalpy as well as possible sources of entropy such as configurational disorder and

Received: March 18, 2011
Published: June 16, 2011
of the constituent primitive cells. Under the independent cells approximation,
\[
\phi(T, \mu) = \frac{\varepsilon_0}{n} - \mu \cdot x_0 - \frac{k_B T}{n} \ln \left( 1 + \sum_{i=0}^{\infty} m_i e^{-\left( E_i - \mu \cdot N_i \right)/k_B T} \right)
\]  
(3)

where \( \varepsilon_0 \) is the ground-state energy per unit cell, \( n \) is the number of atoms per unit cell, and \( x_0 \) is the ground-state composition. For each configuration \( i \), \( m_i \) is the symmetric multiplicity, \( \Delta E_i \) is the change in energy from the ground state, and \( \Delta N_i \) is the change in the number of atoms from the ground state.

The total energy of each atomic configuration was calculated using Density Functional Theory (DFT) with the PBE exchange-correlation functional.\(^\text{16} \) Calculations utilized the projector augmented wave (PAW) method\(^\text{17} \) as implemented in VASP,\(^\text{18} \) neglecting spin–orbit coupling. All unit cell parameters and atomic positions were allowed to relax to find the lowest energy arrangement to within \( 10^{-4} \) eV per primitive unit cell. A final static calculation was performed for an accurate total energy. Energy convergence with respect to \( k \)-points was achieved with a \( \Gamma \)-centered grid with 14 \( k \)-points in the irreducible Brillouin zone.

Configurational arrangements for \( \text{Zn}_8\text{Sb}_7 \) were enumerated by considering all possible interstitial combinations on known \( \text{Zn} \) interstitial sites.\(^\text{3,14} \) Configurational arrangements of \( \text{Zn}_8\text{Sb}_7 \) are much more difficult to enumerate appropriately without guidance from experimentally known defect lattice sites. The configurational disorder then was probed by a systematic enumeration of new possible configurations on the \( \text{Zn} \) sublattice. The specific enumeration process is described later in the Results and Discussion. Configurations with \( \text{Zn} \) vacancies and interstitials deviating from the \( \text{Zn}_8\text{Sb}_7 \) composition are also considered. DFT calculations were performed on select \( \text{Zn}_8\text{Sb}_7 \) configurations since it would be computationally prohibitive to calculate all possibilities. Atomic positions were allowed to relax to a local minimum and were verified to not have settled into identical configurations. While this method is by no means exhaustive in gauging the configurational disorder in \( \text{Zn}_8\text{Sb}_7 \), it does provide a basis for making certain assumptions, to follow in the Results and Discussion.

Phonon density of states and vibrational free energies were calculated using the “supercell” method as implemented in the Alloy Theoretic Automated Toolkit (ATAT).\(^\text{19-21} \) The computational resources needed to compute phonon modes for all \( \text{Zn}_8\text{Sb}_7 \) configurations are prohibitive (360 perturbation structures per configuration per volume), so the phonon modes were only calculated for the nominal configuration. In all, phonon modes were calculated for one \( \text{Zn}_8\text{Sb}_7 \) configuration and several \( \text{Zn}_8\text{Sb}_7 \) configurations as well as end-members \( \text{Zn} \) and \( \text{ZnSb} \) at 0%, 1%, and 2% strain to account for the effects of thermal expansion under the quasi-harmonic approximation.

The vibrational contribution to the free energy is incorporated into the GCP through a nested sum in the partition function.\(^\text{22} \) For each distinct configuration, phonon occupation accounts for small displacements around the local energy minimum, resulting in a temperature-dependent free energy correction.

GCPs were assembled for \( \text{Zn}, \text{Zn}_8\text{Sb}_9, \text{Zn}_8\text{Sb}_7, \) and \( \text{ZnSb} \). Phase equilibrium is determined by equality of two respective GCPs. The equilibrium composition of each phase can be determined by
\[
\nabla_{\mu} \phi(T, \mu) = -x \tag{4}
\]

and the free energy is calculated as
\[
\phi(T, x) = \phi(T, \mu_x) + \mu_x \cdot x \tag{5}
\]

where \( \mu_x \) is the chemical potential that stabilizes the phase at composition \( x \).

The Seebeck coefficient is calculated for the ground-state structures using the Boltzmann transport equation within the constant relaxation approximation.


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**Figure 1.** Structures of the known room-temperature zinc antimonide phases, shown with zinc in blue, \( \text{Sb}_2 \)^+ dimers and isolated \( \text{Sb}^3^- \) in orange. The anionic structure of \( \text{Zn}\text{Sb} \) is exclusively \( \text{Sb}_2 \)^+ dimers, while \( \text{Zn}_8\text{Sb}_9 \) and \( \text{Zn}_8\text{Sb}_7 \) contain both \( \text{Sb}^3^- \) and \( \text{Sb}_2 \)^+ moieties.
time approximation as implemented in the BoltzTraP code. A dense k-point mesh is required to evaluate the Fermi integrals over the entire Brillouin zone. Convergence of the Seebeck coefficient with respect to carrier concentration is achieved in Zn$_8$Sb$_7$ with a 14-point grid. For Zn$_4$Sb$_3$ and ZnSb structures, 16-point grids are used, respectively.

### Results and Discussion

#### Crystal Structure and Charge Counting

The Zn–Sb structures in Figure 1 can all be described using the Zintl–Klemm formalism, in which Zn cations donate electrons to Sb anions which may then form covalent bonds with other Sb to complete their valence shells. A molecular orbital (MO) approach, which includes interactions between Zn and Sb, can also successfully rationalize the electron count. In ZnSb ($P_bca$), all the respective Zn and Sb atoms are symmetrically equivalent. The Zn cations each donate two electrons to an Sb anion, and the Sb atoms form Sb$_2^{4-}$ dimers. A valence-precise structure results with 8 Zn$^{2+}$ and 4 Sb$^{4-}$ per unit cell. One then can rationalize why ZnSb behaves electronically as an intrinsic semiconductor with a band gap between the valence band (dominated by Sb p-states) and the conduction band (composed primarily of Zn $s$-states).

The Zn$_8$Sb$_7$ ($R3c$) framework structure is composed of 30 Sb (orange sites in Figure 1) and 36 Zn (blue sites) in the conventional unit cell. The anionic framework is divided between 6 Sb$_2^{4-}$ dimers and 18 isolated Sb$^{3-}$. A fully occupied cation framework of 36 Zn$^{2+}$ is insufficient to satisfy a valence charge balance. Three additional Zn$^{2+}$ are needed to satisfy the charge balance at a composition of Zn$_{13}$Sb$_{10}$. These additional Zn atoms can occupy any of three symmetrically distinct regions for interstitial sites (pink, green, and brown sites), introducing configurational disorder not present in ZnSb. Thermodynamically, Zn$_8$Sb$_7$ is stable only in a narrow range of composition near Zn$_{12.992}$Sb$_{10}$ which is slightly valence deficient. This explains the persistent p-type doping observed experimentally in ZnSb.

Examining the Zn$_8$Sb$_7$ ($P4/12$) structure reveals some similarities to Zn$_4$Sb$_3$. The anionic Sb framework is only slightly distorted from a high-symmetry structure that can be described with a $P6/m$ space group. There are 10 Sb$_2^{4-}$ dimers and 8 isolated Sb$^{3-}$, all sitting close to points of symmetry. The cation Zn framework exhibits low symmetry with 32 Zn$^{2+}$.

We further investigate the structure of Zn$_8$Sb$_7$ with the help of electron density difference (EDD) plots. The EDD compares the calculated electron charge density with the charge density resulting from the overlap of non-interacting single-atom electronic wave functions. EDD plots thus reveal where charge accumulation and depletion occur as atomic wave functions interact. Charge accumulation between atoms suggests the presence of a covalent bond.

Figure 2 shows the EDD around a diamond moiety in ZnSb, which clearly reveals charge accumulation lobes in a tetrahedral arrangement around each Sb atom. In agreement with a previous molecular orbital study, one lobe of each Sb is shared between two closely spaced Zn atoms, forming a repeated diamond unit.
This same diamond moiety is also apparent in Zn₄Sb₃. Figure 2 shows the EDD for a configuration of composition Zn₁₂Sb₁₀ (no interstitial Zn). In this case, each lone Sb atom shares a lobe with each of two pairs of Zn atoms, forming zigzag chains of diamond moieties. The Sb dimers form a separate linear chain from the diamonds. The presence of interstitial Zn, such as in Zn₁₃Sb₁₀ configurations, breaks up the chain and creates local disorder in the diamond network. High configurational entropy results because there are many possible ways for the interstitial Zn to distort and rearrange the diamond network, all with similar energetic consequences.

In Zn₈Sb₇, we again see the diamond moiety but with added complexity. Nonlinear chains of diamond moieties incorporate both Sb dimers (as in ZnSb) and lone Sb (as in Zn₄Sb₃). All the diamonds are distorted out of plane, as is shown for two of the diamonds in Figure 2. The crystal structure is frustrated in the sense that it cannot settle into a single preferred ordered state, such as in ZnSb, but like Zn₄Sb₃, there are many configurational possibilities that result in similar energetics.

One way to enumerate the possible configurational states is to consider the mismatch of symmetry between the Sb and Zn sublattices. There are six symmetrically equivalent ways to combine the higher symmetry P6/m Sb sublattice with the lower symmetry PT Zn sublattice. By combining these six arrangements into a single lattice, one can discover possible interstitial sites on the Zn sublattice. The combined lattice is shown in Figure 3. All the orange Sb sites map closely to existing sites, as expected. However, the blue Zn sites reveal many new locations. Nearly equivalent sites are combined to form an idealized lattice with 66 new possible Zn sites, shown in pink at the bottom of Figure 3. These sites provide a basis to probe the configurational disorder.

Conconfigurational arrangements involving Zn vacancies on the highly occupied blue sites and Zn interstitials on partially occupied pink sites can be enumerated and the energies calculated from first-principles calculations. This configurational disorder could likely be undetected by electron diffraction analysis due to the low occupation of certain sites. The experimentally predicted partial occupancy results in a composition of Zn₂₉.₅Sb₂₈ which could be explained as an average of 2.1 Zn atoms per unit cell occupying various interstitial sites. The entropy associated with this disorder will be addressed in the Phase Stability section.

**Electronic Structure.** The calculated electronic density of states of Zn₈Sb₇ is shown in Figure 4, along with those for ZnSb and Zn₄Sb₃. As expected from the Zintl—Klemm charge counting, Zn₈Sb₇ is found to be an intrinsic semiconductor like ZnSb and Zn₄Sb₃. The calculated band gap is comparable to that of ZnSb but slightly smaller than that of Zn₄Sb₃. The similar shape and magnitude of the valence band edges of Zn₈Sb₇ and Zn₄Sb₃ suggest a similar hole carrier effective mass. This result alone suggests that Zn₈Sb₇ might have electronic properties similar to those of Zn₄Sb₃. The valence band edge is composed primarily of electronic states localized around the nonbonded Sb atoms. The projected density of states in Figure 4 shows that the valence band is composed primarily of Sb p-orbital character, which is similar to previous studies of Zn₄Sb₃ and ZnSb.¹³

The calculated Seebeck coefficient, S, as a function of (hole) carrier concentration is shown in Figure 5 for 700 K. This assumes a rigid band model with a carrier concentration controlled by shifting the electronic chemical potential away from the intrinsic Fermi energy. For reference, dashed lines show trends derived from a single parabolic band model with effective carrier mass m∗ under the constant relaxation time approximation.
chosen to maximize the power factor, $\alpha S^2$, with electrical conductivity, $\sigma$, calculated under the constant relaxation time approximation. An approximate relaxation time is found by fitting to experimental resistivity data for ZnSb\textsubscript{25} and Zn\textsubscript{4}Sb\textsubscript{3}\textsuperscript{2} and assuming a similar value for Zn\textsubscript{8}Sb\textsubscript{7}. The constant carrier concentration Seebeck coefficient as a function of temperature is shown in Figure 6. Both Zn\textsubscript{4}Sb\textsubscript{3} and Zn\textsubscript{8}Sb\textsubscript{7} have a maximum power factor for a hole concentration of around $5 \times 10^{19}$ cm\textsuperscript{−3} and ZnSb for a concentration of $7.5 \times 10^{19}$ cm\textsuperscript{−3}. It should be noted that in ZnSb it has proven difficult to achieve hole concentrations above $10^{19}$ cm\textsuperscript{−3}. In Zn\textsubscript{4}Sb\textsubscript{3} single-phase material, the hall carrier concentration ranges between $6 \times 10^{19}$ and $9 \times 10^{19}$ cm\textsuperscript{−3}.

Phase Stability. Finally, we consider the thermodynamic phase stability of this new Zn\textsubscript{8}Sb\textsubscript{7} phase. We note that for Zn\textsubscript{4}Sb\textsubscript{3} to be thermodynamically stable, the free energy must fall below the tie-line between ZnSb and Zn\textsubscript{4}Sb\textsubscript{3}. This will prove difficult for Zn\textsubscript{8}Sb\textsubscript{7}, as Zn\textsubscript{4}Sb\textsubscript{3} has high entropy even at room temperature. We start by considering the formation enthalpy at 0 K and then include entropic contributions at finite temperature.

Figure 7 shows the calculated formation enthalpy with respect to decomposition into ZnSb and Zn. This is perhaps not unexpected due to similarities with Zn\textsubscript{4}Sb\textsubscript{3}, which also has positive formation enthalpy at 0 K. However, Zn\textsubscript{8}Sb\textsubscript{7} is known to be thermodynamically stable at higher temperatures$^{14}$ due to both configurational and vibrational entropic contributions to the free energy. These sources might have significant contributions for Zn\textsubscript{8}Sb\textsubscript{7} as well.

Entropy arises in an ensemble when many configurations are energetically accessible. It is apparent from Figure 7 that we will expect some configurational entropy in Zn\textsubscript{8}Sb\textsubscript{7} at finite temperature from the several configurations with similar formation energy. Due to computational limitations on the large unit cell, we have only calculated 30 different configurations at the Zn\textsubscript{8}Sb\textsubscript{28} composition as well as 30 off-stoichiometric configurations. These known configurations represent only a small subset of the possible arrangements of atoms that can be enumerated on the basis of the idealized lattice in Figure 3. Each of our known configurations is likely representative of many other configurations of similar energy. To estimate this, we consider the “mean field” entropy based on the average fractional occupancy, $x_i$ of each site, $i$:

$$S_{nf} = k_B \sum_i \left( x_i \ln(x_i) + (1 - x_i) \ln(1 - x_i) \right)$$

(6)

We can correct this value by assuming that Zn\textsubscript{8}Sb\textsubscript{7} deviates from the mean field value similarly to Zn\textsubscript{4}Sb\textsubscript{3}. For Zn\textsubscript{8}Sb\textsubscript{7}, considering 90% occupancy on the framework sites and 5% occupancy on each of three interstitial sites gives an average mean field entropy of 0.48 $k_B$/atom. This is almost twice as high as the configurational entropy calculated from the grand canonical ensemble, 0.21 $k_B$/atom. For Zn\textsubscript{8}Sb\textsubscript{7}, we consider a Zn...
framework site occupancy of 93% based on the experimentally determined partial occupancy. The remaining Zn is interspersed over 66 possible interstitial sites. This results in a mean field entropy of 0.28 $k_B$/atom, which we reduce by the correction factor for Zn$_4$Sb$_3$ to estimate the configurational entropy for Zn$_8$Sb$_7$ as 0.12 $k_B$/atom. The GCP (eq 3) for Zn$_8$Sb$_7$ is tuned by increasing the multiplicative constants, $m_i$ so that, in the high-temperature limit, $S = -k_B/\partial T = 0.12$ $k_B$/atom (the adjusted mean field entropy). In essence, this procedure combines enthalpy obtained from the *ab initio* calculations with an entropy estimate based on structural similarities with the Zn$_4$Sb$_3$ phase.

The vibrational contributions to the free energy have also been accounted for in the quasiharmonic approximation. Both Zn$_8$Sb$_7$ and Zn$_4$Sb$_3$ have a favorable contribution to the free energy from phonons with respect to Zn and ZnSb. In the high-temperature limit above 300 K, Zn$_8$Sb$_7$ has an approximate vibrational entropy of 0.19 $k_B$/atom, which is slightly less than that of Zn$_4$Sb$_3$ 0.22 $k_B$/atom.

The GCP for each phase was calculated according to eq 3, and the boundary lines of phase equilibria were determined by equality of two respective GCPs. Formation free energy curves, as a function of composition, are shown for Zn$_8$Sb$_7$ and Zn$_4$Sb$_3$ at three different temperatures in Figure 8. The set of blue curves at 650 K correspond to the region of phase decomposition into ZnSb and Zn. At the intermediate temperature in orange, the formation free energy of Zn$_8$Sb$_7$ has dropped below those of Zn and ZnSb. The convex hull connects the lowest energy phase at each composition and includes the respective common tangent construction between Zn$_4$Sb$_3$, Zn$_8$Sb$_7$, and Zn. At this temperature, there is no thermodynamic stability for Zn$_8$Sb$_7$, even though it is more favorable than decomposition to ZnSb and Zn. At the highest temperature in red, we see that the Zn$_8$Sb$_7$ free energy curve touches the convex hull, indicating a region of phase stability. The black dashed line indicates the convex hull without the Zn$_8$Sb$_7$ phase. We see that Zn$_8$Sb$_7$ could have a temperature window of phase stability at high temperature, if there is sufficient entropy as in our estimation. We note that the calculated temperature scale does not correspond exactly to the physical Kelvin scale. Our temperatures likely overpredict the stabilization temperatures for both Zn$_4$Sb$_3$ and Zn$_8$Sb$_7$.

With our plausible assumptions for configurational entropy, we show that Zn$_8$Sb$_7$ can be thermodynamically stable at high temperatures. We also consider two possible reasons as to why Zn$_4$Sb$_3$ has only been observed experimentally in nanoparticulate form: lattice strain and surface energy. *Ab initio* calculations under the GGA typically overestimate the experimentally observed lattice parameter. This is indeed the case with ZnSb and Zn$_4$Sb$_3$, for which calculations predict, respectively, a 1.6% and 2.1% lattice parameter overestimation at 300 K (including the calculated thermal expansion due to lattice vibrations). We would expect to see a linear trend with composition between ZnSb and Zn$_4$Sb$_3$. Contrary to expectation, the calculated lattice parameter of Zn$_8$Sb$_7$ underpredicts the experimentally characterized lattice parameter by 1.0% at 300 K, as shown in Table 1. This error is likely within the limits of accuracy for the experimentally characterized lattice constant, but the presence of lattice strain is possible, due to either a surface stress or other synthetic factors.

Surface effects could explain the more favorable formation of Zn$_8$Sb$_7$ in nanoparticulate form. If the surface energy of Zn$_8$Sb$_7$ was lower than the average surface energy of ZnSb and Zn$_4$Sb$_3$, then for a fixed number of atoms in a nanoparticle, we would expect Zn$_8$Sb$_7$ to be more favored for small particle sizes. Calculating the surface energy for each of these structures would be computationally prohibitive, but we can consider values that might be plausible. As an example, if Zn$_8$Sb$_7$ has a lower surface energy than ZnSb and Zn$_4$Sb$_3$, by 0.05 eV/$\AA^2$ (0.78 J/m$^2$, which is on the order of differences reported in some elemental surface energies$^{27}$), then for a 50 nm particle, Zn$_8$Sb$_7$ would have an energy benefit of 6 meV/atom with respect to ZnSb and Zn$_4$Sb$_3$. At a particle size of 90 nm, the surface energy difference would be negligible. Even if we assume that the surface energy is constant between all phases, we still observe that Zn$_8$Sb$_7$ has a lower bulk modulus than both ZnSb and Zn$_4$Sb$_3$ (Table 1). In a stressed surface condition, we expect the softer phase, Zn$_8$Sb$_7$, to have a more significant energy lowering to the surface contribution according to $P^2/2B$, where $P$ is pressure and $B$ is the bulk modulus. Thus, Zn$_8$Sb$_7$ would be slightly favored over ZnSb and Zn$_4$Sb$_3$. At the pressure required to adjust the calculated Zn$_8$Sb$_7$ lattice parameter to the experimental value (3.4 GPa), the energy correction is 3 meV/atom in favor of Zn$_8$Sb$_7$. We suggest that through some combination of surface energy and lattice strain, Zn$_8$Sb$_7$ might be more favorable under certain conditions.

| Table 1. Bulk Moduli, $B$, as Fit to the Equation of State, $E(V) = (B/2V_0)(V - V_0)^2$ (for Total Energy, $E$, Unit Cell Volume, $V$, and Ground-State Volume, $V_0$), and the Room Temperature Unit Cell Volume (Calculated and Measured) for Three Zn–Sb Phases |
|---|---|---|---|---|
| bulk modulus | unit cell volume ($\AA^3$) |
| eV/$\AA^3$ | GPa | DFT (GGA) | exptl | error (%) |
| Zn$_4$Sb$_3$ | 0.267 | 42.7 | 571 | 536 | 2.1 |
| Zn$_8$Sb$_7$ | 0.240 | 38.5 | 1577 | 1625 | −1.0 |
| ZnSb | 0.248 | 39.7 | 410 | 391 | 1.6 |

### CONCLUSIONS

From our first-principles investigation of Zn$_8$Sb$_7$, we expect the theoretical bulk Zn$_8$Sb$_7$ phase to exhibit good thermoelectric properties. We predict Zn$_8$Sb$_7$ to be entropically stabilized at high temperature if our assumption of configurational entropy holds true. There are also other mechanisms, such as lattice strain or surface energy, that would favor the stability of Zn$_8$Sb$_7$ with respect to ZnSb and Zn$_4$Sb$_3$. The stability of Zn$_8$Sb$_7$ at high temperatures could partially explain the complexity observed in this part of the Zn–Sb phase diagram.

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### ACKNOWLEDGMENT

This work is supported by the U.S. National Science Foundation via Grant No. DMR-0953378, through TeraGrid resources at NCSDA and NCSD under Grant No. TGDMR050013N, the ARO-MURI Materials on the Brink, and the DARPA Nano Materials Program.
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