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Defect-Controlled Electronic Structure and Phase Stability in Thermoelectric Skutterudite CoSb₃

Guodong Li ^{†,‡}, Umut Aydemir [‡], Max Wood [‡], William A. Goddard III [⊥], Pengcheng Zhai [†], Qingjie Zhang ^{*,†}, and G. Jeffrey Snyder ^{*,‡}

[†]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China.

[‡]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, USA.

[⊥]Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, USA.

*Corresponding authors: jeff.snyder@northwestern.edu; zhangqj@whut.edu.cn

Abstract: Controlling extrinsic defects to tune the carrier concentration of electrons or holes is a crucial point concerning the engineering application of thermoelectric semiconductors. To understand the defect-controlled electronic structure in thermoelectric materials, we apply density functional theory (DFT) to investigate the defect chemistry of dopants M ($M = \text{O}, \text{S}, \text{Se}, \text{Te}$) in CoSb₃. DFT predicts that the breakage of Sb₄-rings induced by these dopants produces the unexpected (n- or p-type) conductivity behavior in CoSb₃. For example, energetically dominant O interstitials (O_i) chemically break Sb₄-rings and form O-4Sb five-membered rings, leading to the charge neutral behavior of O_i. While S interstitials (S_i) collapse Te-3Sb four-membered rings within Te doped CoSb₃ leading to a p-type conduction behavior, Se substitution on Sb (Se_{Sb}) breaks the Se-Te-2Sb four-membered ring resulting in a charge neutral behavior of the complex defect Se_{Sb}+Te_{Sb}. Furthermore, the solubility limits of M dopants ($M = \text{S}, \text{Se}, \text{Te}$) are also calculated to provide essential information on single-phase material design. This study provides a new insight to understand the complicated chemical structure in doped CoSb₃, which is beneficial for devising effective doping strategies to develop high-performance bulk thermoelectric materials.

1. INTRODUCTION

Thermoelectric (TE) energy conversion techniques have attracted substantial attention because they can directly convert heat into electricity. Having no moving parts, thermoelectrics

have lots of promising applications such as radioisotope TE power generation and recovery of automobile exhaust heat.¹ The TE conversion efficiency is defined by $ZT = (\alpha^2 \sigma) T / \kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity. The challenge for rationally designing high performance TE materials is to enhance the power factor $\alpha^2 \sigma$ while reducing the κ .²

The guest (filler) and host atom interactions have significant effects on both electrical and thermal transport properties of materials with cage structures.^{3,4} Traditionally, the electropositive guest atoms in a crystal structure rattle inside the voids acting as an additional phonon scattering center, which may remarkably reduce the thermal conductivity to glassy limit.³ The covalently bonded framework on the other hand provides a pathway for efficient charge transport similarly found in a good semiconductor crystal. Among the many types of “phonon-glass-electron-crystal” TE materials,⁵ CoSb₃ based skutterudite has garnered high status and worldwide attention because both n- and p- type doped CoSb₃ exhibit excellent TE and mechanical properties.⁶⁻⁹ Understanding and controlling extrinsic point defects are essential for preparing and optimizing the carrier concentration of CoSb₃ with excellent TE properties. Two defect-chemical approaches are used to optimize the TE performance of CoSb₃. The first one is introducing a filler atom (La, Ce, Yb, Ba, In, Ga, etc.) into the lattice cages of the CoSb₃ structure to remarkably reduce the κ thermal conductivity.¹⁰⁻¹⁶ For example, Shi *et al.* proposed a simple electronegativity rule to determine whether a skutterudite phase with guest atoms can stably form.¹⁶ The filling fraction limit (FFLs) of guest atoms was predicted in CoSb₃ by considering not only the interaction between the guest and host atoms but also the formation of secondary phases.¹⁶ Later, electropositive Ga and In were reported to fill the voids in CoSb₃ through self-compensation interactions between Ga (or In) and Sb.¹⁵ Very recently, CoSb₃ filled with electronegative atoms (S and Se) were successfully prepared with a strong covalent guest-host interactions between S (or Se) and Sb, which leads to very low lattice thermal conductivity.¹⁷ The second approach is substituting Co or Sb atoms with metals or semimetals to tune the electronic properties,¹⁷⁻²³ and lots of experimental studies show VIA-group element (O, S, Se, Te) dopants can significantly influence the TE properties of CoSb₃.^{17,18,24-27}

For Te doped CoSb₃, Te substituting Sb (Te_{Sb}) would be the dominant point defect. For example, Li *et al.* reported Co₄Sb_{12-x}Te_x was successfully synthesized by using a melting method combined with spark plasma sintering (SPS), and the nominal solubility limit of Te substituting Sb was estimated to be $x = 0.55$. The optimized Co₄Sb_{11.5}Te_{0.5} had a zT value of 0.72 at 850 K.²⁴ However, Co₄Sb_{11.5}Te_{0.5} synthesized through a high pressure method followed by SPS had a

maximum zT value of 1.15 at 883 K.¹⁸ Liu *et al.* fabricated $\text{Co}_4\text{Sb}_{12-x}\text{Te}_x$ skutterudite polycrystals through mechanical alloying combined with SPS and found that the nominal solution limit of Te substituting Sb was $x = 0.6$. The maximum zT value of 0.93 was obtained in $\text{Co}_4\text{Sb}_{11.4}\text{Te}_{0.6}$ at 820 K.²⁵ Duan *et al.* prepared $\text{Co}_4\text{Sb}_{12-x}\text{Te}_x$ using solid state reaction and SPS, and found the nominal solubility limit was $x = 0.6$ but the actual solubility limit was $x = 0.272$ by EPMA measurement.²⁰ Wojciechowski *et al.*, however, indicated the actual solubility limit of Te was $x = 0.24$ in $\text{Co}_4\text{Sb}_{12-x}\text{Te}_x$.²⁶ For Se doped CoSb_3 , Wojciechowski *et al.* suggested that Se substituted the Sb site in CoSb_3 , which forms the $\text{Co}_4\text{Sb}_{12-x}\text{Se}_x$ compound.²⁶ Moreover, Duan *et al.* indicated that partial Se element would fill into the void center in Se and Te co-doped CoSb_3 , resulting in the formation of the $\text{Se}_{y-m}\text{Co}_4\text{Sb}_{12-z-m}\text{Te}_z\text{Se}_m$ compound.¹⁷ For S doped CoSb_3 , Duan *et al.* indicated that elemental S can't go into the lattice framework, but would instead go into the void center in S and Te co-doped CoSb_3 .¹⁷ For O doped CoSb_3 , Zhao *et al.* studied the high temperature oxidation behavior of CoSb_3 in air and found the oxide scale of CoSb_3 was the mixture of Sb_2O_3 and CoSb_2O_6 .²⁷ Obviously, the defect thermodynamics of VIA-group element (Te, Se, S, O) doped CoSb_3 , including defect-controlled electronic structure, optimum carrier concentrations and solubility limitation, lacks of systematic study so far.

In order to determine the thermodynamics properties of VIA-group element (O, S, Se, Te) doped CoSb_3 , we applied density functional theory to investigate the point defect chemistry of these dopants in CoSb_3 . We found that these dopants lead to unusual (n- or p-type) conductivity behaviors in CoSb_3 . This can be explained by the breakage of Sb_4 -rings, which is similar to our previous intrinsic defect study of CoSb_3 . In single-atom-doped CoSb_3 , the dominant O interstitial (O_i) defect chemically breaks the Sb_4 -ring and meanwhile forms an interesting O-4Sb five-membered ring, leading to a neutral behavior of O_i , which agrees with the charged defect formation energy calculation. In double-atom-doped CoSb_3 , S interstitials (S_i) can stably form and collapse the Te-3Sb four-membered ring within Te doped CoSb_3 , leading to a p-type conduction behavior and the formation of lone pairs of Te p orbitals, which well explains the previous experimental reports that S filler decreased the electron carrier concentration and thermal conductivity within Te doped CoSb_3 .¹⁷ The calculated electron carrier concentration of Te doping is higher compared with that of Se and S doping. The predicted phase diagram shows that S has a larger solubility within $\text{CoSb}_{3-y}\text{Te}_y$ system than that in the system without Te doping. We believe that the results presented in this theoretical study may stimulate further experimental research to optimize the electronic and thermal properties of the skutterudite CoSb_3 phase as high-performance bulk TE material.

2. METHODOLOGY

All density functional theory (DFT) calculations were carried out within the Vienna *ab initio* Simulation Package (VASP) using the projector augmented wave (PAW) method with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional.²⁸⁻³⁰ The $3s^2 3p^6 3d^8 4s^1$ electrons of Co, $5s^2 5p^3$ electrons of Sb, $2s^2 2p^4$ electrons of O, $3s^2 3p^4$ electrons of S, $4s^2 4p^4$ electrons of Se, and $5s^2 5p^4$ electrons of Te were treated as valence states to generate the PAW potentials. The defect structure calculations of O, S, Se, and Te doped CoSb₃ were performed on a cubic cell containing 32 atoms with a *k*-point grid set of $7 \times 7 \times 7$ Monkhorst-Pack scheme. All charged defect calculations were performed on a $2 \times 2 \times 2$ supercell of the cubic unit cell that contained 256 atoms. The gamma only *k*-point sampling is used for all the supercells. Spin polarization is performed for all calculations. The convergence setups are similar with our prior work on intrinsic defect calculations.³¹

3. RESULTS AND DISCUSSION

3.1 Crystal structure of CoSb₃

The skutterudite CoSb₃ is a body-centered cubic material crystallizing in the space group *Im*-3 (204), as shown in Figure 1. The cubic unit cell contains 8 Co and 24 Sb atoms occupying the 8*c*- and the 24*g*-sites, respectively.³¹ In the unit cell, the Co atomic framework forms eight smaller cubes six of which are centered by Sb₄-rings, while the other two remain empty.

Figure 1. The crystal structure of CoSb₃ with Sb₄ rings. The Co and Sb atoms are represented with blue and brown colors, respectively.

3.2 Point defect structure and defect formation energy

The formation energies of VIA-group (Te, Se, S, O) doped CoSb₃ are systematically investigated to determine the stable point defect structures and (n- or p-type) conductivity behavior. The formation energy of a defect D with a charge state q is written as,³²

$$\Delta H_{D,q} = E_{D,q} - E_0 - \sum_i n_i \mu_i + q(E_v + \Delta E_{pa} + E_F) + \Delta E_{ic} \quad (1)$$

where $E_{D,q}$ is the total energy of the defect structure D , and E_0 is the total energy of the ideal cell. The integer n_i represents the number of atoms of type i (host atoms or impurity atoms) which have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell to form the defect, and μ_i are the atomic chemical potentials corresponding to this change. The atomic chemical potential μ_i is thermodynamically defined as a measure of free energy changes when some atoms (n_i) are removed from ($n_i < 0$) or added to ($n_i > 0$) the system.³² E_v is the eigenvalue of the valence band maximum (VBM) of the ideal bulk, E_F is the electron chemical potential (The electron chemical potential is defined as the Fermi level at $T = 0$) referenced to the VBM. ΔE_{pa} and ΔE_{ic} are the potential alignment correction and image charge corrections in a charged supercell, respectively.^{33,34}

Here, we also investigate the formation of complex defects. The binding energy is defined to consider the formation of a complex defect,³⁵

$$E_b(D_A + D_B) = \Delta H(D_A) + \Delta H(D_B) - \Delta H(D_A + D_B) \quad (2)$$

where $\Delta H(D_A)$ and $\Delta H(D_B)$ are the formation energies of a single point defect D_A and D_B , respectively, $\Delta H(D_A + D_B)$ is the formation energy of a complex $D_A + D_B$, $E_b(D_A + D_B)$ is the binding energy of a complex $D_A + D_B$. A positive binding energy corresponds to defect complexes forming, which are more favorably than single defects.

Three typical extrinsic single point defect sites are considered for M ($M = O, S, Se, Te$) doped CoSb₃: M_{i-7} (M interstitial with 7-fold coordination),³¹ M_{i-v} (M interstitial in the void center), and M_{sb} (M substituting Sb), as shown in Figure S1 in the supporting information. Co, Sb, and M ($M = O, S, Se, Te$) are group 9, 15, and 16 elements, respectively. Obviously, atom M and Sb as p-block elements have similar elemental properties allowing for M_{sb} type defects to form much easier than M_{Co} type defects. All the experimental results show Te_{sb} or Se_{sb} are easier to form than

Te_{Co} or Se_{Co} in Te or Se doped CoSb₃.^{17,18,20,25,26} In addition, our intrinsic defect study reveals that Sb_{Co} has a high formation energy of ~3 eV in the Co rich region,³¹ suggesting Sb_{Co} is very unstable and indeed hard to form. Thus, we didn't investigate M_{Co} in this work. We firstly examined the atomic structure of interstitial M (M_i) because of two possible interstitial sites in CoSb₃ (M_{i-7} and M_{i-v}). The calculated free energy of the neutral O_{i-7} structure in the cubic cell is 2.79 eV lower than that of the O_{i-v} structure, indicating the O_{i-7} is the stable O interstitial site. The free energy of the neutral M_{i-v} is found to be 0.59, 0.95, and 1.28 eV lower than that of the M_{i-7} structure for $M = S, Se, Te$, respectively, indicating the M_{i-v} is the stable interstitial site for $M = S, Se, Te$. Thus, the O_{i-7} and M_{i-v} ($M = S, Se, Te$), structures are chosen for the charged defect formation energy calculations.

Meanwhile, two kinds of complex defects are considered in S and Te co-doped CoSb₃: $S_{Sb}+Te_{Sb}$ and S_i+Te_{Sb} , as depicted in Figures S2 and S3. In the $S_{Sb}+Te_{Sb}$ structure it is found that a placement of S and Te that brings about the longer bond of 3.016 Å has a 0.36 eV lower free energy compared to a placement that results in the shorter bond of 2.886. In the S_i+Te_{Sb} structure it is found that the S filler atom in plane with the Te-3Sb-ring results in 0.35 eV reduction in free energy compared to if S atom is out of plane. Thus, the structures in Figures S2(a) and S3(a) are chosen to perform the charged defect formation energy calculations.

The charged defect formation energies of the above various structures as a function of Fermi energy (E_F) for both Co rich and Sb rich regions, calculated by Eqn. (1), are shown in Figure 2. Here, we also examine the possibility of Se_i+Se_{Sb} , $Se_{Sb}+Te_{Sb}$ and Se_i+Te_{Sb} formation in Se doped and Se+Te co-doped CoSb₃, respectively. Various charged states were calculated for all defects. The slope of the curve represents the charge state of each defect. For M doped CoSb₃, the Co rich region corresponds to the presence of Sb_2M_3 , $CoSb_2$, and $CoSb_3$, whereas the Sb rich region corresponds to the presence of Sb_2M_3 , $CoSb_3$, and Sb . The n-type point defect means the impurity donates electrons to the system, leading to the positive charge state. Similarly, the p-type defect means the impurity accepts electrons from the system, leading to the negative charge state. The neutral defect corresponds to the zero charge state.

In O doped CoSb₃, the formation energy of the neutral O_i defect in the band gap is much lower than the O_{Sb} defect with a -1 charge state both in Co rich and Sb rich regions as shown in Figure 2(a) and (b), indicating the O_i is the dominant neutral defect. It is widely known that O reacts with Sb, leading to the second phase formation of Sb_2O_3 , or $CoSb_2O_6$ in CoSb₃.²⁷ Our study shows that O_i will form in CoSb₃, which is not a contradiction. When the amount of impurity O is small, the impurity O may go into the lattice of CoSb₃ and form O_i . When reaching the doping (solubility) limit, excess O may react with Sb, which leads to the formation of Sb_2O_3 or $CoSb_2O_6$.

as secondary phases.²⁷ In S doped CoSb₃, S_{Sb} with a +1 charge state is the dominant defect in the band gap region for a Co rich system. In the Sb rich region, S_{Sb} with a +1 charge state and S_i with a -2 charge state co-dominate the defect type. However, the calculated equilibrium Fermi level range of S doping as shown in Figure 4(b) suggests that S_{Sb} with a +1 charge state is still the dominant defect in the Sb rich region. In *M* (*M* = Se, Te) doped CoSb₃, the *M*_{Sb} defect with a +1 charge state has a much lower formation energy compared with the *M*_i defect with a -2 charge state in the band gap as shown in Figure 2(e)-(h), suggesting the *M*_{Sb} dominates the n-type single point defect both in Co rich and Sb rich regions. It is noted that the formation energy of Te_{Sb} with a +1 charge state is lower than that of Se_{Sb}, and much lower than that of S_{Sb}, implying that Te_{Sb} is easier to form than Se_{Sb}, and much easier to form than S_{Sb}. This can be attributed to the degree of (Pauling) electronegativity between *M* atom and Sb atom of S (2.58) > Se (2.55) > Te (2.10) > Sb (2.05), and the atomic radius difference of S (1.02 Å) < Se (1.16 Å) < Te (1.35 Å) < Sb (1.38 Å).

Here, each complex defect considered shows a positive binding energy both in Co rich and Sb rich regions as listed in Table 1, suggesting these defects are all favorable. In S+Te co-doped CoSb₃, the S_i+Te_{Sb} complex defect with a -1 charge state has a lower formation energy than the neutral S_{Sb}+Te_{Sb} complex defect both in Co rich and Sb rich regions (See Figure 2(c) and 2(d)), indicating that S_i+Te_{Sb} is the stable p-type defect, which agrees well with previous theoretical prediction that a S filler can be a stable formulation within Te doped CoSb₃.¹⁷ Furthermore, the revealed p-type character of S filler leads to decreased electron carrier concentration in Te doped CoSb₃, explaining the experimental observation that the electron carrier concentration of S_{0.19}Co₄Sb_{11.42}Te_{0.52} ($-1.9 \times 10^{20} \text{ cm}^{-3}$) is much lower than that of Co₄Sb_{11.46}Te_{0.43} ($-5.6 \times 10^{20} \text{ cm}^{-3}$).¹⁷ In Se+Te co-doped CoSb₃, the formation energy of the neutral Se_{Sb}+Te_{Sb} defect is much lower than that of the Se_i+Te_{Sb} defect with a -1 charge state in the Co rich region (Figure 2(e)), suggesting that the Se_{Sb}+Te_{Sb} defect would form in the Co rich region. However, the Se_i+Te_{Sb} defect forms in the Sb rich region because Se_i+Te_{Sb} has a lower formation energy than Se_{Sb}+Te_{Sb} near the conduction band region, as displayed in Figure 2(f). In addition, the positive binding energy of Se_i+Se_{Sb} defect (0.908 and 0.892 eV in Co rich and Sb rich region, respectively) indicates Se_i+Se_{Sb} is more stable compared with the separated Se_i and Se_{Sb} defects. Very recently, by using the annular bright field scanning transmission electron microscopy (ABF-STEM) technique, an experimental study confirmed that the impurity Se is located in the cages in Se-filled Se_{0.17-m}Co₄Sb_{11.31}Te_{0.53}Se_m,¹⁷ which agrees well with our theoretical prediction.

Figure 2. Calculated defect formation energies as a function of Fermi energy: (a) O doped CoSb₃ in Co rich region, (b) O doped CoSb₃ in Sb rich region, (c) S and S+Te doped CoSb₃ in Co rich region, (d) S and Se+Te doped CoSb₃ in Sb rich region, (e) Se and Se+Te doped CoSb₃ in Co rich region, (f) Se and Se+Te doped CoSb₃ in Sb rich region, (g) Te doped CoSb₃ in Co rich region, (h) Te doped CoSb₃ in Sb rich region. The slope of the curve represents the charge state of each defect. The white area represents the band gap region. The zero Fermi energy corresponds to the VBM.

Table 1. The binding energy (in eV) calculated for each complex defect considered in the S+Te and Se+Te co-doped CoSb₃ system, respectively.

	S _i +Te _{Sb}	S _{Sb} +Te _{Sb}	Se _i +Se _{Sb}	Se _{Sb} +Te _{Sb}	Se _i +Te _{Sb}
Co rich	0.994	0.373	0.908	0.426	0.882
Sb rich	0.949	0.337	0.892	0.398	0.868

3.3 Atomistic explanation of extrinsic defects in *M* (*M* = O, S, Se, Te) doped CoSb₃

The stable atomic configuration of the O_i defect shows that the O_i atom chemically breaks the Sb₄-ring with the Sb–Sb atomic distance of 3.753 Å, and forms an interesting O-4Sb five-membered ring with two regenerated O–Sb bonds, as shown in Figure 3(a). The bond length of O–Sb bond is 1.988 Å. This value is consistent with the covalent radii of ~1.977 Å between O and Sb observed in Sb₂O₃.³⁶ The breakage of the Sb–Sb σ-type bond moves down the Sb–Sb antibonding states to produce 2 new lone pairs that require 2 additional electrons, as described in our previous study.³¹ The two new O–Sb covalent bonds generate two shared electron pairs (4 electrons). These bonds provide 2 electrons to the two Sb atoms, compensating for the loss of the bond between them, and also provide 2 additional electrons to chemically saturate the O_i atom with valence O²⁻. Thus, the O_i induced formation of O-4Sb five-membered ring can self-balance its charge state, making the O_i a neutral defect, which agrees with our defect formation energy calculation as shown in Figure 2(a) and 2(b).

The point defect *M*_{Sb} (*M* = S, Se, Te) slightly changes the local atomic structure in non-complex doped CoSb₃, as shown in Figure 3(b). After relaxing the structure, the *M*-3Sb-ring structure remains, with the bond lengths for the *M*–Sb bond changed to 2.750 and 3.116 Å for *M* = S, 2.827 and 3.075 Å for *M* = Se, 2.924 and 3.107 Å for *M* = Te. The VIA-group elements *M* (*s*²*p*⁴) have one more valence electron than Sb (*s*²*p*³). Therefore, these *M*_{Sb} must donate 1 electron

to the system, leading to M_{Sb} as a donor impurity with a +1 charge state, agreeing with the defect formation energy results as shown in Figure 2(c)-2(h).

The complex defect $\text{S}_{\text{Sb}}+\text{Te}_{\text{Sb}}$ breaks the S–Te bond (3.697 Å) and collapses the Te–S–2Sb four-membered ring, as displayed in Figure 3(c). The breakage of the S–Te bond produces 2 lone pairs which require 2 additional electrons from the system. $\text{S}_{\text{Sb}}+\text{Te}_{\text{Sb}}$ can provide 2 additional electrons to the system because S and Te both have one more valence electron than Sb as discussed above, which balances the charge state of this collapsed S–Te–2Sb four-membered ring. Thus, $\text{S}_{\text{Sb}}+\text{Te}_{\text{Sb}}$ is a neutral defect, which is consistent with our charged formation energy calculation in Figure 2(c) and 2(d). Changing S to Se in $\text{Se}_{\text{Sb}}+\text{Te}_{\text{Sb}}$, Figure 3(e), we see the breakage of the Se–Te bond indicated by the long distance of 3.310 Å and the collapse of the Se–Te–2Sb four-membered ring. This once more leads to an overall neutral defect, which is again consistent with the calculated charged formation energy in Figure 2(e) and 2(f).

The complex defect $\text{S}_{\text{i}}+\text{Te}_{\text{Sb}}$ dramatically breaks the Te–3Sb four-membered ring indicated by the Te–Sb atomic distance of 3.489 Å and generates a new S–Sb bond, as shown in Figure 3(d). The bond length of S–Sb bond is 2.609 Å, which is close to the covalent radii (~ 2.585 Å) between S and Sb, as observed in AgSbS_2 .³⁷ The breakage of the Te–Sb bond requires 2 electrons from the system, and the S_{i} atom chemically behaves as valence S^{2-} , which also requires 2 electrons from the system. The new S–Sb covalent bond only generates one shared electron pair, which donates 2 electrons to the system, and Te_{Sb} can donate 1 electron to the system. Combined, the complex defect $\text{S}_{\text{i}}+\text{Te}_{\text{Sb}}$ requires 1 more electron from the system, which leads to $\text{S}_{\text{i}}+\text{Te}_{\text{Sb}}$ as an acceptor complex defect with a -1 charge state, explaining the charged defect formation energy as shown in Figure 2(c) and 2(d). A S filler atom within the Te doped CoSb_3 leads to the formation of Te–3Sb–S chain structure and lone pairs of Te p orbitals, which is similar with the Se–Sn–Se–Sn–Se chain structure in SnSe crystals.³⁸ This explains the extremely low thermal conductivity in S+Te doped CoSb_3 as observed in the previous experiment reports.¹⁷

Similarly, as shown in Figure 3(f), the presence of $\text{Se}_{\text{i}}+\text{Te}_{\text{Sb}}$ breaks the Te–3Sb four-membered ring, and a new covalent Se–Sb bond is generated with the length of 2.808 Å in the $\text{Se}_{\text{i}}+\text{Te}_{\text{Sb}}$ structure. This value is consistent with the radii (~ 2.777 Å) between Se and Sb in Sb_2Se_3 .³⁹ As discussed above, $\text{Se}_{\text{i}}+\text{Te}_{\text{Sb}}$ is a p-type complex defect with a -1 charge state, which agrees with the charged defect formation energy as shown in Figure 2(e) and 2(f).

Figure 3. Local atomic structure of neutral M ($M = \text{O}, \text{S}, \text{Se}, \text{Te}$) doped $\text{Co}_{64}\text{Sb}_{192}$ after relaxation: (a) The O_i structure after relaxation with the O-Sb bond length of 1.988 Å. The long atomistic distance of 3.753 Å represents the breakage of the Sb-Sb bond, as observed in our previous study.³¹ The M atom is represented with the green color. (b) The M_{Sb} ($M = \text{S}, \text{Se}, \text{Te}$) structure after relaxation with the $M\text{-Sb}$ bond lengths of 2.750 and 3.116 Å for $M = \text{S}$, 2.827 and 3.075 Å for $M = \text{Se}$, 2.924 and 3.107 Å for $M = \text{Te}$, respectively. The M atom is represented with the green color. (c) The $\text{S}_{\text{Sb}} + \text{Te}_{\text{Sb}}$ structure after relaxation with the S-Sb and Te-Sb bond lengths of 2.574 and 2.850 Å, respectively. The long atomistic distance of 3.697 Å represents the breakage of the S-Te bond. The S and Te atoms are represented with the yellow and brown

colors, respectively. (d) The S_i+Te_{sb} structure after relaxation with the S–Sb bond length of 2.609 Å. The long atomistic distance of 3.489 Å represents the breakage of the Te–Sb bond. (e) The $S_{sb}+Te_{sb}$ structure after relaxation. The long atomistic distance of 3.310 Å represents the breakage of the Se–Te bond. The Se and Te atoms are represented with the yellow and brown colors, respectively. (f) The Se_i+Te_{sb} structure after relaxation with the Se–Sb bond length of 2.808 Å. The long atomistic distance of 3.427 Å represents the breakage of the Te–Sb bond.

3.4 Defect carrier concentration and solubility limitation in M ($M = O, S, Se, Te$) doped $CoSb_3$

Calculated free carriers and predicted solubility limitation are helpful to optimize a material's carrier concentration and prepare a single-phase material, hence improving a material's thermoelectric properties in the thermoelectric semiconductors.

The defect concentration $c_{D,q}$ in the dilute limit is given by:

$$c_{D,q} = N_{site} \exp\left(-\frac{\Delta H_{D,q} - T\Delta S}{kT}\right) \quad (3)$$

where $\Delta H_{D,q}$ is the formation energy of a defect D in a charge state q , which is calculated by Eqn.

(1). N_{site} is the concentration of possible defect sites determined by the multiplicity of the defect's Wyckoff site. ΔS is the configurational entropy change, which can be estimated by:⁴⁰

$$\Delta S = k \left\{ \ln[N_D(N_D - 1)] - \ln(2N_D) \right\} \quad (4)$$

where N_D is the number of available sites in a fixed concentration of a specific defect. T is the temperature and k is the Boltzmann constant.

Charge neutrality requires:

$$\sum_D \sum_q q c_{D,q} - n + p = 0 \quad (5)$$

where n and p are the free carrier concentrations of electrons and holes defined by:⁴¹

$$n = \int_{E_v}^{+\infty} g(E) f(E; E_F, T) dE \quad (6)$$

$$p = \int_{-\infty}^{E_c} g(E) [1 - f(E; E_F, T)] dE \quad (7)$$

$g(E)$ is the density of states of ideal host cell, and $f(E; E_F, T)$ is the Fermi-Dirac distribution given by:

$$f(E; E_F, T) = \frac{1}{\exp(\frac{E - E_F}{kT}) + 1} \quad (8)$$

Following the procedure described above, the Fermi level (E_F) and free carriers can be determined by iteratively solving the overall charge neutrality requirement, as displayed in Figures 4 and 5. In O doped CoSb₃, because the dominant defect, O_i, is neutral, E_F is exactly the same with that in intrinsic nonstoichiometric CoSb₃.³¹ Here, it can be also concluded that the neutral O_i doesn't change the free carriers of CoSb₃. In Se doped CoSb₃, E_F slightly decreases with the increasing temperature in the Co rich region. The position of E_F (~0.1 eV shown in Figure 4(a)) confirms that the single point defect Se_{Sb} with a +1 charge state is the dominant defect type compared with Se_i+Se_{Sb} complex defect with a -1 charge state. Even though the formation energy of Se_{Sb} in the Co rich region is much lower than that in the Sb rich region, the electron carrier concentration of Se doping in the Co rich region is comparable with that in the Sb rich region as shown in Figure 5(b). This can be attributed to the p-type character of Se_i+Se_{Sb} complex defect. In S, Te doped CoSb₃, E_F increases with the increasing temperature, and goes deeply into the conduction band for Te doping, leading to an n-type conduction behavior. This can also be confirmed by the calculated electron carrier concentration shown in Figures 5(a) and 8(c). E_F and electron carrier concentration in the Co rich condition is much higher than that in the Sb rich condition at high temperature, resulting from the lower defect formation energy of M_{Sb} (M = S, Te) in the Co rich condition compared with that in the Sb rich region. E_F and electron carrier concentration of Te doping are higher than that of S doping, as observed in Figures 4 and 5, which can be explained by the minor (Pauling) electronegativity difference between Te (2.10) and Sb (2.05) atom. In S+Te co-doped CoSb₃, E_F reduces and goes deeply into the valence band with the increasing temperature both in Co rich and Sb rich conditions, resulting in a strong p-type behavior. The calculated hole free carriers as shown in Figure 5(d) further confirms that S filler reduces the electron carrier concentration in Te doped CoSb₃.¹⁷ The annealing temperature region of CoSb₃ is generally around 850 – 1100 K.¹⁴⁻²³ The electron carrier concentration is found to be $10^{20} - 10^{21} \text{ cm}^{-3}$ in Te doped CoSb₃ as depicted in Figure 4(c), which agrees well with the experimental reports.^{18,20,24,26}

Figure 4. Calculated Fermi level (E_F) as a function of temperature both in (a) Co rich and (b) Sb rich conditions.

Figure 5. Calculated free carriers as a function of temperature in (a) S doped CoSb₃, (b) Se doped CoSb₃, (c) Se doped CoSb₃, and (d) S+Te co-doped CoSb₃. The black and red line represents the Co rich and Sb

rich condition, respectively. Reported experimental Hall carrier concentrations at different annealing temperature in Te doped CoSb₃ system are displayed for comparison.

The total composition x of a phase with defects within an equilibrium set of atomic chemical potentials can be calculated by:

$$x = \frac{N_0^i + \Delta N^i}{\sum_i (N_0^i + \Delta N^i)} \quad (9)$$

where N_0^i is the stoichiometric number of atoms of i ($i = \text{Co, Sb, M}$) in M ($M = \text{O, S, Se, Te}$) doped CoSb₃ and ΔN^i is the change in the composition due to the presence of the point defect at a given temperature T , which can be calculated by summing over the carriers c_j of each defect j , weighted by the change in composition N_j^i due to the defect,

$$\Delta N^i = \sum_j N_j^i c_j \quad (10)$$

Using Eqn (9) and (10), we predicted the solubility limits of dopant M ($M = \text{O, S, Se, Te}$) as functions of temperature in CoSb₃ system, as shown in Figure 6. Because the carrier concentration in Co rich condition is much higher compared with that in Sb rich condition (Figure 5), the solubility limit x of dopant M in the Co rich condition is much larger over the entire temperature range. Above the eutectic temperature (900 K) in CoSb₃ – Sb, the solvus boundaries are in metastable equilibrium, which we plot with dashed lines in Figure 6. The solubility limit of Te is higher than Se, and much higher than S. The predicted solubility limit of Te shows agreement with the experimental data,^{20,26} as embedded in Figure 6(d). S has a tiny solubility in pure CoSb₃ system, but it can be further soluble within CoSb_{3-y}Te_y system in the Co rich region due to the lower formation energy of S_i+Te_{Sb} than S_{Sb} as plotted in Figure 2(c) and 2(d). This is consistent with the experimental observations.⁴²

Figure 6. Predicted solubility limits of (a) S in $\text{Co}_4\text{Sb}_{12}$ and $\text{Co}_4\text{Sb}_{12-y}\text{Te}_y$, (b) Se in $\text{Co}_4\text{Sb}_{12}$, and (c) Te in $\text{Co}_4\text{Sb}_{12}$. Experimental solubility limit of Te in $\text{Co}_4\text{Sb}_{12}$ are embedded for comparison. The nominal experimental solubility limit of Te substituting Sb is found to be $x = 0.55 - 0.6$ in $\text{Co}_4\text{Sb}_{12-x}\text{Te}_x$.^{18,20,24-26}

However, the actual solubility limit was found to be $x = 0.272$ and 0.24 by EPMA measurements in Refs. 20 and 26, respectively. Thus, we only compared our predicted solubility limit with the actual solubility limit presented in Refs. 20 and 26.

3.5. Possible role of point defects on transport properties in doped CoSb₃

Present theories and experiments focus on studying the interaction between the guest and host atoms as well as its influence on TE properties of CoSb₃.^{15-17,43} However, the breakage of Sb₄-rings induced by doping atoms is surprisingly overlooked so far. For single-atom-doped CoSb₃, the new interstitial site (M_{i-7}) induces breakage of Sb₄-rings such as O_i as shown in Figure 3(a) and provides a new prospective for understanding the role of doping atoms in CoSb₃ along with its effects on transport properties. Double-atom-doped CoSb₃, S_{Sb}+Te_{Sb} and S_i+Te_{Sb} structures shown in Figure 3(c) and 3(d), are beneficial for further understanding the complicated chemical structure of other dopants in CoSb₃, especially for the controversial group 13 dopants (Ga and In).^{10,15,16,43} The novel S_i+Te_{Sb} structure shown in Figure 3(c) leads to the formation of a lone pair of Te *p* orbitals. This should remarkably reduce the thermal conductivity of CoSb₃ as similarly reported for *e.g.*, bournonites and tetrahedrites,⁴⁴⁻⁴⁷ hence resulting in a high zT value of doped CoSb₃. For example, in Co₄Sb_{12-y}Te_y system, Te_{Sb} is an effective approach to reduce the lattice thermal conductivity (κ_L) from $\sim 10 \text{ Wm}^{-1}\text{K}^{-1}$ to $\sim 3 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature because of point defect and electron-phonon scattering.^{18,20,24-26} S filler atoms within Co₄Sb_{12-y}Te_y further lowers the κ_L to $\sim 1.5 \text{ Wm}^{-1}\text{K}^{-1}$ for S_{0.26}Co₄Sb_{11.11}Te_{0.73} at room temperature.¹⁷ Moreover, S filler atoms decrease the electrical conductivity (σ) within n-type Te doped CoSb₃,¹⁷ contributing to the p-type conduction behavior of S_i+Te_{Sb} observed in Figure 2(c). Meanwhile, due to the typical degenerate semiconducting behavior, S filler atoms increase the Seebeck coefficient (α) within Te doped CoSb₃.¹⁷ In addition to S+Te dopants, many other dopants such as Cl_i + Te_{Sb} and Br_i + Te_{Sb}, etc., might lead to a similar structure shown in Figure 3(c) and can potentially improve the TE properties of CoSb₃ further. We believe this work provides a new defect-engineering strategy to determine the electronic structure and phase stability in doped CoSb₃, which could be applied to other TE and non-TE energy materials with open structures.

4. CONCLUSIONS

We applied density functional theory based defect energy calculations to investigate the point defect chemistry of impurity dopants M ($M = \text{O}, \text{S}, \text{Se}, \text{Te}$) in CoSb₃. We found that the

neutral O_i is the dominant point defect, which can be explained by the breakage of the Sb_4 -ring and the formation of an interesting O-4Sb five-membered ring. M_{Sb} ($M = S, Se, Te$) is more stable than M_i , indicating M_{Sb} is the dominant n-type single point defect in $CoSb_3$. However, Se_i can exist in Se doped $CoSb_3$ by the formation of the complex defect Se_i+Se_{Sb} . Due to the positive binding energy of the complex defect S_i+Te_{Sb} , S_i can stably form and collapse the Te-3Sb four-membered ring within Te doped $CoSb_3$, leading to p-type conduction behavior and the formation of lone pairs of Te p orbitals. Because $Se_{Sb}+Te_{Sb}$ has a lower formation energy compared to Se_i+Te_{Sb} in the Co rich region, Se_{Sb} is easier to form than Se_i within Te doped $CoSb_3$. Se_{Sb} breaks the Se-Te-2Sb four-membered ring within Te doped $CoSb_3$, resulting in a neutral behavior. The solubility limit of Te is higher than Se, and much higher than S. S has a tiny solubility in pure $CoSb_3$ system, but it can be further soluble within $CoSb_{3-y}Te_y$ system in the Co rich region due to the lower formation energy of S_i+Te_{Sb} than S_{Sb} .

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Supporting information: The additional remarks in our calculation, initial single point defect structures for the three types of defects in M ($M = O, S, Se, Te$) doped Co_8Sb_{24} , and initial local atomic structure of neutral $S_{Sb}+Te_{Sb}$ complex defect in S and Te co-doped $Co_{64}Sb_{192}$.

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The TOC Figure: