Thermoelectric Properties of Doped-Cu₃SbSe₄ Compounds: A First-Principles Insight

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Supporting Information

ABSTRACT: This work reports the first systematic study of the effects of substitutional doping on the transport properties and electronic structure of Cu₃SbSe₄. To this end, the electronic structures and thermoelectric parameters of Cu₃SbSe₄ and Cu₃Sb_{1-x}M_xSe₄ (M = Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Bi) were systematically investigated by using density functional theory and the Boltzmann semiclassical transport theory. Substitutional doping at Sb site with IIIA (M = Al, Ga, In, Tl) and IVA (M = Si, Ge, Sn, Pb) elements considerably increases the hole carrier concentration and consequently the electrical conductivity, while doping with M = Bi would be adequate to provide high *S* values. Changes in calculated thermoelectric parameters are explained based on the effects of the dopant element on the electronic band structure near the Fermi level. We also present an extensive comparison between thermoelectric parameters here calculated and available experimental data. Our results allow us to infer significant insights into the search for new materials with improved thermoelectric performance by modifying the electronic structure through substitutional doping.

1. INTRODUCTION

Thermoelectric (TE) materials, which can convert heat into electricity and vice versa, are attracting great attention due to their wide range of potential applications.^{1–4} The performance of a TE material is evaluated by its dimensionless figure of merit (ZT):

$$ZT = S^2\sigma T/k \quad (1)$$

where *S* is the Seebeck coefficient, σ is the electrical conductivity, *T* is the absolute temperature, *k* is the thermal conductivity, and $S^2\sigma$ is the so-called power factor (PF). The thermal conductivity *k* has two contributions:

$$k = k_e + k_l \quad (2)$$

where k_e and k_l are the electronic and the lattice components of the thermal conductivity, respectively. Nowadays, best TE materials are characterized by ZT values above 1. Equation 1 implies that a material suitable for TE applications must have a large *S*, high σ , while the thermal conductivity *k* should be minimized. However, these properties are strongly coupled. As matter of fact, increasing σ by increasing charge carrier concentration usually leads to lower *S* values. The electrical conductivity is also related with the electronic thermal conductivity through the Wiedemann–Franz law; that is, $k_e/\sigma = LT$, where *L* is the proportionality constant known as the Lorenz number.^{5,6}

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Copper-based chalcogenide p-type semiconductors, such as CuInTe₂,^{7–10} Cu₃ZnSnSe₄,^{11,12} Cu₂CdSnSe₄,^{13,14} and Cu₃SbX₄ (X = Se, S),^{15–18} are promising TE materials due to their excellent transport properties and relatively low thermal conductivity. Among them, Cu₃SbSe₄ is one of the most studied compounds, because it possesses large carrier effective mass (i.e., high electrical conductivity), small band gap, as well as abundant, inexpensive, and nontoxic constituent elements.^{19,20} Cu₃SbSe₄ has the Famatinite crystal structure, which can be described as a three-dimensional Cu–Se framework of distorted [CuSe₄] tetrahedrons with one-dimensional array of inserted [SbSe₄] tetrahedrons. This configuration leads to two Cu sites with different Cu–Se bond lengths (see Figure 1). This structure provides adequate electronic transport properties and a noneffective phonon propagation,²¹ which are excellent properties for TE application. However, the ZT of Cu₃SbSe₄ is too small to be used in practice due to the low carrier concentration and resultant poor electrical conductivity.^{16,22}

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Figure 1. Crystal structure of Cu_3SbSe_4 .

Substitutional doping is a well-demonstrated strategy to alter the electronic structure and TE performance of a material.^{2,23} The valence band maximum (VBM) of Cu_3SbSe_4 is mainly due to the hybridization between Cu-3d and Se-4p states, while the conduction band minimum (CBM) is formed by the hybridization between Sb-5s and Se-4p states. In this configuration, the Cu–Se network plays as the hole conduction path. Therefore, the substitution of Sb atoms seems to be the most reasonable strategy to adjust the carrier concentration and fine-tune the TE properties while minimizing the adverse effects on the hole mobility. In this sense, density functional theory (DFT) calculations have shown that p-type doping can certainly be accomplished by replacing Sb atoms, while doping at the Se or Cu site appears to be rather difficult.²⁴

Several experimental works have reported the improvement of TE properties of Cu_3SbSe_4 by doping at Sb sites with elements such as Al,¹⁶ Ga,²⁵ In,^{26,27} Ge,²⁸ Sn,^{17,19,29} and Bi.^{17,21} Moreover, the substitution of Cu by Zn³⁰ or Se by S²⁹ has been also reported. Despite the interest in Cu_3SbSe_4 as TE material and the possibility to improve its TE properties by substitutional doping, no systematic theoretical work on doped Cu_3SbSe_4 is available in the literature. In this paper, we explore the electronic and TE properties of M-doped Cu_3SbSe_4 (M = Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, and Bi) compounds using first-principles calculations and semiclassical Boltzmann theory. Selected doping atoms are isovalent with Sb (P, As, and Bi), or p-dopant (Al, Ga, In, Tl, Si, Ge, Sn, Pb). We are aware that elements such as Tl, Pb, or As are highly toxic or carcinogenic. Even though materials with As (e.g., GaAs),³¹ Pb (PbS and lead halide perovskites),^{32,33} and Tl (TlS)³⁴ are used in optoelectronic devices, we still considered them in the present theoretical study. Despite the interest in Cu_3SbSe_4 as thermoelectric material and the possibility to improve its thermoelectric properties by substitutional doping, no systematic theoretical work on doped Cu_3SbSe_4 is available in the literature. Our results provide information on the substitutional doping effects on the electronic structure and their relationship with the TE properties, as well as useful insights in the search of new materials with improved TE performance by modifying the electronic structure.

2. THEORETICAL DETAILS

One of the most applied theoretical frameworks to study TE properties is based on first-principles calculations combined with the Boltzmann transport theory.^{4,23} Usually, TE materials are narrow bandgap semiconductors. Hence, a proper description of the electronic structure is necessary to obtain accurate results for TE parameters. Several works have reported the electronic structure of Cu_3SbSe_4 and related compounds by using different DFT methods such as GGA, GGA+U, m-BJ exchange potential, and HSE06 exchange-correlation potential.^{24,35,36} Only bandgap values calculated by using HSE06 and GGA+U were in agreement with experimental values (0.1–0.4 eV).^{24,35,36} Unfortunately, accurate methods such as screened hybrid HSE06 functional or quasi particle energy calculations would need too high computational costs.³⁷ As reported by Do et al., very large of U ($U = 15$ eV) for Cu is needed to obtain an accurate bandgap value.^{24,35,36} Other methodologies have been also applied to study the electronic structure of copper-based chalcogenide p-type semiconductor (Cu_3SbS_4). That paper also considers the Coulomb repulsion on the sulfur p-orbitals, leading to $U = 5$ eV for Cu (d-orbitals) and $U = 4$ eV for S (p-orbitals), as well as a bandgap value in good agreement with experimental results.¹⁸

The electronic structure of Cu_3SbSe_4 and M-doped Cu_3SbSe_4 (M = Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Bi) were computed within DFT as implemented in VASP code^{38,39} in combination with the projected augmented wave (PAW) method.^{40,41} The model system Cu_3SbSe_4 was defined through a tetragonal unit cell with 144 atoms ($\text{Cu}_{54}\text{Sb}_{18}\text{Se}_{72}$). Energy calculations were performed with the experimental lattice parameters of the native compound. On the basis of experimental crystal structure available for most of the selected compounds, only slight differences are found due to dopant atoms. Hence, crystal structures of M-doped Cu_3SbSe_4 compounds $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ (M = Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, and Bi) were built by replacing one Sb atom by one dopant atom (M). This substitution level leads to a doping concentration of $x = 0.055$. This is a doping concentration commonly assessed in experimental works. In this work, the PBE exchange correlation functional,⁴² along with the formalism proposed by Dudarev et al. (GGA+U), were applied.⁴³ We use $U_{\text{eff}} = 15$ eV for the Cu 3d states in agreement with our previous work¹⁷ and those ones performed by Dot et al.^{35,36,24} A plane-wave energy cutoff of 450 eV, an energy convergence criterion of 1×10^{-4} eV, and a Methfessel–Paxton first-order scheme were used. For the Brillouin zone integration, a $12 \times 12 \times 12$ Monkhorst–Pack scheme k-point mesh was used.⁴⁴ The effective masses were calculated by using a finite difference method as implemented in *Effective Mass Calculator* developed by A. Fonari et al.⁴⁵ The transport properties were evaluated by employing the Boltzmann semiclassical theory as implemented in BoltzTrap code.⁴⁶ This method is based on two approximations: (i) the constant relation time approximation and (ii) the rigid-band approach. As consequence, the electrical conductivity (σ) and electronic thermal conductivity (k_e) were estimated over the relaxation time (τ).

3. RESULTS

3.1. Electronic Structure of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$. Figure 2 shows the energy band structures of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ (M = Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Bi). Figure 3 collects a summary of bandgap values (E_g)

Figure 2. Electronic band structures of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, and Bi}$). Main energy differences measured at Γ are also displayed. Green, pink, orange, and blue colors stand for the main contribution of Cu, Sb, Se, and M atoms. The zero of energy was set at the valence band energy, while blue dotted line corresponds to the Fermi level (E_{Fermi}).

and Fermi level positions (E_{Fermi}) as a function of the M dopant element. As shown in Figure 2, Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Bi}$) compounds exhibit a direct located at Γ -point. Energy bandgap values are ranged

between 0.17 eV ($M = \text{Tl}$) and 0.28 eV ($M = \text{Si}$). The calculated E_g of Cu_3SbSe_4 is ~ 0.27 eV, which is consistent with experimental data (0.1–0.4 eV).^{24,35,36} Figure 2 also shows the main orbital atomic contributions to the electronic structure.

Figure 3. Calculated energy bandgap values (E_g), position of the Fermi level with respect to the valence band maximum (E_{Fermi}), and density of states effective masses for holes (m_{DOS}^+) in $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, and Bi}$) compounds. Density of states effective masses are in unit of the mass electron (m_0). Dashed lines stand for Cu_3SbSe_4 .

Projected density of states (PDOS) are shown in Figure S1. For the undoped Cu_3SbSe_4 , the electronic structure near the VBM is mainly attributed to Cu 3d and Se 4p states, while the CBM is mainly due to Sb 5s and Se 4p states. The substitution of Sb atoms with p-dopant elements (ns^2p^1 configuration for $M = \text{Al, Ga, In, and Tl}$ and ns^2p^2 configuration for $M = \text{Si, Ge, Sn, and Pb}$) does not cause important changes in the electronic structure composition near the bandgap (VBM is mainly due to the hybridization between Cu 3d and Se 4p states, and the CBM is formed by the hybridization between Sb 5s and Se 4p ones). The bandgap goes between 0.17 and 0.24 eV for IIIA group elements ($M = \text{Al, Ga, In, and Tl}$) and between 0.23 and 0.28 eV for IVA group elements ($M = \text{Si, Ge, Sn, and Pb}$). Note that E_g values decrease with the group number for both IIIA and IVA group elements. The absence of one or two electrons leads to a hole-doped system. Thus, one of the main differences with respect to the native compound is that the Fermi level is shifted within the valence band. Fermi level position lies between -0.11 eV ($M = \text{Ga}$) and -0.03 eV ($M = \text{Si, Pb}$) below the VBM.

For substitutional doping with isovalent atoms (ns^2p^3 configuration for $M = \text{P, As, and Bi}$), the electronic structure near the valence band is not significantly affected, but there are important changes in the occupied band contributions. The main contribution from M atom to the electronic band structure is found in the first conduction band, thus removing the electronic degeneration at Γ -point. Substitution with P or As reduces the bandgap to 0.20 eV, while Bi-doped Cu_3SbSe_4 compound yields the same E_g as the native one. For $M = \text{P, As}$, the first conduction band is located at 0.28 eV (measured at Γ -point) below the remaining conduction bands (mainly due to Se 4p states). Evidently, the maximum contribution to the first peak over the Fermi level is due to M states, while the second peak is a mixture of Sb 5s and Se 4p. Meanwhile, the energy difference between the first and second conduction bands is also ~ 0.27 eV at Γ -point for $M = \text{Bi}$. Nonetheless, this energy difference becomes lower along the Brillouin zone. As a result, the contribution to the total density of states (DOS) of Bi atom is mixed with the contribution of Sb 5s and Se 4p (see Figure S1). It could be concluded that Bi 6s and Se 4p orbitals are more strongly hybridized than M-ns and Se 4p orbitals ($M = \text{P, As}$). This hybridization would lead to the upward shifting of occupied bands, which results in bandgap broadening respect to $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($M = \text{P, As}$).

For degenerate semiconductors, σ and S are related with the effective masses (m^*) through the following equations:^{47,48}

$$\sigma = ne\eta \quad (3)$$

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m_{\text{DOS}}^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (4)$$

where m_{DOS}^* , n (p-type carriers in this work), η , k_B , and h are the density of states effective mass, charge carrier density, carrier mobility, Boltzmann constant, and Planck constant, respectively. Calculated m_{DOS}^* for p-type carriers are shown in Figure 3. We found that m_{DOS}^+ (in unit of the mass electron, m_0) = 0.37 for Cu_3SbSe_4 . Density of states effective mass of holes decreased from IIA group ($m_{\text{DOS}}^+ \sim 0.68$) to isoelectronic dopants elements ($m_{\text{DOS}}^+ \sim 0.32$), while IVA group elements yielded $m_{\text{DOS}}^+ \sim 0.452$. Thus, p-elements lead to stronger changes on m_{DOS}^+ .

Often, improved TE properties rely on the details of the electronic structure and, in particular, on the degeneracy number near the Fermi level. From the viewpoint of electronic band structure, for p-type (n-type) carriers the necessary condition of a high Seebeck coefficient is that the valence band top (conduction band bottom) should be relatively flat, while a high electrical conductivity needs a steep band edge. As said, it becomes quite difficult to simultaneously improve both S and σ . Even more so, if the material only has one VBM (or CBM). Further, the presence of hole (electron) pockets is favorable for achieving better TE properties, since more carriers would be allowed. The total number of hole (electron) pockets is determined by the number of VBM (CBM) in the Brillouin zone and the position of the Fermi level.^{49,50} As seen in Figure 2, N_v (number of degenerate valence bands) of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ at the Γ point on the top of VB is $N_v = 2$. According to the relation between the effective masses and m_{DOS}^* ($m_{\text{DOS}}^* = N_v^{2/3} m^*$), higher N_v will increase m_{DOS}^* and S . Apart from the VBM at the Γ point, there is another valence band extremum (VBE) with little difference in energy that occurs at the M point. At M point, the number of degenerate valence bands is $N_v = 4$ for Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ with $M = \text{P, As, Bi}$ and $N_v = 2$ for $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ with $M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb}$. The energy difference between the VBM at the Γ point and the VBE at the M point (see Figure 2) is ~ 0.05 eV for the native compounds and those ones doped with isoelectronic elements ($M = \text{P, As, Bi}$). Meanwhile, this energy difference decreases up to 0.02 or 0.03 eV for Cu_3SbSe_4 doped with IIIA or IVA group elements, respectively. For $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ with $M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb}$ (i.e., p-doped Cu_3SbSe_4), once the Fermi level crosses the valence bands at least eight hole pockets would be obtained (both Γ and M points have two equivalent points in the Brillouin zone). Small energy differences imply that degenerate energy bands of Γ and M points of the top of the VB simultaneously participate in transport. In addition, doped compounds with $M = \text{Al, Ga, In, Tl}$ also present a VBE over the Fermi level along X-R direction, which would lead to an additional hole pocket. The presence of several hole pockets with almost equal energies is favorable for higher σ .⁵⁰

3.2. Formation Energies. Previously to assess the effects of substitutional doping on TE parameters, the stability of $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ systems have been evaluated through their formation energies. Under equilibrium conditions, the formation energy (E^f) of $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ is calculated as follows:

$$E^f = E_{\text{doped}} - E_{\text{Cu}_3\text{SbSe}_4} - E_M + E_{\text{Sb}} \quad (5)$$

where E_{doped} and $E_{\text{Cu}_3\text{SbSe}_4}$ are the total energies of doped compounds ($\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$) and the pristine one (Cu_3SbSe_4), respectively. E_M and E_{Sb} are the total energies per dopant atom ($M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Bi}$) and Sb (replaced) atom, respectively, in their corresponding bulk phase (see Table S1). A detailed description about formation energy calculation is presented in refs 24 and 51. The same procedure has been previously applied to calculate the formation energies of different doped TE materials.^{52–55} The calculated formation energies are displayed in Figure 4. The values of the formation

Figure 4. Calculated formation energies of $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Bi}$) along with the atomic radii of the dopant elements.

energies are in the -1.84 eV ($M = \text{Si}$) to 2.28 eV ($M = \text{Tl}$) range. Formation energy tendencies of $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ doped with IIIA group ($M = \text{Al, Ga, In, Tl}$) and IVA group ($M = \text{Si, Ge, Sn, Pb}$) elements may be related with the atomic radii (see Figure 4). Dopant elements with larger atomic radii would require higher formation energies. Meanwhile, isoelectronic dopant elements (electronic configuration: s^2p^3 ; $M = \text{P, As, Bi}$) yield favorable formation energies. It is important to point out that the calculated formation energies are negative for most doped compounds, which suggests that substitutional doping at Sb position are energetically favorable. The formation energies are positive for $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ with $M = \text{In, Tl, and Pb}$, indicating that they are thermodynamically more unstable. From Figure 4, it can be concluded that substitutional doping at Sb position with elements such as Al, Si, Ge, and Bi is the most favorable process. In-doped Cu_3SbSe_4 , whose experimental synthesis has been reported, yields $E^f = 0.51$ eV. Hence, low positive formation energies can be overcome through the adequate experimental conditions.

3.3. Thermoelectric Properties of Cu_3SbSe_4 . TE properties of Cu_3SbSe_4 compound have been extensively studied.^{15–17,19–22,25–29,56,57} As discussed below, our results are in agreement with experimental data. TE parameters are evaluated for $T = 300$ – 900 K and hole carrier concentrations (p) between 1×10^{18} and $1 \times 10^{21} \text{ cm}^{-3}$ (see Figure 5), which are considered as the optimum working ranges for TE materials. From Figure 5a, we can see that the Seebeck coefficient increases initially with temperature, then reaches a maximum, and finally decreases inversely proportional to the carrier concentration. The position of this maximum S coefficient is obtained at larger hole carrier concentrations as temperature increases. In the studied hole carrier concentration range, the highest Seebeck coefficient was $557 \mu\text{V/K}$ at 300 K

and $p = 1.0 \times 10^{18} \text{ cm}^{-3}$, which decreases to $245 \mu\text{V/K}$ at 900 K and $p = 1.5 \times 10^{20} \text{ cm}^{-3}$. As seen in Figure 6, the calculated S of Cu_3SbSe_4 is consistent with the experimental data. Most of the experimental data found that the Seebeck coefficient decreases when temperature rises, with a hole carrier concentration $p = (0.08$ – $8.0) \times 10^{18} \text{ cm}^{-3}$ (at $T = 300$ K). The highest experimental value for Cu_3SbSe_4 is $S \approx 496 \mu\text{V/K}$ ($T = 325$ K and $p = 0.08 \times 10^{18} \text{ cm}^{-3}$),¹⁶ even though most of the experimental data show that the highest S values are $\sim 400 \mu\text{V/K}$ at $T = 300$ K. The Seebeck coefficient decreases to $\sim 300 \mu\text{V/K}$ at $T = 600$ – 700 K. For $T = 300$ – 700 K, DFT Seebeck values lie between 338 and $249 \mu\text{V/K}$ at $p = 1.9 \times 10^{19} \text{ cm}^{-3}$ ($T = 300$ K). In general, our results agree well with experimental data and qualitatively predict the evolution of S with temperature. As will be discussed later, the hole carrier concentration of Cu_3SbSe_4 system is overestimated in comparison with experimental data. Using the rigid band model, we could adjust the Fermi level to accurately reproduce the hole carrier concentration. Such an adjustment provides an improvement on the calculated Seebeck values (ranging between 446 and $282 \mu\text{V/K}$ at $T = 300$ and 700 K and $p \approx 5.0 \times 10^{18} \text{ cm}^{-3}$). Unfortunately, the absence of available data for most systems here studied prevents us to apply this fit of the Fermi level. Despite this overestimation of the hole carrier concentration, our results are able to describe the evolution of TE parameters as well as the effects of the substitutional doping (see below).

Since the Boltzmann theory assumes a constant relaxation time (τ), the electrical conductivity (σ) and the electronic thermal conductivity (k_e) are calculated with respect to τ , that is, σ/τ and k_e/τ , respectively. Figure 5b plots the calculated electrical conductivity scaled by relaxation time (σ/τ) as a function of hole carrier concentration at different temperatures. The electrical conductivity increases with increasing T and p . For low hole carrier concentrations σ/τ keeps constant with p . For example at $T = 900$ K, $\sigma/\tau \approx 1.4 \times 10^{18} \text{ S m}^{-1} \text{ s}^{-1}$ and $p < 5 \times 10^{19} \text{ cm}^{-3}$, while σ/τ follows a linear relationship with p for $p > 5 \times 10^{19}$. In this work, the relaxation time is determined by comparing the experimentally measured electrical conductivity σ with DFT-calculated σ/τ values. The relaxation time depends on both the temperature and the charge carrier concentration n . Thus, we used a standard electron–phonon dependence on n and T for τ :^{58,59}

$$\tau = CT^{-1}n^{-1/3} \quad (6)$$

where C is a constant to be determined. To obtain C , we used experimental data of Cu_3SbSe_4 previously published by our group.¹⁷ We reported a maximum Seebeck coefficient $S \approx 369 \mu\text{V/K}$ and $\sigma \approx 3000 \text{ S m}^{-1}$ ($T \approx 400$ K and $p = 5 \times 10^{18} \text{ cm}^{-3}$).¹⁷ In the present work, $S = 304 \mu\text{V/K}$ and $\sigma/\tau = 1.099 \times 10^{18} \text{ S m}^{-1} \text{ s}^{-1}$ (at $T = 400$ K and $p = 4.18 \times 10^{19} \text{ cm}^{-3}$). By comparing theoretical σ/τ with experimental σ , we obtain $\tau = 3.67 \times 10^{-6} T^{-1} p^{-1/3}$, that is, $2.64 \times 10^{-15} \text{ s}$ for $T = 400$ K and $p = 5 \times 10^{18} \text{ cm}^{-3}$. Once estimated τ , Figure 6 displays the calculated electrical conductivity as a function of the temperature for Cu_3SbSe_4 along with experimental data. For most experimental data, the electrical conductivity increases as temperature increases. DFT-calculated electrical conductivities well match the experimental results. For $T = 300$ – 700 K, theoretical σ values vary from $\sigma = 1476$ to 8195 S m^{-1} , while most of the experimental σ values are located between 1000 and 9079 S m^{-1} for this temperature range.

Figure 5. (a–d) Summary of DFT-calculated thermoelectric properties as a function of the hole carrier concentration (p^+) of Cu_3SbSe_4 at different temperatures. (e) Calculated hole carrier of Cu_3SbSe_4 concentration as a function of temperature.

The thermal conductivity k is the sum of the electronic (charge carrier transporting heat) and lattice (phonons traveling through the lattice) contributions: $k = k_e + k_l$. Because the lattice thermal conductivity depends on multiple parameters, its calculation is not straightforward. Full computation of TE parameters by using first-principles calculations entails phonon calculations for evaluation of the lattice thermal conductivity.^{4,23} However, because of their high computational work, phonon calculations are limited to systems with a reduced number of atoms. Therefore, in this work we just focused on the electronic contribution to the thermal conductivity (k_e). As shown in Figure 5c, k_e/τ values show a

rising trend with T and p . Above calculated expression for the relaxation time was used to obtain electronic thermal conductivities (Figure 6). In agreement with experimental data, DFT-calculated k_e values yield increase as T increases, with values ranged between 0.02 and $0.19 \text{ W m}^{-1} \text{K}^{-1}$.

Finally, with the calculated electronic transport parameters, we can evaluate the TE performance. According to eq 1, improvements in the power factor ($S^2\sigma$) will also provide ZT enhancements. Since both S and σ parameters have strongly coupled relationship via carrier concentration, it is valuable to find an optimal carrier concentration for maximizing the power factor and, in general, the TE performance. As shown in Figure

Figure 6. Calculated S , σ , and k_e along with experimental data of Cu_3SbSe_4 as a function of temperature, where p^+ (in holes/ cm^3) represents the hole carrier concentrations at $T = 300$ K.

Figure 7. (a) Calculated hole carrier concentration as a function of temperature of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}, \text{P}, \text{As}, \text{Bi}$) compounds. (b) Calculated hole carrier concentration at $T = 300$ K along with experimental data of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}, \text{P}, \text{As}, \text{Bi}$) compounds.

5d), $S^2\sigma/\tau$ values tend to increase with p . The power factor exhibits the highest values at $p \geq 1 \times 10^{20} \text{ cm}^{-3}$. At high hole carrier concentrations, the power factor also increases upon increasing temperature.

According to T. Takeuchi, ZT can be written as follows:⁶⁰

$$ZT = (S^2\sigma T/k_e) \cdot B \quad (7)$$

where $B = 1/(1 + \kappa_l + \kappa_e)$. The first term of this equation ($S^2\sigma T/k_e$) only depends on the electronic part. Accordingly, it is labeled as the electronic figure of merit (ZT_e). Several conclusions are derived from ZT_e definition: (i) since B value is less than unity, ZT_e must be considered as the superior limit of ZT; (ii) ZT_e removes the dependence of σ and k_e with τ ; (iii) TE performance can be assessed based only on TE parameters obtained from DFT calculations. As seen in Figure 5d, in the temperature range from 300 to 900 K, the highest ZT_e values are obtained at $p > 1 \times 10^{20} \text{ cm}^{-3}$. In this range of hole carrier concentrations, ZT_e yields a similar trend with T and p than the power factor. In short, the TE performance of Cu_3SbSe_4 could be further improved by adequate fine-tuning of the hole carrier concentration. The hole carrier concentration of Cu_3SbSe_4 changes from $p > 1.9 \times 10^{19} \text{ cm}^{-3}$ at 300 K to $2.6 \times 10^{20} \text{ cm}^{-3}$ at 900 K (see Figure 5f).

3.4. Effects of Substitutional Doping on Thermo-electric Properties. 3.4.1. Hole Carrier Concentrations.

Among others, TE properties of Cu_3SbSe_4 can be improved through the adequate optimization of the hole carrier concentration. In Figure 7a, we illustrate the hole carrier concentrations (p) of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ as a function of temperature obtained at the Fermi level. We can see that the carrier concentration increases with increasing temperature. Cu_3SbSe_4 exhibits the lowest value of $p = 1.9 \times 10^{19} \text{ h}^+/\text{cm}^3$ (0.06 holes per unit cell, uc) at $T = 300$ K, while doped compounds exhibit higher values of p of $p \approx 1.0 \times 10^{20} \text{ h}^+/\text{cm}^3$ (0.34 h^+/uc), $8.7 \times 10^{19} \text{ h}^+/\text{cm}^3$ (0.28 h^+/uc), and $3.5 \times 10^{19} \text{ h}^+/\text{cm}^3$ (0.11 h^+/uc) for IIIA, IVA, and VA group elements, respectively. As expected, larger changes in the hole carrier concentration are obtained for p-dopant elements, which

Figure 8. (left) Calculated S , σ/τ , and k_e/τ values as a function of temperature of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}, \text{P}, \text{As}, \text{Bi}$) compounds. (right) Experimental data of S , σ , and k_e .

is related with the position of the Fermi level (located inside the valence bands) and the presence of several hole pockets. Further, the electronegativity difference between Sb and M atom could also influence the hole carrier concentration. According to Pauling scale, the electronegativity of Al (1.61), Ga (1.81), In (1.78), and Tl (1.62) show the largest differences, with the electronegativity of Sb (2.05) leading to higher hole carrier concentration values. As said, calculated hole carrier concentrations are overestimated with respect to experimental data (Figure 7b). Nonetheless, computed hole carrier concentration trends are in agreement with experimental data.

3.4.2. Seebeck Coefficient. The temperature dependence of TE parameters of $\text{Cu}_3\text{Sb}_x\text{M}_{1-x}\text{Se}_4$ compounds is shown in Figures 8 (S , σ/τ , k_e/τ) and 9 ($S^2\sigma/\tau$, ZT_e). For comparative purposes, calculated data of Cu_3SbSe_4 are also included. Figures 8 (S , σ , k_e) and 9 ($S^2\sigma$, ZT) also display available experimental data of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_x\text{M}_{1-x}\text{Se}_4$. Additionally, for the ease of comparison, Figure 10 collects a summary of DFT-calculated

TE parameters at 300 K. As seen in Figure 8a, the Seebeck coefficient of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_x\text{M}_{1-x}\text{Se}_4$ with $\text{M} = \text{P}, \text{As}, \text{Bi}$ exhibits similar dependence on temperature; that is, S decreases with increase in temperature, while S of doped Cu_3SbSe_4 with p-dopant elements ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) yield an opposite behavior with temperature. DFT-calculated S values of M-doped compounds with p-type elements were much lower compared with native compound ($S = 338 \mu\text{V/K}$ at 300). The highest S values of $\text{Cu}_3\text{Sb}_x\text{M}_{1-x}\text{Se}_4$ doped with IIIA and IVA group elements ($S = 27 \mu\text{V/K}$ and $S = 79 \mu\text{V/K}$ at 300 K) was found for $\text{M} = \text{In}$ and $\text{M} = \text{Si}$, respectively. As said above, doping with p-dopant atoms ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) leads to two degenerate valence bands ($N_v = 2$) at M-point (instead of $N_v = 4$ found in Cu_3SbSe_4). This change in N_v could explain, in part, the Seebeck coefficient diminution due to doping with p-dopant atoms. Additionally, in agreement with eq 4, the Seebeck coefficient calculated for $\text{Cu}_3\text{Sb}_x\text{M}_{1-x}\text{Se}_4$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) decreased with increasing hole

Figure 9. (left) Calculated $S^2\sigma/\tau$ and ZT_e values as a function of temperature of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Bi}$) compounds. (right) Experimental data of $S^2\sigma$ and ZT .

carrier concentrations. M-doped Cu_3SbSe_4 with IIIA and IVA elements provide somewhat higher m_{DOS}^+ values (see Figure 3). Hence, the hole carrier concentration seems to play the main role in S behavior upon doping. However, within of the same group, both m_{DOS}^+ and S exhibit similar tendency. Our results are in agreement with experimental data. Previous works have reported a decrease of the Seebeck coefficient for M-doped compounds ($M = \text{Al, Ga, Ge, Sn}$), as well as decreasing values with temperature.^{16–19,25–29}

Both P-doped and As-doped Cu_3SbSe_4 compounds yield similar S values ($S = 260$ and $286 \mu\text{V/K}$, respectively, at 300 K), which are slightly lower than those calculated for Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{Bi}_x\text{Se}_4$ ($S \approx 338 \mu\text{V/K}$ at 300 K). Our results of $\text{Cu}_3\text{Sb}_{1-x}\text{Bi}_x\text{Se}_4$ are somewhat inconsistent with experimental data, which reported improved S values due to bismuth doping.^{17,21} Anew, the qualitative behavior of S within the same group can be explained on the basis of m_{DOS}^+ .

3.4.3. Electrical Conductivity. The temperature dependence of σ/τ of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ is shown in Figure 8b, along with experimental electrical conductivities. For p-dopant elements ($M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb}$), the electrical conductivity decreases as temperature increases from 300 to 900 K. For these compounds, the electrical conductivity is considerably improved by M-doping at Sb site. In addition, the transport behavior changes from semiconductor for the undoped compound to metal-like for doped ones. Therefore, IIIA and IVA group atoms would be effective dopants to

increase the hole carrier concentration and the conductivity. According to eq 3, the electrical conductivity is inversely proportional to the effective masses and directly proportional to the charge carrier concentration. M-doped Cu_3SbSe_4 with IIIA group elements ($M = \text{Al, Ga, In, Tl}$) provide lower σ/τ values than $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ with IVA atoms ($M = \text{Si, Ge, Sn, Pb}$), even though the firsts provide higher hole carrier concentrations (see Figure 7). Hence, lower σ/τ values of M-doped Cu_3SbSe_4 with IIIA group elements ($M = \text{Al, Ga, In, Tl}$) could be related with higher m_{DOS}^+ shown in Figure 3. Experimental data also found that electrical conductivity was significantly increased by Al,¹⁶ Ga,²⁵ In,²⁶ Ge,²⁸ and Sn^{17,19} doping over the investigated range of doping concentrations as well as a change in transport behavior from semiconductor to metal (metal transport behavior was not found for Al- and Ga-doped samples may be due to low doping concentrations, $x = 0.03$ and 0.015 , respectively). The variation of electrical conductivity with temperature of $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ compounds with isoelectronic atoms ($M = \text{P, As, Bi}$) is similar to those described for the undoped compound, which increases with increasing temperature. The replacement of Sb by P, As, or Bi leads to slightly higher σ/τ , which can be correlated with the changes in the hole carrier concentrations (Figure 7) and effective masses (Figure 3). Our theoretical results match well with experimental data of $\text{Cu}_3\text{Sb}_{1-x}\text{Bi}_x\text{Se}_4$,^{17,21} both in the evolution of σ with T and small changes in σ due to Bi doping.

Figure 10. Summary of calculated thermoelectric parameters of $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Bi}$) compounds at $T = 300$ K. Dashed lines stand for Cu_3SbSe_4 .

3.4.4. Thermal Conductivity. Figure S2 collects a summary of experimental measurements of the total thermal conductivity and the lattice contribution of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ compounds ($M = \text{Al, Ga, Ge, Sn, Bi}$). In general, for the undoped Cu_3SbSe_4 compound, the thermal conductivity was found to take values between ~ 2.00 and $3.5 \text{ W m}^{-1} \text{K}^{-1}$ at 300 K and decreased with temperature to values ~ 0.7 – $1.2 \text{ W m}^{-1} \text{K}^{-1}$ at $T \approx 650$ K. As shown, the lattice thermal conductivity entails the main contribution to the total thermal conductivity. For doped compounds, k varies between ~ 1.00 and $3.5 \text{ W m}^{-1} \text{K}^{-1}$ at 300 K and between 0.65 and $2.0 \text{ W m}^{-1} \text{K}^{-1}$ at ~ 650 K. Higher electronic thermal conductivities were measured after the doping with p-dopant elements, which also increased the hole charge carrier concentration ($M = \text{Al, Ga, Ge, Sn}$), while Bi-doped compound provided smaller k values than Cu_3SbSe_4 . In Figure 8c we plotted the electronic thermal conductivity scaled by the relaxation time (k_e/τ) as a function of temperature along with k_e experimental data. In concordance with experiments, DFT-calculated k_e/τ values show a rising trend with T . The largest decreases in comparison with Cu_3SbSe_4 are found for p-dopant elements (at high temperatures), even for dopant atoms of IIIA group. Doping with isoelectronic elements provokes a small increase in k_e/τ with respect to Cu_3SbSe_4 . According to experimental data reported

in Figure 8c, the variation in k_e values due to substitutional doping is smaller than $0.05 \text{ W m}^{-1} \text{K}^{-1}$.

3.4.5. Thermoelectric Performance. Our calculated values of power factor (scaled by the relaxation time) and electronic figure of merit at different temperatures are shown in Figure 9a,b (along with experimental data of $S^2\sigma$ and ZT). High values of $S^2\sigma/\tau$ and ZT_e can be obtained due to large Seebeck coefficient, higher electrical conductivity, and reduced electronic thermal conductivity (for ZT_e). It can be seen that $S^2\sigma/\tau$ increases as temperature increases. Cu_3SbSe_4 and M-doped Cu_3SbSe_4 with $M = \text{P, As, Bi}$ exhibit larger $S^2\sigma/\tau$ and ZT_e values due to their higher values of Seebeck coefficient. Although p-dopant elements ($M = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb}$) provide improved electrical conductivities, p-doped Cu_3SbSe_4 yields lower TE performance (lower $S^2\sigma/\tau$ and ZT_e values) than Cu_3SbSe_4 due to the much lower Seebeck coefficient value. As shown in Figure 9a, calculated $S^2\sigma/\tau$ values follow the same tendency as experimental data of $S^2\sigma$ as a function of temperature. ZT_e and experimental ZT exhibit the same trend with temperature for $M = \text{Al, Ga, In, Tl, Si, Ge, Sn}$, and Pb . For the doping with isoelectronic elements ($M = \text{As, P, Bi}$), the behavior of ZT_e with T is similar to those found for Cu_3SbSe_4 . For Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ compounds ($M = \text{P, As, Bi}$), differences in the behavior of theoretical ZT_e values

Figure 11. DFT-calculated Seebeck coefficient of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($\text{M} = \text{P}, \text{As}, \text{Bi}$) compounds as a function of the hole carrier concentration at $T = 300 \text{ K}$.

and experimental ZT data with temperature are mainly due to the contribution of k_f . Our results are able to describe the improvement in both the hole carrier concentration and electrical conductivity upon doping with IIIA and IVA atom, though the improvement reported for $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ compounds ($\text{M} = \text{Al}, \text{Ga}, \text{Ge}, \text{Sn}$) is not accurately described. Briefly, doping with IIIA and IVA elements will allow higher hole carrier concentration and electrical conductivities. Meanwhile, the substitutional doping with $\text{M} = \text{P}, \text{As}, \text{Bi}$ would prevent S decrease (experimental data reported S improvements by Bi doping). While the Seebeck coefficient is not improved by doping with isoelectronic elements ($\text{M} = \text{P}, \text{As}, \text{Bi}$), this behavior changes due to the hole carrier concentration. On the basis of the rigid-band approach, Figure 11 shows the Seebeck coefficient of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($\text{M} = \text{P}, \text{As}, \text{Bi}$) compounds as a function of the hole carrier concentration at $T = 300 \text{ K}$. Calculated S values of $\text{Cu}_3\text{Sb}_{1-x}\text{Bi}_x\text{Se}_4$ (and $\text{Cu}_3\text{Sb}_{1-x}\text{Bi}_x\text{Sb}_4$) becomes similar or slightly higher than S values of Cu_3SbSe_4 for $p > 1.9 \times 10^{19} \text{ h}^+/\text{cm}^3$ ($p > 5 \times 10^{19} \text{ h}^+/\text{cm}^3$). The largest improvements in S are found for those hole carrier concentrations upon doping with IIIA or IVA group elements ($p = 7.4 \times 10^{19}$ to $1.2 \times 10^{20} \text{ h}^+/\text{cm}^3$). Thus, doping at Sb sites with of both types of atoms (one p-type and one isoelectronic atom) could entail an improvement of ZT_e values based on higher S , σ , and hole carrier concentrations. As matter of fact, we recently reported improved TE properties by codoping Cu_3SbSe_4 with Sn and Bi.

4. CONCLUSIONS

In this paper, the electronic structures and TE transport properties of M-doped Cu_3SbSe_4 compounds at Sb site, that is, $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}, \text{P}, \text{As}, \text{Bi}$), are assessed by using DFT calculations and semiclassical Boltzmann theory. Calculated formation energies are negative for most $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$, which points out that doping at Sb positions would be energetically favorable. The lowest formation energies are found for $\text{M} = \text{Al}, \text{Si}, \text{Ge}$, and Bi . Electronic band structures of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ family systems show a direct bandgap (located at Γ -point), with values ranging between 0.17 eV ($\text{M} = \text{Tl}$) and 0.28 eV ($\text{M} = \text{Si}$). The calculated bandgap of Cu_3SbSe_4 is $E_g = 0.27 \text{ eV}$, in agreement with experimental data ($0.1\text{--}0.4 \text{ eV}$). The analysis of TE properties of Cu_3SbSe_4 can be improved though the adequate fine-tuning of the hole carrier concentration. Our calculations show that doping with p-dopant elements ($\text{M} = \text{Al},$

$\text{Ga}, \text{In}, \text{Tl}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) can increase the number of hole pockets and, in consequence, the hole carrier concentration and the electrical conductivity. However, these p-dopant elements considerable decrease the Seebeck coefficient. Such S reduction is related to the change in the number of degenerate valence bands ($N_v = 2$) at M-point (instead of $N_v = 4$ found in Cu_3SbSe_4) and higher hole carrier concentrations. As regards the substitutional doping with isoelectronic atoms ($\text{M} = \text{P}, \text{As}, \text{Bi}$), the main effects are found in the composition of the CBM, where M dopant atoms provide the main contribution to the first conduction band. We find that good TE performance in doped Cu_3SbSe_4 can be achieved through doping with adequate elements to improve the Seebeck coefficient (doping with isoelectronic elements) and the electrical conductivity (doping with p-dopant elements). Furthermore, we have also performed a comparison between theoretical TE parameters and available experimental data of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ compounds. Our results are in agreement with available experimental data and qualitatively predict general trends upon substitutional doping and temperature, despite DFT-calculated hole carrier concentrations being overestimated with respect to experimental data. On the basis of our theoretical results, we hope that new experimental studies of the missing systems will allow us to adjust the Fermi level to reproduce experimental hole carrier concentrations. Thus, this work offers fundamental insights into the search for new materials with improved TE features, providing information about the modification of the electronic structure through substitutional doping as well as its effects on TE parameters.

■ ASSOCIATED CONTENT

Supporting Information

Crystal structure of Sb and M ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}, \text{P}, \text{As}, \text{Bi}$) atoms used to calculate formation energies; projected density of states of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}, \text{P}, \text{As}$, and Bi) compounds; summary of experimental data for the total thermal conductivity and lattice contribution for holes of Cu_3SbSe_4 and $\text{Cu}_3\text{Sb}_{1-x}\text{M}_x\text{Se}_4$ ($\text{M} = \text{Al}, \text{Ga}, \text{Ge}, \text{Sn}, \text{Bi}$) compounds (PDF)

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Notes

The authors declare no competing financial interest.

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