Band structure engineering in highly degenerate tetrahedrites through isovalent doping†

Xu Lu,*a Wei Yao,a Guiw en Wang,b Xiaoyuan Zhou,*ab Donald Morelli,c Yongsheng Zhang,*d Hang Chi,e Si Hui,f and Ctirad Uhere

g It can be difficult to reduce the electrical resistivity of highly degenerate semiconductors due to their high carrier concentration, impeding the further increase in their thermoelectric power factor. Here we report on an enhancement in the power factor of highly degenerate Cu12Sb4S13–xSex solid solutions, which show a dramatic decrease in the electrical resistivity while maintaining a constant Seebeck coefficient for various contents of Se. Rather than arising from an increased carrier concentration, the reduced electrical resistivity is a consequence of the upward displacement of the valence bands with low effective masses. Using theoretical calculations, we show that these additional valence bands have a similar density of states effective mass to that of the existing conduction valley, thus yielding unchanged Seebeck coefficients. The results suggest that the power factor of highly degenerate semiconductors can be enhanced through careful band structure engineering via isovalent doping.

1. Introduction

The thermoelectric performance of a material is typically quantified using the dimensionless figure of merit, denoted by $zT = S^2T/rk$, where $S$, $\rho$, and $k$ are the Seebeck coefficient, the electrical resistivity and the total thermal conductivity, respectively. The success in improving $zT$ has relied primarily on the strengthening of phonon scattering1 or designing materials with intrinsically low lattice thermal conductivity close to the amorphous limit.2,3 However, to enhance the thermoelectric power factor $S^2/r\rho$ is challenging because the Seebeck coefficient and the electrical resistivity are inherently coupled through charge carrier concentration.4 The usual method to achieve the maximum power factor is to optimize the carrier concentration. However, this approach is not effective in the case of highly degenerate semiconductors having very high carrier concentrations, but still below the optimum values for the maximum power factor. The reason is that non-isovalent doping fails to continually increase the carrier concentration and, instead, more typically leads to diminishing of the carrier mobility on account of the limited solubility.

Tetrahedrite-based thermoelectric materials have received much attention in recent years due to their earth-abundance and good thermoelectric performance.5–9 An undoped tetrahedrite possesses a cubic structure, which consists of 58 atoms in the unit cell, as shown in Fig. 1. The chemical composition of the tetrahe- drite can be described by the formula $\text{Cu}_{120}^{\text{Cu}_{2}^{2+}}\text{Sb}_{4}^{3+}\text{S}_{13}^{2-}$. However, recent results from XPS spectrum analysis imply that Cu$^{2+}$ ions comprise less than 0.2 of the 12 Cu atoms in Cu$_{12}$Sb$_4$S$_{13}$, corresponding to an electron deficiency of roughly 3.6 per unit cell.10 Considering the lattice constant of Cu$_{12}$Sb$_4$S$_{13}$ is about 10.3 Å, an estimated saturated carrier concentration is above $3 \times 10^{21}$ cm$^{-3}$, a very high value compared to conventional thermoelectric semiconductors which typically possess optimum carrier concentrations on the order of $10^{19}$ to $10^{20}$ cm$^{-3}$. In previous studies, transition metal dopants, such as Zn, Mn, Fe, Co and Te, were used to replace Cu.

---

*College of Physics, Chongqing University, Chongqing 401331, P. R. China. E-mail: luxw@cqu.edu.cn; xiaoyuan2013@cqu.edu.cn
†Analytical and Testing Center of Chongqing University, Chongqing 401331, P. R. China
‡Department of Chemical Engineering & Materials Science, Michigan State University, East Lansing, Michigan 48824, USA
§Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, P. R. China. E-mail: yshzhang@theory.issp.ac.cn
*bDepartment of Physics, University of Michigan, Ann Arbor, Michigan 48109, USA
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ta07015a

Fig. 1 Schematic view of Cu$_{12}$Sb$_4$S$_{13}$ crystal structures with cubic and rhombohedral geometries. Blue spheres, brown spheres and green spheres represent Cu, Sb and S atoms, respectively.
and S to tune the electronic transport properties.\textsuperscript{11–17} In most of these cases, the electrical resistivity was increased by transition metal doping: additional valence electrons filled hole states in the valence band, causing diminished power factors. Efforts to enhance the power factor of the tetrahedrite through increasing the concentration of holes have not been successful due to its highly degenerate nature and the limited solubility of p-type doping elements in its crystal lattice. This leaves the issue of how to enhance the power factor of the tetrahedrite an open question.

In recent studies, isovalent substitutions have been shown to be an effective method to enhance the power factor in PbTe\(_{1-x}\)Se\(_x\), and Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) solid solutions through increased band degeneracy near the Fermi level, assisted by temperature or composition variations, and independent of any charge carrier concentration modifications.\textsuperscript{18,19} Also, isovalent doping would lead to local structural perturbations in the crystal lattice, which cause thermal conductivity reduction or charge carrier activation mechanism change.\textsuperscript{20,21} Zhang et al. theoretically predicted Cu\(_{12}\)Sb\(_4\)Se\(_{13}\), an isovalent compound to Cu\(_{12}\)Sb\(_4\)S\(_{13}\), as a promising thermoelectric material with a low lattice thermal conductivity and a high power factor.\textsuperscript{22} Motivated by these predictions, we have performed an experimental study of the Cu\(_{12}\)Sb\(_4\)S\(_{13}\)–Se\(_x\) solid solution. Our results show that these compounds exhibit power factor enhancements via reduced electrical resistivity and an unaltered Seebeck coefficient, and further highlight the possibility of increasing the power factor of highly degenerate semiconductors through band structure engineering.

### 2. Experimental and computational details

#### Sample synthesis and thermoelectric and magnetic property measurements

A series of Cu\(_{12}\)Sb\(_4\)S\(_{13–x}\)Se\(_x\) solid solutions\((x = 0, 0.5, 1, 2)\) were prepared by vacuum melting of a stoichiometric ratio of the pure elements. Details concerning the material synthesis and phase purity analysis can be found in our previous report, which indicates that the tetrahedrite crystal structure is maintained in Cu\(_{12}\)Sb\(_4\)S\(_{13–x}\)Se\(_x\) solid solutions up to \(x = 2\).\textsuperscript{23} The XRD patterns of all samples are shown in the ESI (Fig. S1\textsuperscript{f}). Here, in order to shed light on the interesting fundamental physics of these compounds, we focus on the intrinsic transport properties of these solid solutions at low temperature, trying to minimize the interference of phonons. The electrical resistivity, the Seebeck coefficient, the thermal conductivity and the heat capacity of the prepared samples were measured in the 3–300 K temperature regime using a Quantum Design PPMS instrument. Magnetic property measurements were performed in the same temperature region on a Quantum Design MPMS equipped with a Superconducting Quantum Interference Device (SQUID) using a magnetic field of 1 T. The estimated errors of thermoelectric performance measurement performed on PPMS are 1%, 5% and 5% for the electrical resistivity, Seebeck coefficient and thermal conductivity, respectively.

#### Band structure calculations

For the density-functional theory (DFT) calculations, we used the Vienna \textit{Ab Initio} Simulation Package (VASP)\textsuperscript{24} with the projector augmented wave (PAW) scheme, and the generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE)\textsuperscript{25} for the electronic exchange-correlation functional. The energy cutoff for the plane wave expansion is 450 eV. The Brillouin zone was sampled by Monkhorst–Pack \(k\)-point meshes of \((4 \times 4 \times 4)\).\textsuperscript{26} Atomic positions and unit cell vectors were relaxed until all the forces and components of the stress tensor were below 0.01 eV Å\(^{-1}\) and 0.2 kbar, respectively. In the Se substituted Cu\(_{12}\)Sb\(_4\)S\(_{13}\) calculations, we substituted one/two Se atoms for one/two S atoms in various sites in the Cu\(_{12}\)Sb\(_4\)S\(_{13}\) primitive cell, finding that energetically favorable positions for Se substitution are tetrahedral sites binding with three Cu and one Sb atoms.

#### 3. Results and discussion

##### Thermoelectric properties

Temperature dependent thermoelectric properties of Cu\(_{12}\)Sb\(_4\)S\(_{13–x}\)Se\(_x\) solid solutions\((x = 0, 0.5, 1, 2)\) are shown in Fig. 2. As displayed in Fig. 2a, the electrical resistivity of Cu\(_{12}\)Sb\(_4\)S\(_{13}\) drops by two orders of magnitude from 3 K to 85 K, implying a metal–semiconductor phase transition (MST). Previously, this dramatic decrease in the electrical resistivity was attributed to an order–disorder phase transition caused by a random distribution of Cu\(^{2+}\) ions.\textsuperscript{27} This hypothesis must be ruled out on the basis of the previously mentioned XPS results, which indicated a low concentration of Cu\(^{2+}\).\textsuperscript{28} The above study concluded that the phase transition originates instead from a structural phase transition since, at low temperatures, Cu\(_{12}\)Sb\(_4\)S\(_{13}\) prefers a rhombohedral structure, the energy of which is 70 meV \(\text{fu}^{-1}\), lower than that of the expected cubic structure, as indicated by the theoretical calculation (shown in Fig. 1). Se substitution reduces the electrical resistivity by more than two orders of magnitude in the MST temperature region (Fig. 2a). A similar behavior has been observed in the Cu\(_{12}\)Sb\(_4\)As\(_{0.8}\)S\(_{12}\) solid solutions, in which the internal chemical pressure induced by the unit cell compression led to the suppression of MST.\textsuperscript{29} Here, the unit cell expansion caused by the larger ionic radius of the Se atom gives rise to a similar internal chemical pressure in the crystal structure, impeding the phase change from the cubic to rhombohedral structure below 85 K. This is also confirmed by theoretical calculations, which show that one Se atom substitution in a formula unit reduces the energy difference between the two structures to 23 meV \(\text{fu}^{-1}\). This suggests that finite temperature entropy effects or higher Se concentration might stabilize the cubic structure, which is consistent with the results from other reports.\textsuperscript{5,18,28} Unlike the case of the Cu\(_{12}\)Sb\(_4\)As\(_{0.8}\)S\(_{12}\) solid solution where the resistivity ceases to decrease above the MST and regardless of the increasing As content, converges in all samples at room temperature, the resistivity of Se substituted samples continues to decrease above the MST with respect to both Se content and temperature, albeit at a much slower rate. The difference between As and Se isovalent doping...
can be explained by the fact that the orbitals of S contribute to the top of valence band while those of Sb do not, which will be clarified in the band structure calculations section. As a result, the Se substitution for S involves the modification of the top of the valence band. In contrast, the isovalent doping of As would not yield the same phenomenon as Se doping. For the $x = 1$ sample, the room temperature resistivity drops to 1.39 mohm cm, substantially lower than that of Cu$_{12}$Sb$_4$S$_{13}$ with a resistivity of 2.12 mohm cm. One might be tempted to attribute the lower resistivity to an increased carrier concentration produced by Se doping. However, this would likely reduce the carrier mobility through strengthened alloy scattering. In general, isovalent doping may result in deep acceptor/donor levels and consequently can change the carrier concentration only if the electronegativity difference between the substituting atom and the guest atom is large enough. However, the electronegativities of S and Se are 2.58 and 2.55, respectively (Pauling scale) and such a negligible difference should lead to little if any change in the carrier concentration upon Se substituting for S. Furthermore, energy levels of isovalent impurities often coincide with the band edges, and thus do not contribute additional energy levels to the forbidden gap. Based on the above arguments, we suppose that the carrier concentration of Se substituted samples remains constant and attribute the diminished electrical resistivity to an increase in the mobility of holes induced by a modified electronic structure near the band edge. The noticeable reduction in the electrical resistivity is realized in highly degenerate semiconducting Cu$_{12}$Sb$_4$S$_{13-x}$Se$_x$ solid solutions. Meanwhile, the observed increased resistivity of Cu$_{12-}$ Sb$_4$S$_{10}$Se$_2$ compared with that of the samples with lower Se.

Fig. 2 Electrical resistivities (a), Seebeck coefficients (b), thermal conductivities (c), lattice thermal conductivities (d), power factors (e) and $zT$ values (f) of the Cu$_{12}$Sb$_4$S$_{13-x}$Se$_x$ solid solutions ($x = 0, 0.5, 1, 2$) in the range of 3–300 K.
content may be attributed to intervalley scattering of holes at elevated temperatures.

Turning now to the Seebeck coefficient (Fig. 2b), we see that $S$ remains essentially unchanged with respect to Se content over the whole temperature range, even though the resistivity shows a strong dependence on the Se content. Previous reports showing the decoupling of the thermoelectric transport parameters often involve either (i) an enhanced Seebeck coefficient with a slightly increased resistivity; or (ii) a decreased resistivity with a slightly diminished Seebeck coefficient, typically supported by an observed deviation from the Pisarenko plot of the Seebeck coefficient versus the carrier concentration. A different decoupling mechanism is proposed here for the first time: a decreased electrical resistivity and an unaltered Seebeck coefficient. This mechanism gives a direct evidence of decoupling and thus does not require fitting of the Pisarenko plot with respect to the carrier concentration. We will show that the present decoupling effect actually originates from an increase in the energy of the deeper lying valence bands, thus increasing the band degeneracy near the Fermi level. The Seebeck coefficient of a degenerate semiconductor is given by the well-known Mott relation (eqn (1)),

$$S = \frac{\pi^2 k_B^2 T}{3} B \left[ \frac{\ln(\sigma)}{E_{F}} \right]_{E=E_F} = \frac{\pi^2 k_B^2}{3} T \left[ \frac{1}{n} \frac{dn}{dE} + \frac{1}{\mu} \frac{d\mu}{dE} \right]_{E=E_F}$$

where $k_B$, $T$, $\sigma$, $n$, $\mu$, and $E_F$ are the Boltzmann constant, the absolute temperature, the electrical conductivity, the carrier concentration, the carrier mobility and the Fermi energy, respectively. Normally, the isovalent doping has little influence on the energy dependence of mobility $\frac{dn}{dE}$ in eqn (1). For a given temperature and carrier concentration, in order to maintain a constant Seebeck coefficient, $\frac{dn}{dE}$ should increase to compensate the increased mobility implied by the resistivity results. As the carrier concentration is given by $n(E) = g(E)f(E)dE$, where $g(E)$ and $f(E)$ are the carrier density of states (DOS) and the Fermi distribution function, respectively, the increase in $\frac{dn}{dE}$ is most likely due to the enlarged local DOS near the Fermi level. The same decoupling mechanism was observed for Se substituted tetrahedrites at high temperature.

The calculated power factors of $Cu_{12}Sb_4S_{12-x}Se_x$ solid solutions are shown in Fig. 2e. The power factor of $Cu_{12}Sb_4S_{12}$ is greatly enhanced to 4.6 $\mu$W cm$^{-1}$ K$^{-2}$, roughly a 60% enhancement compared to 2.9 $\mu$W cm$^{-1}$ K$^{-2}$ of $Cu_{12}Sb_4S_{13}$ at 300 K. The Se substitution also leads to a marked reduction in the thermal conductivity, shown in Fig. 2c, in spite of the increased electronic thermal conductivity brought by the enhanced electrical conductivity. The lattice thermal conductivity is calculated by the Wiedemann–Franz law, where the Lorenz number is taken as a constant of $2.0 \times 10^{-8}$ W K$^{-2}$ cm$^{-1}$ and the results are shown in Fig. 2d. As demonstrated by many researchers, the intrinsically low lattice thermal conductivity of tetrahedrites results from the local vibration of Cu atoms in the triangle plan of S atoms, associated with the lone pair electrons of Sb atoms. Clearly, the Se substitution can further reduce the lattice thermal conductivity from low temperature to room temperature. With the increasing Se content, the lattice thermal conductivity is reduced from 1.1 W m$^{-1}$ K$^{-1}$ for the pure sample to 0.7 W m$^{-1}$ K$^{-1}$ for $x = 2$ sample at 300 K, indicating that the point defect scattering plays an important role in this temperature region. Overall, $zT$ values of $Cu_{12}Sb_4S_{12-x}Se_x$ solid solutions are effectively enhanced through isovalent Se doping, from 0.06 for $Cu_{12}Sb_4S_{13}$ to 0.12 for $Cu_{12}Sb_4S_{12}Se$ at 300 K. The doubling of the figure of merit arises from the decreased electrical resistivity and lattice thermal conductivity together with the unchanged Seebeck coefficient.

**Specific heat and magnetic properties**

The DOS near the Fermi level of a semiconductor can be characterized by the Sommerfeld parameter $\gamma$, related to the electronic heat capacity. At low temperatures, the heat capacity can be written as $C_p = \gamma T + AT^2$, where the first term denotes the electronic part of the heat capacity. For a free electron gas, the electronic heat capacity $C_p = \frac{\pi^2 k_B^2}{3} E_F^2 T$, so $\gamma$ is directly proportional to the DOS at the Fermi level, which also holds quite well for d-electron systems. Fig. 3a shows a plot of $C_p/T$ vs. $T^2$ for the $Cu_{12}Sb_4S_{13}$, $Se_x$ solid solution with $x = 0$ and 1. Clearly, the intercept with the vertical axis is the value of $\gamma$. Increasing the content of Se, the intercept value becomes larger, confirming the increase in the DOS as expected. Another experimental demonstration of the modification of the DOS at the Fermi level through Se substitution is displayed in the plot of the magnetic susceptibility as a function of temperature shown in Fig. 3b. Above the MST, the susceptibilities of $Cu_{11}Sb_4S_{13}$ and $Cu_{14}Sb_4S_{12}Se$ both show positive values and follow a common Curie-Weiss behavior. As the temperature decreases, the susceptibility of $Cu_{12}Sb_4S_{13}$ exhibits a dramatic change synchronously with the MST, reaches a negative minimum and rebounds back to a positive value at lower temperatures. This behavior can be attributed to the combined effect of Pauli paramagnetism and core diamagnetism, respectively. The Pauli paramagnetic term is expressed in eqn (2) as

$$\chi(T) = \chi_0 + \frac{\pi^2 k_B^2}{6} \left[ \frac{g(E)^2}{g(E)} - \frac{g(E)}{g(E)} \right]^2 T^2$$

and it describes the response of electrons on the Fermi surface to an excitation, providing a substantial opportunity to study the peculiarities of the DOS at the Fermi level at low temperatures.

In the case of the tetrahedrite, with the Fermi level near the top of the valence band maximum, $g(E_F) < 0$ and thus the coefficient of $T^2$ term is negative, causing the reduction in $\chi(T)$ during the MST. As the temperature decreases, the negative contribution becomes small and thus $\chi(T)$ begins to increase below 50 K. Furthermore, the sharp drop in $\chi(T)$ of $Cu_{12}Sb_4S_{13}$ at the MST indicates the remarkable decline in the DOS at the Fermi level. In contrast, for $Cu_{12}Sb_4S_{12}Se$, the degree of reduction in $\chi(T)$ is diminished, demonstrating that Se substitutions result in the recovery of the DOS's magnitude and the modification of the band structure.
Band structure calculations

The experimental results have already illustrated the possibility of a Se substitution producing additional carrier pockets for carrier transport, leading to effective band structure engineering. By combining these observations with DFT calculations of the electronic structure, a simplified two band model can be constructed which yields a deeper understanding of this mechanism. The calculated electronic structures of Cu$_{12}$Sb$_4$S$_{13}$, Cu$_{12}$Sb$_4$S$_{12}$Se and Cu$_{12}$Sb$_4$S$_{10}$Se$_2$ are shown in Fig. 4, which also presents a schematic illustration of band structure modifications by Se substitution in the Cu$_{12}$Sb$_4$S$_{12}$Se solid solution. To further clarify the details of band structure evolution during Se doping, the magnified band structure at the $\Gamma$ and $P$ points are shown in the ESI (Fig. S2†). From the theoretically calculated band structures, pristine Cu$_{12}$Sb$_4$S$_{13}$ is an indirect band gap semiconductor with the band gap of 1.15 eV; 4 and 3 valence bands are degenerate at $\Gamma$ and $P$, respectively. In addition to orbital degeneracy mentioned above, $P$ point has the symmetry degeneracy of 2. Therefore, the total degeneracy at the $\Gamma$ and $P$ points is 4 and 6, respectively. At the $\Gamma$ and $P$ points, the valence bands are above and below the Fermi level, respectively, which indicates that the contributions to the transport properties from the two points are significantly different. After doping one Se atom in Cu$_{12}$Sb$_4$S$_{13}$, the valence bands at the $P$ point rise up above the Fermi level, which implies that the valence bands at both $\Gamma$ and $P$ points become involved in the electrical transport. Although the orbital degeneracy at $\Gamma$ and $P$ points is weakened, the weight of the high symmetry $P$ point compensates the DOS loss. As can be found in Fig. 5, the top of valence bands of Cu$_{12}$Sb$_4$S$_{13}$ are mainly comprised of 3d orbitals of Cu and p

Fig. 3 $C_p/T$ vs. $T^2$ (2–4 K) (a) and magnetic susceptibility (3–300 K) (b) of Cu$_{12}$Sb$_4$S$_{13}$–xSe$_x$ ($x = 0, 1$).

Fig. 4 Band structures of Cu$_{12}$Sb$_4$S$_{13}$–xSe$_x$ ($x = 0$ (a), 1 (b), 2 (c)). The inset panel in (a) is the first Brillouin zone (BZ) of Cu$_{12}$Sb$_4$S$_{13}$ with high-symmetry points (red points). The inset panel in (b) illustrates the band degeneracy evolution when $x = 1$. 

17100 | J. Mater. Chem. A, 2016, 4, 17096-17103
orbits of S. After one Se atom substitution, the p orbitals of Se also contribute greatly to the valence bands.

Given the above description, we assume the existence of two bands located at the Γ and P points for Cu12Sb4S13-Se, both contributing to transport and denoted as band 1 and band 2, respectively. The total electrical conductivity is then \( \sigma = \sigma_1 + \sigma_2 = e n_1 \mu_1 + e n_2 \mu_2 \). Therefore, the average mobility of Cu12Sb4S13-Se is written as

\[
\mu = \frac{n_1 \mu_1 + n_2 \mu_2}{n_1 + n_2}
\]

where \( \mu_1 \) and \( \mu_2 \) are the carrier mobilities in band 1 and band 2, and \( n_1 \) and \( n_2 \) are the carrier concentrations in band 1 and band 2. When acoustic phonon scattering dominates, the mobility in a semiconductor with the cubic structure is given by

\[
\mu \propto \left( m^* \right)^{\frac{1}{2}}
\]

where \( m^* \) is the average band effective mass. As shown in Fig. 4, the bands at both Γ and P points become more dispersive after Se substitution and this suggests a reduction in the average band effective mass and consequently higher mobilities in both the valence bands of Cu12Sb4S13-Se. The higher mobilities can be simply understood to be a result of the higher degree of covalency in Se substituted samples compared to that of S anions. Indeed, a higher average mobility is observed compared to Cu12Sb4S13. As for the Seebeck coefficient when two bands contribute to the transport, the total Seebeck coefficient is expressed as

\[
S = \frac{S_1 \sigma_1 + S_2 \sigma_2}{\sigma_1 + \sigma_2}
\]

Thus, the overall Seebeck coefficient is the average value weighted by the electrical conductivity of each band. Typically, heavier bands are favorable for large Seebeck coefficients. Nevertheless, as the DOS effective mass is related to the band effective mass, charge carriers in heavy bands would have low mobilities and this causes low electrical conductivity. The conflicting role of the effective mass makes the evaluation of the overall Seebeck coefficient in multiband structures more complex. The band convergence at a constant carrier concentration can cause either increased or decreased Seebeck coefficients, depending on the electronic structure, scattering mechanisms and band anisotropy in each specific case. For example, in Mg2Si1-xSnx solid solutions, the band convergence of heavy and light conduction bands at the content of Snx \( \sim 0.7 \) leads to an enhancement of the Seebeck coefficient but a somewhat increased electrical resistivity.19 In contrast,

<table>
<thead>
<tr>
<th>( \Gamma )</th>
<th>( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu12Sb4S13</td>
<td>1.85m(_0)</td>
</tr>
<tr>
<td>Cu12Sb4S13-Se</td>
<td>1.61m(_0)</td>
</tr>
<tr>
<td>Cu12Sb4S13-Se2</td>
<td>1.51m(_0)</td>
</tr>
</tbody>
</table>
impurity induced additional light conduction bands in Co_{1−x}Ni_{x}Sb_{3} give rise to a significantly decreased electrical resistivity but only a slight decrease in the Seebeck coefficient.\textsuperscript{10} Here, in our work, we attribute the unchanged Seebeck coefficients in Cu_{12}Sb_{4}S_{13−x}Se_{x} solid solutions to similar DOS effective masses at $G$ and $P$ points. Thus, the two degenerate bands contribute roughly equally to the electronic transport and have comparable absolute values of the Seebeck coefficients. As listed in Table 1, the effective masses at $G$ and $P$ points are very similar for a given Se content. In particular, for Cu_{12}Sb_{4}S_{13} and Cu_{12}Sb_{4}S_{12} Se the DOS effective masses at $G$ and $P$ points are 1.61 and 1.68 $m_e$, respectively. When doping two Se atoms in Cu_{12}Sb_{4}S_{13}, an additional band crosses the Fermi level along the $Γ$–$N$ direction, suggesting that the band with the symmetry degeneracy of $N_e = 4$ becomes involved in the electronic transport (Fig. 4c). Nevertheless, no further reduction in the electrical resistivity is observed, most likely due to strong intervalley scattering.

4. Conclusion

In summary, isovalent Se substitution has been employed in the tetrahedrite. The reduction in the electrical resistivity in highly degenerate tetrahedrite compounds is attributed to additional valence bands and the enhanced mobility rather than the increased carrier concentration. Unusually constant Seebeck coefficients and a different form of decoupling between the electrical conductivity and the Seebeck coefficient than reported for other thermoelectric systems are shown to be caused by similar DOS effective masses. Further investigations regarding the effective band degeneracy and carrier mobility would be advantageous, as would be additional experimental studies using advanced characterization techniques. Nevertheless, this work not only shows a new route how to further reduce the electrical resistivity of a highly degenerate semiconductor, but it also gives a detailed explanation for the decoupling mechanism observed to be operative in tetrahedrites, based on the band structure analysis. This illustrates the possibilities of enhancing the thermoelectric power factor in semiconductors having ultrahigh carrier concentration without compromising the electrical conductivity. It should be noted that the decoupling mechanism proposed here can be applied only if the orbitals of the isovalent dopant can contribute to the band edges. Moreover, the large total band degeneracy ($N_e = 14$) in the band structure of tetrahedrites is not fully utilized at present due to orbital splitting and intra/inter valley scattering, leaving much scope for work.

Acknowledgements

This work was supported as part of the Center for Revolutionary Materials for Solid State Energy Conversion, an Energy Frontier Research Center funded by the U.S. Department of Energy, under No. DE-SC0001054. X. L. acknowledges financial support from the Fundamental Research Funds for Central Universities of China with No. 0903005203360. Y. Z. acknowledges financial support from the National Natural Science Foundation of China with No. 11474283. The authors also appreciated the usage of facility in Analytical and Testing Center of Chongqing University.

References


