Enhanced Thermoelectric Properties of Cu_3SbSe_4 Compounds by Isovalent Bismuth Doping

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Abstract

Cu_3SbSe_4 , featuring its earth-abundant, cheap, nontoxic and environmentally-friendly constituent elements, can be considered as a promising intermediate temperature thermoelectric (TE) material. Herein, a series of p-type Bi-doped $\text{Cu}_3\text{Sb}_{1-x}\text{Bi}_x\text{Se}_4$ ($x = 0-0.04$) samples were fabricated through melting and hot pressing (HP) process, and the effects of isovalent Bi-doping on their TE properties were comparatively investigated by experimental and computational methods. TEM analysis indicates that Bi-doped samples consist of Cu_3SbSe_4 and Cu_{2-x}Se impurity phases, which is in good agreement with the results of XRD, SEM and XPS. For Bi-doped samples, the reduced electrical resistivity (ρ) caused by the optimized carrier concentrations and enhanced Seebeck coefficient derived from the densities of states near the Fermi level give rise to a high power factor of $\sim 1000 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 673 K for the $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ sample. Additionally, the multiscale defects of Cu_3SbSe_4 -based materials involving point defects, nanoprecipitates, amorphous phases and grain boundaries can strongly scatter phonons to depress lattice thermal conductivity (κ_{lat}), resulting in a low κ_{lat} of $\sim 0.53 \text{ Wm}^{-1}\text{K}^{-1}$ and thermal conductivity (κ_{tot}) of $\sim 0.62 \text{ Wm}^{-1}\text{K}^{-1}$ at 673 K for the $\text{Cu}_3\text{Sb}_{0.98}\text{Bi}_{0.02}\text{Se}_4$ sample. As a consequence, a maximum ZT value ~ 0.95 at 673 K is obtained for the $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ sample, which is ~ 1.9 times more than that of pristine Cu_3SbSe_4 . This work shows that isovalent heavy-element doping is an effective strategy to optimize thermoelectric properties of copper-based chalcogenides.

1. Introduction

Thermoelectric (TE) materials, dealing with environmental protection and economic development, have gained great interest of research for waste energy recovery, temperature control and heat management in last two decades owing to the direct interconversion between heat and electricity power [1–5]. TE materials like chalcogenides, skutterudites, clathrates and half-Heuslers, etc., are intensively studied for power generation and thermoelectric cooling [6–11]. The efficiency of a TE material is determined by the dimensionless thermoelectric figure of merit, $ZT = S^2 T / \rho \kappa$, where S , ρ , T and κ presents the Seebeck coefficient, electrical resistivity, absolute temperature, total thermal conductivity (including lattice thermal conductivity κ_{lat} and electronic thermal conductivity κ_{ele}), respectively [12, 13]. Generally speaking, an important goal of TE research is to achieve as large ZT value as possible because the efficiency increases nonlinearly with ZT, which approaches the Carnot efficiency as ZT approaches infinity [6]. As known, increasing power factor ($\text{PF} = S^2 / \rho$) or/and depressing κ_{lat} can enhance the ZT values. On one hand, one can use those methods to decouple the internal relationships between S and ρ in order to guarantee a high PF value, such as modulation doping [14], band engineering [15–17], carrier concentration optimization [18–20], carrier blocking [21] and energy filtering effect[22]; On the other hand, to obtain a low κ_{lat} , one can select materials with intrinsically low κ_{lat} [23–25], or strengthen phonon scattering to suppress phonon transports by nanostructure engineering [26–28], alloying [29], and all-scale hierarchical microstructure construction at atomic-, nano- and meso-scale, including point defects [30], dislocations [31], precipitates and boundaries [32, 33]. However, PF is usually along with high κ on

account of the interrelated relationship among the S , ρ and κ_{ele} , which makes the optimization of TE properties and development of high-performance TE materials quite challenging [13]. Furthermore, the exploitation of earth-abundant, cheap, nontoxic TE materials (more economical) is urgently in large-scale practical application of TE devices [7, 34].

On this point, copper based chalcogenides have sprung up as potential TE materials because of their low thermal transport and relatively good electrical transport properties [5, 35, 36]. In particular, Cu_3SbSe_4 , featuring its earth-abundant, cheap, nontoxic and environmentally-friendly elements, has been actively studied as a promising intermediate temperature TE material. Meantime, it shows a narrow band gap (~ 0.29 eV), p -type conductivity with large carrier effective mass ($m^* \sim 1.1 m_e$), and a zinc-blende-derived stannite structure (tetragonal, $I42m$ space group) [37]. However, the low carrier concentration limits high ZT values in pristine Cu_3SbSe_4 , for which how to improve ZT is a research focus. To the best of our knowledge, the Cu-Se bonds can act as the carrier conduction framework while Sb orbitals make less contribution to the valence-band maximum (VBM) in Cu_3SbSe_4 [38]. Consequently, partial substitutions for Sb lattice sites is an effective approach to optimize carrier concentration, such as Ag [13], In [38], Ti [39], Sn [40], Ge [41], Al [42] and other element substitutions [43]. Recently, Dou et al. reported a new strategy to enhance TE properties of Cu_3SbSe_4 via alkali-ion (Na and K) doping, and the peak ZT values reached 0.52 and 0.71 at 673 K for $\text{Cu}_3\text{Sb}_{1-x}\text{Na}_x\text{Se}_4$ ($x = 0.02$ and 0.03) and $\text{Cu}_3\text{Sb}_{0.99}\text{K}_{0.01}\text{Se}_4$, respectively [44]. In contrast to light elements doping, heavy elements doping (Bi, Te, etc.) have more virtues in lowering κ_{lat} because of stronger mass and strain field fluxes, which can block the propagation of phonons [45, 46].

In this article, we report a high-performance Cu_3SbSe_4 -based material via Bi-doping. Isovalent element dopant Bi can reduce ρ by the enhanced carrier concentration and the changed Fermi level, and the κ_{lat} is depressed through the strengthened phonon scattering caused by multiscale defects including point defects, nanoprecipitates, amorphous phases and grain boundaries, respectively. Consequently, a maximum ZT (ZT_{max}) of ~ 0.95 at 673 K is achieved for the $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ compound due to the decoupled internal relationships between electrical and thermal transport properties.

2. Experimental Procedures

Synthesis

The $\text{Cu}_3\text{Sb}_{1-x}\text{Bi}_x\text{Se}_4$ ($x = 0, 0.005, 0.01, 0.015, 0.02, 0.03$ and 0.04) polycrystalline samples were fabricated through vacuum melting and hot pressing (HP) process. Nominal composition of high purity elements (Cu: 99.99%; Sb: 99.99%; Se: 99.999%, Bi: 99.999%) were weighted and placed in quartz tubes, which sealed under high vacuum and then putted into a digitally controlled furnace. The samples were heated at a rate of $20^\circ\text{C}/\text{h}$ to 1173 K with a holding time of 12 h, then cooled to 773 K in 40 h. Finally, the quartz tubes were quenched in water for cooling from 773 K down to room temperature. After quenching, to promote Cu_3SbSe_4 -based compounds homogeneity, the samples were annealed at 573 K

for two days. After that, the obtained ingots were milled into powders by hand in an agate mortar for 30 min and sintering in graphite dies with an inner diameter of 10 mm by HP at 673 K for 2 h under 50 MPa.

Characterizations

The phase structure of bulk samples was checked by using X-ray diffractometer (XRD, Bruker D8 Advance) in the θ -2 θ scan mode with Cu K α ($\lambda = 1.5418\text{\AA}$) radiation as an X-ray source. The surface morphologies and chemical elemental composition of the samples were characterized by field emission scanning electron microscopy (FESEM; Nova NanoSEM450) combined with energy-dispersive X-ray spectroscopy (EDS). The valence state of the elements and chemical composition of the Bi-doped Cu_3SbSe_4 sample was identified by using X-ray photoelectron spectroscopy (XPS) (Escalab 250Xi, Thermo VG Scientific). Transmission electron microscopy (TEM) was performed on a Talos-F200X operated with an acceleration voltage of 200 kV. The Seebeck coefficient (S) and electrical resistivity (ρ) were simultaneously measured by the commercial measuring system (LSR-3) under a helium atmosphere from room temperature to 673 K. The thermal diffusivity (D) was measured by using the laser flash method (Netzsch, LFA-457). The thermal conductivity was calculated from the relationship of $\kappa = DC_p d$, where D , C_p and d are the measured thermal diffusivity, specific heat and density, respectively. The concentration of carrier and transportation in the samples were measured using a Hall apparatus (LAKE SHARE, 7707 A, USA) by the Vander Pauw method under constant magnetic fields of 0.68 T. Densities of sintered samples were conducted by Archimedes' method, which reached over 95% of the theoretical density of Cu_3SbSe_4 (5.86 g cm^{-3}) (Tab. S1).

Computational methods

Theoretical calculations based on DFT were performed using Vienna Ab-initio Simulation Package (VASP) [47, 48]. Generalized gradient approximation (GGA) method with Perdew–Burke–Ernzerhof (PBE) function was used to describe electronic exchange and correlation effects [49]. A supercell consisting of $2 \times 2 \times 2$ pristine cell of Cu_3SbSe_4 (128 atoms, $\text{Cu}_{48}\text{Sb}_{16}\text{Se}_{64}$) were built for randomly replacing Sb atoms with Bi atoms. The kinetic energy cutoff for the plane wave basis was set as 500 eV and the a monkhorst–Pack $3 \times 3 \times 2$ k-point mesh is adopted. All structures were relaxed until the forces exerted on each atom were less than $0.01\text{ eV/\AA}$, and the energy convergence criteria for electronic iterations were assumed to be 10^{-5} eV. The HSE06 model are adopted to calculate the density of states (DOS) [50, 51].

3. Results And Discussion

As seen in Fig. 1a, the crystal structure of the pristine Cu_3SbSe_4 is the tetragonal structure ($I-42m$ space group) [38]. The X-ray diffraction (XRD) patterns of the synthesized $\text{Cu}_3\text{Sb}_{1-x}\text{Bi}_x\text{Se}_4$ ($x = 0-0.04$) compounds are shown in Fig. 1b. The major diffraction peaks match well with the standard peaks of Cu_3SbSe_4 (JCPDS No.85 – 0003) phase, which belongs to the zinc blende structure with tetragonal system. As the concentration of Bi element increases to 0.03, some weak diffraction peaks at the 2 θ

angle of $\sim 24^\circ$, 31° and 65° are observed, indicating the Bi and Cu_{2-x}Se phases [52]. Previous work also demonstrated that Bi phase was precipitated from the matrix as Bi concentration exceeds 0.02 in Cu_3SbSe_4 [45]. It can be deduced that the addition of Bi is propitious to the precipitation of Cu_{2-x}Se phase, which is beneficial to decrease in lattice thermal conductivity.

The morphologies and compositions of Cu_3SbSe_4 -based samples were examined by SEM and EDS analyses. As depicted in Fig. 2, SEM images of the fracture surfaces (Fig. 2a-d) indicate that Cu_3SbSe_4 materials are isotropic and some impurity phases are embedded into the Cu_3SbSe_4 matrix. EDS result demonstrates that the impurity phase contains of Cu and Se elements (Fig. 2e) and the atomic ratio (%) of copper to selenium is 61.31: 32.56, implying that the impurity phase is copper selenide of Cu_{2-x}Se , which is consistent with XRD results. The back-scattered electron (BSE) image of $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ sample clearly present the micro or even nanoscale impurity phases (Fig. S1), which are useful to reduce κ_{lat} by scattering long-wave phonons [46]. The Cu_{2-x}Se with extremely low κ_{lat} can decrease the κ_{tot} of Cu_3SbSe_4 to some degree [52, 53].

XPS is used to check the valence state of elements and chemical composition of the Cu_3SbSe_4 -based samples [54]. The experimental data of XPS spectra peaks of $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ samples are presented in Fig. 3. XPS spectra confirm the presence of Cu, Sb, Se and Bi elements in the Cu_3SbSe_4 -based compounds. As shown in Fig. 3a, Cu 2p core electron peak of specimen is split into two peaks, and the XPS spectra of Cu 2p_{3/2} (931.2 eV) and the Cu 2p_{1/2} (952.5 eV) peaks can confirming indicate the existence of Cu^{1+} in the sample [55]. The Sb 3d spectra can be deconvoluted into two peaks of Sb 3d 5/2 (528.4 eV) and Sb 3d 3/2 (537.7 eV) (Fig. 2b), which can be indexed to Sb^{5+} [56]. The Se 3d spectra can be also split into two peaks at 53.1 eV (3d_{5/2}) and 54.0 eV (3d_{3/2}) (Fig. 2c), which are matched with Se^{2-} of oxidation state [57]. The Bi 4f spectra do not display distinguished changes. Consequently, the components of as-sintered Bi-doped samples are speculated to be consisted of Cu_3SbSe_4 , Cu_{2-x}Se , which is in agreement with XRD and SEM results.

The presence of secondary phase is clearly visualized by employing a high-resolution TEM. The low-magnification images presented in Fig. 4a demonstrate that some impurity phases are distributed in the matrix. As shown in Fig. 4b, a crossed fringe, with interplanar spacing values of 0.5164 nm, which can be indexed to (101) planes of Cu_3SbSe_4 [40]. The 0.2986 nm, 0.1041 nm and 0.1157 nm of spacing are in response to (200), (511) and (422) plane of Cu_2Se , respectively [53]. It can be seen that some amorphous phases exist in the matrix (yellow A presents amorphous phase and C presents crystallized phase). In addition, the interfaces (blue dot lines) among Cu_3SbSe_4 , Cu_2Se and amorphous phases can be clearly observed. All of which are good for reducing lattice thermal conductivity. The SAED pattern, corresponding to (105), (220) planes of Cu_3SbSe_4 , and (111), (220) planes of Cu_2Se , which may be further supposed the as-prepared sample is consisted of Cu_3SbSe_4 and Cu_{2-x}Se [52–54].

To validate our experimental design and investigate the change of electronic properties, the density functional theory (DFT) calculations were performed [13]. To ensure the optimal doping model is consistent with the experiment and guarantee the rationality for theory calculation, the $\text{Cu}_{48}\text{Sb}_{16}\text{Se}_{64}$ and $\text{Cu}_{48}\text{Sb}_{15}\text{Bi}_1\text{Se}_{64}$ structures were constructed. The crystal structure of Bi-doped $\text{Cu}_{48}\text{Sb}_{16}\text{Se}_{64}$ (including the top and side views) is shown in Fig. S2. Bi-doped $\text{Cu}_{48}\text{Sb}_{16}\text{Se}_{64}$. Bi can form four 2.74 Å Bi-Se bonds with the surrounding Se atoms, which is 0.2 Å longer than the original Sb-Se bond, mainly caused by the larger atomic radius of the Bi atom. The DOS of pristine and Bi doped $\text{Cu}_{48}\text{Sb}_{16}\text{Se}_{64}$ is presented in Fig. 5a. After Bi doping, the Fermi level changes from 3.99 eV to 3.77 eV, thus improving electrical transport characteristics. The band gap (E_g) of $\text{Cu}_{48}\text{Sb}_{16}\text{Se}_{64}$ is 0.25 eV, which is basically consistent with previous report [58], and increase to 0.27 eV for $\text{Cu}_{48}\text{Sb}_{15}\text{Bi}_1\text{Se}_{64}$. More importantly, the DOS near the Fermi level (0 eV) are increased, which is composed of the hybridized Cu 3d, Sb 5s, Se 4p and Bi 6s orbitals (Fig. 5b), leading to large Seebeck coefficients

The temperature-dependent electrical transport properties of Cu_3SbSe_4 -based samples are depicted in Fig. 6. As seen in Fig. 6a, the ρ of pristine Cu_3SbSe_4 sample decreases with elevating temperature, indicating that it is non-degenerate semiconductor. However, Bi-doped samples become partially degenerate semiconductors, especially the samples with low Bi content ($x < 0.015$). Clearly, the ρ of all Bi-doped Cu_3SbSe_4 compounds is lower than that of pristine Cu_3SbSe_4 due to the increased carrier concentration (Tab. S1). In comparison with Sb^{5+} (0.62 Å), the bigger radius of Bi^{5+} (0.74 Å) can generate Cu and/or Sb vacancies [45]. Meanwhile, the ρ of the samples increases with increasing Bi content ($x < 0.3$), however, the ρ sharply decreases as $x = 0.03$ and 0.04 because of the relatively high carrier mobility and carrier concentration. In addition, the ρ shows the temperature-independent behavior at high temperature because the intrinsic excitation gradually becomes dominant at 573–673 K, which is similar to the transport behavior of non-degenerate semiconductor.

Figure 6b demonstrates the temperature-dependent S of Cu_3SbSe_4 -based samples. It can be seen that they are p-type conductivity derived from the positive values of S , and the charge carriers in these compounds are holes. After Bi doping, the S first decreases and then rises with increasing temperature, achieving a minimum S , which should be attributed to the α - β phase transition of Cu_{2-x}Se phase [52, 53]. Although the increased hole concentration (Tab. S1) deteriorates S , Bi doping can enhance DOS near Fermi level (E_f) and enlarge E_g according to the DFT calculations, resulting in the relatively large S [45].

Figure 6c presents the temperature-dependent PF of Cu_3SbSe_4 -based samples. It can be seen that the PF values of pristine Cu_3SbSe_4 sample increase with elevating temperature. Besides, PF values of Bi-doped compounds decrease slightly and then increases with rising temperature, and are higher than that of pristine Cu_3SbSe_4 at high temperature, which is attributed to the enhancement of electrical conductivity after Bi-doping. However, the excessive Bi content ($x \geq 0.02$) does not further enhance PF values due to the deteriorated Seebeck coefficient. The maximum PF value of $\sim 1000 \mu\text{Wcm}^{-1}\text{K}^{-2}$ is achieved at 673 K for $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ compound.

(c) power factor of Cu₃SbSe₄-based samples.

The temperature-dependent thermal transport properties of the Cu₃SbSe₄-based samples are displayed in Fig. 7. The D decreases with the increase of temperature and the room-temperature D drops from $\sim 1.7 \text{ mm}^2\text{s}^{-1}$ for pristine Cu₃SbSe₄ to $\sim 1.45 \text{ mm}^2\text{s}^{-1}$ for Cu₃Sb_{0.97}Bi_{0.03}Se₄ sample after Bi doping (Fig. 7a). As presented in Fig. 7b, the κ_{tot} reduces with rising temperature within the range of measurement due to the enhanced lattice vibration scattering at high temperature [11, 59]. Besides, the κ_{tot} of all the Cu₃SbSe₄-based samples decreases after Bi doping, drops from $\sim 3.11 \text{ Wm}^{-1}\text{K}^{-1}$ at 300 K and $\sim 1.03 \text{ Wm}^{-1}\text{K}^{-1}$ at 673 K for pristine Cu₃SbSe₄ to $\sim 2.81 \text{ Wm}^{-1}\text{K}^{-1}$ at 300 K and $\sim 0.69 \text{ Wm}^{-1}\text{K}^{-1}$ at 673 K for Cu₃Sb_{0.985}Bi_{0.015}Se₄ sample. Generally, the κ_{lat} can be calculated by subtracting the electronic part κ_{ele} from the κ_{tot} . According to the Wideman–Franz law Eq. (1):

$$\kappa_{\text{ele}} = L\sigma T \quad (1)$$

where, L is the Lorenz number and can be calculated from Eq. (2) [60, 61]:

$$L = 1.5 + \exp \left[\frac{-|S|}{116} \right] \quad (2)$$

The calculated L values of the Cu₃SbSe₄-based samples are presented in Fig. S3 and L ranges from 1.51 to 2.13 $\text{W } \Omega \text{ K}^{-2}$. The increased κ_{ele} of Bi-doped compounds is shown in Fig. 7c, which can be closely related to electrical conductivity derived from the rising carrier concentration and high carrier mobility. As seen in Fig. 7d, the prominent scattering mechanism of Cu₃SbSe₄-based samples is the phonon-phonon Umklapp scattering, which can be inferred from the relationship of $\kappa_{\text{lat}} \propto T^{-1}$. As expected, the Bi-doping can decrease κ_{lat} in the measured temperature region. On one hand, the isovalent substitutions on Sb can reduce κ_{lat} because of stronger mass and strain field fluctuations, which is similar to the case that In_{Sb} point defects in Cu₃SbSe₄ can scatter high frequency phonons [39]. On the other hand, the heavy element Bi has much larger ionic radius in comparison with Sb, leading to the reduced κ_{lat} . The heat-carrying acoustic phonons can be blocked by softening the chemical bonding interaction in crystal due to the expansion of unit cell [46]. Furthermore, the impurity phase Cu₂Se and amorphous phase with extremely low κ_{lat} can also decrease κ_{lat} of Bi-doped Cu₃SbSe₄ [52, 53]. Consequently, the reduction of κ_{tot} should be attributed to the depressed κ_{lat} caused by the strengthened phonon scattering of multiscale defects involving point defects, nanoprecipitates, amorphous phases and grain boundaries [62, 63]. The lowest $\kappa_{\text{lat}} \sim 0.53 \text{ Wm}^{-1}\text{K}^{-1}$ and $\kappa_{\text{tot}} \sim 0.62 \text{ Wm}^{-1}\text{K}^{-1}$ is achieved at 673 K for the Cu₃Sb_{0.98}Bi_{0.02}Se₄ sample.

The temperature-dependent ZT of Cu_3SbSe_4 -based samples with various Bi concentration is presented in Fig. 8a. Benefiting from the synergistically optimized electrical and thermal transport properties, the ZT values obtains an enhancement at high temperature for Bi-doped compounds, which can reach the maximum ZT value of ~ 0.95 at 673 K for the $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ sample. To further analyze our experimental results, the previous ZT_{max} values of other single-doped Cu_3SbSe_4 samples are listed in Fig. 8b [13, 38–45]. Accordingly, isovalent heavy element Bi doping in Cu_3SbSe_4 compounds can simultaneous optimize electrical and thermal parameters, which is highly effective in improving TE properties.

4. Conclusions

In summary, the improvement of the overall TE properties in p-type Cu_3SbSe_4 was realized by Bi-doping. The results of XRD, XPS, SEM and TEM analysis indicate that Bi-doped samples consist of Cu_3SbSe_4 with Cu_{2-x}Se impurity phases. The ρ of all the isovalent Bi-doped samples is lower than that of pristine Cu_3SbSe_4 because the enhanced carrier concentration, and a high power factor of $\sim 1000 \mu\text{Wcm}^{-1}\text{K}^{-2}$ is achieved at 673 K for the $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ sample. In addition, the multiscale defects of Cu_3SbSe_4 -based materials involving point defects, nanoprecipitates, amorphous phases and grain boundaries caused by Bi-doping can strongly scatter phonons to depress κ_{lat} . Consequently, the thermoelectric properties improve significantly and the maximum ZT value of ~ 0.95 is achieved at 673 K for the $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ sample, which is ~ 1.9 times higher than that of pristine Cu_3SbSe_4 . The present work presents a selectable route to enhance the comprehensive TE properties by isovalent heavy-element doping for other TE materials, which is also important to TE device application.

Declarations

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

Figure 1

(a) The crystal structure of Cu₃SbSe₄; (b) XRD patterns of Cu₃SbSe₄-based samples.

Figure 2

The fracture morphology images of (a) pristine Cu_3SbSe and (b) $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ samples; (c,d) high magnification images of (a,b); (e) the corresponding EDS spectrum of B zone in (d)

Figure 3

XPS spectra of $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ samples: (a) Cu; (b) Sb; (c) Se and (d) Bi.

Figure 4

(a) Low-magnification image and (b) HRTEM image (the inset is SAED pattern) of $\text{Cu}_3\text{Sb}_{0.985}\text{Bi}_{0.015}\text{Se}_4$ sample.

Figure 5

(a) Density of state (DOS) of Cu₄₈Sb₁₆Se₆₄ and Cu₄₈Sb₁₅Bi₁Se₆₄; (b) the corresponding partial density of states (PDOS) of Cu₄₈Sb₁₅Bi₁Se₆₄. The Fermi level was set to zero with red imaginary line marked.

Figure 6

Temperature-dependent (a) electrical resistivity; (b) Seebeck coefficient; (c) power factor of Cu₃SbSe₄-based samples.

Figure 7

Temperature-dependent (a) specific heat capacity C_p , (b) total thermal conductivity κ_{tot} , (c) electronic thermal conductivity κ_{ele} , (d) lattice thermal conductivity κ_{lat} of Cu_3SbSe_4 -based samples.

Figure 8

(a) Temperature-dependent figure of merit (ZT) of Cu_3SbSe_4 -based samples; (b) comparison of ZT_{max} of this work and other Cu_3SbSe_4 systems.