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Enhancement of thermoelectric properties in *p*-type ZnSb alloys through Cu-doping

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ABSTRACT

To meet the growing demand for thermoelectric devices operating in intermediate temperature ranges, it is essential to develop high-performance materials with superior thermoelectric properties and robust mechanical strength. In this study, we systematically optimized carrier concentration by introducing acceptor impurities into ZnSb materials. Our results demonstrate that doping Cu into the Zn site effectively modulates hole carrier concentration, leading to a substantial enhancement in electrical conductivity and a remarkable improvement in power factor (107 %). Consequently, we achieved a high peak *ZT* of 1.04 at 600 K and an average *ZT*_{ave} value of 0.63 within the temperature range of 300–600 K. This yielded a calculated efficiency of $\eta_{max} = 7$ % at $\Delta T = 300$ K, for the Zn_{0.99}Cu_{0.01}Sb sample, which is 134 % higher than that of the pristine ZnSb sample ($\eta_{max} = 2.98$ %). Moreover, the superior hardness and fracture toughness (K_{IC}) of ZnSb samples compared to other state of-the-art thermoelectric materials make them highly desirable for real-time applications.

1. Introduction

In light of the extensive use of fossil fuels worldwide and the concerning state of global warming, researchers have actively explored pathways to revolutionize the energy system [1,2]. Thermoelectric technology offers significant potential for harnessing waste heat and converting it into electricity based on the Seebeck effect [3–6]. The conversion efficiency of thermoelectric devices largely relies on the material's performance, which is determined by the dimensionless figure of merit, $ZT = S^2 \sigma T/\kappa_{tot}$, where *S* is the Seebeck coefficient, σ is the electrical conductivity, *T* is the absolute temperature, and κ_{tot} is the total thermal conductivity, comprising contributions from both carriers (κ_{el}) and lattice vibrations (κ_{L}). Since the electrical transport properties (*S*, σ , κ_{el}) are interconnected through carrier concentration, improving one property affects the others, making it challenging to achieve high *ZT* values. Tuning carrier concentration through elemental doping emerges as an effective strategy for optimizing both electrical conductivity (σ) and power factor (PF = $S^2 \sigma$) [3,7,8].

ZnSb-based alloys are attractive for potential thermoelectric applications in the middle temperature range (500–700 K) [9], due to their combination of advantages, including relatively low cost, lower toxicity, and abundance of their constituent elements in the Earth's crust. These alloys can potentially form two types of thermoelectric phases from Zn and Sb: stable phase like ZnSb and metastable phase like Zn₄Sb₃ [10,11]. Zn₄Sb₃ possesses intrinsically low lattice thermal conductivity (0.2–0.6 W/mK at 300 K) due to the disordered positions of Zn atoms in its crystal lattice [12,13], resulting in a reported maximum *ZT* of 1.4 at 623 K [14]. However, a drawback of Zn₄Sb₃ is its prone to severe decomposition under temperature gradient or an electric field, which limits its practical applications. Conversely, ZnSb offers good stability,

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but its performance is hindered by difficulties in achieving optimal doping levels and its higher lattice thermal conductivity (1.45-3 W/mK at 300 K) [9,15–18].

To enhance the thermoelectric performance of ZnSb, researchers have focused on optimizing carrier concentration through doping with acceptor impurities. Typically, the optimal range of charge carrier concentration for achieving the best ZT values lies within the degenerate doping range (10¹⁸–10²⁰ cm⁻³). However, pristine ZnSb samples exhibit a carrier concentration in the order of 10^{17} cm⁻³, resulting in low ZT values (0.5 at 700 K) [17]. Recent studies have demonstrated significant improvements through various doping strategies. For instance, Sidharth et al. [19] successfully increased the carrier concentration of ZnSb to 1.1 $\times 10^{19}$ cm⁻³ by doping 2 % heterovalent Bi at the Zn site, resulting in a ZT of approximately 0.45 at 573 K. Similarly, Kang et al. [10] optimized the thermoelectric properties of ZnSb alloys through Cr doping, enhancing the carrier concentration to $5.4 \times 10^{18} \text{ cm}^{-3}$ while maintaining low κ_{I} , leading to an improved ZT of 0.67 at 673 K for the Zn_{0.99}Cr_{0.01}Sb composition. Prokofieva et al. [20] reported that 0.1 at% Sn-doped ZnSb increased the carrier concentration to 1.4×10^{19} cm⁻³, resulting in a ZT of 0.85 at 660 K. Additionally, Xiong et al. [21] demonstrated a remarkable increase in ZT to 1.15 at 670 K for 0.2 %Ag-doped ZnSb. This improvement was attributed to the in-situ formation of an Ag₃Sb phase, which promoted both nanostructuring and optimized carrier concentration.

Despite these advances, the charge carrier concentrations in ZnSbbased materials are still below the optimum value ($\sim 2 \times 10^{19}$ cm⁻³) [22], which may be due to several factors. One reason could be low doping efficiency, where the concentration of charge carriers generated per dopant atom is insufficient due to native defects such as vacancies, interstitials, and antisites [23]. Additionally, the maximum possible carrier concentration, known as dopability, may be limited by the solubility of the dopant in the material [10,24]. Consequently, the overall *ZT* values in ZnSb-based compounds remain below unity. Among various dopants, copper ions (Cu⁺) are particularly interesting for ZnSb. Cu has a similar electronic shell structure and comparable physical and chemical properties to Zn [25,26], enabling Cu⁺ ions to easily replace Zn²⁺ ions and potentially optimize the carrier concentration. Therefore, doping Cu into ZnSb alloys could be of great significance for improving their thermoelectric properties.

In addition to thermoelectric properties, the mechanical properties of materials are crucial for ensuring the long-term durability, reliability, and stability of a thermoelectric module during manufacturing and operation. These materials must be robust enough to operate within the temperature range of 500-600 K, which is useful for automotive applications. Consequently, they must withstand high internal thermal stresses caused by rapid temperature cycling between the two ends of the same thermoelectric element [27]. Poor mechanical properties can lead to crack formation, resulting in deteriorated performance under thermal stress [28,29]. Furthermore, severe mechanical vibrations can accelerate the failure process of thermoelectric generator (TEG) devices, particularly in applications such as automotive waste heat recovery [30, 31]. Therefore, research that combines the preparation of ZnSb-based materials with optimized carrier concentration and enhanced thermoelectric and mechanical properties is necessary for power generation applications.

In this work, we doped ZnSb materials with copper (Cu) as an acceptor impurity using the melting-quenching-annealing process. We found that optimizing the hole carrier concentration resulted in a maximum *ZT* of ~1.04 at 600 K, primarily due to a significant enhancement in the power factor by 107 %. Additionally, ZnSb samples exhibited superior mechanical properties compared to other thermoelectric materials.



Fig. 1. SEM images showing the fracture surfaces of spark plasma sintered bulk samples: (a) ZnSb, (b) Zn_{0.99}Cu_{0.01}Sb, (c) Zn_{0.97}Cu_{0.03}Sb, and (d) Zn_{0.9}Cu_{0.1}Sb.

Table 1

X-ray fluorescence (XR) analysis of trace elements in	$Zn_{1-x}Cu_xSb$ (x = 0, 0.01	, 0.03 and 0.1) bulk samples.
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Samples	Zn (wt%)		Sb (wt%)	Sb (wt%)		Cu (wt%)	
	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental	
ZnSb	34.94	33.1±0.04	65.06	66.9±0.27	0.0	0.0	
Zn _{0.99} Cu _{0.01} Sb	34.59	33.8±0.04	65.07	65.8±0.09	0.34	$0.31{\pm}0.01$	
Zn _{0.97} Cu _{0.03} Sb	33.90	$33.5 {\pm} 0.03$	65.08	$65.5 {\pm} 0.10$	1.02	$0.97{\pm}0.01$	
Zn _{0.9} Cu _{0.1} Sb	31.47	$31.2{\pm}0.03$	65.13	$65.8{\pm}0.09$	3.40	$3.0{\pm}0.01$	

2. Experimental section

2.1. Synthesis of alloy powder and bulk samples

Polycrystalline Zn_{1-x}Cu_xSb (x = 0, 0.01, 0.03, and 0.1) samples were synthesized using the melting-quenching-annealing process. Stoichiometric amounts of high-purity elemental Zn (99.999 %, 3–5 mm), Sb (99.999 %, 3–5 mm), and Cu powder (99.999 %, 100 μ m) were weighed and vacuum-sealed in quartz tubes under 10⁻⁵ Torr. The quartz tubes were then heated to 1073 K and maintained at this temperature for 2 h before being quenched in water. Subsequently, the tubes underwent a 24 h annealing process at 773 K to ensure the uniform distribution of the elements. The resulting ingots were ground into fine powders using ball milling for 1 h under an Ar atmosphere. The powder was then loaded into a graphite mold with a diameter of 12.5 mm, and an electric current of 200–1000 A was applied under a pressure of 50 MPa using spark plasma sintering (SPS). During the procedure, the temperature gradually increased to 673 K at a ramp-up rate of 50 °C/min, held for 5 min, and then decreased at the same rate.

2.2. Structural characterization

The crystal structures of the alloys were analyzed using X-ray diffraction (XRD, D8 ADVANCE, Bruker) with a CuK α (λ = 0.154056 nm). The lattice parameters were estimated using the Rietveld refinement method implemented in the TOPAS software. Powder morphology and fracture surface analysis of bulk samples were examined by scanning electron microscopy (SEM, Inspect F, FEI). Elemental mapping was performed using energy-dispersive X-ray spectroscopy (EDS). The quantitative chemical compositions of all the samples were measured with an X-ray fluorescence spectrometer (XRF, ZSX Primus II, Rigaku). Optical bandgap studies were carried out using diffuse reflectance spectroscopy (DRS) with a UV-vis-NIR spectrometer (UV3600, Shimadzu). The absorption coefficient (a/S) was calculated using the Kubelka–Munk equation: $a/S = (1 - R)^2/(2 R)$, where R is the reflectance, a and S are absorption and scattering coefficients, respectively. The bandgap (E_g) of all samples was determined from the graphs plotted against $(F(R)^*hv)^2$ vs energy (eV).

2.3. Thermoelectric and mechanical property measurements

The Seebeck coefficient (*S*) and electrical conductivity (σ) were measured simultaneously in the temperature range of 300–600 K using a four-probe method (LSR-3, Linseis). The κ_{tot} was determined by the product of thermal diffusivity, specific heat, and density of the sintered

pellet. Thermal diffusivity and specific heat were measured via the laser flash method (LFA 457, Netzsch). The density of all the bulk samples was measured using Archimedes principle. Hall carrier concentration (*n*), and mobility (μ) were measured on specimens with dimensions of 8 × 8 × 0.1 mm³ using an HMS-3000 instrument from Ecopia. The hardness of the bulk samples was evaluated at room temperature using a micro-Vickers hardness system (HM-200 Mitutoyo, Japan), applying a load of 50 gf for 15 s. The hardness (HV) values were then converted to GPa by multiplying the HV value by 0.009807. Compressive test specimens were prepared perpendicular to the SPS direction, with dimensions of 6 mm in length and 4 mm in width, and were measured using the MTDI MINOS-100S system.

3. Results and discussion

3.1. Microstructure and phase analysis

Previous studies have shown that grain size influences the thermoelectric properties of bulk samples [15,32]. Therefore, we analyzed the microstructure of the bulk samples using SEM. The microstructure of the fractured surfaces for the Zn_{1-x}Cu_xSb samples are shown in Fig. 1(a-d). It was observed that the average grain size increased from 1.4 µm for ZnSb, to 1.7 μm for Zn_{0.99}Cu_{0.01}Sb, 2 μm for Zn_{0.97}Cu_{0.03}Sb and 3 μm for Zn_{0.9}Cu_{0.1}Sb. To confirm the presence of Cu, we conducted EDS measurements in map mode, as shown in Fig. S1. The Zn, Sb, and Cu maps demonstrate a homogeneous elemental distribution. Interestingly, Cu-rich areas were observed in the high concentration (x = 0.1) doping samples, which is consistent with the XRD results. Additionally, the chemical composition of all samples was determined by X-ray fluorescence spectrometry (XRF), with results listed in Table 1. The experimental composition reasonably matched the nominal composition within the accuracy of the measurements. The relative density of the Cu-doped samples indicated that they attained more than 94 % of their theoretical density ($\sim 6.392 \text{ g/cm}^3$) (see Table 2).

The XRD patterns of the $Zn_{1-x}Cu_xSb$ (x = 0, 0.01, 0.03 and 0.1) samples are shown in Fig. 2(a). All diffraction peaks could be accurately indexed to the orthorhombic ZnSb structure with the *P/bca* space group (JCPDS#04–014–2869). Minor peaks corresponding to elemental Sb were observed in all compositions due to the evaporation of Zn during SPS. Notably, a peak corresponding to the impurity Cu₂Sb phase become evident in the x = 0.1 sample due to the excessive doping of Cu in ZnSb. The major diffraction peaks of (112) and (121) systematically shift to higher angles with increasing Cu doping levels. To comprehend the Cu doping, the XRD results were further examined using Rietveld refinement. The Rietveld refinement pattern for the sample with x = 0.03 is

Table 2

Comparison of relative density, lattice parameters, lattice volume, and R-factors obtained using the Rietveld refinement for $Zn_{1-x}Cu_xSb$ (x = 0, 0.01, 0.03 and 0.1) samples.

Samples	Density (g/cc)	Lattice parameters (Å)		Volume (Å)	R-factors (R-factors (%)		GOF	
		a	b	с		Rexp	R _{wp}	Rp	
ZnSb	6.023	6.215	7.745	8.093	388.99	5.58	8.03	6.18	1.44
Zn _{0.99} Cu _{0.01} Sb	6.345	6.210	7.738	8.086	388.93	5.69	8.22	6.28	1.45
Zn _{0.97} Cu _{0.03} Sb	6.392	6.207	7.736	8.083	388.75	5.71	8.19	6.27	1.43
Zn _{0.9} Cu _{0.1} Sb	6.460	6.203	7.733	8.081	388.58	6.19	7.39	5.65	1.19



Fig. 2. (a) X-ray diffraction patterns of $Zn_{1-x}Cu_xSb$ (x = 0, 0.01, 0.03 and 0.1) samples measured perpendicular to the pressing direction. (b) Rietveld refinement pattern of a $Zn_{0.97}Cu_{0.03}Sb$ sample. (c) Optical band gap of $Zn_{1-x}Cu_xSb$ (x = 0, 0.01, 0.03, and 0.1) samples.



Fig. 3. Thermoelectric properties of Cu-doped ZnSb samples with nominal composition $Zn_{1-x}Cu_xSb$ (x = 0, 0.01, 0.03 and 0.1). Temperature-dependent (a) electrical conductivity (σ), (b) Room temperature carrier concentration and mobility, (c) Temperature-dependent Seebeck coefficient (*S*), (d) Pisarenko plot (*S* vs *n*), (e) Temperature-dependent power factor (*PF*), for the $Zn_{1-x}Cu_xSb$ samples, along with a comparison of the *PF* values for several doped ZnSb alloys reported in the literature. (f) *PF* curves dependent on carrier concentration (*n*) using SPB model compared with experimental data.

shown in Fig. 2(b), showing excellent agreement with the experimental XRD pattern. The refined lattice parameters and unit cell volumes obtained from Rietveld refinement for the different compositions are listed in Table 2. The decrease in lattice parameters and unit cell volume with increasing Cu content is attributed to the smaller atomic radius of the substituted Cu atoms (0.128 nm) compared to the Zn atoms (0.138 nm), resulting in lattice contraction due to the substitution of Zn by Cu atoms.

Fig. 2(c) shows the diffuse reflectance spectroscopy studies of $Zn_{1-x}Cu_xSb$ (x = 0, 0.01, 0.03 and 0.1) samples. Pristine ZnSb exhibits an optical bandgap of $E_g \sim 0.84$ eV. As Cu doping increases, the optical bandgap decreases to 0.83 eV, 0.82 eV and 0.81 eV for x = 0.01, 0.03 and 0.1, respectively, which is consistent with previous reports [16]. This reduction in bandgap is attributed to the formation of impurity states above the valence band (VB), causing the Fermi level moves inside the VB.

3.2. Electrical and thermal properties

The temperature-dependent electrical transport properties of the

Zn_{1-x}Cu_xSb (x = 0, 0.01, 0.03 and 0.1) samples are shown in Fig. 3. In Fig. 3(a), it is observed that σ values of all the samples increases with temperature, indicating typical non-degenerate semiconductor behavior. Moreover, as Cu doping increases, σ shows a significant enhancement across the entire temperature range. For instance, the σ of Zn_{0.9}Cu_{0.1}Sb is 47,105 S/m, approximately 33 times higher than that of pristine ZnSb (1437 S/m) at 300 K.

To gain further insights into the transport mechanism, carrier concentration and mobility were analyzed at 300 K and are presented in Fig. 3(b). The carrier concentration for pristine ZnSb is 4.73×10^{17} cm⁻³, which is comparable to values reported in the literature [17,22]. After Cu doping, the carrier concentration increases significantly to 2.91×10^{19} cm⁻³, close to the theoretically predicted optimum value (2×10^{19} cm⁻³) [22]. The enhanced carrier concentration can be attributed to the occupation of Zn sublattice sites (Cu_{Zn}), where Cu atoms act as acceptor impurities, generating one hole per occupied Zn site. However, Hall mobility decreases from 191 cm²/Vs for ZnSb to 111 cm²/Vs for x = 0.1, representing a reduction of approximately 42 %. This reduction in mobility for all the doped samples is primarily due to carrier



Fig. 4. Temperature-dependent thermal conductivities for $Zn_{1-x}Cu_xSb$ (x = 0, 0.01, 0.03 and 0.1), including (a) total thermal conductivity (κ_{tot}), (b) electronic thermal conductivity (κ_{el}), and (c) lattice thermal conductivity (κ_L).

scattering from the ionized Cu impurities. The presence of Cu₂Sb secondary phase in the x = 0.1 sample also contributes to the reduction of mobility. These results indicate that the significant increase in hole carrier concentration enhances σ with Cu doping.

Fig. 3(c) shows that the *S* values in all samples remain positive across the entire temperature range, indicating hole-dominant *p*-type conduction, consistent with Hall measurements. *S* decreases with increasing Cu doping due to an increase in hole concentration. The electrical transport properties of $Zn_{1-x}Cu_xSb$ are further analyzed using the single parabolic band (SPB) model, where the carriers are primarily scattered by acoustic phonons. The transport parameters can be expressed as follows [33,34]:

$$S = \frac{k_B}{e} \left[\eta - \frac{2F_1(\eta)}{F_0(\eta)} \right] \tag{1}$$

$$n = \frac{16\pi}{3} \left(\frac{2m^* k_B T}{h^2}\right)^{3/2} \frac{(F_0(\eta))^2}{F_{-\frac{1}{2}}(\eta)}$$
(2)

$$\mu = \mu_0 \frac{F_{-\frac{1}{2}}(\eta)}{2F_0(\eta)} \tag{3}$$

$$F_i(\eta) = \int_0^\infty \frac{x^i}{1 + e^{x - \eta}} dx \tag{4}$$

$$\eta = \frac{E_f}{k_B T} \tag{5}$$

where *e* is the electron charge, $k_{\rm B}$ is the Boltzmann constant, η is the reduced chemical potential, x is the reduced energy (the energy divided by product of Boltzmann constant and absolute temperature), h is the Planck's constant, E_f is the Fermi energy and m^* is the effective mass. The Pisarenko plot (S vs n) drawn with a fixed m^* of 0.64 m_e for all samples at 300 K is shown in Fig. 3(d). The experimental data closely align with the Pisarenko plot, indicating that the effective mass remains mostly unchanged (Fig. S2(a)). The deformation potential, which characterizes the perturbation of electronic bands due to acoustic phonon waves, was calculated as a function of x for $Zn_{1-x}Cu_xSb$ [33]. The results show minimized carrier-phonon interaction when Cu substitutes for Zn atoms, except in the x = 0.1 sample, where the presence of a secondary phase is indicated by the grey-colored region (Fig. S2(b)). According to the SPB model, the S is solely determined by the reduced Fermi level. Therefore, by measuring S, the corresponding Fermi level can be inferred. Fig. S2(c) illustrates the variation of S at 300 K with Cu doping, while Fig. S2(d) presents the calculated reduced Fermi level derived from the Eq. (1). With Cu doping in ZnSb, the Fermi level approaches the valence band maxima, as depicted in the schematic diagram in Fig. S3.

The temperature dependence of the power factor (*PF*) is shown in Fig. 3(e). Cu doping enhances the *PF* throughout the measured temperature range due to the significant improvement in σ . Specifically, the

maximum *PF* of 2.82×10^{-3} W/mK² at 575 K was obtained for the x = 0.03 sample, which is higher than that reported for Bi-doped ZnSb [19], Ag-doped ZnSb [21], Ge-doped ZnSb [35], and Ag-Sn co-doped Zn_{1-x}Cd_xSb [7]. Fig. 3(f) shows the *PF* as a function of carrier concentration. The symbols represent the experimentally measured *PF*, while the solid lines depict the theoretically calculated *PF*. The theoretical peak *PF* value occurs at a carrier concentration of 1.7×10^{19} cm⁻³, which is nearly close to the experimental value observed for the Cu-doping content x = 0.03. In accordance with the SPB model, the *PF* of the x = 0.03 sample could be enhanced from 1.43×10^{-3} W/mK² to 1.69 $\times 10^{-3}$ W/mK² through appropriate optimization of *n*. Fig. S4(a) shows the calculated weighted mobility (μ_w) at 300 K and 600 K for the Zn_{1-x}Cu_xSb samples. μ_w was calculated using an approximation of the Drude-Sommerfeld free-electron model [33]:

$$\mu_{W} = \frac{3h^{3}\sigma}{8\pi e (2m_{e}k_{B}T)^{3/2}} \left[\frac{\exp\left(\frac{s}{k_{B}e} - 2\right)}{1 + \exp\left(-5\left(\frac{s}{k_{B}e}\right) - 1\right)} + \frac{\frac{3}{\pi^{2}}\frac{s}{k_{B}e}}{1 + \exp\left(5\left(\frac{s}{k_{B}e} - 1\right)\right)} \right]$$

$$(6)$$

where *h* is Planck's constant, σ is the electrical conductivity, *e* is the electron charge, m_e is the electron mass, k_B is the Boltzmann constant, *T* is the absolute temperature, and *S* is the Seebeck coefficient. It is important to note that μ_W is generally proportional to the maximum achievable PF when the carrier concentration of a materials is optimized [36]. As shown in Fig. S4(a), the μ_W values for x = 0.03 exhibit the maximum value at both 300 K and 600 K, indicating that with suitable carrier concentration tuning, this sample can achieve a higher *PF* compared to the others.

Fig. 4 shows the temperature dependence of κ_{tot} , κ_{el} and κ_{L} for the Zn_{1-x}Cu_xSb samples. The κ_{tot} increased with Cu substitution over the entire temperature range (Fig. 4(a)). For example, at 300 K, κ_{tot} was 1.44 W/mK for pristine ZnSb and increased to 2.26 W/mK for Zn_{0.9}Cu_{0.1}Sb upon Cu doping. κ_{el} is evaluated by applying the Wiedemann-Franz law ($\kappa_{\text{el}} = L\sigma T$, where *L* is the Lorenz number). The Lorenz numbers were calculated using the SPB model, as described by the following equations [37].

$$L = \left(\frac{k_B}{e}\right)^2 \frac{3F_0(\eta)F_2(\eta) - 4F_1^2(\eta)}{F_0^2(\eta)}$$
(7)

The calculated Lorenz numbers are shown in Fig. S5. κ_{el} showed a significant increase with the level of Cu substitution, particularly at high-temperatures, due to the notable increase in σ resulting from the rise in *n* (Fig. 4(b)). Subsequently, κ_{I} was calculated by subtracting κ_{el} from κ_{tot} , as shown in Fig. 4(c). It was observed that κ_{L} values increased



Fig. 5. (a) Temperature-dependent dimensionless figure of merit (*ZT*), (b) average *ZT* (*ZT*_{ave}) in the range of 300–600 K, (c) comparison of peak *ZT* and average *ZT*, and (d) thermoelectric efficiency (η).

with increasing Cu doping, which can be attributed to the increase in grain size, resulting in fewer grain boundaries, as observed in Fig. 1(a-d). Consequently, phonon transport could be facilitated with less scattering in the Cu-doped samples, likely contributing to the higher $\kappa_{\rm L}$. To explore the effect of Cu doping on the thermal stability of the samples, $\kappa_{\rm tot}$ during heating and cooling was measured for the ZnSb and Zn_{0.97}Cu_{0.03}Sb samples, as shown in Fig. S6. It was found that the $\kappa_{\rm tot}$ curves during heating and cooling exhibited similar behavior with almost identical values. These results suggest the samples exhibit good thermal stability during cyclic measurements.

Fig. 5(a) shows the temperature dependence of *ZT* for Cu-doped samples. The introduction of Cu resulted in a notable increase in *ZT* due to the substantial enhancement in the *PF*. A peak *ZT* of ~1.04 at 600 K was achieved for $Zn_{0.99}Cu_{0.01}Sb$, representing a significant improvement of 37 % compared to the pristine ZnSb sample (*ZT* = 0.76). Fig. S4(b) shows the thermoelectric quality factor (B), calculated using μ_w and κ_L based on the following equation [33]:

$$B = \left(\frac{k_B}{e}\right)^2 \frac{8\pi e (2m_e k_B)^{3/2}}{h^3} \quad \frac{\mu_W T^2}{\kappa_L}$$
(8)

The B-factor of the $Zn_{0.99}Cu_{0.01}Sb$ sample shows the maximum value at both 300 K and 600 K, indicating that this sample has the potential to achieve the highest *ZT* when the carrier concentration is optimized.

To ensure stable thermoelectric power generation, high average ZT values are essential across a broad temperature range (300–600 K). The average ZT values can be calculated as follows [38]:

$$ZT_{ave} = \frac{\int_{T_c}^{T_h} Z(T) dT}{\Delta T} \quad \frac{T_c + T_h}{2}$$
(9)

where ΔT is the temperature difference between T_h (hot side temperature) and T_c (cold side temperature). The ZT_{ave} of the $Zn_{0.99}Cu_{0.01}Sb$ sample reached a high value of 0.63, whereas that of pristine ZnSb is 0.28 (Fig. 5(b)). Fig. 5(c) compares the peak ZT and average ZT for our best-performing $Zn_{0.99}Cu_{0.01}Sb$ sample with those reported in the literature for ZnSb compounds. It can be seen that the peak ZT and average ZT of the $Zn_{0.99}Cu_{0.01}Sb$ sample are higher or comparable to those reported for Bi-doped ZnSb [19], ZnSb/SiC [39], Ag-doped ZnSb [21], and Cd-doped ZnSb [40].

The conversion efficiency was estimated using Kim's model [38] (calculation details provided in the supporting information). The calculated engineering power factor PF_{eng} and engineering figure of merit ZT_{eng} with respect to the temperature difference between the hot and cold sides, are shown in Fig. S7. By utilizing PF_{eng} and ZT_{eng} , the maximum conversion efficiency was ~7 % at $\Delta T = 300$ K for the Zn_{0.99}Cu_{0.01}Sb sample, which is 134 % higher than that of the ZnSb sample ($\eta_{max} = 2.98$ %) (Fig. 5(d)). These findings suggest that the substitution of tiny amounts of Cu into Zn sites effectively enhances both ZT and η_{max} , indicating the potential practical applicability of these materials in power generation.

3.3. Mechanical properties

Mechanical stability plays a crucial role in ensuring the longevity of thermoelectric modules. These modules typically operate by recovering waste heat under cyclic temperature gradients, which subjects them to significant thermal shock, stress and mechanical vibrations [27,31]. To assess these effects, the mechanical stability of thermoelectric materials is usually evaluated based on hardness and compressive properties. In this study, micro-hardness and compressive tests were conducted at



Fig. 6. (a) The room temperature Vickers micro-hardness of $Zn_{1-x}Cu_xSb$ alloys with varying Cu content (x = 0, 0.01, 0.03 and 0.1), (b) Comparison of the compressive strength of $Zn_{0.97}Cu_{0.03}Sb$ sample with other thermoelectric materials, and (c) Fracture toughness.

room temperature to explore the mechanical stability of $Zn_{1-x}Cu_xSb$ alloys. Fig. 6(a) shows the room temperature Vickers micro-hardness for the $Zn_{1-x}Cu_xSb$ alloys. The hardness of Cu-doped ZnSb samples decreased as the Cu content increased, primarily due to the increasing grain size. The maximum hardness of 4.35 GPa was obtained for the ZnSb compounds. This value is significantly higher compared to the hardness values reported for various thermoelectric materials such as BiSbTe (0.64 GPa) [3], BiSbTe/SnO₂ (0.95 GPa) [41], Cu₃SbSe₄ (1.14 GPa) [42], Cu_{1.8}S (1.08 GPa) [43], and Mg₃Sb_{1.5}Bi_{0.5} (1.29 GPa) [44]. Fig. 6(b) shows the ultimate compressive strength of the Zn_{1-x}Cu_xSb alloys compared to other thermoelectric materials. Among the Cu-doped samples, the Zn_{0.97}Cu_{0.03}Sb sample showed superior compressive strength of about 180 MPa. This value surpasses that of other thermoelectric materials such as BiSbTe (~ 102 MPa) [3], SnSe (~ 75 MPa) [45], Ag₂Se (~ 88 MPa) [46] and Cu₂Te (~ 16 MPa) [47].

To evaluate the fracture resistance of brittle materials with cracks, the fracture toughness (K_{IC}) was estimated using the Vickers indentation-crack (VIF) technique proposed by Niihara et al. [48], known as the most accurate and successful method for brittle materials, as described below:

$$K_{IC} = 0.0089 \quad \left(\frac{E}{HV}\right)^{2/5} \times \quad \frac{P}{al^{1/2}}; 2.5 \ge \frac{l}{a} \ge 0.25$$
 (10)

where P represents the load (Newtons), HV denotes the Vickers hardness (GPa), E stands for Young's modulus (~ 90 GPa, obtained from literature [39]), *l* represents the crack length obtained from the indentation on the material surface after removing the Vickers indenter (meters), and a denotes the half-diagonal length of the Vickers indentation mark (meters). The Vickers indentation procedure was conducted 10 times on the polished surface of the Zn_{1-x}Cu_xSb samples using a Vickers diamond-shaped indenter with an applied load of 0.49 N and a dwell time of 15 s to generate cracks. The cracks originating from the four corners of the indentation mark can be observed, as shown in Fig. S8. Both the crack length (l) and half-diagonal length (a) were measured using SEM for better accuracy. It was observed that the crack lengths increased with Cu doping and then decreased beyond the addition of 0.03Cu. This phenomenon can be attributed to the formation of a secondary phase of Cu₂Sb when the Cu doping level exceeds 0.03 in ZnSb, consequently increasing resistance against cracking. Fig. 6(c) shows the fracture toughness of the Zn_{1-x}Cu_xSb samples. The K_{IC} decreased slightly from 0.69 MPa $m^{1/2}$ for pristine ZnSb to 0.62 MPa $m^{1/2}$ for 0.03, and then reached a maximum of 0.72 MPa $m^{1/2}$ for 0.1 sample. This value is comparable to or higher that of other thermoelectric materials [39,49]. The possible toughening mechanisms in the Cu-doped samples could be the crack deflection by secondary phase. These results indicate that ZnSb materials can withstand greater thermal and mechanical loads during the preparation of thermoelectric modules. The findings from this study suggest that the enhanced thermoelectric and mechanical properties could be helpful for potential power generation applications.

4. Conclusions

In this work, we systematically investigated both the thermoelectric and mechanical properties of Cu-doped ZnSb samples fabricated by melting, annealing and SPS. The introduction of copper acceptor doping into the Zn site resulted in a significant increase in hole concentration, leading to a substantial enhancement in electrical conductivity and a remarkable improvement in power factor (107 %). However, the PF was found to be 1.43×10^{-3} W/mK² at 300 K, which deviated from the theoretically projected optimum PF (1.69×10^{-3} W/mK²) due to limited solubility. This deviation could potentially be resolved by optimizing the hole concentration through a co-doping to achieve the required optimum hole concentration. Moreover, the maximum fracture toughness (K_{IC}) observed was 0.72 MPa m^{1/2} for the sample with a doping level of 0.1, which is higher than that of other thermoelectric materials. The combination of favorable thermoelectric and mechanical properties makes these materials highly suitable for the fabrication of commercial thermoelectric modules.

CRediT authorship contribution statement

Peyala Dharmaiah: Conceptualization, Methodology, Data curation, Investigation, Writing – original draft, Writing – review & editing. Minsu Heo: Methodology, Formal analysis. Cheenepalli Nagarjuna: Methodology, Formal analysis. Sung-Jin Jung: Investigation, Formal analysis. Sung Ok Won: Resources. Kyu Hyoung Lee: Resources, Formal analysis. Seong Keun Kim: Resources, Formal analysis. Jin-Sang Kim: Investigation. Byungmin Ahn: Resources. Hyun-Sik Kim: Formal analysis. Seung-Hyub Baek: Writing - review & editing, Supervision, Resources, Project administration.

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.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2024.175739.

References

- J. Wang, W. Azam, Natural resource scarcity, fossil fuel energy consumption, and total greenhouse gas emissions in top emitting countries, Geosci. Front 15 (2024) 101757.
- [2] X. Wang, Y. Jiang, Z. Ling, Z. Yuan, J. Shi, Advancements in diffusion barrier layers based on heterogeneous connection of electrode/thermoelectric materials, J. Alloy. Compd. 1001 (2024) 175185.
- [3] C.-h Lee, P. Dharmaiah, D.H. Kim, D.K. Yoon, T.H. Kim, S.H. Song, S.-J. Hong, Synergistic optimization of the thermoelectric and mechanical properties of largesize homogeneous Bi_{0.5}Sb_{1.5}Te₃ bulk samples via carrier engineering for efficient energy harvesting, ACS Appl. Mater. Interfaces 14 (2022) 10394–10406.
- [4] S.-J. Jung, S.-S. Lim, B.-H. Lee, S.O. Won, H.-H. Park, S.K. Kim, J.-S. Kim, S.-H. Baek, Study of the relationship between process parameters, volatility of Te, and physical properties in n-type Bi₂Te₃-based alloys for the reproducible fabrication of high-performance thermoelectric materials, J. Alloy. Compd. 937 (2023) 168476.
- [5] H. Hu, Y. Ju, J. Yu, Z. Wang, J. Pei, H.-C. Thong, J.-W. Li, B. Cai, F. Liu, Z. Han, B. Su, H.-L. Zhuang, Y. Jiang, H. Li, Q. Li, H. Zhao, B.-P. Zhang, J. Zhu, J.-F. Li, Highly stabilized and efficient thermoelectric copper selenide, Nat. Mater. 23 (2024) 527–534.
- [6] Y. Zhou, J. Wang, D. Luo, D. Hu, Y. Min, Q. Xue, Recent progress of halide perovskites for thermoelectric application, Nano Energy 94 (2022) 106949.
- [7] R. Biswas, P.K. Patro, T. Dasgupta, Enhanced thermoelectric performance in Zn_{1-x}Cd_xSb (x = 0-0.375) solid solutions by dynamic optimization of charge carrier concentration, ACS Appl. Energy Mater. 5 (2022) 12752–12759.
- [8] C. Li, Y. Luo, W. Li, L. Yang, W. Ma, Z. Ma, C. Sun, B. Yang, Y. Wei, X. Li, J. Yang, Enhanced power factor and figure of merit through magnesium doping in Sb₂Si₂Te₆, Scr. Mater. 247 (2024) 116090.
- [9] V.C.S. Theja, V. Karthikeyan, S. Nayak, K.U. Kandira, D.S. Assi, V. Kannan, V.A. L. Roy, Facile composite engineering to boost thermoelectric power conversion in ZnSb device, J. Phys. Chem. Solids 178 (2023) 111329.
- [10] S.H. Kang, M. Heo, Y.-J. Jung, J.M. Lee, C. Jeong, S.-M. Koo, W.H. Nam, J.Y. Cho, K.H. Lee, H.-S. Kim, W.H. Shin, Enhanced thermoelectric performance of Cr-doped ZnSb through lattice thermal conductivity reduction below the phonon glass limit, J. Alloy. Compd. 1002 (2024) 175402.
- [11] D. Sidharth, I. Paulraj, V. Lourdhusamy, M. Arivanandhan, C.-J. Liu, Power factor enhancement of β-Zn₄Sb₃-InSb composites via arrays of p-n junction: Mixing p-type and n-type thermoelectric materials, J. Eur. Ceram. Soc. 44 (2024) 954–960.
- [12] J.-J. Wang, S. Sun, L. Lu, H. Du, C.-L. Jia, O. Cojocaru-Mirédin, J. Yang, G. Liu, C. Zhou, G. Qiao, Z. Shi, E. Ma, B. Ge, Y. Yu, M. Wuttig, W. Zhang, Enhancing the thermoelectric performance of β-Zn₄Sb₃ via progressive incorporation of Zn interstitials, Nano Energy 104 (2022) 107967.
- [13] J. Zheng, Y. Tang, Y. Xiang, Y. Tao, K. Shen, L. Shen, W. Ge, P. Yang, S. Deng, High thermoelectric performance and oxidation resistance of (Na, Ga) codoped β-Zn₄Sb₃ thermoelectric materials prepared by the NaCl flux, Cryst. Growth Des. 23 (2023) 2375–2383.
- [14] I.-L. Jen, K.-K. Wang, H.-J. Wu, Aliovalent dilute doping and nano-moiré fringe advance the structural stability and thermoelectric performance in β-Zn₄Sb₃, Adv. Sci. 9 (2022) 2201802.
- [15] R. Biswas, S. Vitta, T. Dasgupta, Influence of zinc content and grain size on enhanced thermoelectric performance of optimally doped ZnSb, Mater. Res. Bull. 149 (2022) 111702.
- [16] J. Palraj, M. Sajjad, M. Moorthy, M. Saminathan, B. Srinivasan, N. Singh, R. Parasuraman, S.P. Patole, K. Mangalampalli, S. Perumal, High thermoelectric performance in p-type ZnSb upon increasing Zn vacancies: an experimental and theoretical study, J. Mater. Chem. A 12 (2024) 13860–13875.
- [17] Q. Guo, S. Luo, Improved thermoelectric efficiency in p-type ZnSb through Zn deficiency, Funct. Mater. Lett. 08 (2015) 1550028.
- **[18]** R. Biswas, V. Srihari, S. Vitta, T. Dasgupta, Vacancy induced anomalies in the electrical transport properties of Ag-doped $Zn_{1-x}Cd_xSb$ (x = 0.375) solid solutions, Appl. Phys. Lett. 120 (2022) 032102.
- [19] D. Sidharth, B. Srinivasan, A.S.A. Nedunchezhian, P. Thirukumaran, M. Arivanandhan, R. Jayavel, Enhancing the thermoelectric performance of nanostructured ZnSb by heterovalent bismuth substitution, J. Phys. Chem. Solids 160 (2022) 110303.
- [20] L.V. Prokofieva, P.P. Konstantinov, A.A. Shabaldin, On the tin impurity in the thermoelectric compound ZnSb: Charge-carrier generation and compensation, Semicond 50 (2016) 741–750.
- [21] D.-B. Xiong, N.L. Okamoto, H. Inui, Enhanced thermoelectric figure of merit in ptype Ag-doped ZnSb nanostructured with Ag₃Sb, Scr. Mater. 69 (2013) 397–400.
- [22] P.H.M. Böttger, G.S. Pomrehn, G.J. Snyder, T.G. Finstad, Doping of p-type ZnSb: Single parabolic band model and impurity band conduction, Phys. Status Solidi (a) 208 (2011) 2753–2759.
- [23] J. Male, M.T. Agne, A. Goyal, S. Anand, I.T. Witting, V. Stevanović, G.J. Snyder, The importance of phase equilibrium for doping efficiency: iodine doped PbTe, Mater. Horiz. 6 (2019) 1444–1453.

- [24] Y. Zhong, F. Lv, X. Zhao, Q. Deng, X. An, Z. He, L. Gan, R. Ang, Extraordinary role of resonant dopant vanadium for improving thermoelectrics in n-type PbTe, Mater. Today Phys. 30 (2023) 100955.
- [25] Z.-H. Zheng, P. Fan, J.-T. Luo, G.-X. Liang, P.-J. Liu, D.-P. Zhang, Enhanced thermoelectric properties of Cu doped ZnSb based thin films, J. Alloy. Compd. 668 (2016) 8–12.
- [26] V. Demontis, M. Isram, N. Abbas Khan, N. Amin, K. Mahmood, F. Rossella, ZnSe nanoparticles for thermoelectrics: impact of Cu-doping, Crystals 13 (2023) 695.
- [27] M. Shtern, A. Sherchenkov, Y. Shtern, N. Borgardt, M. Rogachev, A. Yakubov, A. Babich, D. Pepelyaev, I. Voloshchuk, Y. Zaytseva, S. Pereverzeva, A. Gerasimenko, D. Potapov, D. Murashko, Mechanical properties and thermal stability of nanostructured thermoelectric materials on the basis of PbTe and GeTe, J. Alloy. Compd. 946 (2023) 169364.
- [28] X. Bao, S. Hou, Z. Wu, X. Wang, L. Yin, Y. Liu, H. He, S. Duan, B. Wang, J. Mao, F. Cao, Q. Zhang, Mechanical properties of thermoelectric generators, J. Mater. Sci. Technol. 148 (2023) 64–74.
- [29] H. Wang, G. Han, B. Zhang, Y. Chen, X. Liu, K. Zhang, X. Lu, G. Wang, X. Zhou, AgSbSe₂ inclusions enabling high thermoelectric and mechanical performance in ntype Ag₂Se-based composites, Acta Mater. 248 (2023) 118753.
- [30] Y.J. Cui, K.F. Wang, B.L. Wang, X.Q. Fang, Axial vibration and strength failure analyses of a beam made of thermoelectric materials subjected to time-varying thermal loads, J. Therm. Stress. 47 (2024) 785–797.
- [31] S. Fan, Y. Gao, Fatigue life prediction of annular thermoelectric generators under thermal cycling load, J. Electron. Mater. 52 (2023) 960–970.
- [32] P. Dharmaiah, D.-H. Kim, J.-G. Kwon, Y. Lee, S. Geum, G.-R. Lee, M. Kang, S.-J. Hong, Optimization of mixed grain size structure for enhancement of thermoelectric figure of merit in p-type BiSbTe-based alloys, J. Mater. Sci. 57 (2022) 18131–18141.
- [33] M. Heo, S.-H. Kwon, S.-I. Kim, H. Park, K.H. Lee, H.-S. Kim, Impact of resonant state formation and band convergence in In and Sr co-doped SnTe thermoelectric material evaluated via the single parabolic band model, J. Alloy. Compd. 954 (2023) 170144.
- [34] S.-J. Kim, M. Heo, S.-i Kim, H. Park, J.-Y. Kim, W.-S. Seo, H.-S. Kim, Br dopinginduced evolution of the electronic band structure in dimorphic and hexagonal SnSe₂ thermoelectric materials, RSC Adv. 14 (2024) 7081–7087.
- [35] A. Ostovari Moghaddam, A. Shokuhfar, Y. Zhang, T. Zhang, D. Cadavid, J. Arbiol, A. Cabot, Ge-Doped ZnSb/β-Zn₄Sb₃ nanocomposites with high thermoelectric performance, Adv. Mater. Interfaces 6 (2019) 1900467.
- [36] O. Park, S.J. Park, H.-S. Kim, S.W. Lee, M. Heo, S.-I. Kim, Enhanced thermoelectric transport properties of Bi₂Te₃ polycrystalline alloys via carrier type change arising from slight Pb doping, Mater. Sci. Semicond. Process. 166 (2023) 107723.
- [37] K.H. Lee, S.-i Kim, J.-C. Lim, J.Y. Cho, H. Yang, H.-S. Kim, Approach to determine the density-of-states effective mass with carrier concentration-dependent Seebeck coefficient, Adv. Funct. Mater. 32 (2022) 2203852.
- [38] H.S. Kim, W. Liu, G. Chen, C.W. Chu, Z. Ren, Relationship between thermoelectric figure of merit and energy conversion efficiency, Proc. Natl. Acad. Sci. USA 112 (2015) 8205–8210.
- [39] F. Tseng, S. Li, C. Wu, Y. Pan, L. Li, Thermoelectric and mechanical properties of ZnSb/SiC nanocomposites, J. Mater. Sci. 51 (2016) 5271–5280.
- [40] R. Biswas, S. Mukherjee, R.C. Mallik, S. Vitta, T. Dasgupta, Ultralow thermal conductivity and low charge carrier scattering potential in Zn_{1-x}Cd_xSb solid solutions for thermoelectric application, Mater. Today Energy 12 (2019) 107–113.
- [41] C.Y. Li, J.X. Niu, J.Y. Zhang, D.-B. Zhang, W.F. Cui, Y. Wang, Y.-C. Shi, Z.-H. Ge, Thermoelectric and mechanical properties of Bi_{0.42}Sb_{1.58}Te₃/SnO₂ bulk composites with controllable ZT peak for power generation, J. Eur. Ceram. Soc. 44 (2024) 961–969.
- [42] S. Wei, L. Yu, Z. Ji, S. Luo, J. Liang, T. Wang, W. Song, S. Zheng, Enhancing the thermoelectric and mechanical properties of Cu₃SbSe₄-based materials by defect engineering and covalent bonds reinforcement, J. Alloy. Compd. 997 (2024) 174961.
- [43] Y.-X. Zhang, Y.-K. Zhu, J. Feng, Z.-H. Ge, Precious metal nanoparticles dispersing toward highly enhanced mechanical and thermoelectric properties of copper sulfides, J. Alloy. Compd. 892 (2022) 162035.
- [44] F. Jiang, T. Feng, Y. Zhu, Z. Han, R. Shu, C. Chen, Y. Zhang, C. Xia, X. Wu, H. Yu, C. Liu, Y. Chen, W. Liu, Extraordinary thermoelectric performance, thermal stability and mechanical properties of n-type Mg₃Sb_{1.5}Bi_{0.5} through multi-dopants at interstitial site, Mater. Today Phys. 27 (2022) 100835.
- [45] X. Liu, H. Wang, Y. Chen, B. Zhang, H. Zhang, S. Zheng, X. Chen, X. Lu, G. Wang, X. Zhou, G. Han, Simultaneously optimized thermoelectric and mechanical performance of p-type polycrystalline SnSe enabled by CNTs addition, Scr. Mater. 218 (2022) 114846.
- [46] H. Wang, X. Liu, Z. Zhou, H. Wu, Y. Chen, B. Zhang, G. Wang, X. Zhou, G. Han, Constructing n-type Ag₂Se/CNTs composites toward synergistically enhanced thermoelectric and mechanical performance, Acta Mater. 223 (2022) 117502.
- [47] Z. Zhang, K. Zhao, H. Chen, Q. Ren, Z. Yue, T.-R. Wei, P. Qiu, L. Chen, X. Shi, Entropy engineering induced exceptional thermoelectric and mechanical performances in Cu_{2-y}Ag_yTe_{1-2x}S_xSe_x, Acta Mater. 224 (2022) 117512.
- [48] K. Niihara, R. Morena, D.P.H. Hasselman, Evaluation of K_{Ic} of brittle solids by the indentation method with low crack-to-indent ratios, J. Mater. Sci. Lett. 1 (1982) 13–16.
- [49] L. Zhao, L. Yu, J. Yang, M. Wang, H. Shao, J. Wang, Z. Shi, N. Wan, S. Hussain, G. Qiao, J. Xu, Enhancing thermoelectric and mechanical properties of p-type Cu₃SbSe₄-based materials via embedding nanoscale Sb₂Se₃, Mater. Chem. Phys. 292 (2022) 126669.