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The charge carrier density modulation in off-stoichiometric ZrNiSn leads to enhanced thermoelectric performance

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ABSTRACT

The off-stoichiometry i.e., $ZrNi_{1+\delta}Sn (0<\delta<1)$, and carrier modulation are the two approaches that have separately been found effective mainly to reduce thermal conductivity and improve power factor, respectively. This work explores the combined effect of both of these approaches by tuning the carrier density by varying the Sb-concentration in off-stoichiometric $ZrNi_{1.04}Sn$, which shifts the conduction band towards the Fermi level as confirmed by the band structure calculations. The maximum thermoelectric figure-of-merit $ZT\sim0.95$ at ~873 K was achieved in the optimum composition $ZrNi_{1.04}Sn_{0.975}Sb_{0.025}$. For evaluating the device applicability of the synthesized materials, the cumulative temperature dependence (CTD) model was applied, predicting the single leg maximum efficiency $\sim8.6\%$ at $\Delta T \sim 546$ K. A series of calculations have been performed to predict electronic band structure and electronic transport properties to unearth the underlying physics. The microhardness and fracture toughness were determined to ensure that the enhanced thermoelectric performance is not deteriorating mechanical robustness.

1. Introduction

The waste heat dumped in the environment needs to be cut down to reduce global warming. Thermoelectric has gained tremendous attention in the past few decades due to its ability to generate electricity using waste heat [1], as well as cooling applications [2]. The figure of merit, $ZT = S^2 \sigma T/\kappa$ is the widely recognized parameter for determining TE performance of the material, where, *S*, σ , *T*, and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. $S^2 \sigma$ is the power factor (α) which determines the electronic performance of the TE material.

In mid-to-high temperature range, some of the highly potential materials are GeTe [3,4], skutterudites [5,6], and half-Heusler (HH) alloys [7,8]. ZrNiSn-based HHs are more attractive owing to their mechanical robustness and stability [9,10]. However, its TE performance needs to be enhanced to develop efficient thermoelectric generators (TEGs). In view of this, Hf has been widely explored as the most effective dopant for achieving high TE performance in ZrNiSn [11,12]. However, Hfs high cost and scarcity are of significant concern [13]. Therefore, the quest for efficient Hf-free ZrNiSn HHs is highly desirable which are more promising economically as well as environmentally. The primary strategies of thermoelectric performance enhancement mainly involve power factor enhancement, reduction of thermal conductivity, or their combination. Several approaches such as carrier density modulation [14–17], electron energy filtering [18], and resonance doping [19,20] have been found effective to improve the power factor of ZrNiSn; whereas, nanostructuring [21], nanoinclusion/nanocomposite [22,23], off-stoichiometry [24,25], doping/alloying [7,26,27], are for reducing the thermal conductivity. Among these approaches, carrier density modulation is a well-established approach for power factor enhancement. Several studies suggest the effectiveness of carrier density modulation using different dopants such as Ta [7,16], La [26], Nb [17,28], Sb [15,29,30], and Cu [31] for enhancing the power factor. Here, it may be noted that Sb has emerged out as a potential dopant for tuning the

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carrier concentration which leads to the enhancement in α . Xie et al. [30] have investigated the intrinsic disorder and Sb-doping in ZrNiSn HH alloys and exhibit the maximum *ZT* ~0.8 at ~875 K in ZrNiSn_{0.99}Sb_{0.01} HH alloy. Akram et al. [29] exhibit a maximum ZT of 0.83 at 923 K in Hf_{0.25}Zr_{0.75}NiSn_{0.985}Sb_{0.015} by tuning Sb-content leading to the carrier density modulation. Further, the stoichiometric modulation i.e., Ni_{1+δ} (0 < δ < 1) in ZrNiSn [24,25,32,33] has been established to enhance the TE performance by reducing the thermal conductivity and also increases the power factor. In our recent study, we investigated the off-stoichiometric composition ZrNi_{1.04}Sn with isoelectronic Ge-doping and found a significant enhancement in *ZT* [34].

In the present work, we synergistically combined the charge carrier density modulation with off-stoichiometry, and studied the effect of charge carrier density modulation in the off-stoichiometric composition ZrNi_{1.04}Sn by using Sb as dopant at Sn-site. The samples ZrNi_{1.04}Sn_{1-x}Sb_x (x = 0.01-0.04) were synthesized employing arc melting followed by spark plasma sintering. The temperature-dependent electronic and thermal transport properties were measured, and the results were compared with ZrNi_{1.04}Sn and ZrNiSn reported in our earlier works [27,34]. The energy conversion parameters were calculated using the cumulative temperature dependence (CTD) model [35-37], exhibiting maximum efficiency of ~8.6% at ΔT ~ 546 K in the sample $ZrNi_{1.04}Sn_{0.975}Sb_{0.025}$ showing maximum peak $ZT \sim 0.95$ at ~873 K. Further, to deepen the insight into the physics of experimental results, we also performed the electronic band structure and electronic transport properties calculations employing density functional theory (DFT). The mechanical robustness has been studied, which is also a pre-requisite for fabricating TE devices.

2. Experimental details

To synthesize the samples of compositions $\text{ZrNi}_{1.04}\text{Sn}_{1-x}\text{Sb}_x$ (x = 0.01– 0.04), the elements Zr, Ni, Sn, and Sb of high purity were taken in the stoichiometric proportion and then arc melted using arcmelter (MAM-1) under an inert atmosphere of argon gas. The arcmelted buttons were remelted after flipping several times to ensure stoichiometric uniformity. The ingots obtained post arc-melting were ground using a mortar-pestle to a fine powder. The fine powder was then consolidated in a 12.7 mm inner diameter graphite die and sintered at ~1473 K under ~50 MPa by employing spark plasma sintering (SPS; Dr. Sinter, 725). The density of all of the synthesized samples was measured using the instrument (ML204/A01, Mettler Toledo) based on Archimedes' principle.

The phase investigation was performed using X-ray diffraction (XRD; Rigaku Miniflex II), and the Rietveld refinement was executed utilizing the FullProf Suite package. The field emission scanning electron microscope (FESEM; TESCAN MAGNA GMH) and energy dispersive X-ray spectroscopy (EDS; EDAX OCTANE ELECT SUPER) were employed for surface morphology and elemental analysis, respectively. The thermal diffusivity (*D*) was determined by employing laser flash an

alyzer (LFA; Linseis 1000). Then samples were cut into rectangular shapes to measure the Seebeck coefficient (*S*) and electrical resistivity simultaneously using ULVAC, ZEM 3. The specific heat (C_P) was determined by employing a differential scanning calorimeter (DSC; NET-ZSCH, 404 F3). Charge carrier concentration and carrier mobility were determined at room temperature using the Hall effect measurement system (HEMS, Nanomagnetics). Future Tech equipment (FM-e7) was employed for determining the microhardness and fracture toughness of all well-polished samples, whereas, more details can be found in our earlier study [34].

3. Computational details

The DFT-based calculations have been carried out by using Vienna Ab-initio Simulation Package (VASP) [38]. VASP considers the projected augmented wave scheme for pseudo-potential calculations of elements. We opted Perdew-Burke-Ernzerhof [39,40] exchange correlation functional form of generalized gradient approximation. The use of AM05 functional [41-43] results precise structural parameters of pristine HH-ZrNiSn, as discussed in our earlier report [34] and therefore adopted in the present work also. We opted the supercell approach while following doping of Ni and Sb in HH-ZrNiSn system and therefore multiplying pristine unit cell by $3 \times 3 \times 3$ along x, y, and z-direction. For the expansion of plane wave basis sets, we have used 550 eV cutoff energy including with Γ -centered $4 \times 4 \times 4$ k-points mesh. Integration of the first Brillouin zone was performed by using Gaussian smearing method while considering smearing width of 0.10 eV. In order to predict electronic transport properties of alloys, the BoltzTraP code [44] was used. Before to perform any calculations we first minimize residual force on atoms up to $\leq 0.01 \text{ eV/Å}$. All the results reported here were extracted while keeping very tight energy convergence criteria of 10⁻⁶ eV.

4. Results and discussion

The X-ray diffraction (XRD) spectra of all the samples $ZrNi_{1.04}Sn_{1.x}Sb_x$ (x = 0.01–0.04)) are shown in Fig. 1(a) which confirms the formation of half-Heusler phase. Further, the Rietveld refinement of all the XRD patterns was executed to extract the lattice parameters along with other fitting parameters which is shown in Table 1, here, no significant change in lattice constant was observed with Sb-doping owing to the comparable atomic radius of Sn and Sb [30,45]. The Rietveld refined pattern of the representative sample $ZrNi_{1.04}Sn_{0.975}Sb_{0.025}$ is shown in Fig. 1(b).

The surface morphology and elemental analysis of the representative sample $ZrNi_{1.04}Sn_{0.975}Sb_{0.025}$ were investigated employing field emission scanning electron microscope (FESEM) and energy dispersive X-ray spectroscopy (EDS) analysis, shown in Fig. 2 which indicates the in-situ evolution of minor secondary phases in the synthesized material. The region a_1 is representing the main matrix and its EDS analysis is



Fig. 1. (a) X-ray diffraction pattern of $ZrNi_{1.04}Sn_{1.x}Sb_x$ (x = 0.01–0.04), (b) Rietveld refined XRD pattern of the representative $ZrNi_{1.04}Sn_{0.975}Sb_{0.025}$ sample.

Table 1

The Rietveld refinement details of $ZrNi_{1.04}Sn_{1-x}Sb_x$ (x = 0.01–0.04).

x	R _p	R _{wp}	R _e	χ^2	a (Å)	
0.01	19.6	16.0	7.89	4.095	6.1179	
0.02	18.7	19.0	7.03	7.334	6.1170	
0.025	20.7	18.5	7.25	6.538	6.1141	
0.03	17.7	14.8	8.96	2.718	6.1164	
0.035	17.9	16.1	7.57	4.494	6.1133	
0.04	21.9	19.7	8.15	5.827	6.1106	

shown in Fig. $2(a_1)$ which exhibits the stoichiometry close to the nominal. The bright and dark grey contrast are visible as the secondary regions in the main matrix. The EDS analysis of the bright grey region shown in Fig. 2(a2) indicates the minor secondary phase of Ni-Sn. Fur-



ther, the EDS analysis of the dark region given in Fig. $2(a_3)$ exhibits the Zr-rich phase. Furthermore, the Sn-Zr binary minor phase is determined in Fig. 2(b & b₁), also the substantial Ni-excess phase can be found in Fig. 2(c & c₁). Fig. 3 exhibits the microstructural analysis of the sample ZrNi1 04Sn0 99Sb0 01 showing the excess of Ni content in the primary matrix and Zr-rich secondary phase is also visible, which is very similar as of the microstructure of the ZrNi_{1.04}Sn₀₉₇₅Sb_{0.025}. The presence of Sb in both the samples has been realized. However, similar kinds of in-situ secondary minor phases along with the full-Heusler phase were also observed in isoelectronic Ge-doped ZrNi_{1.04}Sn [34]. Here, it is worth mentioning that the expected full-Heusler (FH) phase due to an excess amount of Ni, which was obtained in our earlier study [34] is not visible in the microstructure of the present study but we cannot rule out its complete absence. The adopted processing route in this work is similar to our previous work on off-stoichiometric ZrNiSn [34] which demon-

Ar. 04

32.32

34.78

31.13

1.77

1.20

2.01

95.55

2.32

1.91

0.23

Fig. 2. FESEM and EDS analysis of ZrNi_{1.04}Sn_{0.975}Sb_{0.025}.



Fig. 3. FESEM and EDS analysis of ZrNi1.04Sn0.99Sb0.01.

strates detailed microstructural investigation; whereas, the present work focuses on the effect of carrier density modulation on transport properties.

To deepen our understanding of the electronic properties of the Sbdoped ZrNi1,04Sn system, we have performed the electronic structure calculations. The dispersion curves of $ZrNi_{1.04}Sn$ [34] and Sb-doped $ZrNi_{1.04}Sn$ systems are illustrated in Fig. 4(a) and (b), respectively. In the case of ZrNi1.04Sn, the narrow direct energy band gap of 0.12 eV was predicted between the valence band maximum (VBM) and CBM at the X-point of the Brillouin zone [34]. Looking at Fig. 4(a) and (b), it is clear that the doping of Sb in $ZrNi_{1.04}Sn$ results in the shift of CBM below to the Fermi energy level with no significant change in the nature of bands and energy gap, exhibiting the transition of semiconductor ZrNi1.04Sn to degenerate semiconductor Sb-doped ZrNi1.04Sn. In order to understand the effect of Sb-doping on the transport properties of ZrNi1 04Sn, we focus on the calculations of electrical conductivity scaled by relaxation time (σ/τ) and Seebeck coefficient (S) while varying temperature and the results have been presented and compared with ZrNi_{1 04}Sn [34] in Fig. 4(c-f). From Fig. 4(c-f), it is obvious that the σ/τ of Sb-doped ZrNi_{1 04}Sn increases while the S decreases which is an outcome of semiconductor to degenerate semiconductor transition. In a nut shell, the Sb-doping is responsible for semiconductor to degenerate semiconductor transition without affecting the shape of the bands. It is important to mention here that σ/τ and *S* follow inverse proportional relation while increasing the temperature.

The observed electronic transport properties of the samples ZrNi_{1.04}Sn_{1-x}Sb_x are shown in Fig. 5. The temperature dependent electrical conductivity (σ) is shown in Fig. 5(a). It is clear from Fig. 5(a) that the electrical conductivity of Sb-doped samples is higher than that of the pristine ZrNi_{1.04}Sn. The Hall effect measurement was performed at room temperature (RT) to understand electronic transport properties. The Hall carrier concentration (n_H) and mobility (μ_H) are given in Fig. 5 (b), exhibiting the enhanced n_H and μ_H in Sb-doped compositions. Here, it is worth mentioning that the observed simultaneous enhanced n_H and μ_H are out of line with their usual trade-off relationship, however, with Sb-doping such kind of behavior has been observed earlier [30,45]. These improved n_H and μ_H collectively contribute to the enhanced σ . Further, σ increases with temperature of pristine ZrNi_{1.04}Sn and thus exhibits the semiconducting type behaviour, whereas, with Sb-doping the semiconducting nature starts diminishing, and above 2.0 at% of Sbdoping, it completely exhibits degenerate semiconducting behaviour. The transition from semiconductor $(ZrNi_{1.04}Sn)$ to degeneratesemiconductor (Sb-doped ZrNi_{1.04}Sn) is in well accordance with the band structure, shown in Fig. 4(a and b), which exhibits the shifting of CBM below the Fermi level when Sb is doped in $ZrNi_{1.04}Sn$. Our observed behavior of electrical conductivity with Sb-doping in offstoichiometric ZrNi_{1.04}Sn HH is in good agreement to that of determined earlier in Sb-doped ZrNiSn-based HH alloys [29,30,45]. The maximum $\sigma \sim 2.55 \times 10^5 \text{ Sm}^{-1}$ at ~873 K was observed in ZrNi_{1.04}Sn_{0.96}Sb_{0.04} which is ~147% higher than that of pristine ZrNi_{1.04}Sn [34] and also it exhibits more than two-fold enhancement than pure ZrNiSn [27].

The temperature dependence of Seebeck coefficient (*S*) of all the samples is shown in Fig. 5(c). A reduction in |S| is observed with increasing Sb-doping in ZrNi_{1.04}Sn which is in accordance with the observations made earlier in Sb-doped ZrNiSn-based HH alloys [29,30,45]. The Pisarenko curve was plotted using the single parabolic band (SPB) model under the consideration of scattering by acoustic phonons, employing the following relations [46,47].

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

$$= 4\pi \left(\frac{2m^{*}k_{B}T}{h^{2}}\right)^{3/2} F_{1/2}(\eta)$$
⁽²⁾

Hall carrier concentration, $n_H = \frac{n}{r_H}$, Hall factor, $r_H = \frac{3}{2}F_{1/2}(\eta) \frac{F_{-1/2}(\eta)}{2F_0^2(\eta)}$, Fermi integral, $F_j(\eta) = \int_0^\infty \frac{e^j de}{1+Exp(e-\eta)}$, where, k_B is the Boltzmann constant, e is the electronic charge, m^* is the density of

is the Boltzmann constant, e is the electronic charge, m^* is the density of states effective mass, T is the temperature, and h is Planck's constant.

It is clear from the pisarenko plot, shown in Fig. 5(d), that the density of states carrier effective mass is unaltered with Sb-doping, suggesting no significant change in the shape of electronic bands which is also visible in the theoretically predicted band structure shown in Fig. 4(a and b). Therefore, the reduction in |S| with Sb-doping may be ascribed to the enhanced n_H , shown in Fig. 5(b). For a better understanding, we have calculated the reduced chemical potential using equation (1). The reduced chemical potential shown in Fig. 5(e), exhibits the systematic increment with increasing Sb-concentration, suggesting the shifting of the conduction band towards the Fermi level along with increasing depth of penetration and thus leading to the enhancement of charge carrier concentration. The shifting of the CBM below the Fermi level is well supported by the band structure calculation shown in Fig. 4(a and b). Further, |S| is decreasing with temperature for undoped ZrNi_{1.04}Sn; whereas, it is increasing with temperature for Sb-doped ZrNi_{1.04}Sn, which is in well agreement with the literature [29,30,45]. Thus, it can be concluded that the charge carrier concentration is the foremost parameter governing the electronic transport. The reduction in |S| was observed comparatively lower than that of the enhancement in the electrical conductivity, which was realized in $\text{ZrNi}_{1.04}\text{Sn}_{0.96}\text{Sb}_{0.04}$ showing



Fig. 4. Calculated electronic transport properties of ZrNi_{1.04}Sn (left panel) (Reprinted with permission from Ref. [34]. Copyright 2022 American Chemical Society.) and Sb-doped ZrNi_{1.04}Sn (right panel): (a, b) electronic band structure, (c, d) electrical conductivity scaled by relaxation time, (e, f) Seebeck coefficient.

 $|S| \sim 120.84 \,\mu V/K$ at ~ 873 K which is $\sim 38\%$ lower than that of the pristine ZrNi_{1.04}Sn [34] and $\sim 42\%$ lower than that of pure ZrNiSn [27].

The power factor (α) describes electronic performance derived synergistically from the *S* and σ . The α is depicted in Fig. 5(f), exhibiting substantial enhancement in all the Sb-doped samples compared to pristine ZrNi_{1.04}Sn. Further, α of all the samples ZrNi_{1.04}Sn_{1-x}Sb_x enhances with increasing temperature and a maximum value ~4.6 × 10⁻³ Wm⁻¹K⁻² at ~873 K has been achieved for the composition ZrNi_{1.04}Sn_{0.975}Sb_{0.025} which is ~16% higher than that of the pristine ZrNi_{1.04}Sn [34] and ~30% enhanced than pure ZrNiSn [27].

The temperature dependent thermal conductivity (κ) was determined employing the relation $\kappa = DC_P d$ by using the measured thermal diffusivity (D), specific heat (C_P), and mass density (d), shown in Fig. 6 (a). Also, it is clear from Fig. 6(a) that the κ of Sb-doped samples at RT is higher than that of the pristine ZrNi_{1.04}Sn, these results are in well accordance with the literature [30,45]. We have observed the lowest $\kappa \sim 3.9 \text{ Wm}^{-1}\text{K}^{-1}$ at ~624 K and $\kappa \sim 4.0 \text{ Wm}^{-1}\text{K}^{-1}$ at ~873 K for the composition ZrNi_{1.04}Sn_{0.99}Sb_{0.01} HH alloy which is lower than that of the earlier reported in Hf-free Sb-doped ZrNiSn-based HH alloys [30,45]. Further, here it is also noted that the observed κ is even lower than that of the Hf-contained Sb-doped ZrNiSn-based HHs [29,48]. At

~873 K, we have observed the maximum reduction of ~10% in κ realizing ~3.99 Wm⁻¹K⁻¹ in ZrNi_{1.04}Sn_{0.99}Sb_{0.01} compared to that of pristine ZrNi_{1.04}Sn [34], and this κ is ~18% lower than that of pure ZrNiSn [27]. To understand how Sb-doping affects κ , we have separated electronic thermal conductivity (κ_e) and lattice thermal conductivity (κ_l) using the relation $\kappa = \kappa_e + \kappa_l$, and shown in Fig. 6(b) and (c), respectively.

The κ_e was calculated using the Wiedemann-Franz relation $\kappa_e = L\sigma T$, where, *L* is Lorenz number calculated using the relation $L = 1.5 + \exp\left[-\frac{|S|}{116}\right]$, where *L* is in 10⁻⁸ W Ω K⁻² when *S* in μ VK⁻¹ [49]. The κ_e is higher in Sb-doped samples than that of the pristine ZrNi_{1.04}Sn sample due to the reason that Sb-doped ZrNi_{1.04}Sn are tending towards the degenerate semiconductors owing to the increasing charge carrier concentration. The κ_e increases with temperature in all the samples, contributing significantly to κ at the high temperature shown in Fig. 6 (b). And it was observed that the maximum $\kappa_e \sim 4.06 \text{ Wm}^{-1}\text{K}^{-1}$ at 873 K of ZrNi_{1.04}Sn [34], and it is ~243% higher than that of pure ZrNiSn [27]. Further, the κ_l of the samples ZrNi_{1.04}Sn_{1-x}Sb_x is shown in Fig. 6(c). The κ_l is decreasing with increasing temperature due to the enhanced scattering of phonons at high temperatures. The reduction in κ_l with Sb-



Fig. 5. (a) Electrical conductivity, (b) carrier concentration and mobility, (c) Seebeck coefficient, (d) Pisarenko plot, (e) reduced chemical, and (f) power factor, of $ZrNi_{1.04}Sn_{1.x}Sb_x$ (x = 0.01–0.04) samples. For comparison the data of pristine $ZrNi_{1.04}Sn$ (Reprinted with permission from Ref. [34]. Copyright 2022 American Chemical Society.) and pure ZrNiSn (Reprinted with permission from Ref. [27]. Copyright 2019 American Chemical Society.) are taken from our earlier studies.

doping might be the collective outcome of phonon scattering owing to the point defects due to Sn/Sb and interfaces of secondary phases. The maximum reduction of ~65% was observed in ZrNi_{1.04}Sn_{0.975}Sb_{0.025} at ~873 K than ZrNi_{1.04}Sn [34] and showing $\kappa_l \sim 1.0 \text{ Wm}^{-1}\text{K}^{-1}$ at 873 K, which is ~73% lower than that of pristine ZrNiSn [27]. The realized reduction in κ_l was overcompensated by the enhanced κ_e leading to the increment of the total thermal conductivity in Sb-contained samples than that of pristine counterpart ZrNi_{1.04}Sn, except for two samples, ZrNi_{1.04}Sn_{0.99}Sb_{0.01} and ZrNi_{1.04}Sn_{0.975}Sb_{0.025} at high temperature, and the lowest $\kappa \sim 4.0 \text{ Wm}^{-1}\text{K}^{-1}$ at ~873 K was observed in ZrNi_{1.04}Sn_{0.99}Sb_{0.01} due to the optimization of κ_e and κ_l .

The temperature-dependent figure of merit (*ZT*) of the samples $\text{ZrNi}_{1.04}\text{Sn}_{1-x}\text{Sb}_x$ is shown in Fig. 6(d). The maximum *ZT* ~0.95 at ~873 K in the sample $\text{ZrNi}_{1.04}\text{Sn}_{0.975}\text{Sb}_{0.025}$ was achieved due to the synergistic optimization of α and κ . The enhancement in *ZT* has been successively achieved as the *ZT* of $\text{ZrNi}_{1.04}\text{Sn}$ [34] is ~22% higher than that of pure ZrNiSn [27], and further, the *ZT* of $\text{ZrNi}_{1.04}\text{Sn}_{0.975}\text{Sb}_{0.025}$ is ~22% higher than pristine $\text{ZrNi}_{1.04}\text{Sn}$ [34]. In view of this, a maximum of ~48% enhancement was observed by synergistically combining the two approaches of off-stoichiometry along with charge carrier modulation. Here, it is worth mentioning that the present study realized an excellent high α ~4.6 \times 10⁻³ Wm⁻¹K⁻² at ~873 K in the sample ZrNi_{1.04}Sn_{0.975}Sb_{0.025}, and further enhancement in *ZT* may be achieved

by reducing the thermal conductivity and maintaining the power factor.

For device performance analysis, we opted the cumulative temperature dependence (CTD) model [35–37] and predicted the single leg energy conversion performance parameters such as engineering figure of merit (*ZT*)_{eng}, output power density (P_d) at maximum efficiency, and maximum energy efficiency considering the leg thickness of t = 2 mm and cold end temperature T_c = 323 K, employing the following relations. The maximum energy conversion efficiency as noted:

$$\eta_{\max} = \eta_C \frac{\sqrt{1 + (ZT)_{eng} \left(\frac{\hat{\alpha}}{\eta_C} - \frac{1}{2}\right)} - 1}{\hat{\alpha} \left(\sqrt{1 + (ZT)_{eng} \left(\frac{\hat{\alpha}}{\eta_C} - \frac{1}{2}\right)} + 1\right) - \eta_C}$$

Where, $\eta_C = (T_H - T_C)/T_H$ is the Carnot efficiency, T_C and T_H are the temperature of the cold and hot end, respectively, and $\hat{\alpha}$ is a dimensionless intensity factor of the Thomson effect, $\hat{\alpha} = \frac{S(T_h)\Delta T}{\int_{T_c}^{T_h} S(T)dT}$, and $(ZT)_{eng}$ is the engineering figure of merit and given as:

Fig. 6. (a) Thermal conductivity, (b) electronic thermal conductivity, (c) lattice thermal conductivity, and (d) Figure of merit, of $ZrNi_{1.04}Sn_{1.x}Sb_x$ (x = 0.01–0.04) samples. For comparison the data of pristine $ZrNi_{1.04}Sn$ (Reprinted with permission from Ref. [34]. Copyright 2022 American Chemical Society.) and pure ZrNiSn (Reprinted with permission from Ref. [27]. Copyright 2019 American Chemical Society.) are taken from our earlier studies.

$$(ZT)_{eng} = \frac{\left(\int_{T_c}^{T_h} S(T) \, dT\right)^2}{\int_{T_c}^{T_h} \rho(T) \, dT \int_{T_c}^{T_h} \kappa(T) \, dT} \Delta \Sigma$$

The output power density at maximum efficiency is expressed as

$$P_d = \frac{(PF)_{eng}\Delta T}{4t}$$

where $\Delta T = T_H - T_C$ is the temperature gradient.

The temperature dependence consideration of the thermoelectric properties in CTD model, makes it more consistent for predicting the TE device performance. ZT evaluates the material performance at a certain temperature or for very short difference of temperature due to temperature-independent consideration of properties, whereas, (ZT)ene is considered as the better evaluator of TE material and device for large temperature difference condition. The calculated $(ZT)_{eng}$ of all the samples is shown in Fig. 7(a), exhibiting the increasing trend with increasing temperature gradient and the maximum value of $(ZT)_{eng} \sim 0.46$ at $\Delta T \sim 546$ K. This maximum (ZT)_{eng} is ~41% enhanced than that of predicted for pristine ZrNi_{1.04}Sn [34] and ~109% higher than that of pure ZrNiSn [27]. The P_d increases with increasing temperature gradient and we observed that the P_d is more likely to follow the trend of $(PF)_{ene}$ with Sb-doping as shown in the inset of Fig. 7(b). The maximum value of P_d ~14.5 Wcm⁻² at ΔT ~546 K was predicted for the two samples $ZrNi_{1.04}Sn_{0.975}Sb_{0.025}$ and $ZrNi_{1.04}Sn_{0.975}Sb_{0.035}\text{,}$ due to its maximum $(PF)_{eng} \sim 2.1 \text{ Wm}^{-1}\text{K}^{-1}$. The maximum efficiency of ~8.6% at ΔT ~546 K was projected for the composition ZrNi_{1.04}Sn_{0.975}Sb_{0.025} which is ~24% higher than predicted for pristine ZrNi_{1.04}Sn [34], and ~73% enhanced than pure ZrNiSn [27], shown in Fig. 7(c). For comparing our energy conversion performance parameters, we have extracted the

 $(ZT)_{eng}$ and η_{max} using the TE data reported in the literature showing $ZT\sim1$ which is comparable with our maximum $ZT\sim0.95$ at ~873 K and shown in Fig. 7(d). Here, it is worth noting that our peak ZT at high temperature is among the lowest values of the compared data, however, our $(ZT)_{eng}$ is among the highest values, as shown in Fig. 7(e). Here, it may be noted that a lot of work has been carried out by various groups, but in the present study, we have extracted $(ZT)_{eng}$ for very few of them. The η_{max} lies in the highest values following the $(ZT)_{eng}$ among the compared data at high-temperature gradient shown in Fig. 7(f), exhibiting that $(ZT)_{eng}$ is the more crucial parameter rather than peak ZT for defining the energy conversion performance.

Apart from the high TE performance, the mechanical strength of the material is equally desirable to design the sustainable efficient TE device. For ensuring the robust mechanical properties of HH alloys, we have determined the microhardness and fracture toughness of all the samples $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (x = 0.01-0.04). These properties are compared with the pristine $\text{ZrNi}_{1.04}\text{Sn}$ and other $\text{ZrNi}\text{Sn}_{1.2}\text{Sb}_x$ (the mechanical properties are compared with the pristine $\text{ZrNi}_{1.04}\text{Sn}$ and other $\text{ZrNi}\text{Sn}_{1.2}\text{Sb}_x$ (the mechanical properties i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i.e. microhardness and fracture toughness of the $\text{ZrNi}_{1.04}\text{Sn}_{1.x}\text{Sb}_x$ (the mechanical properties) i

5. Conclusion

In the present work, we have attempted carrier concentration modulation using Sb as a dopant in off-stoichiometric ZrNi_{1.04}Sn at the Sn site. The alteration of reduced chemical potential modulates the carrier concentration in ZrNi_{1.04}Sn_{1-x}Sb_x when increasing Sb-concentration. The improved n_H and μ_H results in the tremendous enhancement in σ . The increased σ is significantly contributing to the enhancement of α and raised it to 4.6×10^{-3} Wm⁻¹K⁻² at ~873 K in ZrNi_{1.04}Sn_{0.975}Sb_{0.025}.

Fig. 7. (a) Engineering *ZT*, (b) output power density at maximum efficiency (inset: engineering power factor), (c) maximum conversion efficiency, of $ZrNi_{1.04}Sn_{1.x}Sb_x$ (x = 0.01-0.04) samples. For comparison, the data of pristine $ZrNi_{1.04}Sn$ (Reprinted with permission from Ref. [34]. Copyright 2022 American Chemical Society.) and pure ZrNiSn (Reprinted with permission from Ref. [27]. Copyright 2019 American Chemical Society.) are taken from our earlier studies and calculated the thermoelectric power conversion performance parameters. For comparison of (d) figure of merit *ZT*, (e) Engineering *ZT*, and (f) maximum conversion efficiency, of the representative sample $ZrNi_{1.04}Sn_{0.97}Sb_{0.25}$; the data are taken with permission from Ref. a [24], Ref. b [15], Ref. c [34] and calculated the thermoelectric power conversion performance parameters.

Further, the lattice thermal conductivity was reduced enormously, but it was overcompensated by enhanced κ_e . Therefore, no considerable decrement in κ was observed. The maximum *ZT* ~0.95 at ~873 K was attained in the composition ZrNi_{1.04}Sn_{0.975}Sb_{0.025} and the single leg maximum energy conversion efficiency ~8.6% at ΔT ~546 K was predicted employing the CTD model. Further, the experimental results are well supported with electronic structure calculations based on density functional theory. Here, it is worth emphasizing that, the mechanical robustness is intact even after the enhanced TE performance, which is making the proposed composition more suitable for designing the TE generator.

Author credit

K.K.J.: Material synthesis, characterization, data analysis, and prepared the first draft of the manuscript.

A.K.V.: Formal analysis.

N.K.U., R.S.: Methodology.

D.K.S., S.K.: Theoretical calculations and analysis. **B.G.:** Conceptualization, visualization, review, and editing.

Data availability

The data that support the findings of this study is available upon request from the authors.

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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Fig. 8. Microhardness and fracture toughness with their standard deviation of $\text{ZrNi}_{1.04}\text{Sn}_{1-x}\text{Sb}_x$ (x = 0.01–0.04), compared with our earlier study $\text{ZrNi}_{1.04}\text{Sn}$ (Reprinted with permission from Ref. [34]. Copyright 2022 American Chemical Society.), and other ZrNiSn based HHs Ref. a [50], Ref. b [51].

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