



Enhanced Thermoelectric Performance of a New half-Heusler Derivative Zr₉Ni₇Sn₈ Bulk Nanocomposite: Enhanced Electrical Conductivity and Low Thermal Conductivity

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1. Introduction

Thermoelectricity, being simplest technology for the conversion of thermal energy to electrical energy has attracted a renewed attention for application in power generation. In the past decade, most efforts have been concentrated on thermoelectric research dealing with designing of new materials or optimizing the existing materials to increase their conversion efficiency. The greatest challenge in this direction lies in the optimization of three competing physical material property parameters perceived in the expression of the dimensionless thermoelectric figure of merit,¹ $ZT = (\alpha^2 \sigma T) / \kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, T the absolute temperature and κ is the thermal conductivity. The modification to any of these physical parameters α , σ and κ often adversely affects the other due to their interdependence and hence limits to a substantial increase in the overall ZT .

The best possible strategy for increasing ZT is to decouple the thermoelectric parameters; α , σ and κ by doping, solid solution alloying and nanostructuring approaches. These concept have been demonstrated theoretically and experimentally in several systems, such as, Bi_2Te_3 ,²⁻⁶ $\text{AgPb}_m\text{SbTe}_{2+m}$ (LAST),⁷ TeAgGeSb ,⁸ PbTe ,^{9,10} SiGe ¹¹ and Zintl phase compounds.¹²⁻¹⁵ Despite their high ZT , these materials are not viable for economic and large scale commercial applications because their constituents are expensive and toxic.

Among several thermoelectric materials, HH compounds have been identified not only as a promising class of thermoelectric materials¹⁶⁻¹⁹ but also they possesses various properties such as magnetic,^{20, 21} topological insulator,^{22,23} shape memory,^{24,25} thermoelectric¹⁶⁻¹⁹ etc with their varying VEC. They are constituted with cheap, non-toxic elements and easy to synthesize at large scale. Moderately high σ due to narrow band gap and high α due to high slope of density of

1 state near the Fermi level, despite the excellent electronic properties, these materials exhibit low
2 ZT because they are associated with their relatively high κ .

3 In the past decades, several approaches such as controlled doping, solid solution alloying and
4 nanostructuring in HH compound have been adopted to disrupt the heat carrying phonons in
5 order to achieve significant reduction in their κ . Recently, a chemical disorder of full-Heusler
6 (FH) at atomic scale in half-Heusler matrix, so called Atomic-Scale Structural Engineering of
7 Thermoelectrics (ASSET) approach has been employed in both p-type MCoSb (where M= Ti,
8 Zr, Hf) and in n-type MNiSn HH to reduce further κ . Moreover, it has also been reported that
9 the κ in half-Heusler material can be significantly reduced by making super cell of HH with
10 increased unit cell based on varying VEC which has been derived in Ru₉Zn₇Sb₈. It has been
11 claimed that a significant reduction in κ , about one quarter of that of most normal HH is obtained
12 due to superstructure of HH in Ru₉Zn₇Sn₈.²⁶ It is also suggested that the compound Ru₉Zn₇Sb₈
13 and its analogues M₉Zn₇Sb₈ (M= Fe, Co, Rh) could serve as a new structure type for exploring
14 new thermoelectric materials. Despite this, a further reduction in their κ could make these
15 materials more efficient for commercial applications.

16 The concept of nanostructuring and nanocomposites has been observed to improve the
17 efficiency of thermoelectric devices for power generation due to their capability of decoupling
18 the competing physical parameters; σ , α and κ , leading to an enhancement in ZT. The
19 nanocomposite materials could be either single-phase nanomaterials or nanoinclusions embedded
20 in a host bulk matrix, the latter being the mainstream of the nanocomposite approach. The
21 micron-scale and nanometer-scale inclusion in nanocomposite facilitates some of the limitations
22 that otherwise arise from interrelated α , σ and κ in their counterpart bulk materials.²⁷⁻²⁹ The
23 nanocomposite thermoelectric materials exhibit several requisite features for the optimization of

1 high ZT, such as, (1) numerous grain boundaries which can scatter phonons effectively for the
2 reduction in κ ^{30,31} (2) mechanisms of energy dependent scattering of electrons at interfaces
3 between the matrix and nanoinclusions i.e., electron filtering effect^{32,33} for improvement for
4 power factor ($\alpha^2\sigma$) (3) electron injecting phenomenon induced by nanoinclusions (4) quantum
5 confinement regime which alter the electronic structure and phonon dispersion relations^{7,29,34} (5)
6 morphological tailoring of nanocomposite thermoelectric materials due to dimension reduction,
7 grain refinement and size reduction of a second phase.³⁵⁻³⁹

8 However, despite of all these interesting features, inherent limitations of the composite
9 materials can also be noted in the light of established theory of effective medium approximation
10 (EMA) by Bergman and Fel.^{40,41} This study demonstrates that the σ and κ of a composite cannot
11 substantiate for improvement in comparison with that of either best or worst thermoelectric
12 parameters of the separate component of the composite if the contribution from the phase
13 interface/ boundary is of little worth.^{40,41} The thermoelectric properties calculated by them for the
14 binary composite indicated that the ZT of the composite could never exceed the highest ZT of
15 each separate component phase, although enhancement in the power factor could be achieved.
16 This proof-of-principle of EMA theory was demonstrated experimentally by Heremans et.al.⁴² in
17 a composite of high thermopower Bi matrix and high electrically conducting inclusions of Ag.
18 However, recently the nanocomposites based on PbTe,^{9,10} CoSb₃,⁴³⁻⁴⁵ Bi₂Te₃,²⁻⁶ Mg₂Si,¹² and
19 HH^{10,46-49} as matrix phase substantiate simultaneous improvement in power factor and reduction
20 in κ leading to an increased ZT. It may be emphasized that the enhancement in ZT in most of
21 these nanocomposites resulted almost entirely from a drastic reduction of the lattice thermal
22 conductivity (κ_l), due to increased phonon scattering at several interfaces and grain boundaries.
23 In such nanocomposites, the dispersed nanoparticles are designed to scatter the phonon more

1 effectively than electrons because mean free path of phonons is comparable to the grain size
2 while the micro-particles matrix forms a connected network for electron transport. This leads to
3 partial decoupling of the thermal and electronic transport. Thus, it is expected that the
4 nanocomposite containing more fine particles may have low σ and low κ . Furthermore, the α
5 usually does not change significantly by changing the grain size and hence the ZT value could be
6 tuned by reducing κ by optimizing the volume percentage of fine inclusions.

7 In the present work, a new undoped off-stoichiometric HH-based composition $Zr_9Ni_7Sn_8$
8 having VEC of 17.25 per formula unit which is larger than 18 for normal $ZrNiSn$ HH has been
9 synthesized in order to obtain either the superstructure of HH if it occurs similar to the report in
10 $Ru_9Zn_7Sb_8$ or if it results to a phase segregation forming a composite phase material. We noticed
11 that despite the formation of a single phase supercell of HH phase, two separate phases of HH
12 (space group; $F\bar{4}3m$; cubic) and Ni_3Sn_4 (space group; $C2/m(12)$; monoclinic) were stabilized
13 resulting into a HH composite phase. In order to ascertain the phases obtained, the composition
14 $Zr_9Ni_7Sn_8$ has been optimized by several synthesis routes such as solid state reaction, ball-
15 milling and arc-melting. The resulting composite has high reproducibility which has been
16 verified by various synthesis approaches. We observed that this large mismatch in VEC number,
17 comparing with that of $Ru_9Zn_7Sb_8$ (VEC=15.75 per formula unit), does not allow this
18 composition to be stabilized electronically as supercell of HH; rather it causes to lead the system
19 to the phase separation, resulting in a composite of HH $ZrNiSn$ and Ni_3Sn_4 phase. Interestingly,
20 despite the metallic nature of Ni_3Sn_4 a (with larger κ at room temperature than that of the HH
21 phase), a drastic reduction in thermal conductivity (~56%) was observed, which might be
22 originated from the dampening of lattice thermal conductivity ($\kappa_{lattice}$) by metallic Ni_3Sn_4
23 inclusion rather than acting as an accelerated path for thermal transport. Moreover, the interfaces

1 of HH and Ni_3Sn_4 phase disrupt the phonon transport which leads to medium-to-long wavelength
2 phonon scattering, thus resulting in reduction of κ_{lattice} . The nanostructuring (employed by
3 mechanical ball milling) further induces increased density of such hetero-interfaces of HH/ Ni_3Sn_4
4 which yields a further reduction in thermal conductivity, leading to a ZT of 0.90 at 773K. Such
5 *in-situ* bulk nanocomposite (BNC) in $\text{Zr}_9\text{Ni}_7\text{Sn}_8$ with VEC=17.25 per formula unit which is
6 smaller than 18 for normal HH ZrNiSn , resulted into partitioning of a precursor phase into
7 primarily two thermodynamically stable phases, provides an additional control on the
8 optimization of thermoelectric parameters for enhancement of ZT. The present strategy of
9 fabricating *in-situ* bulk nanocomposite by decreasing VEC below that of HH leads to high ZT
10 via drastic reduction in thermal conductivity may extend to explore several compositions in XYZ
11 (X=Ti, Zr, Hf, Y= Ni, Co, Z= Sn, Sb) family of half-Heusler.

12 **2. Experimental Details:**

13 The stoichiometric compositions of ZrNiSn , $\text{Zr}_9\text{Ni}_7\text{Sn}_8$ and Ni_3Sn_4 phase were prepared by
14 melting zirconium (Zr; 99.99%, Alfa Aesar), nickel (Ni; 99.99%, Alfa Aesar), and tin (Sn;
15 99.99%, Alfa Aesar) powders using an arc-melting process. All the elemental powders for each
16 stoichiometry were mixed together and cold pressed into cylindrical pellets further use in Arc
17 melts. The congealed melts were re-melted several times in the arc melter each after turning
18 them over to ensure homogeneity. The melted ingot was then annealed at 1173 K for one week
19 under vacuum in a quartz tube. All the final ingots were pulverized into fine powder and
20 consolidated employing spark plasma sintering (SPS) technique at temperatures of 1073 K and
21 pressure of 50 MPa for holding time of 10 minutes using graphite dies with a 12.7 mm central
22 cylindrical opening to dense pellets. In the present study, ZrNiSn is designated as HH, $\text{Zr}_9\text{Ni}_7\text{Sn}_8$
23 is termed as bulk composite (BC). A part of the annealed sample of $\text{Zr}_9\text{Ni}_7\text{Sn}_8$ was further milled

1 for 30 hours to reduce their grain sizes. The mechanically milled nanopowder of $Zr_9Ni_7Sn_8$ was
2 then consolidated at the same conditions using SPS to get 12.7 mm diameter sample of
3 nanostructured composite, which is designated as bulk nanocomposite (BNC). The samples were
4 characterized by powder X-ray diffractometer (Rigaku Mini Flex II), Scanning Electron
5 Microscopy (SEM) and Transmission Electron Microscopy (TEM ; Technai G² T³⁰; W-Twin
6 operating at 300 KV) to study their phases, homogeneity, average grain sizes, and the grain-size
7 distribution of the minor phases.

8 The electrical conductivity and Seebeck coefficient were measured simultaneously by
9 employing the commercial equipment (ULVAC, ZEM-3) in the temperature range 300 to 773K
10 on samples of polished bars of about $3 \times 2 \times 10$ mm. The electrical conductivity was measured in
11 four probe geometry. The thermal diffusivity was measured with disks of 12.7 mm in diameter
12 and 2 mm in thickness in the same temperature range using a laser flash system (Linseis, LFA
13 1000). The disc specimen used for thermal diffusivity was sprayed with a layer of graphite in
14 order to minimize errors due to emissivity. Specific heat was determined by a Differential
15 Scanning Calorimeter (DSC 822^e Mettler Toledo). The thermal conductivity was calculated as
16 $\kappa = \alpha \cdot C_p \cdot \rho$ where α , C_p and ρ are the thermal diffusivity, specific heat capacity and density,
17 respectively.

18 Reproducibility of the thermoelectric properties was realized within 3% under the same
19 experimental conditions. The density of the sintered samples was measured using an
20 Archimedes' kit and was observed to be >98% of the theoretical density.

21

22

23 **3. Results and discussion:**

1 3.1 Structural Characterization

2 The XRD patterns of SPSed normal half-Heusler-ZrNiSn (HH), Bulk composite-Zr₉Ni₇Sn₈
3 (BC) and Bulk nanocomposite- Zr₉Ni₇Sn₈ (BNC) are presented in Fig. 1. All the peaks in XRD
4 patterns corresponding to ZrNiSn sample (Fig. 1a), could be well indexed with cubic crystal
5 system (space group $F\bar{4}3m$). Fig. 1b shows the XRD pattern which indicates a co-existence of
6 two separate phases namely, HH as major phase and monoclinic Ni₃Sn₄ (space group; C2/m (12)
7 as minor phase. The Reitveld refinement (Fig. 1c) of BC Zr₉Ni₇Sn₈ using the full proof software
8 has been performed to calculate the lattice parameters in the composites, which is shown in table
9 1. Thus, despite formation of supercell, as reported in Ru₉Zn₇Sb₈,²⁶ the Zr₉Ni₇Sn₈ results into a
10 composite material consisted of slightly large unit cell of HH in comparison to the normal
11 ZrNiSn HH (Fig. 1b). This expansion of unit cell of HH becomes more prominent in BNC
12 Zr₉Ni₇Sn₈ sample (Fig. 1d). Moreover, a subtle peak broadening in HH peaks (Fig. 1d) were also
13 noted indicating the reduced size of the HH grains in BNC sample prepared by nanostructuring
14 route.

15 In order to further identify the phases and microstructural details, the SEM and TEM of
16 BC and BNC samples have been performed. SEM morphology of BC sample shown in Fig. 2a,
17 clearly reveals a two phase contrast, indicating a composite comprising of two phases. The
18 EDAX analysis of this sample in Fig. 2b and Fig. 2c, clearly reveal the dark grey contrast
19 (marked as dotted curves) as HH phase while light grey contrast (marked as square box) as
20 Ni₃Sn₄ phase. The EDAX result (Fig. 2c) obtained from light grey contrast grain shows a
21 composition Ni_{3.01}Sn_{4.1}Zr_{0.3} indicating additional Zr which might have originated from the grain
22 boundary of Ni₃Sn₄ obtained during phase separation.

1 In order to confirm the phases present in BC $Zr_9Ni_7Sn_8$ sample, the TEM has also been
2 carried out. Two phase contrast in the bright field TEM images (Fig. 2d) is witnessed which is
3 consistent with the phases shown in SEM images (Fig. 2a). For the clarity in the phase contrast, a
4 high magnification image in TEM is recorded, which is shown in Fig. 2e. The selected area
5 electron diffraction (SAED) pattern taken from light contrast portion (the dotted area) in Fig. 2e,
6 shown in the inset, reveals the dotted marked area to be HH phase. The EDAX analysis from the
7 black contrast (Fig. 2e) confirms it to be again Ni_3Sn_4 - type phase (not shown here). The
8 formation of Ni_3Sn_4 -type phase within the HH matrix in $Zr_9Ni_7Sn_8$ resulting from arc melting,
9 could be attributed to occur due to phase separation during cooling. A single solid solution of all
10 the elements at high temperature decomposes into thermodynamically stable phases of HH and
11 Ni_3Sn_4 -type phase at lower temperature. TEM characterization of BNC sample, synthesized by
12 nanostructuring route, was also performed. Fig. 3a represents bright field TEM images obtained
13 BNC sample clearly showing a co-existence of two phase contrast together with highly dense
14 packed grains and of smaller sizes. HRTEM image shown in Fig. 3b, confirms that the dark
15 precipitates correspond to (-5, 1, 1) planes of Ni_3Sn_4 phases, while SAED pattern in Fig. 3c,
16 obtained from grey contrast, corresponds to [-1 1 1] zone axis of HH. The microstructure (Fig.
17 3a), obtained from the BNC sample, elucidates a high density of grains with smaller sizes as
18 compared to the normal BC. The size of HH grains of BNC sample range from 45 to 170 nm,
19 which is much smaller than the grains ranging from 0.3 to 2 μm for BC sample. Thus, the present
20 microstructural analysis reveals that BNC sample consists of all-scale hierarchical architectures
21 starting from nanoscale Ni_3Sn_4 (4-25 nm) to mesoscale HH grain boundaries (45-170 nm).

22 **3.2 Thermoelectric Properties**

1 In order to understand the impact of such *in-situ* fabricated composite with multiple
2 dimensions length scale on thermoelectric properties, the $Zr_9Ni_7Sn_8$ both BC and BNC samples
3 have been subjected to thermal and electronic transport measurements. The electronic and
4 thermal transport properties of BC and BNC samples have been studied and compared with the
5 normal HH. Fig. 4 shows the temperature dependence of various electrical and thermal
6 parameters which contributed towards ZT. The electrical conductivity of all the samples
7 increases monotonically with increasing temperature, displaying a characteristic feature of
8 semiconducting materials. The room temperature σ of BC sample of $Zr_9Ni_7Sn_8$ is observed to be
9 significantly higher in comparison to that of HH. However, the BNC sample exhibits two
10 striking features i.e. reduction in σ compared to BC sample but higher than normal HH
11 counterpart and a weak temperature dependency of $\sigma(T)$. For instance, room temperature values
12 of σ of HH, BC, and BNC are 632 S/cm, 1140 S/cm and 1010 S/cm, respectively. This
13 corresponds to an increase in σ of $\sim 80\%$ for BC and $\sim 60\%$ for BNC, compared to normal HH
14 $ZrNiSn$. The increased σ of BC and BNC sample might be resulting from its large carrier density
15 induced by doping of HH matrix by the metallic Ni_3Sn_4 -type phase. Fig. 4b shows the
16 temperature dependence of Seebeck coefficient (α) of HH, BC, BNC which indicates them to be
17 n-type materials. The value of room temperature α of BC and BNC sample is significantly
18 lowered compared to its bulk HH counterpart and this decrease is associated with the increase in
19 their corresponding σ . For instance, room temperature value of α in HH, BC and BNC are -122, -
20 56.8, and -84.3K, respectively which corresponds to $\sim 115\%$ and $\sim 45\%$ decrease compared to its
21 value of HH counterpart.

22 In order to understand the behavior of electronic transport, room temperature Hall-effects
23 measurement have been performed on HH, BC, and BNC samples to measure the carrier density.

1 The carrier mobility was calculated from electrical conductivity value. The BC sample exhibited
 2 a carrier concentration of $1.6 \times 10^{20}/\text{cm}^3$ and mobility $\sim 42 \text{ cm}^2/\text{Vs}$ while the BNC sample yielded
 3 a carrier concentration of $9.3 \times 10^{19}/\text{cm}^3$ and mobility $\sim 72 \text{ cm}^2/\text{Vs}$. The carrier concentration and
 4 mobility for the HH sample was found to be $2.4 \times 10^{19}/\text{cm}^3$ and $\sim 167 \text{ cm}^2/\text{Vs}$ respectively. The
 5 large increase in σ of BC is attributed to the increased carrier density arising from doping of HH
 6 with Ni_3Sn_4 precipitates. The observed decrease in α of BC and BNC sample compared to the
 7 bulk counterpart matrix of HH is consistent with the increased carrier densities in comparison to
 8 HH counterpart. Remarkably, the increase in α for BNC sample compared to that of BC sample,
 9 could be attributed to the observed reduction in carrier density at around 300K which might have
 10 resulted due to filtering of low energy carrier by scattering at potential barrier created at the
 11 interfaces of HH/ Ni_3Sn_4 , similar to that proposed by Faleev et.al.⁵⁰ in BNC sample. Such
 12 filtering effect will not occur in BC sample due to submicron size of Ni_3Sn_4 phase. The optimum
 13 size of inclusions ranging from 2-20 nm only promotes such filtering effect as suggested by
 14 Faleev et al.⁵⁰

15 A plausible explanation of mechanism of increasing α of BNC than its bulk counterpart BC
 16 sample may also be discussed in the frame of a model involving the scattering factor and reduced
 17 Fermi energy proposed by Nolas et.al.⁵¹ where α is expressed as:

$$18 \quad \alpha = \frac{\pi^2}{3} \frac{K_B}{e} \left(r + \frac{2}{3} \right) \left(\frac{1}{\xi} \right)$$

19 Where K_B is the Boltzmann constant, r is the scattering factor and ξ is the reduced Fermi energy.
 20 A significant decrease in the carrier concentration in nanocomposite (BNC) $\text{Zr}_9\text{Ni}_7\text{Sn}_8$ as seen
 21 from the Hall data, may reduce the Fermi energy and consequently result in an increased α as
 22 compared to its BC sample. Additionally, the increase in α of BNC sample may also be

1 attributed to an increased scattering factor r , apparently from the potential barrier scattering
2 effect.⁵² It is worth mentioning here that similar effects have also been reported in HH
3 ZrNiSn/ZrO₂ based nanocomposites.⁵² Nevertheless, further studies may be required to
4 understand the mechanism leading to increase in the scattering factor and the electron filtering
5 effects. Thus, it appears that the overall effect of metallic Ni₃Sn₄ inclusions on the electronic
6 transport of nanocomposite might be related to several factors, such as optimum size, the carrier
7 concentration, potential profile in the bulk matrix and the position of the Fermi level compared to
8 its bulk counterpart of BC. The temperature dependence of power factor, plotted in Fig. 4c, is
9 found to decrease in both BC and BNC sample as compared to the HH counterpart. This
10 decrease in power factor in both the samples is attributed to drastic reduction in α due to metallic
11 Ni₃Sn₄ doping in HH as compared to its value in HH counterpart.

12 In addition to α and σ , the thermal conductivity, κ is also an important parameter for
13 thermoelectric material. The thermal conductivity is calculated by taking the product of
14 diffusivity, specific heat and density of the sample. These data for the samples are shown in the
15 supplementary information as Fig. S1, Fig. S2 & table T1 respectively. The value of κ of sample
16 BC is significantly reduced by -56% in comparison to the HH as shown in Fig. 4d. This drastic
17 reduction in the κ in BC sample may be partly attributed due to lattice expansion of HH which
18 leads to the lattice softening resulting from weak chemical bonding resulting to dampening of the
19 phonon propagation in addition to the interface scattering of phonons from phase boundaries.
20 This observation is similar to our earlier report.⁴⁶ Interestingly, the κ of BNC sample is
21 significantly reduced by ~81% as evident from Fig. 4d in comparison to that of normal HH
22 counterpart. Significantly reduced κ of BNC sample may be assigned to high density of

1 HH/Ni₃Sn₄ hetero-interfaces in addition to notable mesoscale grain boundaries for enhanced
2 scattering of phonons ranging from large-to-medium-to short wavelength.

3 In order to understand the details about the effect of interfaces on the κ_l of the samples
4 BC and BNC samples, the lattice thermal conductivity (κ_l) was calculated by subtracting the
5 electronic part of thermal conductivity (κ_e) from the total thermal conductivity (κ),⁵⁴ using
6 Wiedemann-Franz law. The Wiedemann-Franz law is invoked to calculate the electronic part of
7 the thermal conductivity, by a relation $\kappa_e = L_0\sigma T$, where L_0 is the Lorenz number,⁵⁵ $L_0 = 2.48 \times$
8 $10^{-8} \text{ W}\Omega\text{K}^{-2}$, for a metallic-like material and the bipolar contribution was taken into account by
9 assuming $\kappa_l \approx 1/T$.⁵³ Fig. 4e suggests that for the HH sample, $\kappa_e = 0.31 \text{ W/mK}$ and $\kappa_l = 10.57$
10 W/mK (at room temperature) whereas, for the samples BC and BNC, the κ_e , were obtained to be
11 0.52 W/mK and 0.49 W/mK respectively, and κ_l ; 4.03 W/mK and 2.86 W/mK , respectively. Thus
12 it can be easily inferred from the Fig. 4e that κ_l dominates over κ_e with its significantly low value
13 from HH to BNC samples. It was noted that a 60% and 72% decrease in κ_l is observed for the
14 samples BC and BNC, respectively, in comparison to its value of HH. This significant reduction
15 in lattice thermal conductivity κ_l is primarily contributing to a large enhancement in ZT for BC
16 and BNC samples. For instance, BC sample exhibits a ZT ~ 0.38 at 773K and BNC estimates a
17 ZT ~ 0.90 at 773K which is 87% and 300% higher than that of the HH. The variation in ZT as a
18 function of temperature is shown in Fig. 4(f). The stability of the material and consistency of
19 electronic transport properties have been verified by measuring the electrical conductivity and
20 Seebeck coefficient with samples after 10 weeks kept at room temperature and also with the
21 samples annealed at 850 °C for 24 hrs. which are presented in supplementary information (Fig.
22 S3 & S4 respectively). We do not find a significant change in the value of electrical conductivity
23 and Seebeck coefficient (Fig. S3 & S4) in the composites. The temperature dependent α , σ and κ

1 of both BC and BNC were observed to be consistent in magnitudes and also in trends of α and σ
 2 suggesting the material to be chemically stable in nature.

3 4 **3.3 Bergman-Fel Effective Medium Model: Calculation of effective thermoelectric** 5 **parameters**

6 In order to discuss our observed results, Bergman-Fel effective medium model^{40,41} has been
 7 used to calculate the effective value of thermoelectric parameters. This model relates the
 8 effective electrical conductivity $\sigma_{(E)}$, effective thermal conductivity $\kappa_{(E)}$ and effective Seebeck
 9 coefficient $\alpha_{(E)}$ for a composite containing random dispersion of nearly spherical particles
 10 inclusions in a matrix medium. If one assumes a matrix medium such as HH as A and inclusion
 11 of Ni₃Sn₄ as B in the present study and σ_A and σ_B the electrical conductivities, α_A and α_B the
 12 Seebeck coefficients, κ_A and κ_B as the thermal conductivities of the constituents A & B
 13 respectively, then the effective σ_E , κ_E and α_E for such composite can be given as:

14

15

$$16 \quad \sigma_E = \sigma_A + \frac{\phi}{D} \left(\frac{\delta_\sigma}{d_{BA}} + \frac{1-\phi}{3} \frac{\sigma_A}{d_A} \right) \text{----- (1)}$$

$$17 \quad \kappa_E = \kappa_A + \left(\frac{\delta_\kappa}{d_{BA}} + \frac{1-\phi}{3} \frac{\kappa_A}{d_A} \right) \text{----- (2)}$$

$$18 \quad \alpha_E = \left[\alpha_A \sigma_A + \frac{\phi}{D} \left(\frac{\delta_{\alpha\sigma}}{d_{BA}} + \frac{1-\phi}{3} \frac{\alpha_A \sigma_A}{d_A} \right) \right] \frac{1}{\sigma_E} \text{----- (3)}$$

$$19 \quad \alpha_E = \left[\alpha_A \sigma_A + \frac{\phi}{D} \left(\frac{\delta_{\alpha\sigma}}{d_{BA}} + \frac{1-\phi}{3} \frac{\alpha_A \sigma_A}{d_A} \right) \right] \frac{1}{\sigma_E}$$

20

21 Where ϕ is the volume fraction of Phase B and

$$\delta_{\sigma} \equiv \sigma_B - \sigma_A, \delta_{\kappa} \equiv \kappa_B - \kappa_A,$$

$$d_A \equiv \frac{\sigma_A \kappa_{\sigma}}{T} - (\alpha_A \sigma_A)^2, d_{BA} \equiv \frac{\delta_{\sigma} \delta_{\kappa}}{T} - \delta_{\alpha\sigma}^2$$

1 and

$$D \equiv \left(\frac{\delta_{\sigma}}{d_{BA}} + \frac{1-\phi}{3} \frac{\sigma_A}{d_A} \right) \left(\frac{\delta_{\kappa}}{T d_{BA}} + \frac{1-\phi}{3} \frac{\kappa_A}{T d_A} \right) - \left(\frac{\delta_{\alpha\sigma}}{d_{BA}} + \frac{1-\phi}{3} \frac{\alpha_A \sigma_A}{d_A} \right)^2$$

2

3 The calculation of effective TE parameters for composite was performed considering 25% of

4 volume fraction of Ni₃Sn₄ inclusions in HH matrix, as obtained by Reitveld refinement.

5 Accordingly, the $\sigma_{(E)}$, $\alpha_{(E)}$ and $\kappa_{(E)}$ of bulk HH/Ni₃Sn₄ composite are calculated using equation

6 (1), (2) & (3) respectively and plotted in Fig. 4 a, b & d, respectively. The σ , α and κ of Ni₃Sn₄

7 phase is shown in the inset of Fig. 4 a, b & d, respectively. It can be clearly noted from Fig. 4a

8 and Fig. 4b that the calculated data for σ_E and α_E presents slightly deviated trend with small

9 variations in their magnitude as compare to the observed experimental results for BC sample.

10 This slight deviation in σ_E and α_E is expected which can be attributed to the presence of a trace

11 amount of third phase of Zr at grain boundary of Ni₃Sn₄ as evidenced by SEM-EDAX analysis

12 (Fig. 2c). However, when compared to the calculated data for BNC sample, neither σ_E and nor α_E

13 matches with the experimental results for BNC sample which is quite expected as model

14 assumed for micron sized inclusion phase rather than nano-sized inclusion in the matrix phase. It

15 is interesting to mention here that the Hall data and transport properties, discussed in section 3.2

16 have also witnessed the filtering effect and interface boundary scattering in our BNC sample

17 which supports to the violation of the assumptions of Bergmann-Fell model and hence the

18 inconsistency of calculated and observed thermoelectric parameter were observed.

19 The size and distribution of Ni₃Sn₄ nano-inclusion in the composite influences the

20 transport properties of BNC sample. It is important to mention that the BNC sample exhibited a

1 rather high α (in Fig. 4b) without changing the carrier concentration in comparison to its BC
2 counterpart. The exact reason for this result is not yet clearly known. However, it could be an
3 energy filtering mechanism, similar to that proposed by Faleev et.al.,⁴⁹ as discussed in section
4 3.2. In the present work, low energy carriers might have filtered out by the scattering at potential
5 barrier created at the interface between HH and metallic Ni₃Sn₄ phases and thus improving α in
6 BNC sample in comparison to its BC counterpart as discussed previously. Thus, the optimum
7 size and density of the Ni₃Sn₄ precipitates could be an important factor responsible for enhancing
8 the ZT.

9 The results obtained in the present work motivate to design *in-situ* bulk composite
10 consisting of HH and metallic inclusions Ni₃Sn₄ in an off-stoichiometric HH composite with
11 VEC smaller than 18 for drastic reduction in κ and simultaneous improvement in the electrical
12 transport. However, further work is needed to explore several compositions of half-Heusler of
13 XYZ family to assess the precise impact of such composite material on the thermoelectric
14 properties. Moreover, optimization of several processing conditions and their impact on
15 thermoelectric properties in Zr₉Ni₇Sn₈ may be the future avenue of present research.

16 4. Conclusions

17 An off-stoichiometric composition of HH namely Zr₉Ni₇Sn₈ having VEC of 17.5 per unit
18 formula which is smaller than 18 for most stable normal ZrNiSn HH, exhibits an *in-situ*
19 composite of HH/Ni₃Sn₄ rather than forming a superstructure of HH. Such *in-situ* composites
20 enables to the optimization of high ZT ~0.38 at 773K, which is 87% higher in comparison with
21 that of the normal HH counterpart. Interestingly, nanostructuring of BC sample further enhanced
22 ZT to ~ 0.90 at 773K which is ~300% higher than normal HH counterpart. The enhancement in
23 ZT for BC and BNC sample is primarily due to significant reduction in their κ with simultaneous

1 improvement in electrical conductivity as compared to the normal HH counterpart. Our finding
2 stimulates the search for several off-stoichiometric compositions based on varying VEC in wider
3 family of XYZ (X=Ti, Zr, Hf, Y= Ni, Co, Z= Sn, Sb) with composition $X_{1+x}Y_{1-x}Z$ where
4 significant reduction in thermal conductivity and electronic transport can be optimized for high
5 ZT. Further controlling the distribution of metallic inclusions by fine tuning the growth
6 parameters through appropriate thermal-treatment and with or without doping could be a
7 promising future strategy for enhancing the ZT of several compositions of HH family.

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23 **Figure Captions:**

- 24 **Fig.1.** X-ray diffraction patterns of (a) ZrNiSn HH (b) BC Zr₉Ni₇Sn₈, HH derivative (c) Reitveld
25 refinement of Zr₉Ni₇Sn₈ showing a composite which are well indexed with HH and Ni₃Sn₄
26 phases Blue ticks are Bragg positions out of which the upper blue ticks correspond to the HH,
27 and lower blue ticks are for Ni₃Sn₄ phase and (d) Bulk nanocomposite (BNC) Zr₉Ni₇Sn₈
- 28 **Fig.2.** (a) SEM morphology of BC Zr₉Ni₇Sn₈ showing a composite consisting two phases of HH
29 (dotted circle), Ni₃Sn₄ (Square box) and small pores. (b) EDAX-SEM recorded from the dotted

1 portion [Fig. 2a], shows the presence of all the elements and quantification shows a phase very
2 close to the HH. (c) EDAX-SEM obtained from the region marked as square box (fig. 2a) shows
3 the presence of Ni, Sn & Zr elements and quantification shows a phase very close to Ni_3Sn_4 -type
4 phase with Zr surrounding the grain boundaries of Ni_3Sn_4 phase (d) Bright field TEM image also
5 shows two contrasts in the sample which confirm the presence of two phases. (e) High
6 magnification TEM image clearly shows two phases. The inset, shows SAED pattern
7 corresponding to dotted region, reveal HH phase with zone axis $[1 \bar{1} 1]$.

8 **Fig.3.** (a) TEM image of $\text{Zr}_9\text{Ni}_7\text{Sn}_8$ -BNC showing varying grain sizes 45 to 170 nm of HH
9 indicated by dotted lines and varying sizes 5 to 25 nm of Ni_3Sn_4 shown by square boxes (b)
10 HRTEM image shows the two phases; HH and Ni_3Sn_4 with $(-5, 1, 1)$ lattice planes (c) SAED
11 pattern corresponding to dotted region, showing HH phase with zone axis $[1 \bar{1} 2]$

12 **Fig.4.** Temperature dependence of thermoelectric properties of ZrNiSn normal HH, $\text{Zr}_9\text{Ni}_7\text{Sn}_8$
13 bulk composite (BC), $\text{Zr}_9\text{Ni}_7\text{Sn}_8$ bulk nanocomposite (BNC), Ni_3Sn_4 [in inset] and calculated
14 effective thermoelectric parameters for composite using Bergemen and Fel model (a) electrical
15 conductivity (b) Seebeck coefficient (c) power factor (d) total thermal conductivity (e) lattice and
16 electronic thermal conductivity (f) calculated thermoelectric figure of merit (ZT)

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