Implication of nanostructuring of bulk nanocomposite $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ on the optimization of high thermoelectric performance

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Abstract

Nanostructuring approach on TiNiSn-based half-Heusler (HH) thermoelectric materials (TE) has been well established as the most prominent paradigm for achieving high figure of merit (ZT). Herein, we have extended this approach on our previously reported bulk nanocomposite (BNC), containing HH and Full Heusler (FH) with little traces of Ti_6Sn_5 phase in a stoichiometric composition $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ for the optimization of high thermoelectric performance. A synergistic effect of nanostructuring of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ bulk nanocomposite (BNC) on its thermoelectric properties was noticed, revealing an enhanced value of $ZT \sim 0.83$ at 773 K. This enhancement in ZT value is mainly ascribed to significant reduction in thermal conductivity ($\kappa \sim 1.0$ W/mK at 773 K), through modification in grain as well as phase boundary scattering. The marginal enhancement in Seebeck coefficient observed is attributed to charge carrier filtering effect at the interface of HH/FH phases.

Keywords Half-Heusler · Nanostructuring · Thermal and electronic transport · Spark plasma sintering

Introduction

Innovative developments in small-scale energy conversion technologies have gained enormous attention, especially in the utilization of low-potential heat energy. Thermoelectric (TE) energy converters, in particular, thermoelectric generators (TEG), occupy an important niche in modern technology and have a big potential for application in future energy-harvesting technologies, as well [1–5]. However, comparatively low efficiency of thermoelectric materials and devices makes a wide-scale expansion of this technology economically non-profitable. Therefore, the final goal of fundamental investigations in the field of thermoelectric is to search for cost-effective, non-toxic, and highly efficient

materials for TEGs. The thermoelectric figure of merit (ZT) [6], given below, gauges the efficiency of thermoelectric materials:

$$ZT = \frac{\alpha^2 \sigma T}{\kappa}, \quad (1)$$

where α , σ , and κ (where $\kappa = \kappa_e + \kappa_p$) is the thermopower, electrical conductivity, and thermal conductivity accounting both electronic (κ_e) and phonon (κ_p) contributions, respectively, and T is absolute temperature. High ZT can be achieved via enhancing α , σ , and reducing κ . However, the simultaneous optimization of these three transport properties is a highly challenging task due to their close interdependencies. As α increases, σ usually decreases which in turn affects κ_e based on the Wiedemann–Franz law [6].

In the past few years, doping, band engineering, solid solution alloying, PGEC (phonon-glass electron-crystal), nanostructuring, and spin fluctuation driven effect on electronic transport have been the prime focus for tuning thermoelectric parameters simultaneously for optimizing large ZT in different class of materials [6–12]. However, unfortunately, a large number of high ZT materials are either toxic or expensive which makes them irrelevant for practical use in thermoelectric generators (TEG) [13, 14]. (The practical use of several high ZT thermoelectric materials in thermoelectric generators (TEG) is difficult due to either high cost

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or toxic nature.) Thus, study of cost-effective and non-toxic materials is relevant for thermoelectric device fabrication at a large scale.

Among several TE materials, the TE materials based on HH [15] have been shown to be potential thermoelectric materials as they include abundant non-toxic components, and also, they offer distinct structural advantages for designing bulk nanocomposites [16, 17]. In addition to this, they are site selective, such that if substituted on one site, there usually created lot of defects/disorder which further gets energetically minimized via phase separation of other inter-metallic phases [18–20]. It is well documented that Heusler class of materials is very important from the waste-heat utilization perspective [21], provided that high ZT materials can be produced at low cost.

Although, (Zr,Hf)NiSn-based (n-type) [22–26] and (Zr,Hf)CoSb-based (p-type) [27–29] HH materials have shown decent ZT values with Hf being used as an ingredient element, it makes these materials highly expensive which resists their deployment in developing thermoelectric generators (TEG) for commercial application [13, 14]. Recently, a new family of NbFeSb-based p-type half-Heusler alloys has been discovered with high performance ($ZT > 1.0$) [30–33] which advances the applications of HH materials. An n-type counterpart of Hf-free p-type is essential for finding suitable applications with the existing materials. One may consider an alternative option with Hf-free TiNiSn-based n-type HH materials and these have been optimized with enhanced ZT [34, 35]. A high ZT near 1 has been achieved at 823 K in TiNiSn via modified synthesis route by Gurth et al. [34]. Two methods are commonly used to increase the thermoelectric efficiency, the alloying, and the nanostructuring. Alloying is a traditional method for modification of thermoelectrics, while aiming at the suppression of the thermal conductivity due to lattice part, and it also modified the band structure of the material, i.e., improved electronic properties. On the other hand, nanostructuring (nanocomposite) is the modern approach targeted on both phonon and electron transports to achieve high ZT. The bulk nanocomposite having multiphase nanoinclusions can lead to enhancement in the ZT value; and this is via reducing thermal conductivity at boundaries and increasing power factor. This is caused either by modification of the band structure or by the effect of carrier filtering.

In many TE materials, nanostructuring has been observed to improve the ZT by reduction of thermal conductivity. Through the modification only in grain boundaries, there is an increase in phonon scattering from various interfaces between the grains [36, 37] or through an increase in Seebeck coefficient due to charge carrier filtering [38–40]. Nanostructuring on the bulk nanocomposite provides a constructive combination of modifying grain as well as phase

boundaries for effective phonon scattering and, hence, to optimize the thermoelectric performance. In the present work, we have investigated the effect of nanostructuring of our previously reported Ti₉Ni₇Sn₈ bulk nanocomposite (Nano-BNC) which is a composite having $97.1 \pm 0.12\%$ HH phase, $2.6 \pm 0.2\%$ in FH and traces of metallic Ti₆Sn₅ phase for the optimization of high ZT [41]. The phase separation and long-term stability of present composite material have been detailed in our earlier report [41]. Interestingly, a reasonably good ZT ~ 0.83 at 773 K has been demonstrated for nanostructured Ti₉Ni₇Sn₈ bulk nanocomposite (Nano-BNC) which resulted from a synergistically combined effect of modifying grains and phase boundary scattering. Furthermore, the cost of this material is estimated to be almost 15% cheaper than the best ZT ~ 1.2 at 823 K in Hf-free n-type HH material [34]. The cost estimation has been performed using reports [13, 42, and 43]; though the ZT value of present material is lower than 1.0 compared to that of Hf containing n-type HH materials [19, 44, 45], but lower cost with such reasonably good ZT ~ 0.83 at 773 K justifies these materials to be used in large-scale applications.

Experimental details

The polycrystalline samples having stoichiometric compositions of TiNiSn, Ti₉Ni₇Sn₈, and TiNi₂Sn with high-purity elements were prepared by Arc-melting process. All the elemental powder for each stoichiometry was mixed using mortar and pestle, cold-pressed to make cylindrical pellets, and arc melted several times in the presence of high-purity argon atmosphere for making a homogeneous alloy. These homogenized alloys were crushed to make fine powders and subsequently densified using spark plasma sintering (SPS) technique up to 800 °C temperature and by applying 50 MPa pressure for 10 min. Here, TiNiSn; as HH (half-Heusler), TiNi₂Sn; as FH (Full Heusler), Ti₉Ni₇Sn₈; as BNC (Bulk Nanocomposite) are abbreviated. A part of the annealed sample of Ti₉Ni₇Sn₈ (BNC) was further milled by planetary ball milling (HEBM, Fritsch, Pulverisette-4) to reduce the grain sizes of the bulk nanocomposite Ti₉Ni₇Sn₈ for 30 h. The nanopowder of Ti₉Ni₇Sn₈ was subjected to SPS to obtain a dense pellet of nanostructured bulk nanocomposite (Nano-BNC) of Ti₉Ni₇Sn₈. The density (ρ) of these SPSed pellets/samples was measured using an Archimedes' kit and was observed to be greater than 99% of their theoretical density. Microstructure investigation was performed by TEM (transmission electron microscopy, Technai G²T³⁰) of all the samples. There are three steps involved in the preparation of samples for TEM investigation [41]. For computing the thermoelectric properties, σ (T) and α (T) were obtained using ULVAC, ZEM3 equipment. Moreover, thermal diffusivity (d) and specific heat (Cp) measurement were performed

using laser flash system; Lineseis, LFA 1000 and differential scanning calorimetry (DSC) instrument; 822°Mettler Toledo, respectively. Thermal conductivity was calculated using the formula, $\kappa = d \times C_p \times \rho$. To obtain carrier concentration, Hall measurement was carried out employing the Van der Pauw method at room temperature. Both sample preparation procedure and thermoelectric measurements of Nano-BNC were carried out three times to confirm their reproducibility. The values were realized to spread within 3% under the same experimental conditions.

Results and discussion

Microstructural characterization

The detail TEM investigation is performed on a Nano-BNC sample of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ to investigate the minor details of microstructure of nanostructuring of bulk nanocomposite in the present work. The TEM investigation of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ —BNC has already been presented in our previous report by Misra et al. [41] revealing the confirmation of three phases namely HH TiNiSn , FH TiNi_2Sn , and Ti_6Sn_5 . Figure 1 exhibits a bright-field TEM image obtained from the sample of nano-BNC. The micrograph (Fig. 1a) clearly shows the grain size of HH phase (marked as rectangle) varying from 25 to 100 nm, while the grain size of FH inclusion phase (marked as dotted circle) varies from 3 to 10 nm. The trace amount of Ti_6Sn_5 phase as white precipitate is also noted as another minor phase. This uniform distribution of inclusions at multiple length scales of grain size distribution integrates many exciting mechanisms such as electron injection, electron filtering jointly with an ample range of phonon dispersal to realize elevated ZT. Figure 1b presents SAED along $[1\ 1\ -1]$ zone axis parallel to the electron beam, obtained from the dotted white lines confirming it to be HH phase with a lattice parameter of 6.14 Å. Furthermore, the dotted circle area as shown in Fig. 1a has been magnified showing the lattice scale image (Fig. 1c) along (220) plane of FH phase. Fast Fourier Transform (FFT) was generated corresponding to the feature displayed (Inset Fig. 1c) revealing full-Heusler phase with $[1\ -1\ -2]$ zone axis.

Electronic transport properties

To investigate the effect of nanostructuring on bulk nanocomposite for further optimization of the thermoelectric properties, the Nano-BNC sample of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ have been subjected to measurements of electronic transport. For better visibility of improvement in electronic transport of nanostructured BNC sample, we have compared the present result with our reported data of TiNiSn HH and BNC sample of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ [41]. The present result is also compared with

Fig. 1 **a** Low-magnification TEM micrograph of the $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ (Nano-BNC) displaying two phase contrasts of HH phase (marked as dotted white lines) and FH inclusions (marked as yellow-colored circle) along with the trace amount of Ti_6Sn_5 phase (marked as blue-color rectangle); **b** selected area electron diffraction pattern (SAED) obtained from the dotted white lines showing the HH phase along the $[1\ 1\ -1]$ zone axis; **c** HRTEM image obtained along (220) plane of FH phase revealing a lattice scale image. The fast Fourier transform (FFT) taken from this lattice scale image as shown in the inset confirms the black contrast to be FH phase

TiNiSn synthesized via modified route by Gurth et al. [34]. Figure 2 represents the electronic transport characteristics of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ Nano-BNC with temperature and compared with that of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ BNC and TiNiSn HH materials [34, 41]. One can notice that the nanostructuring of BNC sample so-called Nano-BNC exhibits significantly reduced electrical conductivity (σ) at room temperature. Moreover, the $\sigma(T)$ of Nano-BNC sample increases with rising temperature showing semiconducting behavior rather than to remain almost

Fig. 2 Temperature dependence of **a** the electrical conductivity, σ (T); **b** the Seebeck coefficient, α (T); **c** the power factor, P.F. ($\sigma\alpha^2(T)$) of Ti₉Ni₇Sn₈ Nano-BNC

constant up to 150 °C as in case of BNC sample and which was further found to be increasing with rising temperature. We also noticed that increase in α is associated with decrease in the electrical conductivity. However, in case of Nano-BNC sample, surprisingly, the temperature variations of α (T) and σ (T) trends displayed are rather unusual, as it indicates a weak correlation between these parameters.

The carrier concentration ($n = 1/R_H e$) from Hall measurement and mobility at room temperature using relation $\sigma = ne\mu$ was computed (Table 1). The carrier concentration of Nano-BNC sample was estimated to be $\sim 1.2 \times 10^{19}/\text{cm}^3$, which was observed to be decreased with respect to Ti₉Ni₇Sn₈ BNC ($n \sim 2.8 \times 10^{19}/\text{cm}^3$) [41]. The reduced value of carrier concentration is abnormal in case of Nano-BNC sample which may be due to the low energy electron filtering at the interfaces of HH/FH phases as reported by Faleev et al. [46] and by others [47–50]. Figure 2b exhibits α (T) of Nano-BNC samples which was compared with that of BNC and HH sample [34, 41]. The α (T) value of Ti₉Ni₇Sn₈ Nano-BNC sample at 323 K temperature is largest as compared to that of Ti₉Ni₇Sn₈ BNC and TiNiSn HH. For instance, α (T) at room temperature for Ti₉Ni₇Sn₈ Nano-BNC is $-61.2 \mu\text{V/K}$ which is $\sim 12.5\%$ larger than the value of $-54.4 \mu\text{V/K}$ obtained for Ti₉Ni₇Sn₈ BNC [41] and $\sim 40\%$ larger than that of normal TiNiSn HH [41], as shown in

Fig. 2b. This enhancement in α can be attributed to the electron filtering effect as suggested in many other reports [47–50].

A plausible explanation for this mechanism in which an increased value of α was observed for Ti₉Ni₇Sn₈ Nano-BNC as compared to that of Ti₉Ni₇Sn₈ BNC sample and TiNiSn HH can be given on the basis of the model proposed by Nolas et al. [51] and can be articulated as:

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

Here, r is the scattering factor, k_B ; the Boltzmann constant, and ξ ; the reduced Fermi energy. In our present work, the reduced carrier concentration in Ti₉Ni₇Sn₈ Nano-BNC sample decreases the Fermi energy which leads to increase in α (T) in comparison to its Ti₉Ni₇Sn₈ BNC and TiNiSn HH. Moreover, increased α can be ascribed to an augmented r as well based on potential barrier scattering effect [52]. These results are consistent with a similar type of report on HH ZrNiSn/ZrO₂-based bulk nanocomposites [53]. Exclusively, the behavior of α (T), from the room temperature, and strange observations of α (T) and σ (T) were found to be simultaneously increasing with rising temperature. To investigate the complex behavior in

Table 1 Room-temperature physical parameters such as lattice parameter (a), Hall coefficient R_H , carrier concentration n , Hall mobility μ , carrier effective mass m^* , and carrier relaxation time τ

Sample name	TiNiSn HH (Ref. [41])	Ti ₉ Ni ₇ Sn ₈ BNC (Ref. [41])	Ti ₉ Ni ₇ Sn ₈ Nano-BNC (present result)
Hall coefficient R_H (m^3C^{-1})	1.05×10^{-7}	2.23×10^{-7}	5.20×10^{-7}
Carrier concentration n (cm^{-3})	5.9×10^{19}	2.8×10^{19}	1.2×10^{19}
Hall mobility μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	72	210	257
Effective mass (m^*/m_e)	0.305	0.232	0.149
Carrier relaxation time τ (s)	1.25×10^{-14}	2.78×10^{-14}	2.17×10^{-14}

and free electron rest mass m_e of Nano-BNC samples and compared with HH, BNC for understanding of nanostructuring effect

the transport properties of Nano-BNC sample, a Pisarenko plot which relates the $\alpha(T)$ and carrier density may be discussed as follows:

$$\alpha = \left(\frac{8\pi^2 \kappa_B^2}{3qh^2} \right) m^* T \left(\frac{\pi}{3n} \right)^{\frac{2}{3}}. \quad (3)$$

Assuming single parabolic bands up to 573 K, the Pisarenko plot of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ Nano-BNC is constructed together with TiNiSn HH, $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ BNC for comparison (Fig. 3). In this graph, α corresponds to the particular effective mass (m^*) and m^* of materials was estimated from n by Eq. (3) and the slope of α vs T . The estimated m^* at 323 K are noticed to be $0.305m_e$ for HH, $0.232m_e$ for BNC, and $0.149m_e$ for Nano-BNC, respectively. The m^* was found to be varying for all the composites and does not satisfy the single parabolic band indicating a complexity in the electronic structure of these composites at Fermi level.

Power factor

Figure 2c shows the calculated value of power factor of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ Nano-BNC samples as a function of temperature and is compared with that of reported TiNiSn HH and $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ BNC [34, 41]. The power factor of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ Nano-BNC sample is slightly smaller than that of bare $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ BNC sample [41]. This is mainly due to the considerable decrease in $\sigma(T)$ associated with effective electron scattering.

Fig. 3 Pisarenko plot at 323 K showing the dependence of the Seebeck coefficient $\alpha(T)$ on the electron carrier concentration (solid line) for $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ Nano-BNC and compared with that of TiNiSn (HH) and $\text{Ti}_9\text{Ni}_7\text{Sn}_8$

Thermal transport properties

Figure 4a shows $\kappa(T)$ of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ Nano-BNC samples and is compared with that of TiNiSn HH and $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ BNC [34, 41]. Regardless of temperature, the $\kappa(T)$ of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ Nano-BNC samples have been observed to be decreased significantly when compared to that of TiNiSn HH and BNC samples. The reduced value of $\kappa(T)$ may be ascribed to a synergy integrated for both phase and grain boundaries scattering in the present $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ Nano-BNC sample.

Interestingly, an ultra-low thermal conductivity ($\kappa \sim 1.0$ W/mK at 773 K) of $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ Nano-BNC sample was observed yielding to a high ZT ~ 0.83 at 773 K. It may be mentioned here that the phonons which have mean free paths ranging from short to mid can be scattered by modifying phase boundaries due to FH phase precipitation, Ti_6Sn_5 embedded in the HH matrix, while phonons having large mean free path can be scattered by numerous number of grain boundaries modified during the nanostructuring of bulk nanocomposite. The Wiedemann–Franz law is used to estimate $\kappa_e = L\sigma T$, where L is the Lorentz number and $k_l = \kappa - \kappa_e$. Here, exact determination of Lorentz number with varying temperature is essential to estimate the correct value of κ_e and hence, in turn, k_l . This finding is very important to closely understand the boundary engineering effect on reduction of k_l . The Lorentz number varying with temperature is plotted in Fig. 5a for all the samples. Figure 5b also shows the relation between Lorentz number and Seebeck coefficient along with the estimated value of L based on single parabolic band model with acoustic phonon scattering (SPB-APS model) with a degenerated limit of Lorentz number [54].

Figure 4d shows κ_e vs T of Nano-BNC sample and the same is compared with that of the HH, BNC sample [41]. Consistent with the increasing σ with temperature, the κ_e was observed to enhance for all the samples with temperature. The k_l of Nano-BNC sample as displayed in Fig. 4c shows that k_l decreases with increasing temperature. As a result, the Nano-BNC sample displayed an ultra-low thermal conductivity (~ 1.0 W/mK) which is $\sim 76\%$ lower than that of TiNiSn HH [41] at 773 K temperature and $\sim 62\%$ lower than that of the BNC sample [41]. It is worth mentioning that such structural modification by incorporating the phase and grain boundary engineering leads to the reduced k_l which is about more than six times reduction when compared to k_l of TiNiSn for the best reported high ZT by Downie et al. [25].

The reduction in κ can be ascribed by synergistic effect of nanostructuring on bulk nanocomposite to modifying phase as well as grain boundaries or in other words known as boundary engineering approach as shown in the schematic diagram Fig. 6. This reduction is attributed to increased phonon scattering by various grain boundaries formation as well as the phase boundaries created due to the formation of nano inclusions of TiNi_2Sn FH and Ti_6Sn_5 in $\text{Ti}_9\text{Ni}_7\text{Sn}_8$

Fig. 4 Temperature dependence behavior of **a** the total thermal conductivity, κ (T) of Ti₉Ni₇Sn₈ Nano-BNC and its comparison with that of reported TiNiSn (HH), Ti₉Ni₇Sn₈ (BNC) [41]; **b** calculated effective thermal conductivity for the composites Ti₉Ni₇Sn₈ (BNC) using

the effective medium theory and Maxwell–Eucken approximations; inset of **b** shows the total thermal conductivity of FH TiNi₂Sn; **c** the lattice thermal conductivity, κ_L (T) of Ti₉Ni₇Sn₈ Nano-BNC; **d** the electronic thermal conductivity, κ_e (T)

Nano-BNC sample, as presented in Fig. 6. The effective κ for Ti₉Ni₇Sn₈ Nano-BNC and Ti₉Ni₇Sn₈ BNC samples has been calculated theoretically via considering the minimal effect of Ti₆Sn₅ phase through Maxwell–Eucken approximations equation given below [55]:

$$k = \frac{\kappa_1 v_1 + \kappa_2 v_2 \frac{3\kappa_1}{2\kappa_1 + \kappa_2}}{v_1 + v_2 \frac{3\kappa_1}{2\kappa_1 + \kappa_2}} \quad (4)$$

Here, k is the effective thermal conductivity for the composite, where κ_1 , κ_2 is the thermal conductivity due to continuous phase, i.e., HH matrix, and dispersed phase, i.e., FH, respectively, and v_1 and v_2 stand for the volume fractions of HH and FH, respectively. Using above model, the thermal

conductivity of Ti₉Ni₇Sn₈ Nano-BNC samples was calculated and found to be much deviated as compared to the BNC sample, as shown in Fig. 4a, b [41], which could be due to the effect of nanostructuring; though the trends of the thermal conductivity graph were almost similar to this theoretically calculated model value as inclusion phases are same in Ti₉Ni₇Sn₈ Nano-BNC sample.

Thermoelectric figure of merit

Estimated thermoelectric figure of merit (ZT) of Ti₉Ni₇Sn₈ Nano-BNC is presented in Fig. 7a which have been compared with that of bare TiNiSn HH and Ti₉Ni₇Sn₈ BNC sample [34, 41]. A maximum ZT ~0.83 at temperature of 773 K for Ti₉Ni₇Sn₈ Nano-BNC was optimized, which was

Fig. 5 **a** Temperature-dependent Lorenz number (L) of $\text{Ti}-9\text{Ni}_7\text{Sn}_8$ Nano-BNC and TiNiSn (HH) and $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ (BNC) for comparison; **b** Relation between Lorenz number (L) and Seebeck coefficient, α (T)

for all samples along with the estimated value of L based on single parabolic band model with acoustic phonon scattering (SPB-APS model) with degenerated limit of Lorenz number

Fig. 6 Strategies for reduction in thermal conductivity via using boundary-engineered approach on TiNiSn -based HH materials starting from micrograined bulk TiNiSn to form phase and grain boundary modified nanostructured BNC $\text{Ti}_9\text{Ni}_7\text{Sn}_8$

noticed to be significantly enhanced ($> 300\%$) than $ZT \sim 0.20$ at 773 K for pure TiNiSn and $\sim 170\%$ enhanced than that of BNC sample ($ZT \sim 0.32$ at 773 K) [41]. This large enhancement in the ZT for $\text{Ti}_9\text{Ni}_7\text{Sn}_8$ Nano-BNC was realized due to observed ultra-low κ ($\sim 74\%$) as compared to bare TiNiSn (HH) and BNC samples [41]. This favorable condition of

drastic reduction in κ is attributed to the structurally modified grains as well as phase boundaries by means of precisely performing the engineering on the composition to form bulk nanocomposite and its nanostructuring via ball milling.

Figure 7b displays a comparison of ZT in the present research work with several other n-type HH based TE

Fig. 7 **a** Temperature dependence of the thermoelectric figure of merit of Ti₉Ni₇Sn₈ Nano-BNC; **b** comparison of the thermoelectric figure of merit of Ti₉Ni₇Sn₈ Nano-BNC with some state-of-the-art N type thermoelectric materials

materials. ZT for various state-of-the-art HH materials compared (Fig. 7b) is from higher temperature side, i.e., above 773 K [56–60]. These ZTs if compared at 773 K with the ZT of materials carried out in the present work, ZT of all the state-of-the-art HH materials found to be smaller at 773 K. Moreover, the expensive elements like Hf or Zr and toxic element Pb involved in such HH materials limit their large-scale industrial application and making them economically non-profitable and also have a harsh impact on the environment. It is worth mentioning here that TiNiSn-based nanostructured bulk nanocomposite studied in the present work is the most cost-effective and non-toxic alternative option with such reasonably high ZT along with easy synthesis route can provide an emerging pathway for large-scale applications.

Compatibility factor

The thermoelectric compatibility factor (S) is an essential parameter to be calculated for designing the highly efficient TE devices [61]. $S(T, \alpha)$ is given by:

$$S(T, \alpha) = \frac{\sqrt{1 + ZT} - 1}{\alpha T}. \quad (5)$$

This factor gives an idea about the feasibility of the materials with another counterpart to be deployed in thermoelectric devices. Figure 8a displays the estimated value of compatibility factor of Ti₉Ni₇Sn₈ Nano-BNC which has been compared with that of bare TiNiSn HH and Ti₉Ni₇Sn₈ BNC with increasing temperature. The compatibility factor of Ti₉Ni₇Sn₈ Nano-BNC was observed to be $\sim 3.9 \text{ V}^{-1}$ at 773 K. This value of S is much higher than that of the bare

TiNiSn HH sample and BNC sample, as shown in Fig. 8a, which is ascribed to simultaneous effect of high ZT and low α at high temperature.

The compatibility factors of the present materials are compared with reported materials, as shown in Fig. 8b. “The comparison reveals that Ti₉Ni₇Sn₈ (Nano-BNC) exhibits reasonably good compatibility factor which is either slightly larger in comparison to few materials or even comparable to few other reported materials as depicted in Fig. 8. Thus, it can be noticed that the present material offers possibility of high probability of being segmented with even other class of compounds other than its own family of compounds. However, it is always suggestive to use materials with similar Compatibility Factor for p and n-type components for thermoelectric device fabrication.” This material has a broad range for segmentation with other TE materials (approximately 2 times) to yield high TE device efficiency, benefitted in TE power production [62–65].

Concluding remarks and future prospects

In the present study, effect of nanostructuring of our previously reported bulk nanocomposite Ti₉Ni₇Sn₈ has been investigated for the optimization of high ZT. Interestingly, a significant reduction in thermal conductivity without deteriorating electronic transport properties is observed due the synergistic effect of nanostructuring of bulk nanocomposite (i.e., Ti₉Ni₇Sn₈ BNC). Nanostructuring of BNC sample leads to modify grain and phase boundary scattering which result in enhanced value of ZT ~ 0.83 at 773 K in Nano-BNC sample. This enhanced value of ZT could be realized due to an

Fig. 8 **a** Temperature-dependent thermoelectric compatibility factor (S) for TiNiSn (HH), Ti₉Ni₇Sn₈ (BNC), and Ti₉Ni₇Sn₈ (Nano-BNC); **b** comparison of the compatibility factors of Ti₉Ni₇Sn₈ (Nano-BNC)

with the compatibility factor (S) for some state-of-the-art n-type thermoelectric materials with high ZT

ultra-low thermal conductivity ($\kappa \sim 1.0$ W/mK at 773 K) and due to marginal enhancement in Seebeck coefficient ($\sim 18\%$ larger in comparison to TiNiSn HH). The severe reduction in κ was resulted on account of scattering of all short-to-long-range phonons from the distinct microstructures obtain via several nanostructured grain boundaries and interface boundaries, while an increase in Seebeck coefficient is corroborated to carrier filtering effect. We strongly believe that rapid energy-efficient processed materials employing arc melting followed by mechanical milling provide an easy path for developing such strategically modified TE materials via synergizing two approaches of phase boundary and grain boundary scattering together for optimizing high ZT.

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Compliance with ethical standards

Conflict of interest The authors declare that there have no conflicts of interest.

Code availability Not applicable.

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