Thermoelectric properties, efficiency and thermal expansion of ZrNiSn half-Heusler by first-principles calculations

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Abstract

In this work, we try to understand the experimental thermoelectric (TE) properties of a ZrNiSn sample with DFT and semiclassical transport calculations using SCAN functional. SCAN and mBJ provide the same band gap \(E_g\) of \(\sim 0.54\) eV. This \(E_g\) is found to be inadequate to explain the experimental data. The better explanation of experimental Seebeck coefficient \(S\) is done by considering \(E_g\) of 0.18 eV which suggests the non-stoichiometry and/or disorder in the sample. In the calculation of \(S\) and other TE properties temperature dependence on chemical potential is included. In order to look for the possible enhanced TE properties obtainable in ZrNiSn with \(E_g\) of \(\sim 0.54\) eV, power factor and optimal carrier concentrations are calculated. The optimal electron and hole concentrations required to attain highest power factors are \(\sim 7.6 \times 10^{19}\) cm\(^{-3}\) and \(\sim 1.5 \times 10^{21}\) cm\(^{-3}\), respectively. The maximum figure of merit \(ZT\) calculated at 1200 K for n-type and p-type ZrNiSn are \(\sim 0.5\) and \(\sim 0.6\), respectively. The % efficiency obtained for n-type ZrNiSn is \(\sim 4.2\%\) while for p-type ZrNiSn is \(\sim 5.1\%\). The \(ZT\) are expected to be further enhanced to \(\sim 1.1\) (n-type) and \(\sim 1.2\) (p-type) at 1200 K by doping with heavy elements for thermal conductivity reduction. The phonon properties are also studied by calculating dispersion, total and partial density of states. The calculated Debye temperature of 382 K is in good agreement with experimental value of 398 K. The thermal expansion behaviour in ZrNiSn is studied under quasi-harmonic approximation. The average linear thermal expansion coefficient \(\alpha_{\text{ave}}(T)\) of \(\sim 7.8 \times 10^{-6}\) K\(^{-1}\) calculated in our work is quite close to the experimental values. The calculated linear thermal expansion coefficient will be useful in designing the thermoelectric generators for high temperature applications.

Keywords: thermoelectric properties, efficiency, thermal expansion, thermoelectric generator, chemical potential, band gap

(Some figures may appear in colour only in the online journal)

1. Introduction

Thermoelectric materials are one of the technologically important materials for small scale power generation applications through waste heat recovery. In a thermoelectric material generation of electricity takes place by the motion of charge carriers driven by flow of heat across a temperature gradient [1, 2]. This process in the solid state thermoelectric device leads to power generation useful enough for many applications. At many places where heat released is unused, like in automobiles, industry, many heating appliances in homes or offices, high performance computing (HPC) centres etc., thermoelectric generators (TEG) can be applied. This helps in providing, an alternative to conventional fuel sources, usefulness of waste heat through electricity generation and lesser impact on environment. The advantages of thermoelectric
materials at applications are that they are scalable according to application, portable, lesser in weight, noise-free and less expensive [3].

The dimensionless figure of merit $ZT$ for a thermoelectric material is given by the relation,

$$ZT = \frac{S^2 \sigma T}{\kappa + \kappa_{\text{ph}}}. \quad (1)$$

The above relation gives a measure of efficiency of a thermoelectric material. As the equation suggests, to have high a $ZT$, the Seebeck coefficient $S$, electrical conductivity $\sigma$, thermal conductivity $\kappa$ should be high and electronic part and phonon part of thermal conductivity ($\kappa_e$ and $\kappa_{\text{ph}}$, respectively) should be lower at any temperature $T$. But, the quantities deciding the $ZT$ are counter related and hence achieving good value of $ZT$ is a task of optimization among these quantities [4, 5]. Also, there is a constant effort in the areas of thermoelectric research to reduce the thermal conductivity by methods like nanostructuring, alloying and to enhance $S$ and $\sigma$ by suitable doping [4].

With the help of density functional theory (DFT) and computational tools, materials with suitable electronic structure are being discovered which can be further tuned to get good thermoelectric efficiency [6]. Materials with $ZT$ value closer to or greater than 1.0 can be considered for application in commercial TEGs.

The ability of a TEG to convert heat into electrical power is given by its efficiency $\eta$. The maximum efficiency $\eta_{\text{max}}$ of a TEG is given by [7, 8]

$$\eta_{\text{max}} = \frac{T_h - T_c}{T_h} \sqrt{1 + \frac{ZT - 1}{\sqrt{1 + ZT} + T_c/T_h}}. \quad (2)$$

Here, $T_h$ is hot end temperature, $T_c$ is cold end temperature, $ZT$ is the figure of merit of the thermoelectric material used in the TEG and $T_h$ is average temperature. The above formula suggests that efficiency of TEG is mainly dependent on temperature difference between hot and cold end and also on the $ZT$ of the material used in the TEG [1, 8]. The TEG consists of number of n-type and p-type thermoelements (or legs) connected electrically in series. In order to have good efficiency, materials with high $ZT$ are desirable to use as legs of TEG.

The efficiency of TEG is also dependent on the operating temperature of the cold and hot ends. Even though the efficiency of TEG is not quite high still they are suitable in applications where sources of energy (e.g. space applications RTEGs), reliability and silent operation are more important [9]. For a practical application of a material in TEG, apart from its high value of $ZT$, considering the properties such as bulk modulus, thermal expansion and melting point etc. are also important. The material with high melting point, hardness and high bulk modulus, and less expensive are advantageous from the application point of view.

The possession of narrow bands with high Seebeck coefficient, tunable band gap and charge carrier concentration are the features making the Heusler compounds to be explored for thermoelectric applications with the only hindering factor being their relatively high thermal conductivity [10]. ZrNiSn belongs to the family of half-Heusler compounds with valence electron count 18 and has semiconducting ground state [11]. The experimentally reported band gap for ZrNiSn by the resistivity measurement is $\sim 0.18$ eV [12]. The ZrNiSn compound shows high $S$ values and moderately high value of $\kappa$ which make it promising material to explore for high temperature thermoelectric application. But, the $\kappa$ of the undoped ZrNiSn is $\sim 10-6$ Wm$^{-1}$ K$^{-1}$ (300–900 K) which is relatively higher compared to oxide or telluride materials [13, 14].

Due to the higher power factor in ZrNiSn based compounds, much attention has been given in exploring the possibility to enhance the ZT. Shen et al [13] reported the thermoelectric properties of undoped and Pd substituted ZrNiSn compounds. A maximum $ZT$ value of $\sim 0.7$ at 800 K was observed for the Hf$_{0.5}$Zr$_{0.5}$Ni$_2$Pd$_{0.5}$Sb$_{0.1}$Sb$_{0.9}$ compound. Sb doping at the Sn site in ZrNiSn was found to enhance the $ZT$ value to $\sim 0.8$ at 800 K in the work of Culp et al [15]. In the n-type (Hf,Zr)NiSn samples Chen et al have observed a $ZT$ of $\sim 1.2$ at 800 K through proper annealing [16]. Theoretically, Zou et al have given the explanation of experimental thermoelectric properties of doped ZrNiSn and Z$_{0.5}$Hf$_{0.5}$Ni$_2$Sn compound using DFT and transport calculations [17]. But, an attempt to understand the experimental thermoelectric properties of undoped ZrNiSn samples is lacking in the literature. Moreover, high temperature thermal expansion behaviour becomes an important parameter when designing TEG which is calculated here and compared with experimental data.

Therefore, in the present work, the experimental thermoelectric properties of a ZrNiSn compound [13] is explained using DFT and transport calculations. SCAN functional is used to study the electronic structure and transport properties. To calculate the thermoelectric properties, temperature dependent shift in chemical potential is considered. Further, the $S$, $\sigma$ and $\kappa_e$ of ZrNiSn with band gap 0.54 eV are predicted. Importance of considering doping in the ordered ZrNiSn with band gap of 0.54 eV is shown by exploring the possibility of improving $ZT$ upto $\sim 1.2$ for p-type doping. We have calculated the optimal doping concentration which would yield highest power factor for n-type and p-type material which are $7.6 \times 10^{10}$ cm$^{-3}$ and $1.5 \times 10^{11}$ cm$^{-3}$, respectively. The figure of merit for n-type and p-type ZrNiS is estimated which are $\sim 0.5$ and $\sim 0.6$ at 1200 K, respectively. Applying the method of segmentation, efficiency of n-type and p-type materials are estimated. The obtained efficiency of n-type material is $\sim 4.2\%$ and that of p-type material is $\sim 5.1\%$ for cold and hot end temperature of 300 K and 1200 K, respectively. By doping with heavy elements to reduce $\kappa$ for the ordered ZrNiSn the $ZT$ are predicted to be enhanced to $\sim 1.1$ and $\sim 1.2$ for n-type and p-type compounds, respectively at 1200 K. Thus, through this work, emphasis of preparing doped ZrNiSn samples without disorder is theoretically studied by exploring the possible enhancement in $ZT$. The phonon properties are studied by calculating phonon dispersion, total and partial density of states. The estimated Debye temperature is $\sim 382$ K which is close to the experimental value of 398 K. Under the quasiharmonic approximation, the thermal expansion of ZrNiSn is studied. The calculated average linear thermal expansion coefficient $\alpha_{\text{ave}}$ is $\sim 7.8 \times 10^{-6}$ K$^{-1}$. This value is in quite good
agreement with the experimentally reported value of $11.0 \times 10^{-6}$ K$^{-1}$ from the high temperature XRD measurement.

2. Computational details

The DFT calculations are performed using full-potential linearized augmented plane wave (FP-LAPW) method based WIEN2k [18]. Using WIEN2k, the ground state total energy, electronic structure and forces on atoms are calculated. Meta-GGA SCAN [19] is used as the exchange–correlation (XC) functional in this work. For the convergence of electronic total energy, a criterion of $10^{-4}$ Ry/cell is selected. In the ground-state total energy calculations, a dense $k$-point mesh of $50 \times 50 \times 50$ is used in order to get computationally proper transport properties further. The transport properties of the compound are calculated using BoltzTraP [20] program based on semiclassical Boltzmann transport theory. The doping in BoltzTraP is considered through the shift in chemical potential. The lattice parameter used in this work is optimized by fitting Birch–Murnaghan (BM) EOS [21] to energy vs volume curves.

The force constants and phonon properties are calculated using phonopy [22] under supercell and finite displacement method (FDM). In order to calculate the forces on atoms in WIEN2k, a supercell of size $2 \times 2 \times 2$ is constructed of the conventional unit cell. Under an approximation termed quasi-harmonic approximation (QHA) as implemented in phonopy [22] we calculate thermal expansion of ZrNiSn. In QHA the electronic density on phonon frequencies are introduced through harmonic approximation in order to get the thermal properties.

Electronic total energy and force calculations are carried out at 21 volumes points varying from $-5\%$ to $+5\%$ of equilibrium unit cell volume. In order to find out volume corresponding to minimum total free energy at different temperatures (0 K to 1300 K in steps of 100 K), BM EOS is used at each temperature (figure 9(a)). The Brillouin zones of the supercells are sampled by $5 \times 5 \times 5$ $k$-point mesh. A force convergence criteria of 0.1 mRy/bohr is used in the force calculation.

3. Results and discussion

The ZrNiSn compound belongs to the class of half-Heuslers and has cubic $C1_b$ structure with spacegroup F43m (no. 216). In half-Heusler structure theoretically three inequivalent atomic arrangements are possible [10]. The calculated total energy of other two possible atomic arrangements are $\sim 2.5$ eV/f.u and $\sim 3.0$ eV/f.u higher, respectively compared to ground state of the compound which is semi-conducting. In the ground state structure the Wyckoff positions of Zr, Ni and Sn atoms are 4b (1/2, 1/2, 1/2), 4c (1/4, 1/4, 1/4) and 4a (0, 0, 0), respectively. The ground state structure is used for the further electronic structure, transport properties and phonon calculations. The ZrNiSn compound with valence electron per formula unit of 18 satisfies the Slater–Pauling rule for half-Heusler compounds suggesting non-magnetic in nature. In order to know the magnetic ordering, the spin-polarized DFT and magnetic KKR calculations are performed and found that the compound has no magnetic ordering in the ground state. The magnetic susceptibility measured at 300 K by Hlil et al [23] also suggested the compound to be of Pauli paramagnetic character. The experimental value of lattice constant taken from the literature [24, 25] is 6.110 Å. The volume optimization procedure is carried out to find out the ground state equilibrium lattice constant. The equilibrium lattice constant after fitting the BM equation of state to the total energy vs unit cell volume curve is 6.092 Å. The calculated lattice constant using SCAN XC functional is in close agreement with the experimental value.

3.1. Electronic structure

The electronic dispersion of ZrNiSn is calculated using SCAN XC functional which is presented in figure 1. The SCAN is found to describe the electronic dispersion features (group velocity, effective mass) more appropriately relative to LDA, PBE or mBJ and thus giving improved transport properties [26, 27]. As can be seen from the electronic dispersion the ZrNiSn is a semiconductor with an indirect band gap of 0.54 eV. For this compound, mBJ [28] calculation performed is also giving the value of indirect band gap of 0.55 eV. The values of band gaps obtained from SCAN and mBJ match very well with each other and also to the earlier reported value from LDA and PBE [11, 17]. In the figure dashed line in the middle of the gap represents the Fermi level ($E_F$) and the bands that would contribute significantly to transport are numbered from 1 to 4 (referred with symbols B1 to B4 from here on and in table 1). In the ZrNiSn compound, the conduction band minimum (CBM) is at the X-point and the triply degenerate valence band maximum (VBM) at the Γ point which was also seen in case of full-Heusler compounds studied in our earlier work [27]. The degeneracy of bands B2 and B3 can be
observed fully along the \( L-\Gamma -X \) \( k \)-path. This is a useful feature for a thermoelectric material since, more states are available for occupation of charge carriers near the Fermi level. Also, the bands B2 and B3 are narrower causing charge carriers to have more effective mass and thus higher contribution to Seebeck coefficient. The lift in degeneracy of the band B1 with other two bands can be seen on moving away from the vicinity of \( \Gamma \)-point.

The effective mass \( m^* \) of charge carriers in a material is one of the key quantities for understanding the transport behaviour of that material. The \( m^* \) values of charge carriers in terms of mass of electron (\( m_e \)) for bands B1 to B4 are calculated and listed in Table 1. In order to find the \( m^* \), parabola is fitted in the neighbourhood of band extrema where the charge carriers behave more like free particles. In the table, the notation for instance, \( \Gamma -\Gamma L \) denotes the \( m^* \) calculated in the vicinity of \( \Gamma \) point along \( \Gamma \) to \( L \) direction. Clearly, the band B1 is lighter band with lesser \( m^* \) and the charge carrier conductivity will be higher in this band. The bands B2 and B3 being degenerate have same \( m^* \) values in all the directions listed except in \( X-W \) direction. The values of \( m^* \) for B3 are \( \sim 2.42 \) and \( \sim 2.50 \) times larger than \( m_e \) in \( \Gamma -L \) and \( X-W \) directions, respectively. The effective mass for the conduction band B4 is \( \sim 3.56 \) along \( X-\Gamma \) direction indicating lower mobility for electrons in the vicinity of CBM in ZrNiSn.

### 3.2. Transport properties

In this section, the Seebeck coefficient \( S \) and other electrical transport properties of ZrNiSn compound are explained through transport calculations. Using the calculated values of \( S \), an understanding of the experimental \( S \) of the ZrNiSn compound is made. The experimental data of ZrNiSn compound is taken from the work of Shen et al [13] which is presented in figure 2(a). At temperature of 300 K, the calculated value of \( S \) is \( \sim 574 \mu \) VK\(^{-1} \) for the ZrNiSn compound. But, the calculated value is positive and far from the experimental value of \( \sim 125 \mu \) VK\(^{-1} \) at the same temperature. In the experimentally prepared Huesler compounds, generally non-stoichiometry or inter-mixing between two sites are observed. This can make the position of the chemical potential \( \mu \) to shift away from the middle of the gap. Therefore, considering the change in \( \mu \) may be required in order to explain the observed negative value of experimental \( S \). On taking into account the shift in \( \mu \) from the middle of the gap, the best matching corresponding to experimental \( S \) value was found at \( \mu \) of \( \sim 337 \) meV towards conduction band region. The Seebeck coefficient values corresponding to the \( \mu \) of \( \sim 337 \) meV are plotted in figure 2(a). As can be observed from the figure, the calculated \( S \) values are close to experimental values upto \( \sim 500 \) K and above \( 500 \) K starts to deviate from the experimental curve. Also, the magnitude of calculated \( S \) is showing an increasing trend upto 1200 K whereas the experimental data is showing increasing trend only upto \( \sim 700 \) K and above which reduction in \( |S| \) values are observed.

At this point it is important to note that the theoretically obtained band gap (0.54 eV) is higher compared to reported experimental band gap [12] of 0.18 eV and \( S \) of a material is highly dependent on the value of band gap. This may be the reason for the observed differences in the calculated and experimental \( S \). Thus in order to explore the band gap dependence and to understand the observed deviation compared to experimental \( S \), the band gap is set to the experimentally observed band gap \( E_g \) of 0.18 eV [12]. The reduction in \( E_g \) is considered by a rigid shift of conduction bands in transport properties calculation. Such an approach is found to be appropriate under rigid band approximation in some of the earlier works, not expecting much distortion in the bands due to defects or disorder [17, 29]. The variation of \( S \) with chemical potential for ZrNiSn with \( E_g \) of 0.18 eV is plotted in figure 2(b). In the figure, the dashed line represents chemical potential, \( \mu = 0 \) at the middle of the gap for intrinsic ZrNiSn at \( T = 0 \) K. The chemical potentials for the \( n \)-type and \( p \)-type compound with the addition of impurities or doping are represented by positive and negative values in the \( \mu \)-axis, respectively. From the figure one can observe that the best agreement with the experimental value of \( S \) is found for \( \mu \) of \( \sim 156 \) meV at 300 K. The calculated values of \( S \) for the \( \mu \) of \( \sim 156 \) meV are plotted in figure 2(a). The nature of the \( S \) curve thus calculated is showing improvement qualitatively (non-monotonic temperature dependence) compared to that of \( S \) curve calculated with \( E_g \) of 0.54 eV. But, the values of \( S \) are still further away from the experimental value. Here, it is important to note that the \( \mu \) considered till now in calculating \( S \) are only doping dependent and not temperature dependent (fixed \( \mu \)). But, the \( \mu \) in a material is also dependent on temperature and hence the transport properties calculated are going to be depend on it. Therefore, we move on to include the temperature dependence on \( \mu \) along with the doping dependence.

In case of nondegenerate semiconductor \( (E_g \gg k_B T) \) at any temperature \( T \), the number of electrons in conduction band per unit volume \( (n_c(T)) \) and the number of holes in valence band per unit volume \( (p_v(T)) \) are given as [30],

\[
n_c(T) = N_c(T)e^{-(E_c - \mu)/k_BT} \tag{3}
\]

\[
p_v(T) = P_v(T)e^{-(\mu - E_v)/k_BT} \tag{4}
\]

where,

\[
N_c(T) = \frac{1}{4} \left( \frac{2m_e k_BT}{\pi \hbar^2} \right)^{3/2} \tag{5}
\]

\[
P_v(T) = \frac{1}{4} \left( \frac{2m_h k_BT}{\pi \hbar^2} \right)^{3/2} . \tag{6}
\]
Here, $k_B$ is Boltzmann constant, $\mu$ is chemical potential, $E_v$ ($E_c$) is the energy at the CBM (VBM) and $m_c$ ($m_v$) is the geometric mean of the eigenvalues of effective mass tensor at CBM (VBM), respectively. The above relations are for the case when the CBM and VBM are nondegenerate.

But, in case of the degenerate CBM and VBM, the equations for $N_c(T)$ and $P_v(T)$ will be modified as [30],

$$ N_c(T) = \frac{1}{4} \left( \frac{2k_B}{\pi \hbar^2} \right)^{3/2} \sum_{\alpha} (m_{\alpha c}^2 T)^{3/2} \quad (7) $$

$$ P_v(T) = \frac{1}{4} \left( \frac{2k_B}{\pi \hbar^2} \right)^{3/2} \sum_{\alpha} (m_{\alpha v}^2 T)^{3/2} \quad (8) $$

where, $\alpha$ denotes the index of the degenerate band at CBM or VBM indicating a sum over each such minimum or maximum.

Then from the above relations, the chemical potential $\mu$ in case of an intrinsic semiconductor is given by,

$$ \mu = E_v + \frac{1}{2} E_g + \frac{1}{2} k_B T \ln \left( \sum_{\alpha} (m_{\alpha v}^2 T)^{3/2} / \sum_{\alpha} (m_{\alpha c}^2 T)^{3/2} \right) \quad (9) $$

where, $E_g$ is the band gap of the semiconductor.

We employed the above relation to include temperature dependence on $\mu$ to calculate the $S$, electrical conductivity per relaxation time ($\sigma/\tau$) and electronic thermal conductivity per relaxation time ($\kappa_e/\tau$). The values of $m_{\alpha v}$ calculated for the three degenerate valence bands at VBM are 0.35, 0.62 and 0.69, respectively. Similarly, the value of $m_c$ for the non-degenerate conduction band is 0.93. The Seebeck coefficient thus obtained is shown in Figure 2(a). The nature of the $S$ calculated with temperature dependent $\mu$ has not improved much with respect to the one calculated with fixed $\mu$ except for the crossover above 950 K. The possible reason for the deviation compared to the experimental data may be due to temperature dependence of the both band gap [31] and dispersion curves which are not considered here.

In Figure 2(c), $\sigma/\tau$ calculated by considering change in $\mu$ with temperature is shown. The increasing trend of $\sigma/\tau$ in 300–1200 K range can be seen. The $\sigma/\tau$ value is changing from $\sim 0.91 \times 10^{19}$ to $\sim 2.79 \times 10^{19} \Omega^{-1} \text{m}^{-1} \text{s}^{-1}$ in the temperature range considered. The trend of calculated $\sigma/\tau$ by including temperature dependence on $\mu$ is in agreement with the trend of experimental conductivity [13]. Also, the $\kappa_e/\tau$ for ZrNiSn is calculated by considering the temperature dependence on $\mu$ which is shown in figure 2(d). We also extracted the electronic
thermal conductivity $\kappa_e$, from the experimental data of resistivity [13] using the Wiedemann–Franz law in order to compare with the trend of calculated $\kappa_e/\tau$ and to further get the lattice part ($\kappa_{\text{ph}}$) of ZrNiSn from the experimental $\kappa_e$. The nature of the calculated $\kappa_e/\tau$ qualitatively agrees with the experimental $\kappa_e$ of the sample plotted in Figure 2(e).

The above discussion of the results showed the inclusion of the proper band gap value and temperature effect on $\mu$ to explain the transport coefficients of ZrNiSn sample. But, now the question arises what could be the right band gap value of pure ZrNiSn? Because, the experimental values of $S$ and $\rho$ as reported by Schmitt et al [14] at 300 K are $\sim 325 \mu \text{VK}^{-1}$ and $\sim 1 \times 10^{-3} \Omega \text{m}$, respectively. These values are higher compared to that of the work of Shen et al [13]. The magnitude of $S$ in reference [14] is decreasing with increase in temperature and also the behaviour of $S$ is different. Similarly, $\rho$ values in reference [14] are higher compared to that of reference [13] which indicate that effective gap in ZrNiSn sample may be different compared to that of Shen et al [13]. Also, for instance, in the experimentally prepared Heusler samples, there are chances of excess Ni [32–34] or deficiency of Ni leading to non-stoichiometric compound. Other possibility is the mutual substitution between the Sn and Zr atoms leading to Sn/Zr antisite disorder [35] or Ni/vacancy antisite disorder [36]. This defect or disorder may lead to reduction in the overall gap of the compound.

In order to qualitatively check the effects of defect and disorder previously mentioned in ZrNiSn we performed the density of states calculations using Korringa–Kohn–Rostoker (KKR) method under coherent potential approximation (CPA) [37]. In KKR-CPA calculations, the disorder or defect is taken care through an effective medium. Since, none of these atoms have variable coordinates for the Wyckoff positions, the relaxation of atomic positions are not considered. However, it is important to note that in KKR-CPA calculations, the effects due to local relaxations of the lattice are not taken care [38]. Thus, for more accurate quantitative descriptions one can make use of models such as independent sublattice model [38] or effective tetrahedron method [39]. But, such a detailed study is not considered here, concerning the scope of the present work. The calculations showed the appearance of electronic states in the gap region leading to reduction of the effective gap. The effect of Sn/Zr antisite disorder on the size of gap studied by Öğüt et al [11] and Qiu et al [40] also showed the reduction in effective gap. Therefore it appears that experimentally prepared samples in reference [13] is not pure (non-stoichiometric or disordered) and the band gap in pure ZrNiSn may be higher than the reported experimental

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Figure 3. The variation of (a) Seebeck coefficient $S$, (b) electrical conductivity $\sigma$ and (c) electronic thermal conductivity $\kappa_e$ with temperature for ZrNiSn ($E_g = 0.54$ eV). (d) Power factor per relaxation time with change in chemical potential $\mu$. 

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value. The SCAN and mBJ calculations are predicting that pure ZrNiSn may have band gap of \(\sim 0.54\) eV. Therefore, it is interesting to study the thermoelectric properties of pure ZrNiSn and to see how they can be further enhanced.

In this direction the thermoelectric properties of pure ZrNiSn are first systematically predicted. For the calculations, the electronic relaxation time \(\tau_e\) are obtained by fitting the experimental \(\sigma\) and \(\kappa_e\) data. Later, the possibility of achieving higher \(ZT\) and efficiency in ZrNiSn based compounds by doping are explored through power factor calculations. The obtained electronic transport power factor of ZrNiSn with band gap of 0.54 eV are presented in figure 3. The Seebeck coefficient of pure ZrNiSn is shown in figure 3(a). The value of \(S\) is positive suggesting that contribution to thermoelectric voltage in ZrNiSn are mainly from holes even upto 1200 K. The maximum value of \(S\) is \(\sim 443\) \(\mu\) V K\(^{-1}\) at 300 K and starts to reduce with the increase in temperature. At 1200 K, the value of \(S\) reaches \(\sim 58\) \(\mu\) V K\(^{-1}\). The calculated \(\sigma\) and \(\kappa_e\) of ZrNiSn with temperature are shown in figures 3(b) and (c), respectively. Both the \(\sigma\) and \(\kappa_e\) show an increasing behaviour with temperature. Upto \(\sim 600\) K, the value and change in \(\sigma\) (or \(\kappa_e\)) is lower but as temperature increases large increase in \(\sigma\) (or \(\kappa_e\)) can be observed due to the excitation of more charge carriers across the band gap as in the case of a semiconductor.

Enhancing the power factor of a thermoelectric material by doping is one of the strategies to get higher figure of merit. Theoretically, one can predict the value of doping or proper carrier concentration that enhances power factor through the power factor versus chemical potential plot. In order to find the optimal carrier concentration values which can yield higher power factor, we have plotted \(S^2\sigma/\tau\) (PF) as a function of \(\mu\) in figure 3(d). The figure 3(d) shows PF curves at temperatures from 300 to 1200 K. In the figure, the consecutive temperatures from 300 K to 1200 K are to be read in the order of peak height. As can be seen from the figure there are two peaks corresponding to maximum PF at 1200 K. In the n-type region of doping the maximum PF peak is at \(\mu\) of \(\sim 435\) meV. The optimal electron doping corresponding to this \(\mu\) of \(\sim 435\) meV is \(\sim 7.6 \times 10^{19}\) cm\(^{-3}\) which gives the maximum power factor. At 1200 K, the value of PF at \(\sim 435\) meV is \(\sim 100 \times 10^{14}\) \(\mu\) WK\(^{-2}\) cm\(^{-1}\)s\(^{-1}\). Similarly, in the p-type doping region the maximum value of PF can be obtained at \(\mu\) of \(\sim 401\) meV below the middle of the gap. For this value of \(\mu\) representing hole doping the maximum PF value is \(\sim 130 \times 10^{14}\) \(\mu\) WK\(^{-2}\) cm\(^{-1}\)s\(^{-1}\) which is higher than PF obtained from electron doping in this compound. The optimal value of hole concentration needed to attain this maximum PF in ZrNiSn related to \(\mu\) of \(\sim 401\) meV is \(\sim 1.5 \times 10^{21}\) cm\(^{-3}\).

Further, to evaluate the material for thermoelectric application we calculated figure of merit, \(ZT\) for the doped ZrNiSn compounds with optimal electron and hole doping estimated before. The lattice part of thermal conductivity \(\kappa_{ph}\) (table 2) required to calculate \(ZT\) is obtained by subtracting electronic contribution \(\kappa_e\) (figure 2(d)) from the total thermal conductivity data of undoped ZrNiSn from reference [13]. The extracted \(\kappa_{ph}\) is extrapolated to higher temperatures (>1000 K) and used in the calculation of \(ZT\). The \(\kappa_e\) and \(S^2\sigma\) values at the \(\mu\) corresponding to the optimal carrier concentrations are obtained using the electronic relaxation time obtained earlier. The calculated \(ZT\) for both the n-type and p-type doping corresponding to \(\sim 7.6 \times 10^{19}\) cm\(^{-3}\) and \(\sim 1.5 \times 10^{21}\) cm\(^{-3}\), respectively are shown in figure 4 for the temperature range of 300–1200 K. As can be seen from the figure, the \(ZT\) value is increasing with temperature. This nature of \(ZT\) suggests doped ZrNiSn compounds can be used for application in high temperature region. The figure of merit for p-type doping is higher compared to \(ZT\) due to n-type doping. At 1200 K, the value of \(ZT\) are \(\sim 0.5\) and \(\sim 0.6\) for n-type and p-type compounds, respectively. In order to find the elements for doping, we tried Sc, In, Y, Co, Cu, Zn, Sb as n-type or p-type of substitution. Out of these elements tried, Y doping is found to give states close to top of the valence band leading to p-type, while Zn doping is giving states close to the bottom of conduction band leading to n-type doping. This indicates that these elements can be experimentally tried as doping elements. These suggested elements can be doped in appropriate concentration to achieve the higher power factor values.

### Table 2. The lattice part of thermal conductivity \(\kappa_{ph}\) extracted from reference [13] and used in the calculation of \(ZT\).

| Temperature (K) | \(\kappa_{ph}\) (Wm\(^{-1}\)K\(^{-1}\)) |
|-----------------|----------------------------------|
| 300             | 11.13                            |
| 350             | 10.13                            |
| 400             | 9.30                             |
| 450             | 8.57                             |
| 500             | 7.90                             |
| 550             | 7.30                             |
| 600             | 6.75                             |
| 650             | 6.29                             |
| 700             | 5.91                             |
| 750             | 5.57                             |
| 800             | 5.33                             |
| 850             | 5.22                             |
| 900             | 5.19                             |
| 950             | 5.09                             |
| 1000            | 4.99                             |

![Figure 4. The figure of merit \(ZT\) for the doped ZrNiSn compounds as a function of temperature \(T\).](image)
The values of $ZT$ predicted are fairly high for the doped ZrNiSn compounds to be considered for high temperature thermoelectric applications. But, here it is important to note that in predicting the $ZT$, we have used the $\nu_{\text{ph}}$ of the undoped ZrNiSn from reference [13] which is higher compared to its doped compounds. As can be seen in reference [13], doping the Zr site with heavy element Hf and Ni site with Pd one can systematically reduce the thermal conductivity and enhance $ZT$. So, if we use the $\nu_{\text{ph}}$ for the doped sample from the experimental data and consider in $ZT$ calculation, then the predicted $ZT$ for n-type and p-type ZrNiSn compounds at 1200 K can be enhanced to $\sim 1.1$ and $\sim 1.2$, respectively. These value of $ZT$ obtained are higher compared to that of the maximum $ZT$ ($\sim 0.7$) obtained in the work of Shen et al [13]. Therefore, our work highlights the importance of considering doping for the pure ZrNiSn half-Heusler (band gap of 0.54 eV) to get further improvements in $ZT$.

Since, both the n-type and p-type doped ZrNiSn compounds have reasonably good value of $ZT$, it is desirable to consider the two materials for high temperature applications. The n-type and p-type materials can be used as n- and p-type legs in thermoelectric generators (TEGs). Therefore, the assessment of a material for TEG application can be done by calculating its efficiency. An approach of segmentation to calculate the efficiency of thermoelectric materials was given in the work of Gaurav et al [8]. In this method the module is divided into number of segments (or slices) depending on the hot and cold end temperatures ($T_h$ and $T_c$, respectively) and temperature difference $\Delta T$ across the each segment. The details of the methodology can be found in the reference [8]. The efficiency of each module is calculated by keeping the $T_c$ fixed at 300 K and varying the $T_h$ in steps of 100 K up to 1200 K. The efficiency thus calculated for both n-type and p-type legs are plotted in figure 5. As can be seen from the figure the % efficiency of p-type module is higher than the n-type module. For the hot end temperature of 1200 K, the efficiency of n-type module is $\sim 4.2\%$ and that of p-type module is $\sim 5.1\%$. It is to be noted that if the improved $ZT$ values estimated earlier are used, further enhancement in the efficiency can be obtained.

The efficiency is lesser compared to Bi$_2$Te$_3$ or PbTe [8], but the ZrNiSn compounds have other advantages as half-Heusler materials. This compound is thermally stable, has high melting point [41], easy to prepare and due to the non-toxic nature of elements the ZrNiSn based compounds can be considered for high temperature thermoelectric applications [10]. For a proper design of a TEG, considering the thermal expansion of the material becomes an important aspect. Thus, in order to calculate the thermal expansion coefficient and to see how good the thermal expansion in ZrNiSn (which is an unharmonic effect) can be explained by the forces calculated through DFT with supercell-FDM approach and quasi-harmonic approximation, we have performed phonon calculations. The obtained phonon related properties and thermal expansion of ZrNiSn are discussed in the next section.

### 3.3. Phonon properties and thermal expansion

The phonon dispersion of ZrNiSn compound is calculated along high symmetric directions which is shown in figure 6. There are six optical and three acoustic phonon branches as can be seen in the dispersion plot for the ZrNiSn half-Heusler. The number of optical phonon modes per $k$-point are three lesser compared to that of the full Heuslers with formula unit of type $X_3YZ$. The optical and acoustic phonon branches are separated by a small gap of $\sim 1.5$ meV. Around 30 meV there are three branches corresponding to optical phonons of higher energy.

Further, we have calculated phonon total density of states (DOS) and partial DOS to see the contribution of different atoms to acoustic and optical vibrational modes of the spectrum. The figure 7 shows the phonon total DOS per unit cell and phonon partial DOS per atom for ZrNiSn compound. The total DOS plot shows, in the region around $\sim 13$, $\sim 22$, $\sim 30$ meV, three main peaks, respectively. As can be seen from the phonon partial DOS plot, the acoustic vibrational modes are predominantly from the heavier Sn atom. The Ni atom being lighter in mass contributes significantly to the higher energy optical phonons in the neighbourhood of $\sim 30$ meV.

The Debye frequency $\omega_D$ which is a measure of maximum phonon frequency is $\sim 33$ meV in case of ZrNiSn as computed from total DOS. Using the value of $\omega_D$, the calculated Debye temperature $\Theta_D$ for ZrNiSn is $\sim 382$ K. The value of $\Theta_D$
indicates that all the vibrational modes in ZrNiSn are excited above 382 K. The value of $\Theta_D$ for ZrNiSn is relatively lower compared to the $\Theta_D$ of full Heusler compounds studied in our previous work [27, 42]. Rogl et al have reported $\Theta_D$ of 398 K for ZrNiSn compound from sound measurements [43]. The value of $\Theta_D$ calculated in the present work is in quite good agreement with the experimental value. The variation of phonon part of specific heat at constant volume $c_v$ with temperature calculated under harmonic approximation is shown in figure 8. As can be seen from the plot, above 400 K the variation in $c_v$ is almost constant and is quite close to the Dulong–Petit value of $\sim 75$ J mol$^{-1}$K$^{-1}$.

For any material involving in applications where it is subjected to large temperature variations, understanding of its thermal expansion behaviour becomes important. In the design of TEGs where the materials used in modules experience temperature gradient, thermal expansion parameter needs to be taken into account. Therefore, a study of the thermal expansion in ZrNiSn is carried out in the present work. The linear thermal expansion coefficient $\alpha(T)$ of ZrNiSn compound is calculated under quasi-harmonic approximation.

The calculated $\alpha(T)$ for ZrNiSn from temperature 0 to 1300 K is presented in figure 9(a). The figure 9(a) shows, the variation of total free energy with change in volume of primitive unit cell, at a given temperature. Here, the total free energy at a given temperature $T$ and particular volume $V$ is defined as $F = [U_{el}(V) - U_{el}(V_0)] + F_{ph}(T; V)$. The $F$ obtained is the sum of the Helmholtz free energy of the phonon part $F_{ph}(T; V)$ and relative ground state electronic total energy $U_{el}(V) - U_{el}(V_0)$, where $V_0$ is equilibrium volume $V_0$ at 0 K. This $F$ vs volume plot is useful in obtaining the equilibrium volumes at different temperatures. For each curve in figure 9(a), the minimum $F$ point gives equilibrium volume at that temperature. In figure 9(a) each such minimum energy point is connected through the solid (red) line from temperature 0 to 1300 K. Using the obtained equilibrium volume at each temperature from figure 9(a), the variation of primitive cell volumes of ZrNiSn compound with increase in temperature is plotted in figure 9(b). Above $\sim$100 K the volume is increasing monotonically with temperature. The volume of ZrNiSn at 1300 K is increased by an amount of $\sim 2.3\%$ from its room temperature volume. In order to compare with the experimental thermal expansion data in the work of Jung et al [41], we calculated average linear thermal expansion coefficient from the volume vs temperature data in figure 9(b). The average linear thermal expansion coefficient is calculated using the below formula:

$$\alpha_{ave}(T) = \frac{1}{a_{RT}} \left( \frac{a(T) - a_{RT}}{T - T_{RT}} \right),$$

here, $a_{RT}$ is lattice constant at room temperature $T_{RT}$ and $a(T)$ is lattice constant at temperature $T$. The value of $\alpha_{ave}(T)$ calculated is $\sim 7.8 \times 10^{-6}$ K$^{-1}$ in the temperature range 300–1000 K. Experimental value of $\alpha_{ave}(T)$ from dilatometer measurement (313–963 K) is $12.1 \times 10^{-6}$ K$^{-1}$ and from high temperature XRD measurement (323–673 K) is $11.0 \times 10^{-6}$ K$^{-1}$ [41]. The value of $\alpha_{ave}(T)$ calculated under quasi-harmonic approximation using the forces calculated from DFT with supercell-FDM approach is in quite good agreement with the experimentally reported values.

Using the primitive cell volumes at different temperature data in figure 9(b) first, the volumetric thermal expansion coefficient is calculated. The volumetric thermal expansion coefficient is given by $\gamma(T) = 3/9 \times \alpha(T)$. For the cubic structure, considering uniform expansion in three directions [30] the linear thermal expansion coefficient $\alpha(T)$ can be obtained from $\beta(T)$ as $\alpha(T) = (1/3)\beta(T)$. Thus obtained $\alpha(T)$ in the 0 to 1300 K temperature range for ZrNiSn is presented in figure 9(c). The value of $\alpha(T)$ for ZrNiSn is rising rapidly till $\sim 200$ K and reaches maximum value of $\sim 7.9 \times 10^{-6}$ K$^{-1}$ around 450 K. After 450 K, thermal expansion rate in ZrNiSn is reducing upto 1300 K. The calculated $\alpha(T)$ gives a measure of the extent to which change in length can occur in a thermoelectric material during heating or cooling. This quantity can be used in analyzing the thermal stress or thermal fatigue of a thermoelectric material under its working conditions. The product of elastic modulus and linear thermal expansion coefficient is a useful quantity to analyse the thermoelectric materials for thermal fatigue [44, 45]. Lesser value of this product indicates lesser thermal fatigue in that material. Thus, one can take into account this parameter when designing a TEG module or a hybrid TEG using segmentation of two
4. Conclusions

In our work, electronic structure of ZrNiSn is calculated using SCAN XC functional. The effective mass values are calculated at the conduction and valence band extrema under parabolic approximation. The obtained indirect $E_g$ of $\sim 0.54$ eV from SCAN and mBJ are in agreement with previous reports. The experimental $S$ values of a ZrNiSn sample is explained using DFT and transport calculations. The calculated $E_g$ of $\sim 0.54$ eV is found to be inadequate to explain the experimental $S$ of the sample. It is observed that considering the $E_g$ of 0.18 eV improves the nature of the calculated $S$. The need for considering $E_g$ of 0.18 eV to understand $S$ suggested that synthesized sample is not ordered and motivated to explore the possible improvement in TE properties from the ordered ZrNiSn. The calculated $E_g$ of $\sim 0.54$ eV is found to be inadequate to explain the experimental $S$ of the sample. It is observed that considering the $E_g$ of 0.18 eV improves the nature of the calculated $S$. The need for considering $E_g$ of 0.18 eV to understand $S$ suggested that synthesized sample is not ordered and motivated to explore the possible improvement in TE properties from the ordered ZrNiSn.

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