Isoelectronic Sn-Ge substitution effect on electronic and thermoelectric properties of ZrNiSn compounds: a DFT Study

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Abstract. In this work, we have studied the Isoelectronic Sn-Ge substitution effect on electronic and thermoelectric properties of ZrNiSn compounds using the density functional theory and Boltzmann transport equations. The calculation shows that band gap decreases with doping and exhibit semiconductor nature. The negative value of Seebeck coefficient of all systems indicates that conduction is due to electrons. With increase in concentration of Ge, Seebeck coefficient decreases, while electrical conductivity and electronic thermal conductivity increases. At \( x=0.125 \), the maximum value of power is attained at 1200 K, which is equal to \( 9\times10^{-11}V^2SK^{-2}ms^{-1} \).

1. Introduction

Intensive attention has recently been paid to energy conversion using thermoelectric principles, which can directly convert both waste heat and solar energy into electricity. At absolute temperature \( T \), the performance of thermoelectric materials is characterized by dimensionless figure of merit [1], which is defined as

\[
ZT = \frac{S^2\sigma T}{k}
\]

where \( S, \sigma, T, k \) are Seebeck coefficient, the electrical conductivity, absolute temperature, total thermal conductivity respectively.

Efficient thermoelectric materials have high seebeck coefficient, high electrical conductivity and low lattice thermal conductivity. In present time, discovering new classes of materials are great challenge in the field of thermoelectric research. Half-Heusler [HH] compounds are intermetallic alloys [2,3] and interesting in thermoelectric field due to high seebeck coefficient and good chemical stability. At room temperature, the value of seebeck coefficient of MNiSn (M=Zr,Hf,Ti) alloys lies in -200 to -400 \( \mu \)V/K (n-type) range[4,5]. The performance of these materials improves by doping. According to the literature, doping on Sn sites tunes the carrier concentration [6] and on M sites gives mass fluctuations which reduce the lattice thermal conductivity [7]. Thus enhance their properties. For pure ZrNiSn compounds, experimentally it was found that the maximum dimensionless figure of merit about 0.3 achieved at 900K [7]. In Zr_{0.5}Hf_{0.5}NiSn compound, maximum ZT value was achieved about 0.5 at 700K [8]. Recently, R.Akram et al [9] reported that ZT =0.53 achieved at 923 K for compound La_{0.01}Zr_{0.99}NiSn. At 800K, ZT~0.6 was achieved in Zr_{0.5}Hf_{0.5}NiSn while Doping of 20\% Pd in this compound enhance the ZT~0.7 at same temperature [10]. Yuanteng liu et al was found that in Ti_{0.1}Zr_{0.9}NiSn compound doping of 2.5\% Ge gives 70% reduction in lattice thermal conductivity [11]. At 693K, the maximum dimensionless figure of merit 1.5 was achieved in Ti_{0.5} (Zr_{0.5} Hf_{0.5})_{0.5} NiSn_{0.998} Sb_{0.002} by N.
Shutoh et al [8]. From previously study, it is confirmed that ZrNiSn promising acts as good thermoelectric materials like SiGe, PbTe, Bi2Te3 (ZT_max~1). On the theoretical side, using ab initio calculations and the Boltzmann calculations, Yang et al [12] was studied electronic transport properties of ZrNiSn compounds. D. F. Zou [13] et al was investigated the electronic structure and thermoelectric properties of Zr0.5Hf0.5NiSn compound. Theoretical research on half heusler materials is very rare.

To the best of our knowledge, Theoretical calculations as well as experimental investigation for this doped system are not available in the literature. This study might be provide guidance to future researchers.

2. Computational Methodology:
ZrNiSn system has the cubic MgAgAs-type structure, corresponding to (group no. 216) space group. To simulate the ZrNiSn1-xGex compound, we have constructed 2*1*1 super cell which contains 24 atoms (8 Zr atoms, 8 Ni atoms and 8 Sn atoms).

In this study, we adopted same methodology which we have used in our earlier work [14]. The electronic structure calculations were performed using density functional theory (DFT) based on plane wave pseudo potential method as implemented in the Quantum Espresso package [15]. The Local Density approximation (LDA) of Perdew-Wang [16] was used for exchange –correlation functional. The cutoff for the kinetic energy was set to 40 Ry for the plane-wave expansion of the electronic wave functions. The charge-density cutoff was kept at 400Ry and the marzari-vanderbilt cold smearing size was fixed at 0.003 Ry. The Brillouin zone integration was performed using Monkhorst–Pack scheme [17] with 4 × 8 × 8 meshes. The lattice constant of ZrNiSn1-xGex (x=0, 0.125, 0.25) system was optimized until the total energy converged to at least 10^-6 Ry, and the forces between atoms became smaller than 10^-4 Ry/bohr. For the density of state (DOS) calculation, we used tetrahedron method with 16x16x16 denser k-point mesh.

In order to calculate the thermoelectric transport properties, we have used BoltzTraP code [18] which is based on semi classical theory Boltzmann theory.

3. Results and Discussion
3.1. Electronic Structures
The calculated lattice constant of pure system is 6.15Å and this is in good agreement with the experimental work reported by W. Jeitschko et al [19].The calculated band gap of pure and doped ZrNiSn systems are summarized in Table 1. The calculated band gap of pure ZrNiSn compound is 0.622eV which is comparable with the previous theoretical work [20]. In the experimental work, the band gap of ZrNiSn is 0.18eV [21] which is very small as compared to the calculated value. We calculated the band gap for perfect crystal, that’s why our reported value is larger than the experimental value [20]. According to the literature, during the experimental work, the band gap shrink due to structural imperfections such as anti-site defects which are inherent feature of HH compounds [22, 23]. The calculated band structure of ZrNiSn1-xGe (x=0, 0.125, 0.25) systems are depicted in figures 1. In ZrNiSn1,Ge systems, the highest occupied valance band (HOVB) and the lowest unoccupied conduction band (LUCB) are lies at Γ high symmetry point. So that, pure and doped systems are a direct band gap semiconductors. Here occurrence of direct band gap for all systems is due to the band folding because in our work we used supercell. As the concentration of Ge (0≤ x ≤ 0.250) increases, the Fermi level shifts from the bottom of Conduction band to the top of valence band as shown in the fig. 2(d ) The valence electron of Ge and Sn are equal in number, therefore it neither acts as a donor and acceptor. Due to the lower electronegativity of Sn than the Ge, it loses the electron from the outer shell and thus the carrier concentration increases.
Table no. 1 Calculated electronic band gaps of ZrNiSn_{1-x}Ge_x in comparison with previous results

| System       | This work(eV) | Previous calculations(eV) | Experimental values |
|--------------|--------------|--------------------------|---------------------|
| ZrNiSn       | 0.622        | 0.5[20]                  | 0.18[21]            |
| ZrNiSn_{0.875}Ge_{0.125} | 0.619        | ----                     | --------            |
| ZrNiSn_{0.75}Ge_{0.25}    | 0.618        | ----                     | --------            |

To have an explicit understanding of the interaction between the different orbitals of atoms, the total DOS and projected density of states (PDOS) has been calculated and depicted in the Fig. 2 and 3. It’s clear from PDOS that at x=0, 0.125 the bands below 2eV are due Sn s orbitals but at x=0.25 the bands are also due to the Sn s- and Ge s- orbitals and in this range no contribution of all other atoms. At x=0, the bands spans below the Fermi level are due to Zr-d, Ni-d and Sn-p orbitals, in this range Ni-d orbitals give high contribution as compared to other atoms and there are negligible contribution of Zr-s ,Ni-s-p and Sn –s orbitals. Above the Fermi level, at x=0, the bands are due the Zr d ,Sn s and p orbitals but there is negligible contribution due to the orbitals of Ni atom. At x=0.125, the bands spans below Fermi level due to Zr-d,Ni-d,Sn-p and Ge-p and at x=0.25 the band spans due to Zr-d ,Ni-d, Sn-p, Ge-p and all other orbitals contribute negligible. At x=0.125, above Fermi level the bands are due to the, Zr-s, d, Sn-s, p and Ge-p orbitals and at x=0.250 these are due to the Zr-s, d, Sn-s, p, Ge-p, s orbitals.

Fig.1. Calculated Band structure of ZrNiSn_{1-x}Ge_x compound (0 ≤x≤0.25)
Fig. 2. Calculated Density of states of ZrNiSn$_{1-x}$Ge$_x$ compound (0 ≤ x ≤ 0.25)

Fig. 3. Calculated Projected Density of states of ZrNiSn$_{1-x}$Ge$_x$ compound (0 ≤ x ≤ 0.25)
3.2. Thermoelectric properties:

In this subsection, a quantitative investigation on thermoelectric properties of pure and Ge doped ZrNiSn is undertaken. The variation of Seebeck coefficient ($S$) as the function of temperature is depicted in Fig 4(a). For pure and doped system, the sign of Seebeck coefficient is negative, which indicates that the conduction is due to the electrons. For pure system, the value of Seebeck coefficient increases with increase in temperature, but at 1000K it decreases due to presence of minority carriers and our this result is in good agreement with the work reported by H. Mutta et al [7]. The Seebeck coefficient in terms of carrier concentration ($n$) is expressed as:

$$ S = \frac{8\pi^2k_B^2m^*}{3e^2h^2} T \left[ \frac{n}{3n} \right]^{1/3} $$

(2)

Where $k_B$ is Boltzmann constant, $m^*$ is effective mass and $n$ denotes the carrier concentration. According to the equation (2), Seebeck Coefficient is inversely proportional to the carrier concentration. Therefore, the absolute value of Seebeck coefficient of doped systems decreases with increase in the concentration of Ge.

Fig. 4(b) shows the electrical conductivity scaled by relaxation time ($\sigma/\tau$) of pure and doped system as the function temperature. The electrical conductivity in terms of carrier concentration ($n$) and mobility ($\mu$) is given as:

$$ \sigma = ne\mu $$

(3)

Where $e$ is electronic charge and $\mu$ is mobility. Therefore according to equation (3), with increase in concentration, the electrical conductivity increases.

But at high temperature range, there is a minor decrease in the electrical conductivity for pure and doped system. This is due to decrease in the mobility ($\mu \alpha T^{-3/2}$) [24, 25]. According to equation (3), electrical conductivity is not only a function of carrier concentration but also function of mobility. Therefore, decrease in mobility results into decrease in electrical conductivity for all systems. For pure system, our calculated electrical conductivity follows the same trend reported by D. F. Zou et al [13].

Fig 4 (c) shows the electronic thermal conductivity of ZrNiSn$_{1-x}$Ge$_x$ ($0 \leq x \leq 0.250$) as the function of temperature. The electronic thermal conductivity ($k_e$) in terms of carrier concentration ($n$) expressed as:

$$ k_e = \frac{n\pi^2\tau k_B^2}{3m^*v_e} $$

(4)

In previous subsection, (figure 2(d)) we discuss that with increase in concentration of Ge ($0 \leq x \leq 0.250$) Fermi level and band gap also decreases (table1). The availability of states near the fermi level with increase in concentration results into more thermal excitation of electrons at all temperature ranges. Therefore, at all temperature range, addition of more thermal excited charge carriers increases charge carriers concentration in the conduction band. According to equation (4), electronic thermal conductivity directly depends upon carrier concentration ($n$), therefore electronic thermal conductivity increase with increase in the concentration. In our work, the calculated value of the electronic thermal conductivity for pure system follows same trend as reported by Liu et al [26].

To finalized, our study, we calculate the power factor scaled by relaxation time ($S^2 \sigma/\tau$) of ZrNiSn$_{1-x}$Ge$_x$ system which is equal to the product of square of Seebeck coefficient and electrical conductivity:

$$ P= S^2\sigma $$

(5)

The calculated power factor of pure and doped system as the function of temperature is shown in Fig. 4(d). For pure system, the power factor follows the same trend as reported by Liu et al [26]. At $x=0.125$, the maximum power factor is attained. In doped systems, the enhancement in the power factor is due to increase in the electrical conductivity. In this work, we conclude that electrical conductivity plays a major role to enhance the power factor.
Fig.4: Variation of (a) Seebeck coefficient ($S$) (b) Electrical conductivity ($\sigma/\ell$) (c) Electronic Thermal conductivity ($k_e$) (d) Power factor ($S^2\sigma/\ell$) with temperature.

4. Conclusion:

In this work, an attempt is made to employ first-principle calculations in order to predict the effect of Ge substitution on Sn sites in ZrNiSn half heusler system. As concentration of Ge ($0 \leq x \leq 0.250$) increases, Seebeck coefficient and band gap decreases. But the electrical conductivity and the electronic thermal conductivity increases. The increase in the carrier concentration is due to lower electronegativity of Sn which increase the electrical conductivity and electronic thermal conductivity. The negative sign of Seebeck coefficient of all systems indicates that the conduction is due to electrons. The maximum power factor is achieved at $x=0.125$.

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