DFT study of ZnSb thermoelectric material and its thermoelectric properties.

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Abstract:-

*ZnSb is a binary compound of zinc antimonide thermoelectric material. It can work in room temperature range or higher temperatures from 300K to700K. It is an intermetallic semiconductor compound in nature. This paper presents the first principle study (DFT) of undoped ZnSb material and investigated the crystal structure, electronic structure and band gap dependent properties like Seebeck coefficient, electrical conductivity, thermal conductivity, power factor at room temperature and higher temperatures. The power factor increases from 2.59 * 10^{-3} W/m.K^2 to 6.13*10^{-3} W/m.K^2. It is a higher reported value of PF not reported by any other research.*

Keywords- **DFT, ZnSb, electronic structure, Seebeck coefficient, electrical conductivity, power factor**

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1. Introduction:-

Thermoelectric materials work on the phenomenon of the Seebeck effect and the Peltier effect. Conversion of heat into electricity is known as the Seebeck effect. The conversion of heat possible by a thermocouple, this thermocouple made by two different types of heat reservoir, one sink and another one is a source. The temperature difference between source and sink creates voltage difference and this may cause of Seebeck effect (ΔV/ ΔT) [1]. The total performance of the device is represented by the thermoelectric figure of merit ZT.

$$ZT = \frac{S^2\sigma}{(ke+kl)}T \quad \text{---------- (1)}$$

Where Z is the Figure of merit, T is the absolute temperature, S is the Seebeck coefficient, σ is the electrical conductivity, k_e is the electronic thermal conductivity and k_l is the lattice thermal conductivity [2].

ZnSb thermoelectric material belongs to pbca space group 61. It has orthorhombic crystal structure. This contains $8Zn^{2+}$ cations and $4Sb^{24-}$ dimers per unit cell. ZnSb possesses higher power factor as compared to β-Zn_4Sb_3, but it has relatively high thermal conductivity because of simple crystal structure. This leads to overall low TE performance [3]. The ZnSb thermoelectric material has significant thermoelectric properties like it can work at medium temperature range (450 -800K) and utilize waste heat of industry for their applications [4, 5]. As compared to Zn_4Sb_3, ZnSb is phase stable and has relatively high carrier mobility and seebeck coefficient, so yielding a high power factor [6]. Zn-Sb alloy was used for fabricating the thermoelectric generators since 1870 [7]. A large interest in ZnSb followed and was benefitted by the progress

on semiconductors since 1950s. The thermoelectric generator prototype built by p-ZnSb and n-$Bi_{91}Sb_9$ with an efficiency of 0.63% [8].

2. DFT Model and Methodology

2.1 Crystal structure:-

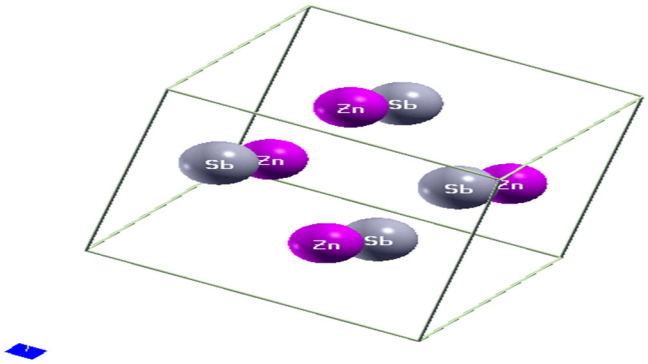

Figure 1, Unit cell structure of ZnSb, pink for Zn, grey for Sb.

DFT is a computational quantum mechanical modelling used in Physics, chemistry and material science for the investigation of electronic structure of many body systems. This paper used this modelling for the investigation of ZnSb thermoelectric material. This material belongs to the Pbca space group no. 61 with an orthorhombic crystal structure. For the simulation and modelling of crystal structure and its parameter, used quantum espresso [9] open-source package for simulation and modelling of material [10]. Initially taken a=6.2016 A^0, b=7.7416 A^0, and c=8.0995 A^0 for self consistency calculation (SCF) [11] and uniform k-point grid. It has 8 no. of atoms/unit cell. Set kinetic energy cut-off to 44 Ry. And charge density cut-off to 352 Ry. Where Ry (Rydberg) is the unit of Energy. This structure optimized by Vanderbilt ultrasoft pseudopotential and Perdew-Burke-Ernzerhof (PBE) energy exchange-correlation functional [12] and the structure was successfully conserved after 13 iterations. This unit cell contains 4 no. of Zn atoms and 4 no. of Sb atoms.

2.2 Electronic (Band) structure:-

The energy gaps of the semiconductors are used in thermoelectric energy convertors is rather small; this leads to the possibility of minority carrier conduction. The maximum seebeck coefficient of a material is closely related to the energy gap. The calculation required to know the relative carrier concentrations and mobilities of two types of carriers. Here, is a relation between the carrier concentration and reduced Fermi energy [13].

$$n = 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2} \exp(\eta_n) \text{ ---------- (2)}$$

$$p = 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2} \exp(\eta_p) \text{ ---------- (3)}$$

Where η_n and η_p are connected together and the energy gap E_g,

$$\eta_n + \eta_p = - \frac{E_g}{kT} = - \eta_g \text{ ---------- (4)}$$

Parameter C is define as

$$C = \left(\frac{\mu_n}{\mu_p}\right)\left(\frac{m_n^*}{m_p^*}\right)^{3/2} \text{ ---------- (5)}$$

Where m_n^* and m_p^* are the density of states masses for the electrons and holes. Then

$$\frac{\sigma_n}{\sigma_p} = C \exp(\eta_n - \eta_p) \text{ ---------- (6)}$$

Maximum seebeck coefficient will be found when the Fermi level lies sufficiently far from both the valence and conduction bands for classical statistics. Exceptional cases will also possible when energy gap is very small or when the parameter C is either very large or very small [14].

In this study, Band structure computed by taking 8 high symmetry k points and 40 k-points in between each set of k -point's grid and set occupation to fixed. In figure 2, a total of 80 bands were computed in this calculation. After 13 iterations, the computed band gap is 0.3962 eV the result best match with [15, 29]. Further perform the DOS and Non-SCF calculation for obtaining the Fermi energy. So, increase the k - point's grid by 12x12x12.

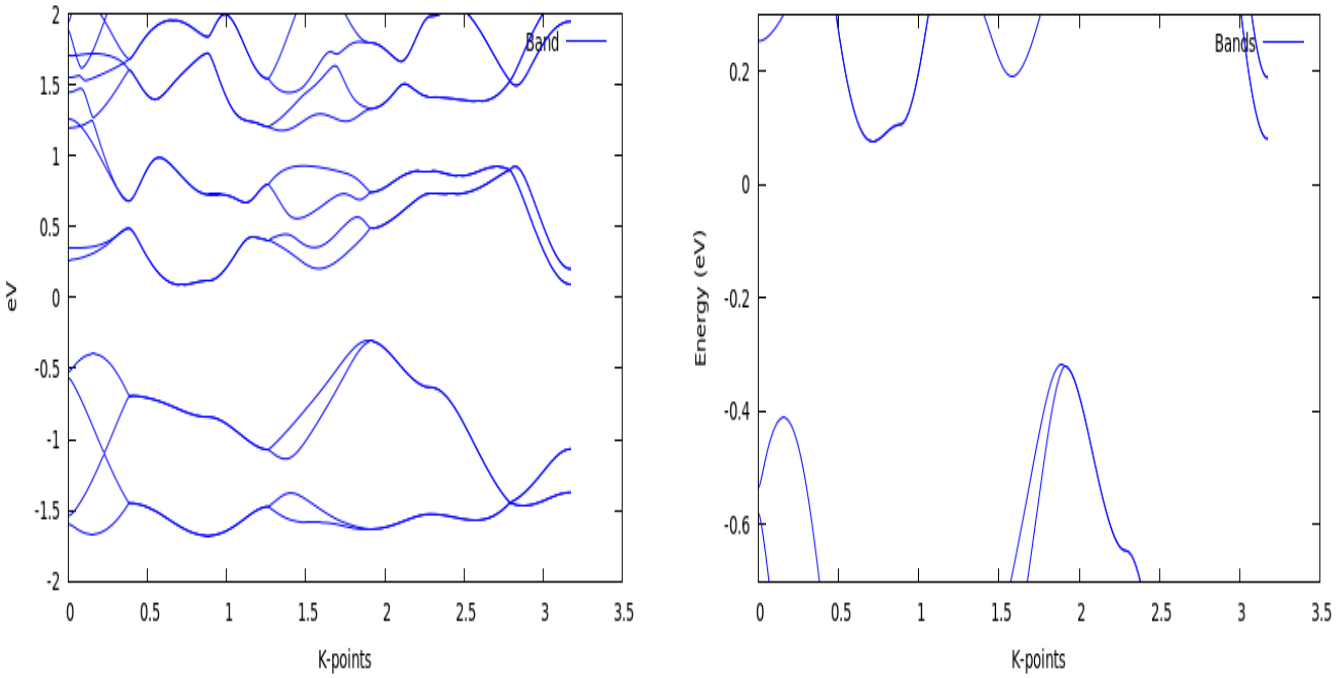

Figure 2, Electronic structure (Band Gap) Eg= 0.3962 eV

3. Methodology to improve ZT

It is important to enhance the figure of merit (ZT) of the material. For doing that work there are two ways one is to decrease the thermal conductivity K [16-20] and second is to increase the power factor ($S^2\sigma$) [21-22]. For reducing the thermal conductivity, use to embed

nanostructure into the bulk materials [20] and for increasing the thermopower S or enhancing the power factor is done by improving the carrier concentration and resonant distortion [23]. It is experimentally proved by Zau et al., the introduction of Cu_3SbSe_4 nano inclusions increases the thermopower S, by EFM [24]. So, both resonant eDos distortion and EFM used separately to enhance the Seebeck coefficient.

4. Result and discussion

4.1 Transport (Thermoelectric) Properties:-

Transport Properties were calculated by using semi-classical Boltzmann's Transport properties calculation package BoltzTraP2 [25]. It used a smoothed Fourier interpolation algorithm to calculate band gap dependent properties. Transport properties in semiconductors depend on various parameters like Transport coefficients, electron distribution, and electron scattering mechanism. The Transport process involves a flow of charge or energy or both. These flows arise due to external causes like an electron field and temperature gradient known as forces. So the sum of flow of electron and flow of energy can be written as W [26].

$$\vec{w} = (\pi - \frac{\mu}{e})\vec{\imath} - \lambda . gradT \quad \text{---------- (7)}$$

Second parameter is electron distribution, may be by external fields, diffusion and collision process in Boltzmann equation.

$$\frac{df}{dt} = (\frac{\delta f}{\delta t})_{field} + (\frac{\delta f}{\delta t})_{diff} + (\frac{\delta f}{\delta t})_{coll} \quad \text{---------- (8)}$$

Third parameter is electron scattering, this scatter electrons are phonons. If a material has more than one number of atoms per unit cell than optical phonons take part in the scattering [D.M.Rowe ed 26]. The scattering of phonons solve by electron distribution. In this scattering elecron-phonon system produces entropy.
Here, plot the graph between chemical potential and seebeck coefficient in fig. 3. Fermi energy adjusted manually to plot the Seebeck coefficient, and refined fermi energy is subtracted from the obtained chemical potential (μ-Ef) for smoothing of the graph. Taken (μ-Ef) on x-axis and Seebeck coefficient on y-axis of the graph. For the calculation of Boltzmann's Transport properties, used constant relaxation time (τ), which was equal to 10^{-14} sec [25, 28].

4.1.1. Density of States:-

DOS represents the number of electron states per unit volume per unit energy at a particular energy level. DOS generally determine spacing between energy bands for semiconductors. Eq.9 is used for the calculation of Density of states of bulk (3-d) materials.

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{Eg - E} \quad \text{---------- (9)}$$

4.1.2. Electrical Conductivity:-

Electrical conductivity is the product of charge carriers and their mobility.

$$\sigma = ne\mu \quad \text{---------- (10)}$$

Mobility is given by

$$\mu = e\tau / m_e \quad \text{----------(11)}$$

Where μ is the mobility of the carriers, m_e is the effective mass and τ is the mean scattering time. The carriers thermally excited across the band gap for the occurrence of conduction.

$$\sigma=\sigma_0 \exp(+Eg/K_BT) \quad \text{---------- (12)}$$

Conductivity is the resultant of both the electrons and holes.

$$\sigma=ne\mu_e + pe\mu_h \quad \text{---------- (13)}$$

Where n is the carrier concentration of electrons, μ_e is the mobility of electrons, p is the carrier concentration of holes and μ_h is the mobility of holes. two methods are there to obtain high electrical conductivity is that one way is very small or narrow band gap to excite the electrons across the $Eg < K_BT$. Second is by using very high mobility carriers [27 Tritt T.M.]. Fig.3 Represent the electrical conductivity with respect to temperature in kelvin. The electrical conductivity is found to be 9.84 x 10^5 (σ/τ) (1/ohm.m) at 300K and 1.10 x 10^6 (1/ohm.m) at 700K. The graph represents the continuous increment in the electronic conductivity with respect to the incremented temperature. The 10^6 range of the electrical conductivity shows that metal like electrical conductivity [31].

4.1.3. Seebeck Coefficient:-

Seebeck coefficient is known as thermopower or thermoelectric power of material. It is a magnitude of an induced voltage with respect to the temperature difference across the material which induced by Seebeck effect. The Seebeck coefficient is defined as:-

$$S = \Delta V / \Delta T \quad \text{---------- (14)}$$

It is also known as the heat per carrier over temperature or in other words entropy per carrier.

$$S \approx C / q \quad \text{---------- (15)}$$

Where C is the specific heat and q is charge of carrier [Chaiken 1990]. In semiconductors, a charged particle first excite across the band gap Eg. In this case, thermopower is given by the heat per carrier is a product of electronic specific heat and temperature divided by number of carriers (N)

$$S \approx C_{el}\, T/N \quad \text{---------- (16)}$$

$$S \approx \frac{C_{el}}{Q} \approx \left(\frac{K_B}{e}\right)\frac{E_G}{K_BT} \quad \text{---------- (17)}$$

Where, E_F is the fermi level or chemical potential related to the energy. The thermopower larger than the characterize value 87 μV/K and increases with decreasing temperature and vice-versa. In semiconductors exists both type of conduction either by electrons or holes. Negative thermopower by electron contribution and positive thermopower by holes contribution [27 Tritt,T.M.]. Fig. 4, Represents the Seebeck Coefficient with respect to the temperature. Seebeck coefficient shows the continuous increment with respect to the incremented temperature range. It

is 148.9 μV/K at 300K and 177.7 μV/K at 700K. This result best match with result of Reference [15].

4.1.4. Thermal conductivity:-

Thermal conductivity is known as the transfer of heat through a material, either by electrons or phonons.

$$K = K_L + K_E \quad \text{---------- (18)}$$

Where, K_L and K_E are the lattice and electronic thermal contributions respectively. According to Wiedemann-Franz relationship thermal conductivity and electrical conductivity is related to each other.

$$K_E = L_0 \sigma T \quad \text{---------- (19)}$$

The Lorentz number is given by

$$L_0 = \frac{\pi^2}{3}\left(\frac{K_B}{e}\right)^2 \text{---------- (20)}$$

Where, $L_0 = 2.45 \times 10^{-8}\ V^2K^{-2}$ assume an elastic scattering mechanism. So that mean scattering time of electrons and phonons is the same. One of the important factors is to minimize the thermal conductivity. Thermal conductivity can be modifying by chemical substitutions or alloy scattering of phonons. According to slack 1979 the concept of minimum lattice thermal conductivity is,

$$K_L \approx V_s C L_{ph} \quad \text{---------- (21)}$$

Where, C is the heat capacity, V_s is the velocity of sound and L_{ph} is the mean free path of phonons. Fig. 5, Represents the thermal conductivity with respect to temperature. At 300 K, thermal conductivity is 0.210 W/m K and when the temperature raises thermal conductivity increases and reported 0.877 W/m K at 700 k temperature. Due to high thermal conductivity ZnSb does not have a high figure of merit (ZT).

4.1.5. Power Factor:-

The power factor is defined as $S^2\sigma$ and S and σ both are strongly dependent on carrier concentration (typically around $10^{19}\ cm^{-3}$) doping of a suitable material will enhance the value of ZT and power factor [27 Tritt, T.M.]. Fig. 6, Represents the power factor with respect to temperature. As the temperature increases, the power factor of the material also increases. The power factor is 2591 μW/ (mK^2s) $x10^{14}$ at 300K and 6138 μW/ (mK^2s) $x10^{14}$ at 700 K temperature. The obtained power factor is high enough because of high electrical conductivity. These results are more than the experimental results of [15].

The figure of merit is known as the thermoelectric efficiency. The BoltzTraP code could not calculate the lattice thermal conductivity because of constant relaxation time τ and only electronic thermal conductivity is calculated. Z is strongly dependent on the phonon scattering

and grain boundary scattering mechanism. At a time best thermoelectric materials are semiconductors because of Fermi level is close to the band edge [29]. This type of material has the value of ZT≈ 1. The value of figure of merit can be increased by increasing seebeck coefficient and electrical conductivity or by decreasing the lattice thermal conductivity.

Fig.7, Represents the variation in power factor with respect to carrier concentration. At the particular carrier concentration of holes means at ~3 x 10^{22} cm^{-3}, the power factor goes to increase. At this point, the power factor reaches a value. When the temperature is 300K and achieves 2906 μW/ (mK^2s) x10^{14} and gradually increases with an incremented temperature range and achieves 6195 μW/ (mK^2s) x10^{14} at 700K. Usually, the state-of-the-art thermoelectric materials are heavily doped with carrier concentrations of the range of 10^{19} -10^{21} cm^{-3} [5]. Doping is an effective method to improve the thermoelectric performance of the bulk material.

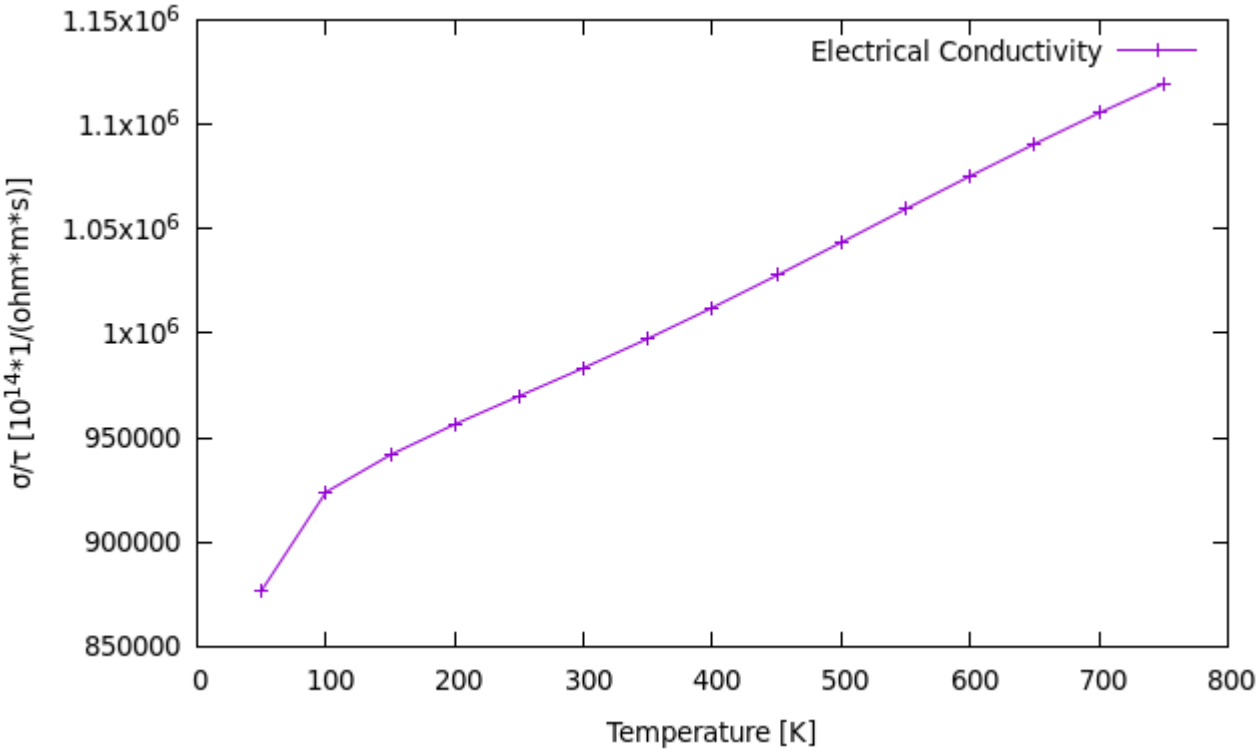

Figure 3. Electrical conductivity with respect to temperature.

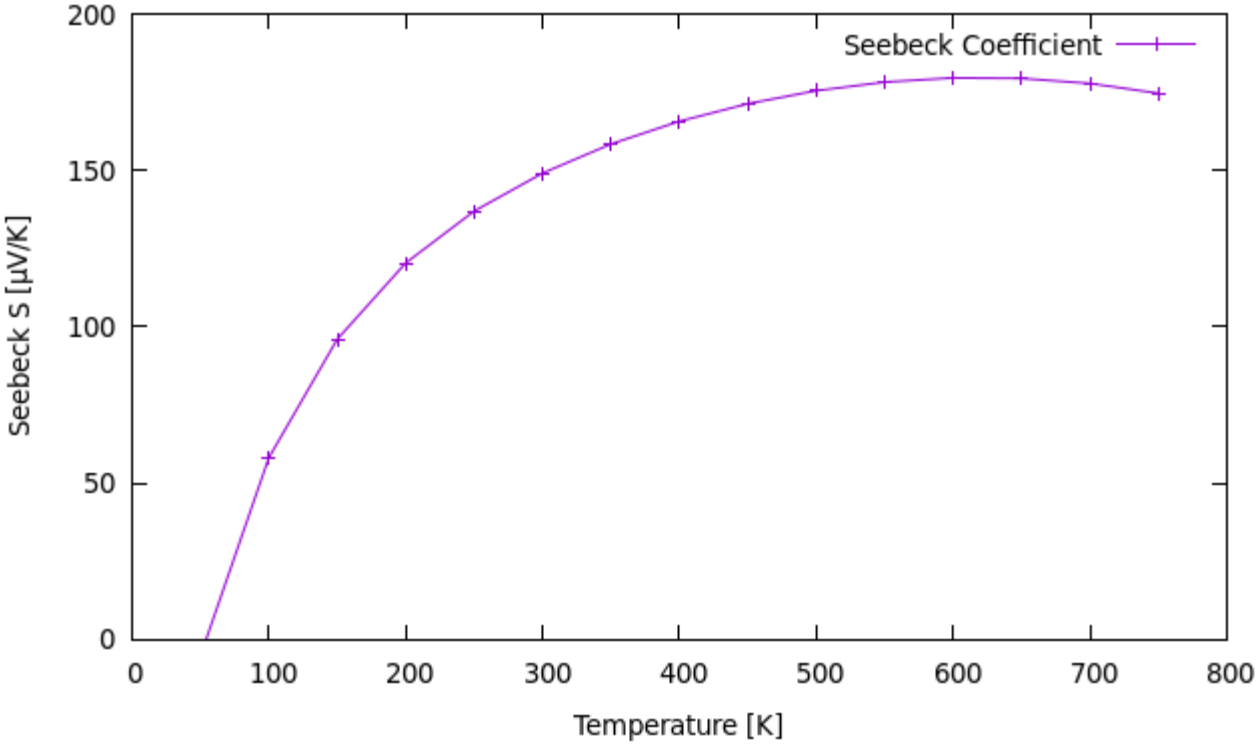

Figure 4. Seebeck coefficient with respect to temperature.

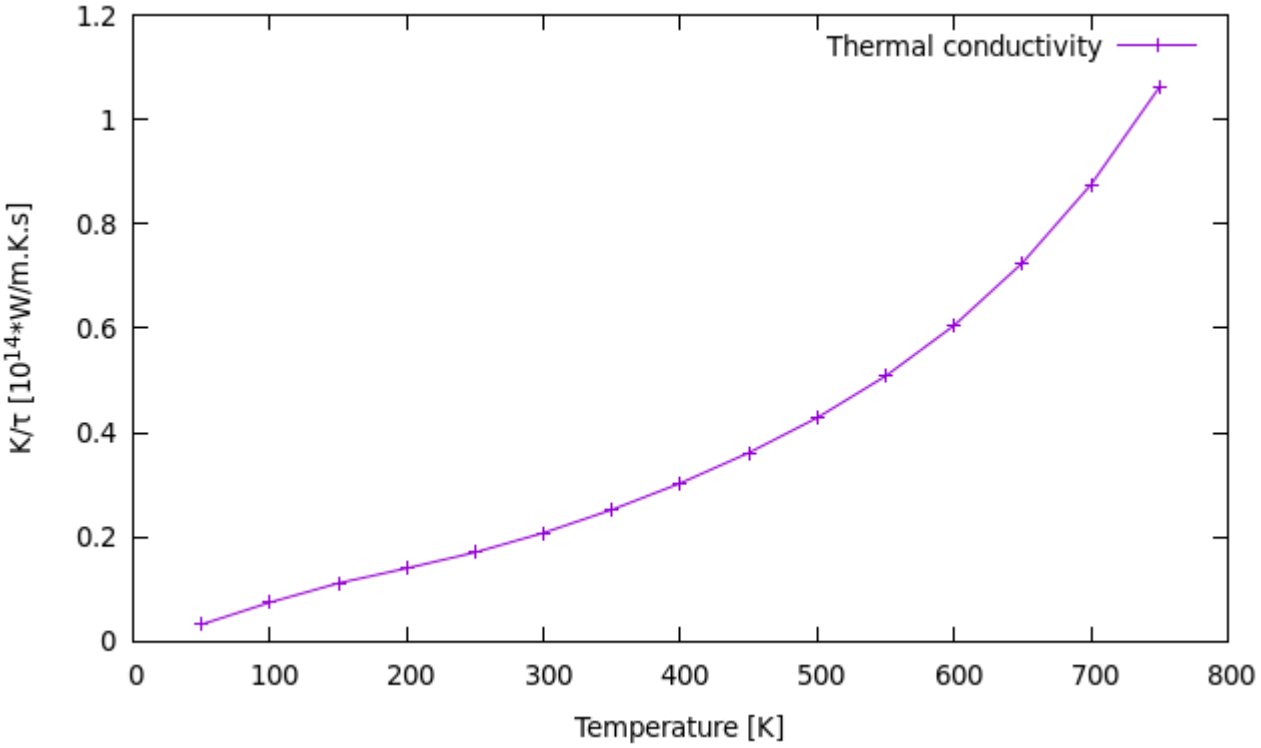

Figure 5. Thermal conductivity with respect to temperature.

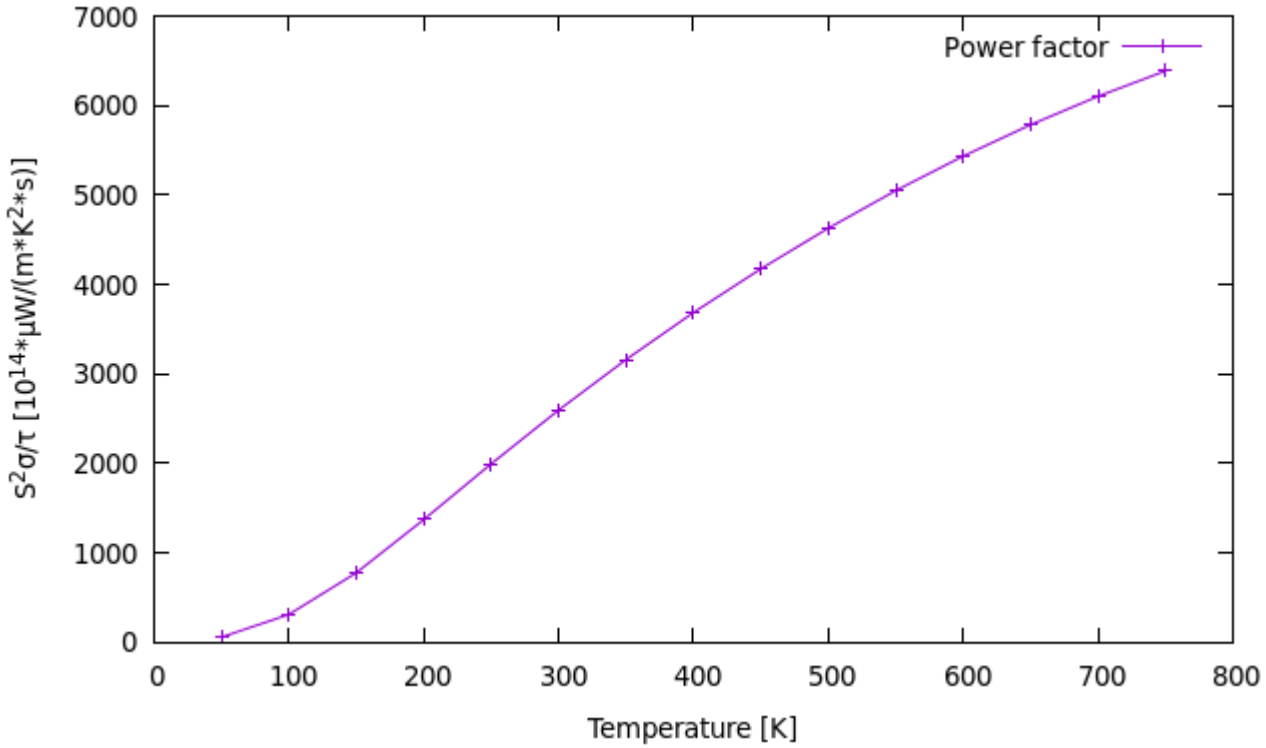

Figure 6. Power factor with respect to temperature.

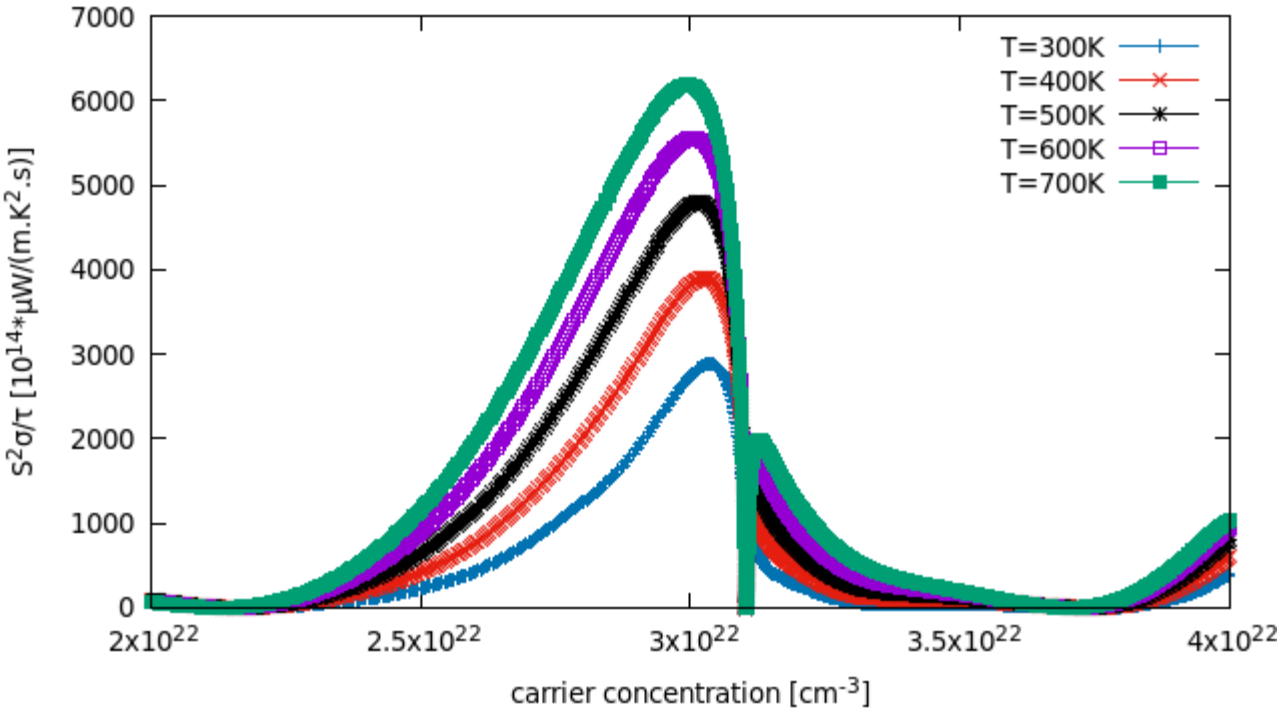

Figure 7. Power factor with respect to carrier concentration

The First principle DFT study found, listed parameter followed by table 1.

Table 1

Investigated parameters	ZnSb at 300K	ZnSb at 700K	Outcomes of this research best match with others
Conductivity Type	p	p	p [30]
Electrical Conductivity (σ/τ) [1/ohm.m.s x 10^{14}]	9.84 x 10^5	1.10 x 10^6	10^4 [30]
Carrier concentration N (cm^{-3})	10^{22}	10^{22}	
Seebeck Coefficient S (μV/K)	148.9	177.7	353 at 300K [15]
Thermal Conductivity (K/τ) [10^{14} x W/m.K.s]	0.210	0.877	0.05519 at 300 K [15]
Power Factor $S^2σ/τ$ [μW/(mK^2s)x10^{14}]	2591	6138	2.81x10^{-3} W/mK^2 at 300 K [15]

5. Conclusion

The undoped ZnSb is a p-type semiconductor thermoelectric material. Simulation and modelling of unit cell structure of ZnSb done in this research, and found the band structure of that material which is very small band gap according to thermoelectric performance. It can perform very well at room temperature and high temperatures. There is good carrier concentration of holes to achieve a higher power factor. It corresponds to ~3 x 10^{22} cm^{-3} holes at 300 – 700 K, at this concentration achieves the best results match with experimental values. The electrical conductivity is 10^2 times more.The power factor increases from 2.59 * 10^{-3} W/m.K^2 to 6.13*10^{-3} W/m.K^2. It is a higher reported value of PF not reported by any other research. All the studies indicate that this material is best performing at room temperature range (300 K). By appropriate change in the carrier concentration of holes or by doping a competitive material could be achieves better results of (ZT) figure of merit.

Competing Interests:-
The authors declare that there are no competing interests regarding the publication of this paper.

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