

**THERMOELECTRIC PROPERTIES OF XFeSb (X=Ta, Nb)
HALF-HEUSLER COMPOUNDS FROM FIRST PRINCIPLE**

BY

AHMED RIDWAN ADESOYE

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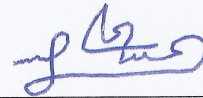
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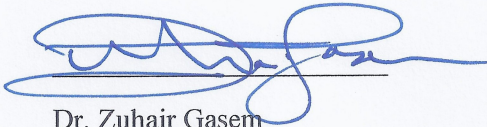
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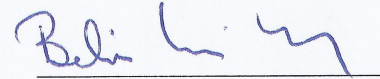
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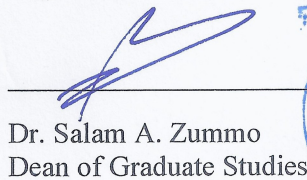
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(Advisor)



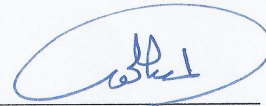
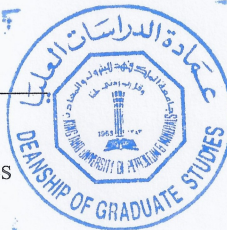
Dr. Zuhair Gasem
Department Chairman



Dr. Bekir Yilbas
(Member)



Dr. Salam A. Zummo
Dean of Graduate Studies



Dr. Abdellah Al-Sunaidi
(Member)

30/12/19
Date

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This work is dedicated to Almighty Allah for giving me the grace to complete my MSc. programme and for his blessings on me and the entirety of my family.

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ABSTRACT

Full Name : [Ahmed Ridwan Adesoye]
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Half-Heuslers (HH) are intermetallic compounds which have drawn a significant research interest over the past decades and have been widely studied as potential materials for thermoelectric applications. This present work focuses on the investigation of the thermoelectric properties of pure and doped XFeSb (X=Ta, Nb) half Heusler compounds from first principle and semi classical Boltzmann theory. Rigid Band Approximation (RBA) method and Supercell approach were employed to investigate the thermoelectric properties of XFeSb. Very low figure of merit values of ~ 0.021 and ~ 0.002 were recorded at 950K for pure TaFeSb and NbFeSb respectively. These values increased to ~ 0.355 and ~ 0.454 for the Mn-doped TaFeSb and Co-doped TaFeSb respectively. Also, the zT values for NbFeSb increased to ~ 0.254 and ~ 0.040 for the Mn-doped NbFeSb and Co-doped NbFeSb respectively all at 950K. The results obtained also showed that XFeSb did not show rigid band behavior.

ملخص الرسالة

عنوان الرسالة: دراسة للخصائص الكهروحرارية لمركبات Half-Heusler وبالتحديد مركبات XFeSb ($\text{X}=\text{Ta}, \text{Nb}$) باستخدام المحاكاة بطريقة (المبدأ الأولي – first principle)

التخصص: علم وهندسة مواد

تاريخ الدرجة العلمية: ديسمبر 2019

(Half-Heuslers) هي مركبات بين فلزية " Intermetallic " حازت على اهتمام واضح في مجال البحث العلمي خلال الأعوام الماضية، وقد درست بشكل موسع كمواقد قابلة للاستخدام في التطبيقات الكهروحرارية – تحويل الحرارة إلى كهرباء والعكس-. البحث الذي بين أيدينا يركز على استكشاف الخصائص الكهروحرارية لمركبات " XFeSb ($\text{X}=\text{Ta}, \text{Nb}$) " النقية والمعالجة بالتطعيم، وهذه المركبات من نوع Half-Heusler سنقوم بدراستها بالمحاكاة على الحاسب باستخدام (المبدأ الأولي) و (نظرية بولتزمان نص الكلاسيكية). في هذا البحث سننهج طرقتي (المجموعة الجامدة التقريبية – Rigid band approximation) و (الخلية الكبرى – Supercell) لاستكشاف الخصائص الكهروحرارية للمركبات المذكورة آنفا. حصلنا من خلال بحثنا على قيم منخفضة لـ (figure of merit) – والذي يعبر عن كفاءة المادية كهروحراريا- وكانت القيم قرابة 0.021 و 0.002 في درجة حرارة 950 كلفن لمركبات TaFeSb و NbFeSb على التوالي. ارتفعت هذه القيم لمركب TaFeSb إلى 0.355 و 0.454 بعد التطعيم بالمنجنيز للقيمة الأولى، والتطعيم بالكوبالت للقيمة الثانية. كذلك ارتفع هذه القيم لمركب NbFeSb إلى 0.254 و 0.040 بعد التطعيم بالمنجنيز للقيمة الأولى، والتطعيم بالكوبالت للقيمة الثانية، كلها عند درجة حرارة 950 كلفن. كل هذه النتائج أشارت في النهاية كذلك إلى أن مركبات XFeSb لا تتبع في سلوكها إلى اتباع طريقة (المجموعة الجامدة).

CHAPTER 1

INTRODUCTION

Generation of electricity from heat has been a subject of great interest to scientists and engineers ever since Seebeck discovered the flow of charge due to temperature gradient in the 1820's [1], [2]. This phenomenon generally referred to as 'Thermoelectricity' became so appealing to researchers because it posed the possibility of converting waste heat into useful electrical energy. Advancement in this field has made possible the realization of thermoelectric power generator, thermocouple, watches driven by body heat etc. In fact, people have thought of forming a hybrid system of solar panel and thermoelectric generator to take full advantage of the heat and light energy from the sun[3], [4]. However, one of the major drawbacks in this field is the fact that most of the materials which have been identified to serve this purpose (usually referred to as the thermoelectric materials) produce a very little amount of electrical energy which limit their use for high electrical energy generation. Thermal stability of the material used is also important and poses a great challenge. Some of the materials which have been identified in the literature as potential materials for thermoelectric applications include but not limited to ; 2-D materials [5]–[7], Skutterudite [8], [9], Oxides[10], [11]. A special type of intermetallic compounds generally referred to as Half Heuslers have also been reported as good thermoelectric materials. Ever since the discovery of this special class of intermetallic compound by Heusler in 1904. Many authors have worked on theoretical calculations to predict thermodynamic stability of over a thousand of these compounds some of which were later synthesized in the

laboratory. Other authors have also focused on predicting the thermoelectric properties of these compounds from first principle calculations using Density Functional Theory (DFT). The advantage of using this method is that it is more convenient, less expensive and reduces the time of discovery. Very recently, Zhu et.al predicted the stability TaFeSb half Heusler compound from DFT calculation, synthesized this compound in the laboratory and then studied its thermoelectric properties. It was reported in their work that this compound possesses zT as high as 1.5 [12], [13]. This value of 1.5 was remarkable as this was higher than most of the previously reported zT values for the other class of materials. As reported by Masood et al. in their review [3], that a zT value >2 is required for thermo power application while a $zT > 3$ is required for cooling applications. Therefore, it is imperative to carry out more fundamental research in order to understand and engineer the structure of this class of materials. As this will increase their potential for thermoelectric applications. In this work, we focus on elucidating the thermoelectric properties of doped TaFeSb and a similar compound NbFeSb by carrying out first principle calculations from Density Functional Theory (DFT). The following subsections give the fundamentals of thermoelectricity, a review on thermoelectric materials and the basics of the computational method used to study the thermoelectric properties of materials.

1.1 Thermoelectric Generator and the Conversion Efficiency

A thermoelectric generator is the one which is able to generate electrical energy from thermal energy or from temperature gradients. This usually comes in thermoelectric modules being composed of a matrix formed by multiple thermoelectric joints usually

connected in series to increase the output voltage and parallel to increase the output current. Each junction in a thermoelectric generator consists of both p-type material and n-type material. The junctions are electrically connected in series and thermally connected in parallel usually by copper conductor and are surrounded by a ceramic cover as shown in figure 1 below. Commercially available thermoelectric modules have various specifications according to their applications. These may vary from 4mm thick and 3mm wide, up to 5mm thick with 60 mm. The range of heat transfer can be between 1W to 125 W [14], [15]. The conversion efficiency of a thermoelectric generator which is the fraction of heat energy that can be converted into electrical energy and the maximum output power density can be obtained from equations 1 and 2 below respectively;

$$\eta_{max} \frac{T_h - T_c}{T_h} \times \frac{\sqrt{1 + zT} - 1}{\sqrt{1 + zT} + \frac{T_c}{T_h}} \text{---(1)}$$

Where T_h is the Temperature at the hot side, T_c is the Temperature at the cold side and zT is the figure of merit.

$$\omega_{max} \frac{T_h - T_c}{4L} S^2 \sigma \text{---(2)}$$

Where S is the Seebeck coefficient, σ is the electrical conductivity and L is the thermoelectric leg

From this equation, it is apparent that the efficiency of a thermoelectric generator is directly related to a dimensionless figure of merit (zT) and the maximum power output is dependent on $S^2 \sigma$ (Power factor). These power factor and the figure of merit depend on material

properties such as Seebeck coefficient, electrical conductivity and thermal conductivity which shall be discussed in the subsequent sections. The variation of the thermoelectric generator conversion efficiency with the temperature and figure of merit is shown in figure 3.

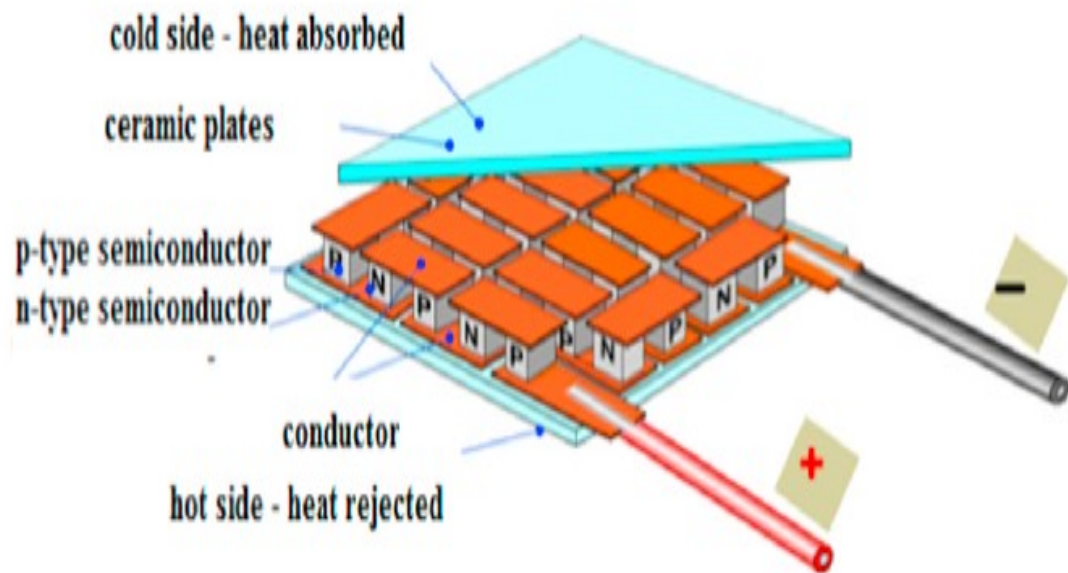


Figure 1. Internal structure of a thermoelectric module



Figure 2. Full thermoelectric module

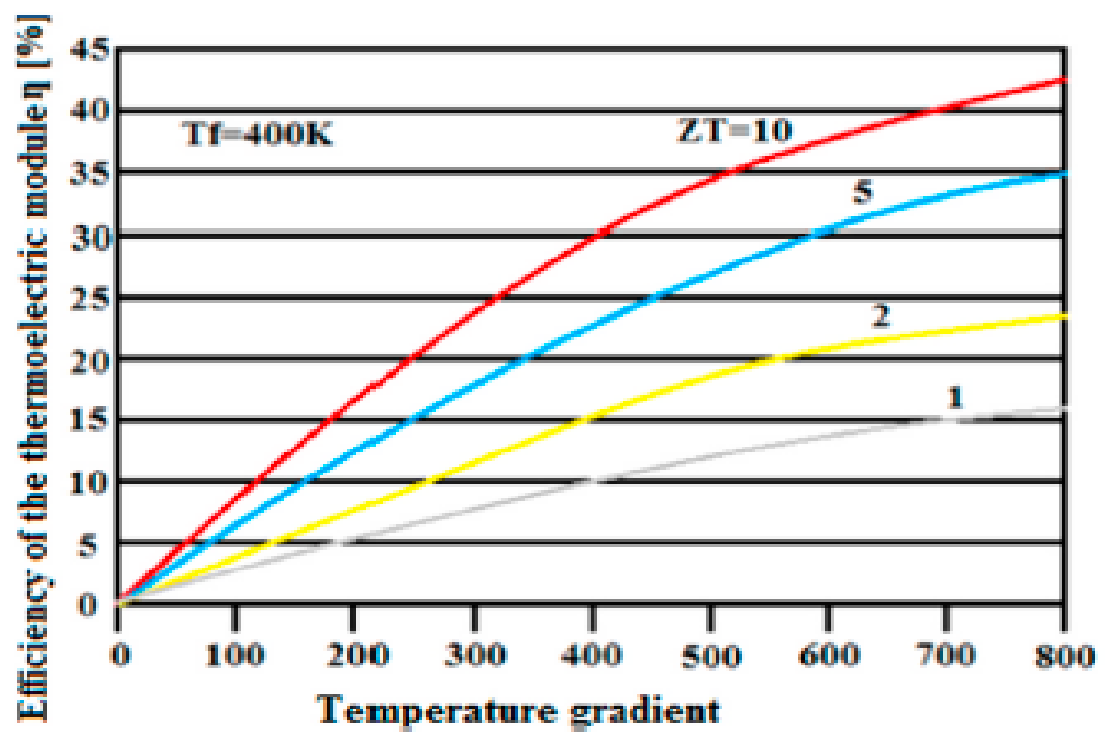


Figure 3. Efficiency of a thermoelectric module versus temperature gradient

1.2 Thermoelectric Materials

As mentioned in the previous section, thermoelectricity refers to a phenomenon which allows conversion of heat into electrical energy [1], [2]. Materials which show good thermoelectric properties are referred to as thermoelectric materials and these materials can be used for various applications such as the generation of electricity from waste heat, cooling systems and refrigeration [16], [17]. This section gives a review on some of the widely studied thermoelectric materials namely; 2-D thermoelectric materials, oxides, Skutterudite and the half Heusler thermoelectric materials.

1.2.1 2-D Thermoelectric materials

Following the experimental realization of a monolayer PbSe₂. Dan Qin et. al. investigated the electronic as well as thermal properties of this novel 2-D material by performing first principle calculation based on density functional theory (DFT) and Boltzmann transport theory. It was reported in this work that monolayer PbSe₂ is a semiconductor with an indirect band gap and hole mobility which can go as high as 1929cm² V⁻¹ s⁻¹. This high hole mobility resulted in improved transport properties of monolayer PbSe₂. They also found an anisotropic transport property of monolayer PdSe₂ and reported low value of lattice thermal conductivity ($k \sim 3 \text{ W m}^{-1} \text{ K}^{-1}$) along x-direction at 300K. The enhanced transport properties and the low lattice thermal conductivity of monolayer PbSe₂ resulted in a zT value of 1.1 for the p-type doped monolayer PbSe₂ along x-direction at 300K [18]. Also, after a successful synthesis of 2-D graphene-like carbon allotrope popularly known as graphyne. Its thermoelectric performance was investigated by P.H.J et. al. In their work,

first principle calculation was performed for both electron and phonon which was augmented with Boltzmann transport theory. A maximum value of zT of 1.5 for p-type and 1.0 for n-type were obtained at an intermediate temperature of 600K for this material. This work revealed that γ -graphyne has an outstanding thermoelectric property that is significantly better than that of the widely known graphene. The reason given for these outstanding properties was the carbon-carbon triple bond in γ -graphyne and the band gap opening [19]. Gandhi et. al. investigated and compared the thermoelectric performance of two dimensional MXenes, M_2CO_2 with $M=Ti, Zr$ or Hf . The thermoelectric properties were calculated by solving electron and phonon transport equations for three MXenes (Ti_2CO_2 , Zr_2CO_2 and Hf_2CO_2). The aim was primarily to evaluate the effect of metal M on the thermoelectric properties of MXenes. The electronic band structure and density of states of the respective MXenes revealed Ti_2CO_2 with the least band gap of 0.33eV and Hf_2CO_2 having the highest 1.00eV. It was concluded from this work that the energy band gap seems to increase with increasing the atomic mass of M , and again the larger Seebeck coefficient observed for n-doping as compared to p-doping was attributed to the differences in effective masses of charge carriers. The lattice contribution to thermal was found to be least for the Ti_2CO_2 as the acoustic phonon showed the strongest dispersion. Consequently, the highest thermoelectric figure of merit was predicted for Ti_2CO_2 [20]. Eddwi et. al. very recently studied the thermoelectric properties of 2-D Dirac materials using Boltzmann transport equation and the relaxation time approximation, it was reported in this work that gapped 2-D Dirac material exhibit higher thermoelectric properties than the gapless 2-D Dirac. The optimal band gap to improve the figure of merit in this material type was reported to be between $6k_B T$ - $18k_B T$ where k_B is the Boltzmann constant and T is the

temperature in kelvin. The authors also claimed that the figure of merit for this material can go many times higher than commercially available thermoelectric materials in the most ideal case where the lattice conductivity was considered to be very small [21]. The electronic structure and electronic properties of Selenene and Tellurene were studied by Lin et. al. using DFT calculation. It was reported in this work that both Selenene and Tellurene exhibited three-phonon limited thermal conductivity. It was also concluded in this work that the extremely low lattice thermal conductivity in Tellurene was due to the prominent anharmonic phonon scattering. High effective mass and Seebeck coefficient were observed along the arm-chair direction [7]. Following this work, Sharma et. al. investigated the thermoelectric properties of Tellurene from first principle calculation and semiclassical Boltzmann transport equation, it was reported in this work that Tellurene exhibited anisotropic lattice thermal conductivity of $0.43\text{Wm}^{-1}\text{K}^{-1}$ along x direction and $1.29\text{Wm}^{-1}\text{K}^{-1}$ along y direction. It was also reported in this work that optical phonon played a key role in the extremely low lattice thermal conductivity of tellurene which led to a room temperature figure of merit of 0.8 along x at a hole concentration of $n=1.2\times 10^{11}\text{cm}^{-3}$ [22]. Lee et.al. also worked on thermoelectric properties of 2-D SnS_2 and reported a negative correlation between electrical conductivity within the nano-range of SnS_2 sample. This led to a maximum figure of merit of 0.13 at 300K a value claimed to be approximately 1000 times higher than the previously reported value for the bulk SnS_2 . They also obtained a Seebeck value of 37.7mVK^{-1} for a 16nm thick SnS_2 sample [6].

1.2.2 Thermoelectric Oxides

Miller et. al. adopted high throughput calculation approach to screening a large number of oxides for thermoelectric applications where they assessed about 7350 oxides. They found

that n-type SnO is a promising material for thermoelectric applications. They reported lattice thermal conductivity value of $0.75 \text{ Wm}^{-1}\text{K}^{-1}$ at a temperature of 525K for bulk polycrystalline SnO. They also obtained a hole mobility value of $30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature for this material type [11]. Jiangang et. al. worked on Bi_2PdO_4 oxide from first principle calculations and reported this material as a promising material for thermoelectric applications with huge power factor and low lattice thermal conductivity. It was predicted from this work that Bi_2PdO_4 is a stable p-type thermoelectric material with low lattice thermal conductivity [10]. Dehkordi et. al. revealed a new way to improve the thermoelectric properties of SrTiO_3 oxide using a novel method to prepare Pr-doped SrTiO_3 which was reported to increase the figure of merit of perovskite SrTiO_3 oxide. A power factor of $1.3 \text{ Wm}^{-1}\text{K}^{-1}$ at 500°C was obtained, the high power factor was attributed to enhanced carrier mobility resulting from the formation of Pr-rich grain boundary [23]. Using first principle calculation and semi classical Boltzmann transport theory the effect of strain on the thermoelectric properties of CuO was studied by Absike et. al. In this work, they applied both compressive (-2%) and tensile strain (2%) to CuO and explored the effects on its thermoelectric properties. They reported that the Seebeck coefficient was found to be positive for the strained compared to the unstrained. The carrier concentration for the strained CuO was also found to increase with the increase in temperature [24]. Khandy et. al. explored the electronic structure, magnetic and thermoelectric properties of double perovskite $\text{Sr}_2\text{HoNbO}_6$ adopting first principle calculation approach. In this work, a max value of the figure of merit of ~ 0.9 was obtained at room temperature for $\text{Sr}_2\text{HoNbO}_6$ [25]. The effect of V co-doping of Nb- SrTiO_3 was also studied by Ozdogan et. al. from density functional theory. A higher increase in carrier density was observed for V

dopant than for Nb dopant. While in Nb-SrTiO₃ a high carrier density counteracts a high thermoelectric figure of merit, the trend is inverted by V co-doping. The mechanism leading to this behavior is explained in terms of a local spin-polarization introduced by the V ions. It was shown in this work that magnetic co-doping could be a prominent way to improve the thermoelectric properties of a material [26].

1.2.3 Skutterudite Thermoelectric Materials

Through dislocation engineering, Meng and co-workers were able to improve the thermoelectric properties of Ce-filled Skutterudite single phase. Single phase p-type Ce-filled Skutterudite was achieved by liquid phase compaction method. It was then reported that the dense dislocation array led to reduced lattice thermal conductivity with no significant influence on carrier transport. A high figure of merit of ~ 1.1 at a temperature of 723K was obtained for the liquid phase compacted Ce_{0.8}Fe₃CoSb₂ alloy [8]. Saeed et. al. explored the thermoelectric properties of binary semiconducting Skutterudites from first principle calculations and semi classical Boltzmann transport theory. The compounds were CoP₃, CoAs₃, IrP₃, IrAs₃, IrSb₃, CoSb₃, RhAs₃, RhSb₃ where CoSb₃ was reported to have the highest Seebeck coefficient at room temperature. However, in terms of electrical conductivity RhAs₃ was reported to have the highest value of $3.736 \times 10^5 \text{ ohm}^{-1} \text{ m}^{-1}$. It was also reported in this work that the Seebeck coefficient values for these compounds were almost constant at high temperature. This was attributed to the activation of minority charge carriers at high temperatures [9].

1.2.4 Half Heusler Thermoelectric Materials

The effect of Vanadium vacancy on the thermoelectric properties of VCoSb half Heusler compound was studied by Huang et. al. A figure of merit of 0.6 and the power factor of $29\mu\text{Wcm}^{-1}\text{K}^{-2}$ were obtained at 873K for the non-stoichiometric $\text{V}_{0.9}\text{CoSb}$ sample. It was concluded in this work that moderate vacancy can cause improvement in the thermoelectric properties of VCoSb. However, higher vacancy may create more CoSb impurities which may reduce the thermoelectric properties of VCoSb [27]. Joshi et. al. studied electronic and thermoelectric properties of MCoSb (M=Ti, Zr, Hf) using Full Potential Linearized Augmented Plane Wave (FP-LAPW) method based on Density functional theory and semi classical Boltzmann transport theory. It was reported in this work that MCoSb is a narrow indirect band gap semiconductor. They also obtained the highest figure of merit for the TiCoSb at 800K and the order of figure of merit for the MCoSb within the 600K-900K temperature range from lowest to highest is $\text{HfCoSb} < \text{ZrCoSb} < \text{TiCoSb}$ [28]. Synordzki et. al. worked on the thermoelectric properties of ScNiSb half Heusler obtained by arc melting and spark plasma sintering technique. They reported that ScNiSb possessed a fairly high positive Seebeck coefficient $\sim 240\mu\text{VK}^{-1}$ close to 450K. However, small conductivity was obtained which resulted in low power factor $< 1 \times 10^{-3} \text{Wm}^{-1}\text{K}^{-2}$ in the 2K-950K temperature range. A maximum figure of merit of ~ 0.1 was obtained at $\sim 820\text{K}$.

1.3 Thermoelectric Coefficients and the Computational Method

The most important factor which determines the thermoelectric properties of materials is a dimensionless quantity known as the figure of merit zT . This quantity is defined as the product of Seebeck coefficient squared and electrical conductivity (generally referred to

as the power factor) divided by the sum of electronic and lattice thermal conductivity (equation 3)[3], [17], [29].

$$zT = \frac{S^2 \sigma}{k_e + k_l} \text{--- -- -- -- -- (3)}$$

Where S is the Seebeck coefficient, σ is the electrical conductivity, k_e is the electronic contribution to thermal conductivity and k_l is the phonon contribution to thermal conductivity

1.3.1 Seebeck Coefficient

The flow of charge carriers due to temperature gradient is referred to as the Seebeck effect, the voltage produced is usually proportional to the temperature gradient where the constant of proportionality is referred to as the Seebeck coefficient which is often referred to as the Thermopower in thermoelectric. From Mott's relation, the Seebeck coefficient is given by:

$$S = \frac{\pi^2 K_B^2 2m^*}{|e|\hbar^2 (3n\pi^2)^{2/3}} T \text{--- -- -- -- -- (4)}$$

From this equation it is apparent that S is proportional to the charge carrier effective mass which is also dependent on the electronic structure as follows;

$$m^{*-1} = \frac{\partial^2 E(k_\alpha)}{\partial^2 k_\alpha} \text{--- -- -- -- -- (5)}$$

From equation (4) S is proportional to the temperature and inversely proportional to the charge carrier concentration. This explains why S increases as T increases and decreases with increase in doping concentration. It is also important to mention that since charge carrier mobility is inversely proportional to the charge carrier concentration as seen in the relation below:

$$\mu = \frac{\sigma}{ne} \text{----- (6)}$$

Therefore, S is proportional to the charge carrier mobility. i.e. the higher the charge carrier mobility the higher the Seebeck coefficient. Band degeneracy has been reported to improve the charge carrier mobility and hence increase in S for Half Heusler compounds. For instance, Zhu et. al. reported that the band degeneracy in ZrCoBi half-Heusler compound enhanced the hole transport which improved the Thermopower [12].

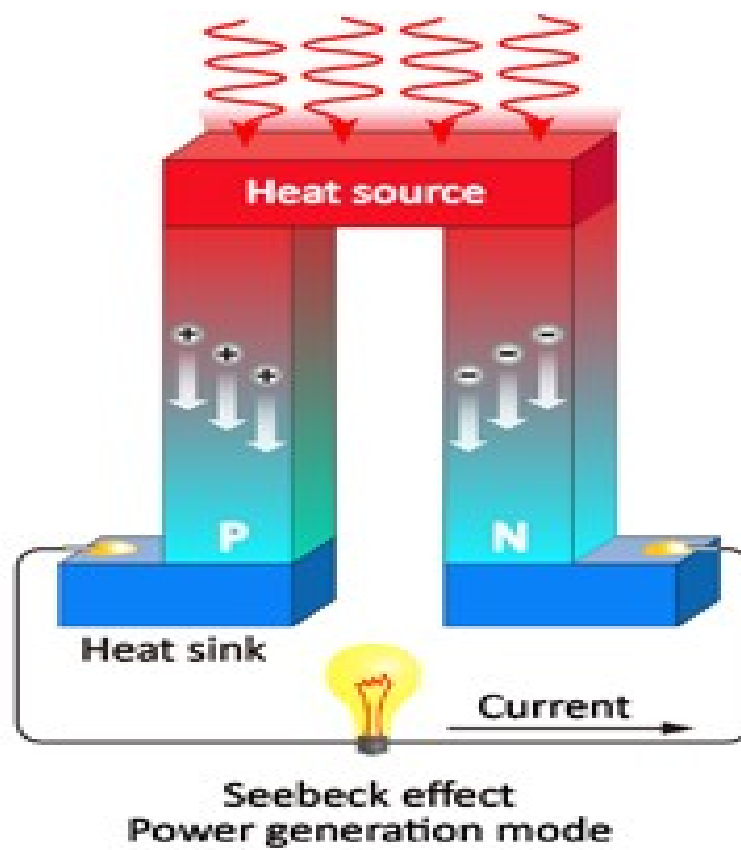


Figure 4. Seebeck effect

1.3.2 Electrical and Thermal Conductivity

Electrical conductivity is a measure of the flow of charge carriers under the influence of applied electric field while electronic and lattice thermal conductivities are measures of the heat transfer by electrons and phonon vibration respectively.

The electrical conductivity of material σ is related to the $N(E_f)$ and the fermi velocity as thus:

$$\sigma = \frac{1}{3} e^2 v_f^2 \tau N(E_f) \text{ --- (7)}$$

where e is the electronic charge, v_f is fermi velocity t is the relaxation time and $N(E_f)$ is the population density or charge carrier concentration at or close to fermi. The concentration of charge carriers or the population density ($N(E_f)$) depends on the density of state $g(E)$ which is the number of allowed energy states available to electrons within a certain energy range and $f(E)$ (The fermi Dirac distribution function) which gives the probability of occupancy. This is illustrated in the equation given below:

$$N(E_f) = \int g(E) f(E) dE \text{ --- (8)}$$

In order to calculate the thermoelectric properties of material based on the above equations, electronic band structure and density of states of the material need to be obtained using the Density Functional Theory (DFT) calculation, the results can then serve as input file for BoltzTraP2 which solve Boltzmann Transport Equation (BTE) to calculate the

transport coefficients (Electrical conductivity, Seebeck coefficient and Electronic thermal conductivity). From (3.), zT is proportional to the PF ($S^2\sigma$) and is inversely proportional to the sum of electronic and lattice thermal conductivities. But since materials with high electrical conductivity are usually characterized by high electronic thermal conductivity and vice versa, this implies that materials with high Seebeck coefficient and low lattice thermal conductivity are often desired for thermoelectric applications.

1.3.3 Density Functional Theory (DFT)

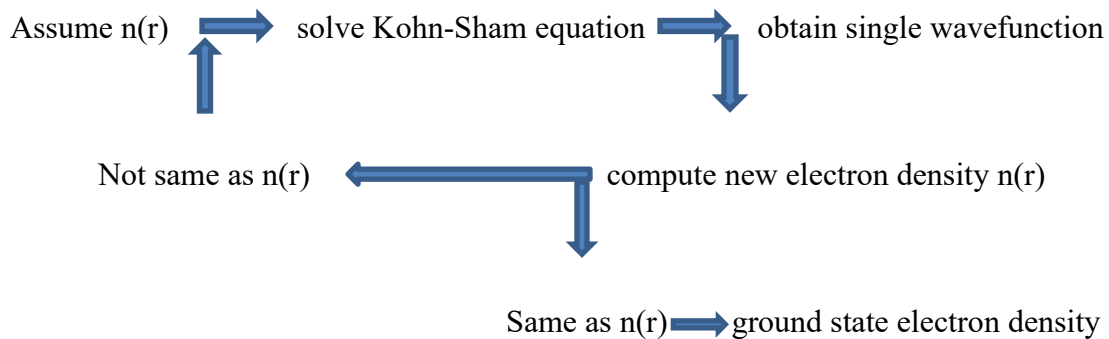
Density functional theory (DFT) is a computational method used to describe the properties of the material from first principle calculation i.e. by solving Schrodinger equation (Eqn. 9.) [30]. This method has long been used in condensed matter Physics and computational Chemistry to predict the stability and properties of compounds [17], [31]. Density functional theory (DFT) calculation has been helpful in the discovery and identification of new compounds for new and existing applications as it assists in reducing the cost of research and shorten the time of discovery. The whole idea of DFT is to provide a simpler way of solving a very complex Schrodinger equation for a many body system. This is made possible by the transformation of the wave function into electron density functional, which is expressed as the square of the wavefunction [32]. In fact, the name density functional theory came as a result of the use of electron density functional. By this transformation, a $3N$ dimensional problem for an atom (where N is the number of electrons) is reduced to 3-dimensional problem. Two theorems allow for the determination of the ground state electron density, the first which states that the energy is a unique functional of electron density shows the strong dependence of energy of a many body system on the electron density [33]. The second theorem which states that the electron density which minimizes

the energy is the ground state electron density allows for the realization of the ground state of the system [33]. Based on these theorems the ground state energy can be obtained from which other properties of the system can be obtained.

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(x)\psi = E\psi \text{ --- (9)}$$

1.3.4 Kohn-Sham Equation and the Self-Consistency Scheme

Kohn-Sham equation is a single electron Schrodinger equation which can be solved to obtain a single wavefunction for an electron (see equation below) [32]. The self-consistency scheme is a scheme used in DFT to obtain the ground state electron density. In this scheme an electron density is assumed and substituted into the Kohn-Sham equation, the Kohn-Sham equation is then solved to obtain a single wavefunction. This wavefunction is then used to calculate the new electron density, if it is same with the assumed value, then the ground state density is obtained. If not, the steps are repeated until ground state electron density is obtained. This is illustrated below:



1.3.5 Boltztrap2 Code and the Rigid Band Approximation

BoltzTraP2 code developed by Madsen et al., provides a Fourier sum of the quasi particle energies and their derivatives as shown in equation (10) and (11) below [34], [35]. This method calculates the transport coefficients by adopting Rigid Band Approximation (RBA) which assumes temperature and doping independence of the band structure. This method also adopts a Constant Relaxation Time Approximations (CRTA) which assumes the Seebeck coefficient and the Hall coefficient to be independent of scattering rate [36]. Under these assumptions the transport distribution function is given by [10]:

$$\tilde{\varepsilon}_k = \sum_{\pi} c_{\pi} \sum_{R \in \pi} \exp(ik \cdot R) \text{ --- (10)}$$

$$\nabla \tilde{\varepsilon}_k = i \sum_{\pi} c_{\pi} \sum_{R \in \pi} \exp(ik \cdot R) \text{ --- (11)}$$

Where π are so called stars denoting a set of symmetry-equivalent lattice vectors.

$$\sigma(\varepsilon, T) = \int \sum_{\pi} v_{b,k} v_{b,k} \tau_{b,k} \delta(\varepsilon - \varepsilon_{b,k}) \frac{dk}{8\pi^3} \text{ --- (12)}$$

This is then used to evaluate the moments of generalized transport coefficients as thus:

$$\mathfrak{I}^{(\alpha)}(\mu; T) = q^2 \int \sigma(\varepsilon, T) (\varepsilon - \mu)^{\alpha} \left(-\frac{\partial f^{(0)}(\varepsilon; \mu, T)}{\partial \varepsilon} \right) d\varepsilon \text{ --- (13)}$$

$$\sigma = \mathfrak{I}^{(0)} \text{ --- (14)}$$

$$S = \frac{1}{qT} \frac{\mathfrak{I}^{(1)}}{\mathfrak{I}^{(0)}} \text{ --- (15)}$$

$$k_e = \frac{1}{q^2 T} \left(\frac{(\mathfrak{I}^{(1)})^2}{\mathfrak{I}^{(0)}} - \mathfrak{I}^{(2)} \right) \text{ --- (16)}$$

One major advantage of using BoltzTraP2 to calculate transport coefficient is that it provides an easier way to obtain the group velocity from the k-space derivatives of the quasi-particle energies.

1.4 Half- Heusler Compounds

Ever since the discovery of Heusler compounds by Heusler in 1903, thousands of these compounds have been reported in the literature [37]–[39]. A unique class of these compounds commonly of the form XYZ are generally referred to as the Half Heusler. The XYZ configuration is based on electronegativity where X is the most electropositive, Y is less electropositive than X and Z is the most electronegative element. X and Y are mostly transition metals, but in some cases can also be rare earth metal or a main group element [40]. While Z is usually a main group element. Examples of half Heusler compounds are TaFeSb, ZrCoSb, NbFeSb, TiNiSn etc. [13], [41], [42]. These compounds have been reported to possess several surprising and outstanding properties which allow them to be used for a variety of applications ranging from electronic, spintronic to thermoelectric applications. They have been thought of to possess characteristics like the binary compound semiconductors such as GaAs, InSb etc. [40].

1.4.1 Crystal Structure

Half Heuslers are compounds with the space group of (216, F43m Cl_b), the crystal structure can be imagined as the combination of zinc blend and rock salt sublattices or can as well be imagined as a zinc blend structure with filled octahedral sites[40], [43]. In this structure, the corresponding Wyckoff positions that are filled with X, Y and Z atoms are 4a (0, 0, 0), 4b ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), 4c ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$). MgAgAs and MgCuSb structures are generally the prototype

structures assigned to half Heusler compounds. In the MgAgAs structure, the MgAg form the ionic bond dominated rock salt sublattice, while the AgAs form the covalent zinc blende sublattice. However, they can also crystallize in MgCuSb where MgSb represents the ionic sublattice while CuSb form the covalent zinc blende sublattice. Factors which determine which of these structures half Heusler crystallizes in include, difference in the atomic sizes and the ionic character of the constituent atoms. In these structures, the positions of each of the constituent elements (XYZ) follow three inequivalent atomic configuration types (Type I, Type II and Type III). This is essential in the theoretical calculation as placing any of the constituent atoms in the wrong position will result in wrong computational results. In type I, X sits on the 4a Wyckoff positions, Y sit on 4b while Z sits on the 4c Wyckoff positions. In Type II, the Z sits on 4a, X sits on 4c and Y sits on 4b Wyckoff positions. In Type III, Y sits on the 4a, Z sits on 4b while X sits on 4c Wyckoff positions. A different possible configuration for TaRuAs (an example of HH compound) is shown in the figure below. The most common atomic configuration types in half Heuslers are Type I and type II[40]. However, it is important to test for the stable atomic configuration type for any chosen half Heusler compound before proceeding with a theoretical calculation.

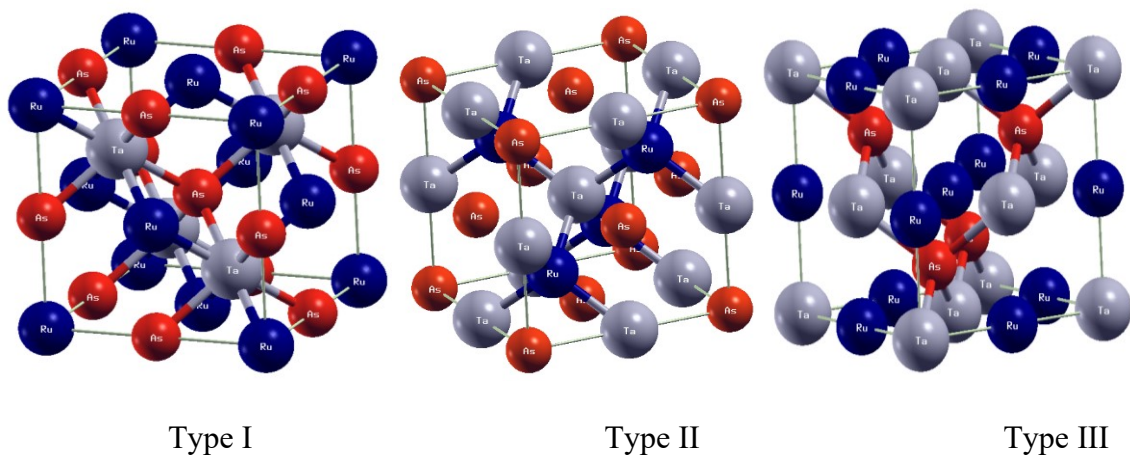


Figure 5. Different possible configuration types in TaRuAs half-Heusler

1.4.2 Magnetism

The magnetic properties of HH can be understood from the valence electrons model where the X element donates all its valence electrons to the more electronegative elements (Y and Z) to attain d^{10} and s^2p^6 stable configurations for Y and Z respectively [44]. This process requires 18 valence electrons hence, referred to as the 18-valence electron rule. The interesting thing about this is that half Heuslers which obey this rule are magnetic. This is in accordance with the Slater Pauling 's rule[45], [46] shown below:

$$m_{XYZ} = N_v - 18 \text{ --- (17)}$$

where m_{XYZ} is the magnetic moment and N_v is the valence electron

Compounds which obey 18-electron rule (i.e. $N_v=18$), when substituted in this equation will have the magnetic moment of 0. In most cases, a deviation from this rule implies compound is magnetic and crystallizes in a different structure other than the half Heusler structure. An exception to this is the MnNiSb which deviates from the 18-valence electron and show 22 electron system but crystallizes in HH structure [47]. This unique class of HH compound is ferromagnetic and its ferromagnetism is associated with the tendency of 'd' electrons localization [47].

CHAPTER 2

LITERATURE REVIEW

2.1 Thermoelectric Properties of XFeSb (X=Ta, Nb)

The realization of Cu_2MnSn intermetallic compound in 1903 by Heusler paved way for the discovery and investigation of a new and interesting class of materials generally referred to as the half Heusler compounds. Since 1903 till date over 2000 of such have been identified in the literature [37]–[39]. Many authors have worked on the discovery and thermodynamic analysis of over a thousand half Heusler (HH) compounds using theoretical calculations. Gautier et. al investigated about 400 HH compounds and used theoretical calculation to check their thermodynamic stabilities, among these 400 HH compounds, only about 54 were reported to be stable from their calculation[48]. Subsequently, 15 of these compounds were synthesized in the laboratory to verify their prediction. Carrete et. al. also carried out a thermodynamics analysis on 450 HH compounds and predicted that only 77 are stable[39]. Zakutayev et. al. also carried a study on the thermodynamic stability of V-IX-IV family of HH compounds where (V= V, Nb, Ta; IX=Co, Rh and Ir and IV=C, Si, Ge, Sn and Pb)[49]. Among the 29 missing compounds, only about 8 were found to be stable in their work. The thermoelectric properties of some of these reported stable HH compounds have been widely studied and well documented in the literature [12], [50], [51] where it became apparent that HH compounds are a class of materials characterized by high Seebeck coefficient, moderate resistivity, good thermal stability and most importantly high zT. Consequently, HH compounds serve as potential materials for the thermoelectric

application. Some authors have attributed their outstanding thermoelectric performance to structural order, mass fluctuations and high band degeneracy[13]. The addition of foreign atoms into the lattice of HH structure happens to have a considerable effect on the thermoelectric properties of the compound, this is as a result of a considerable increase in the charge carrier concentration which consequently affect the electronic properties. This is also accompanied by the reduction of lattice thermal conductivity due to the scattering effect caused by the strain induced in the lattice by the foreign atom. Among different classes of thermoelectric materials, XFeSb (where X = Nb, Ta) half-Heusler compounds are considered particularly promising with a high figure of merit which was attributed to mass fluctuation and heavy hole band character [7-9]. Junjie et al. investigated the role of Ta doping at the Nb site of NbFeSb in enhancing the thermoelectric figure of merit and concluded that the lattice thermal conductivity was reduced as a result of the large mass fluctuation between Ta and Nb [8]. Hangian et. al. reported a high figure of merit of 1.5 for $Ta_xTi_{1-x}FeSb$, which was attributed to large phonon scattering due to Ti doping at the Ta site [9]. Naydenov et al. very recently also showed the effect of Ti-doping at Ta site in improving the power factor of $Ta_{1-x}Ti_xFeSb$ [52]. Grysiv et al. also verified the role of Ti doping on the formation and physical properties of $Ta_{1-x}Ti_xFeSb$ [53]. All these authors have focused on the doping at X sites and most of the theoretical calculations have focused on virtual doping by Rigid Band Approximation (RBA). They evaluated the doping effects by virtue of the shift in fermi level due to addition of dopants. However, the validity of this approach for practical purpose is still questionable as this is clear from a considerable difference that is often encountered between theoretical predictions by this method and experimental results. Other authors have also shown that the validity of this method

depends on the compound and the type of dopant or impurity introduced[54], [55]. For instance, Man-Soon Lee et al. reported that introduction of dopant into the lattice of a compound can cause a significant change in the band structure which results to removal of existing degeneracy that lowers the S predicted by RBA[56]. Thus, it is important to carry out first principle calculations on doped XFeSb that explicitly include the dopant atom.

In this work, we adopt a supercell approach to elucidate the effects of dopants atoms at Fe sites on the thermoelectric properties of XFeSb ($X=\text{Ta, Nb}$). For the sake of comparison, first principles calculations were carried out and RBA was employed to evaluate the thermoelectric properties of both p-type and n-type XFeSb, this was then followed by thermoelectric properties calculations of the compounds in question by forming supercells which explicitly contained the dopant atoms.

2.2 Aim and Objectives

The aim of this work is to investigate the thermoelectric properties of pure and doped XFeSb ($X=\text{Ta, Nb}$) intermetallic compounds. This would be achieved by the following objectives:

1. First principle calculation on Mn and Co-doped TaFeSb and NbFeSb within the framework of DFT as implemented in the Quantum Espresso package.
2. Determination of Seebeck Coefficient, Electrical Conductivity and Electronic Contribution to Thermal Conductivity which would be obtained by solving the electron Boltzmann Transport Equation (BTE) as implemented in the BoltzTrap2 software.
3. Evaluate the Lattice Thermal Conductivities for both pure and doped compounds using Slack's equation.

CHAPTER 3

METHODOLOGY

First principle calculation was carried out within the framework of Density Functional Theory (DFT) for the half Heusler compound as implemented in QUANTUM ESPRESSO software[57]. I started with structural optimization of undoped TaFeSb and NbFeSb, followed by band structure and density of states calculations using the Quantum Espresso software [10]. The exchange–correlation potential was treated in the generalized gradient approximation, the cut-off energy was set to 700eV for TaFeSb and 650eV for NbFeSb. The k-mesh of 8x8x8 was used for TaFeSb and 6x6x6 was used for NbFeSb. Higher k-mesh of 24x24x24 were used to obtain the thermoelectric properties in BoltzTraP2. The crystal structure of each of these materials was relaxed and a value of 10^{-7} eV was set for the total energy convergence criterion. Similarly, a value of 0.001 eV/Å was set as the force convergence criterion and this was adopted throughout the calculation. The effects of doping were obtained by Rigid Band Approximation (RBA) approach from BoltzTraP2. The electronic transport properties were obtained by solving Boltzmann transport equations for electrons as implemented in the BoltzTraP2 software[58]. This approach stated here has been successfully employed in other to model the thermoelectric properties of various HH compounds. The temperature dependent relaxation time was measured by using the equation below, the values obtained by [52] at 300K were used to obtain the constant of proportionality.

$$\tau = \frac{K}{T^{3/2}} \text{-----} \text{---(18)}$$

The lattice thermal conductivities for the pure compounds were obtained from the elastic properties of the compounds using Slack equation and Jia et. al. approach [59], [60] given in the equations shown (16) below.

$$k_{int} = A \frac{\Theta_D^3 V_a^{1/3} m_{av}}{\gamma^2 n^{2/3} T} \text{---(19)}$$

Where Θ_D is the Debye Temperature, V_a is the unit cell volume per atom in ($\text{\AA}$), m_{av} is the average mass of the compound in (amu), T is the Temperature, n is the number of atoms per unit cell, γ is the Grüneisen parameter, A is a parameter given by:

$$A = \frac{2.43 \times 10^{-6}}{1 - \frac{0.514}{\gamma} + \frac{0.228}{\gamma^2}} \text{---(20)}$$

The Grüneisen parameter and the parameter A are obtained from the elastic properties as thus:

$$\gamma = \frac{3}{2} \left(\frac{1 + \nu}{2 - 3\nu} \right) \text{---(21)}$$

Where ν is the Poisson's ratio which can be obtained from the transverse and longitudinal velocities as thus:

$$\nu = \frac{1 - 2 \left(\frac{v_t}{v_l} \right)^2}{2 - 2 \left(\frac{v_t}{v_l} \right)^2} \text{---(22)}$$

Where v_t is the transverse velocity and v_l is the longitudinal velocity

$$v_l = \sqrt{\frac{B_H + \left(\frac{4}{3}\right) G_H}{\rho}} \text{-----} (23)$$

Where B_H is the bulk modulus, G_H is the shear modulus and ρ is the density

$$v_t = \sqrt{\frac{G_H}{\rho}} \text{-----} (24)$$

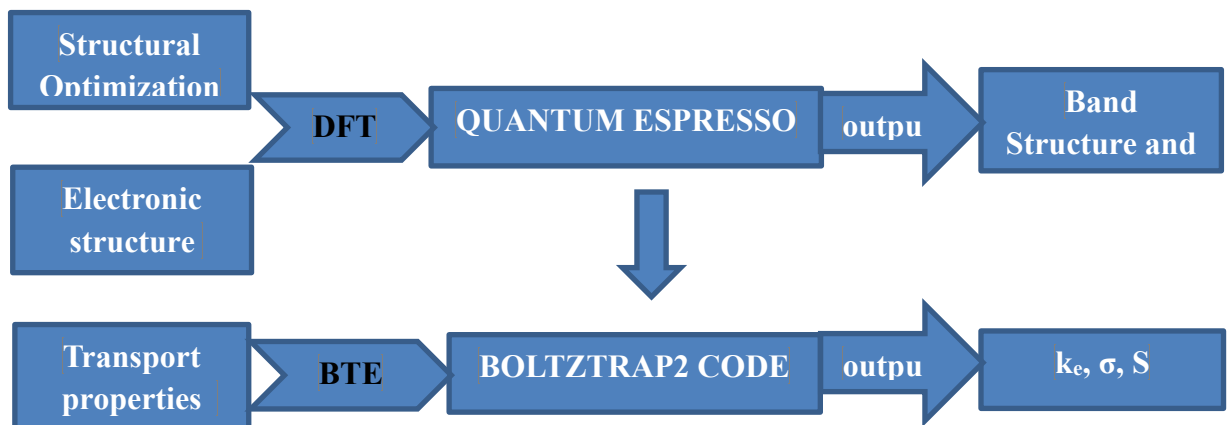
$$v_{av} = \left[\frac{1}{3} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \right]^{-1/3} \text{-----} (25)$$

$$\Theta_D = \frac{h}{2\pi k_B} \left(\frac{6\pi^2 n}{V_a} \right)^{\frac{1}{3}} \text{-----} (26)$$

Where h is the Planck's constant and k_B is the Boltzmann constant

Further work would involve the Fourier interpolation of lattice thermal conductivity by solving the Boltzmann transport equation for phonons as implemented in ShengBTE code[61].

Below is the flow chart of the computational method:



CHAPTER 4

RESULTS AND DISCUSSION

4.1 Thermoelectric Properties of Pure XFeSb (X= Ta, Nb)

In this section, first the stable configuration of XFeSb and thermodynamic stability of XFeSb are discussed, this is then followed by the discussion of the electronic structure of pure XFeSb and then the thermoelectric properties of XFeSb. The results obtained for the two compounds are then compared.

4.1.1 Identification of Stable Configuration of TaFeSb

To begin with, the stable atomic configuration within the unit cell of TaFeSb compound was verified among the three different atomic configurations (the type I, type II and type III) which HH usually crystallizes in, see section 1.3.1. This was done by running self-consistent function (SCF) calculations to obtain the total energy for each configuration from first principle. The three configuration types in TaFeSb are shown in the figures below:

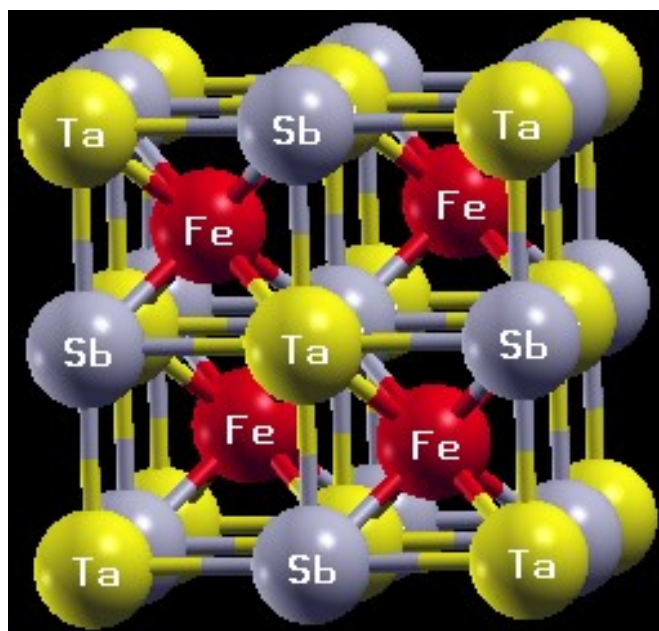


Figure 6. Type I TaFeSb

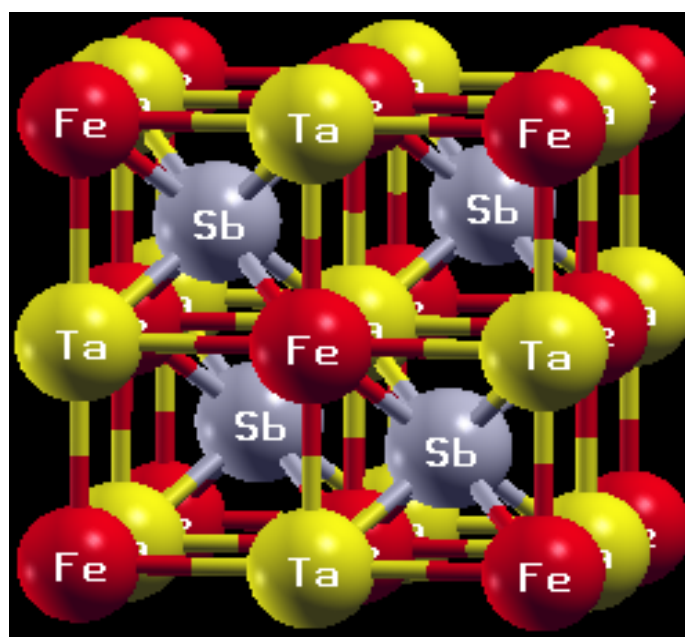


Figure 7. Type II TaFeSb

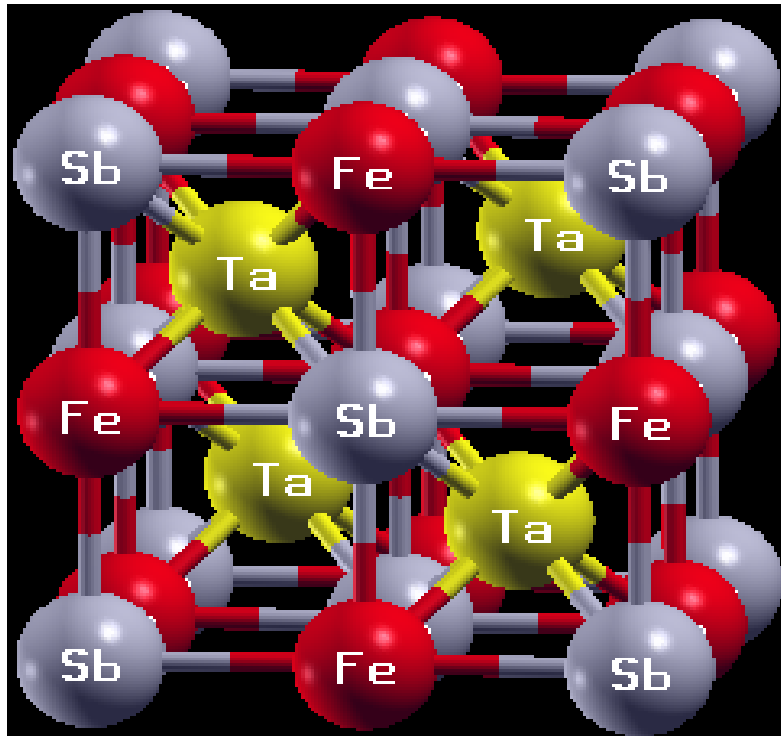


Figure 8. Type III TaFeSb

Table 1 Total energy for 3-atomic configuration types

TaFeSb	Total Energy (Ry)	Total Energy (eV)
I	-221.479	-3013.44
II	-221.253	-3010.37
III	-221.205	-3009.72

Based on the results shown in table i above, the minimum energy corresponds to type I configuration. This implies that the most stable atomic configuration type for TaFeSb compound is type I as a result, type I configuration was chosen for all calculations for TaFeSb.

4.1.2 Thermodynamic Stability of TaFeSb

To also verify the thermodynamic stability of the compound at absolute zero (i.e. to be sure that TaFeSb will not dissociate into its constituent elements) and also obtain the enthalpy of formation for TaFeSb, we carried out SCF calculations to obtain the total energy for each of the constituent elements and then for the compound. We then obtained the energy difference as shown in table ii below. Based on our results, we found that TaFeSb was stable with the enthalpy of formation of $\Delta H = -1.24574 \text{ eV/atom}$.

Table 2 Total energy for Ta, Fe, Sb and TaFeSb

	Total Energy (Ry)	Total Energy (eV)
Ta	-140.19	-1907.42
Fe	-61.1287	-831.717
Sb	-19.886	-270.569
TaFeSb	-221.479	-3013.44
		$\Delta H = -1.24574$ eV/atom

4.1.3 Convergence Tests and Determination of Lattice Parameter for TaFeSb

In order to obtain full-Fourier transform of the density of state and to ensure highly accurate prediction of material properties in our calculations, convergence tests were conducted for the Plane-Wave Cutoff and the Brillion-Zone Sampling (k-mesh). In our calculations, k-point and cutoff energy were considered to converge when the energy difference was 5meV. This energy convergence criterion was chosen because the value is so small that it cannot cause any significant change in the properties of the material. From our results for TaFeSb, the cutoff energy and k-mesh converged at a value of 700eV and 512 (8x8x8) respectively. These values were used throughout our calculations to obtain the electronic structure and electronic properties of TaFeSb. In other to obtain the lattice parameter of the TaFeSb, we carried out several self-consistent calculations (SCF) and plotted a graph of total energy against different values of the lattice parameter. From our results (figure x), a value of 5.951Å correspond to the minimum energy and consequently taken as the equilibrium lattice constant of TaFeSb, this value is comparable to an experimental value of 5.9Å obtained by [13].

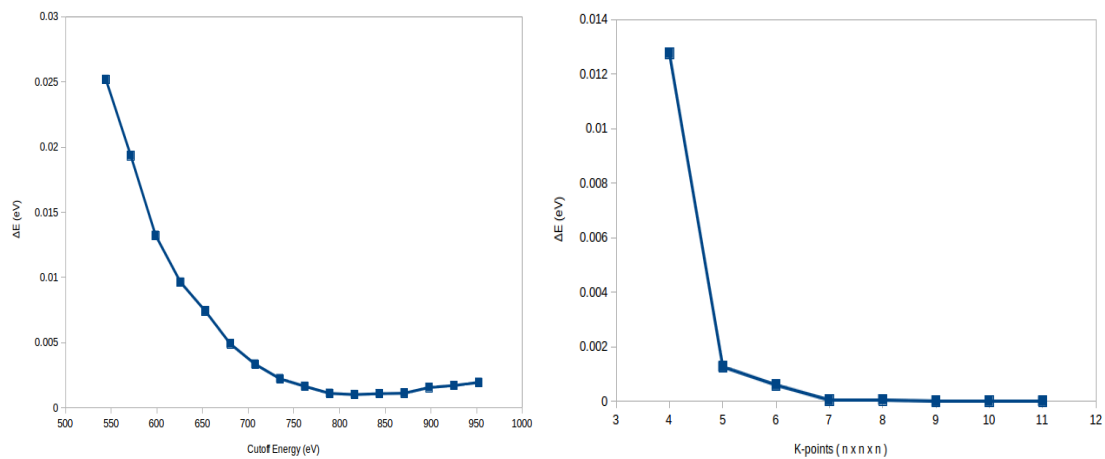


Figure 9. left: Energy change(eV) versus Cutoff Energy(eV) Right: Energy change (eV) vs k-mesh

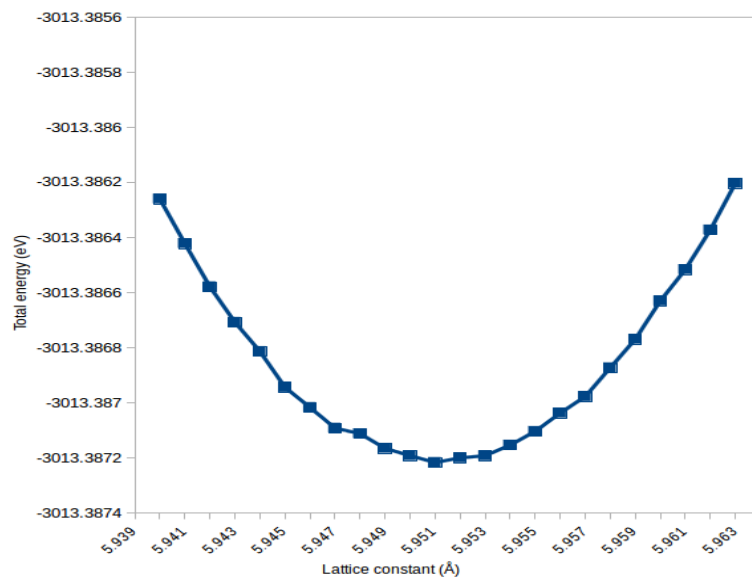


Figure 10. Total energy (eV) versus Lattice constant(Å)

The total energy versus lattice constant plot was fitted to Birch equation of state, the equilibrium lattice constant was obtained as $a_0=5.95126\text{\AA}$ and the value of Bulk modulus (B_0) for TaFeSb was obtained to be 175.3GPa, this value is comparable to other theoretical predictions by [52], [53].

4.1.4 Electronic Structure of TaFeSb

Using the converged parameters with the obtained lattice parameter for TaFeSb, the band structure and Projected Density of State (PDOS) of TaFeSb were obtained (figure 11 and 12). From the graph, the conduction band minimum (CBM) is situated at X-point while the valence band maximum (VBM) is situated at the L-point. It then turned out that TaFeSb is a semiconductor with an indirect band gap of magnitude $E_g=0.848\text{eV}$. This was in perfect agreement with the value of 0.85eV obtained by [52]. It can also be inferred from the Projected Density of State graph (figure 12) that the major contributor to the states in the valence band is Fe followed by the Ta. However, the major contributor in the conduction is the Ta followed by the Fe. The band gap of TaFeSb was found to be higher than that of the NbFeSb (which will be shown in the subsequent sections). The relatively large band gap of TaFeSb resulted in low electrical conductivity at room temperature as a result, the power factor of pure TaFeSb at room temperature was found to be very low. The band degeneracy observed at the L and gamma points is indicative of high Seebeck coefficient for TaFeSb. This will be discussed further in the subsequent sections.

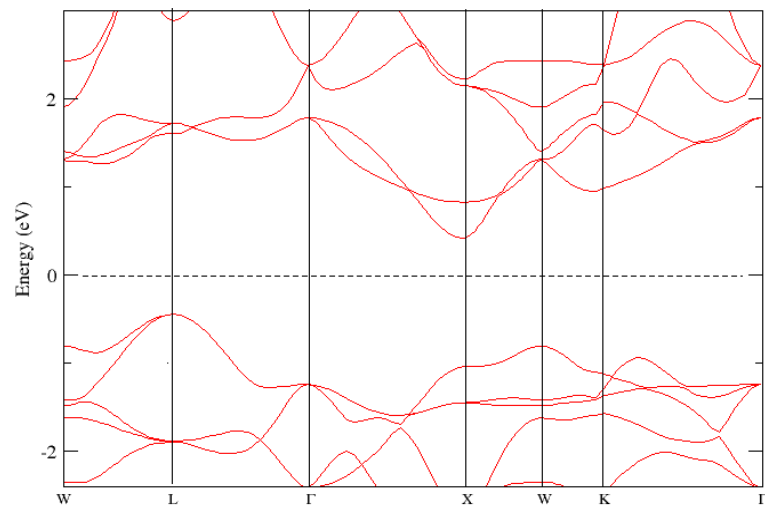


Figure 11. Band structure of TaFeSb

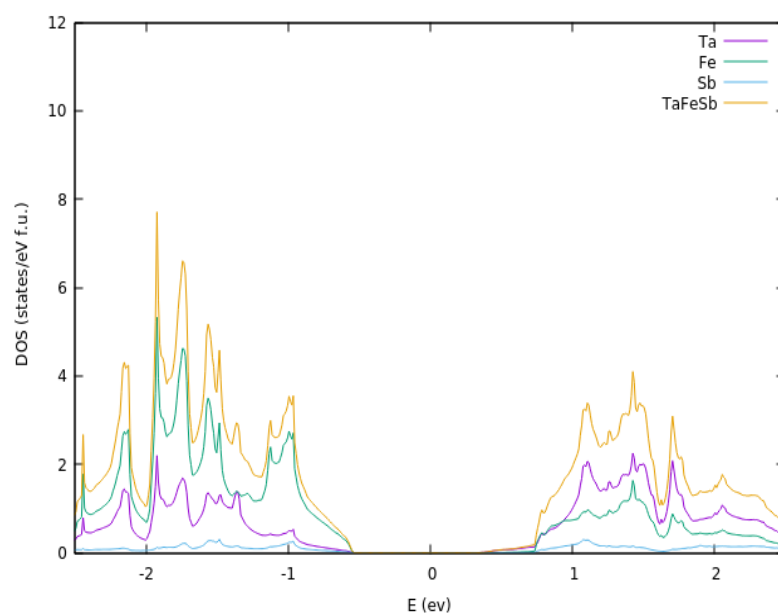


Figure 12. DOS of TaFeSb

4.1.5 Identification of Stable Configuration of NbFeSb

Like the case of TaFeSb, the stable atomic configuration for NbFeSb compound was verified, the results obtained are shown in table III. The possible configurations types in NbFeSb are depicted below:

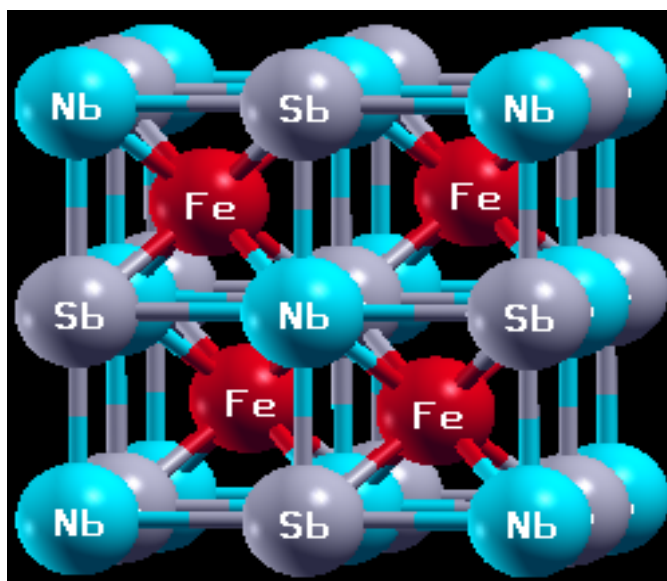


Figure 13. Type I NbFeSb

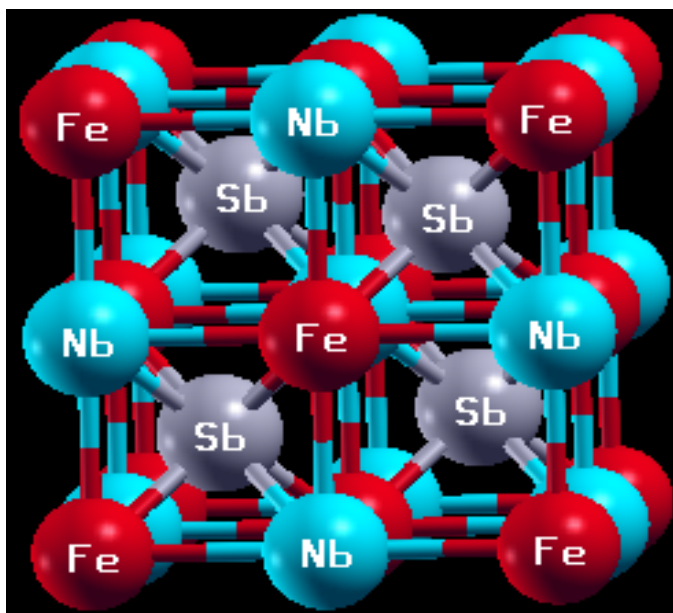


Figure 14. Type II NbFeSb

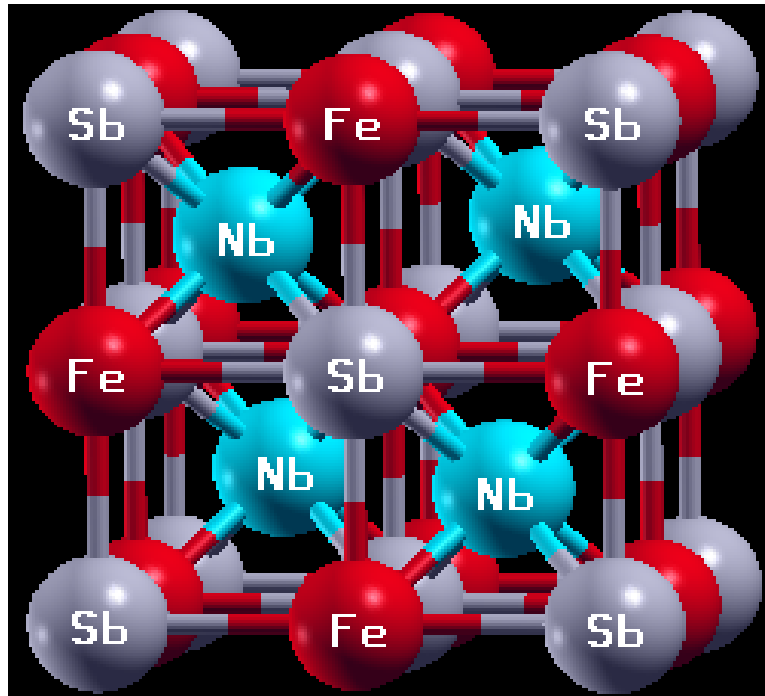


Figure 15. Type III NbFeSb

Table 3 Total energy of 3-atomic configuration types for NbFeSb

NbFeSb	Total Energy (Ry)	Total Energy (eV)
I	-199.235	-2710.79
II	-199.017	-2707.83
III	-198.985	-2707.38

It is also apparent from these results that type I was the most stable configuration as this gave rise to minimum total energy as compared to other configuration types.

4.1.6 Thermodynamic Stability of NbFeSb

Following the same approach to check the thermodynamic stability of TaFeSb and obtain the enthalpy of formation. It was found that NbFeSb was stable with the enthalpy of formation of $\Delta H = -1.26187 \text{ eV/atom}$ as shown in the table iv below:

Table 4 Total energy for Nb, Fe, Sb and NbFeSb

	Total Energy (Ry)	Total Energy (eV)
Nb	-117.942	-1604.72
Fe	-61.1287	-831.717
Sb	-19.886	-270.569
NbFeSb	-199.235	-2710.79
		$\Delta H = -1.26187\text{eV/atom}$

4.1.7 Convergence Tests and Determination of Lattice Parameter for NbFeSb

The convergence test was also conducted for NbFeSb like the case of TaFeSb, and the following results were obtained (Figure 16, 17). In this case, the plane wave cutoff was found to converge at a value approximately equal to 600eV and the k-mesh was found to converge at about 343 (7x7x7). These values were used for electronic structure and electronic properties calculations for NbFeSb. Also, like what was done in the case of TaFeSb, we carried out several self-consistent calculations (SCF) and plotted a graph of total energy against different values of the lattice parameter to obtain the equilibrium lattice constant of NbFeSb. From our results (figure 17), a value of 5.96Å corresponds to the minimum energy and as a result, taken as the equilibrium lattice constant of NbFeSb, this value is comparable to other theoretical value of 5.96Å obtained by [52]. Even though it may be argued that TaFeSb is supposed to possess larger lattice parameter because of the larger atomic radius of Ta as compared to Nb, but this would not have a significant effect on the lattice parameter because both atoms sit at 4a Wyckoff position in the lattice. Nevertheless, the value of 5.96 Å obtained for NbFeSb was slightly above the experimental value of 5.95 Å obtained by [62].

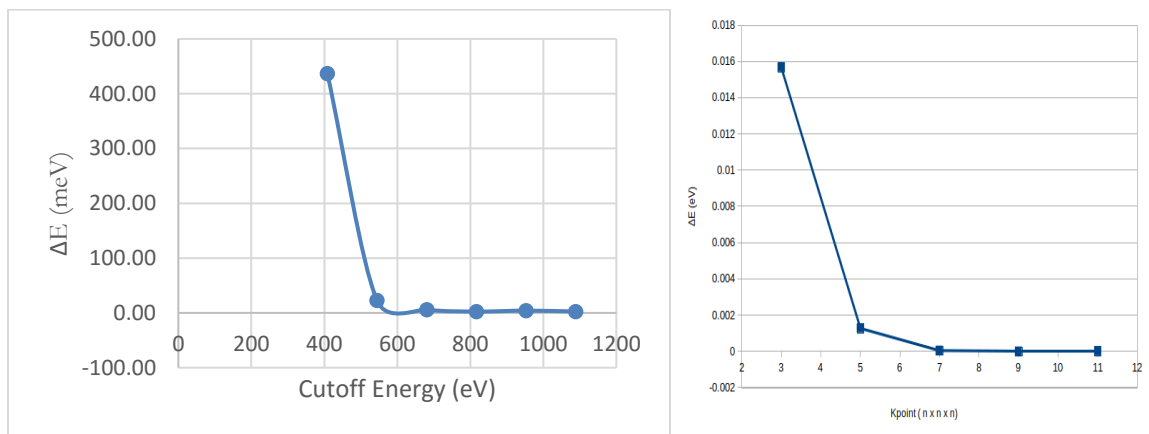


Figure 16. Left: Energy change(eV) vs Cutoff (eV), Right: Energy change (eV) vs k-mesh

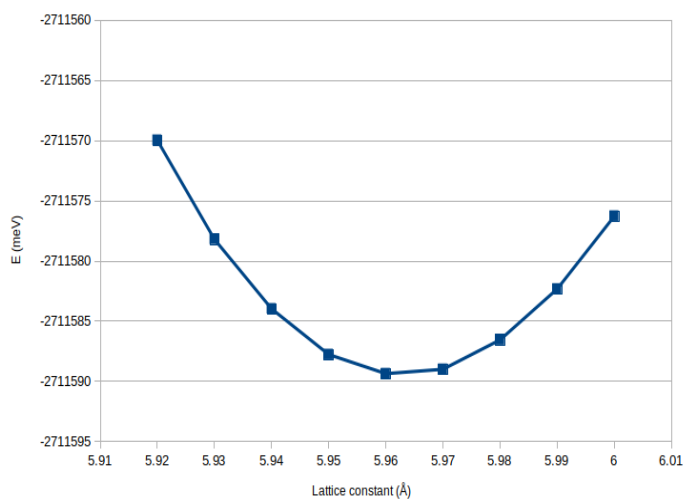


Figure 17. Energy (eV) vs Lattice constant ($\text{\AA}$)

Also, by fitting the total energy versus lattice constant plot in Birch equation of state, the equilibrium lattice constant was obtained as $a_0=5.96303\text{\AA}$ and the value of Bulk modulus (B_0) for NbFeSb was obtained to be 235.2GPa. It is important to point out that this value was higher than that obtained by [52].

4.1.8 Electronic Structure of NbFeSb

Using the converged parameters with the obtained lattice parameter for NbFeSb, the band structure and DOS of NbFeSb were obtained (figure 18 and 19). From the band structure plot, the conduction band minimum (CBM) is situated at X-point while the valence band maximum (VBM) is situated at the L-point like the case of TaFeSb. Therefore, NbFeSb is a semiconductor with an indirect band gap of magnitude $E_g=0.53\text{eV}$. This value which is very much smaller than the energy gap of TaFeSb is in perfect agreement with other theoretical calculation results [52]. The relatively small band gap of NbFeSb resulted in relatively higher electrical conductivity at room temperature as compared to the TaFeSb. The Projected Density of State graph (figure 19) shows that the major contributor to the states in the valence band is Fe followed by the Ta. However, the major contributor in the conduction is the Ta followed by the Fe as in the case of TaFeSb.

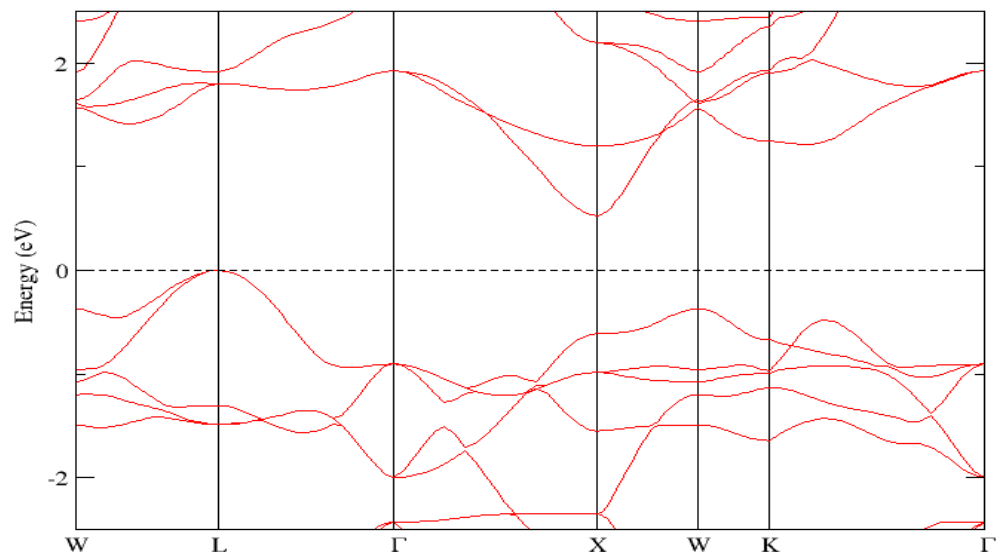


Figure 18. Left: Band structure of NbFeSb Right: DOS of NbFeSb

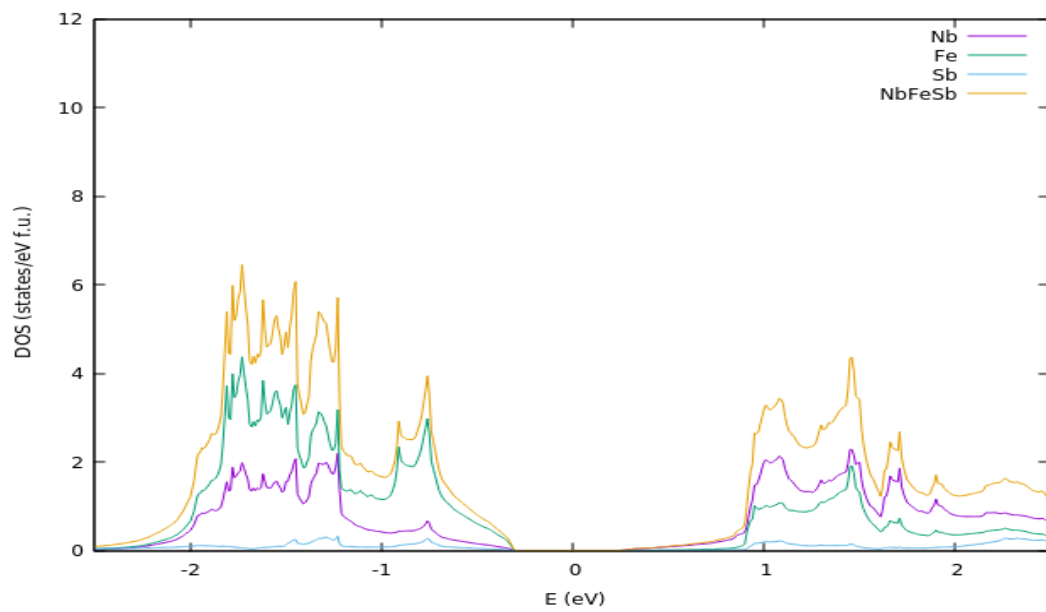


Figure 19. DOS of NbFeSb

4.1.9 Thermoelectric Properties of Pure XFeSb

The following graphs show the dependence of the thermoelectric properties of pure TaFeSb and NbFeSb on temperatures. Figure 20 shows that the electrical conductivity for both TaFeSb and NbFeSb. From this graph, we could see that at a temperature below 300K the electrical conductivity is approximately zero for both compounds. However, the electrical conductivity for NbFeSb starts to increase when the temperature goes slightly above room temperature. The increase in conductivity can be ascribed to the thermal excitation due to temperature increase which causes the generation of charge, Semiconductor behavior carriers. In the case of TaFeSb, no noticeable increase is observed until when the temperature goes slightly above 500K, this is due to the relatively larger band gap of TaFeSb as compared to NbFeSb. It is important to mention here that the results obtained follow a similar trend with the experimental results even though there is a sharp increase in the electrical conductivity at temperature range above 500K for TaFeSb which is in contrast with the experimental result for TaFeSb by [13] This is probably due to the fact that the output of BoltzTraP2 is conductivity divided by the relaxation time and this relaxation time depends on several factors such as temperature and the band edge and since this is not the main focus of this work, we only considered dependence on temperature. From the Seebeck versus Temperature plot (figure 21), it can be noted that TaFeSb behaves as n-type with negative Seebeck coefficient at low temperature range, (200K-300K). However, at higher temperature TaFeSb behaves as p-type which, since half Heusler compounds are aimed for high temperature applications, this implies that at the operating condition TaFeSb is likely going to behave as p-type. NbFeSb behaves as n-type for a larger temperature range of (200K-600K), above this temperature range the compound

behaves as p-type. Also, the Seebeck coefficient versus temperature plot (figure 20-right) shows that TaFeSb has higher Seebeck coefficient as compared to NbFeSb for all temperature range above room temperature. Since Seebeck coefficient effects the Power Factor (PF) more than the electrical conductivity, then we observe higher PF for TaFeSb than NbFeSb (see figure 21-left) even though NbFeSb possesses higher electrical conductivity. It is also worth noting that these results indicate that TaFeSb will probably yield a better figure of merit (zT) value than the NbFeSb. Again, the higher electrical conductivity of NbFeSb will undoubtedly result in higher electronic thermal conductivity for NbFeSb than for TaFeSb as observed in (figure 21-right). High electronic thermal conductivity is undesired as this will lower the figure of merit. This explains why TaFeSb will produce a higher zT value as compared to NbFeSb. The lattice thermal conductivity for both compounds were estimated from Slack's equation [59]. The results are shown in figure 22-left, where it is clear that lattice thermal conductivity which is the phonon contribution to thermal conductivity for both compounds at each temperature are approximately the same. Figure 22 right shows the variation of the zT for each compound with Temperature where the value of zT for TaFeSb is higher than that of NbFeSb at all temperatures as expected.

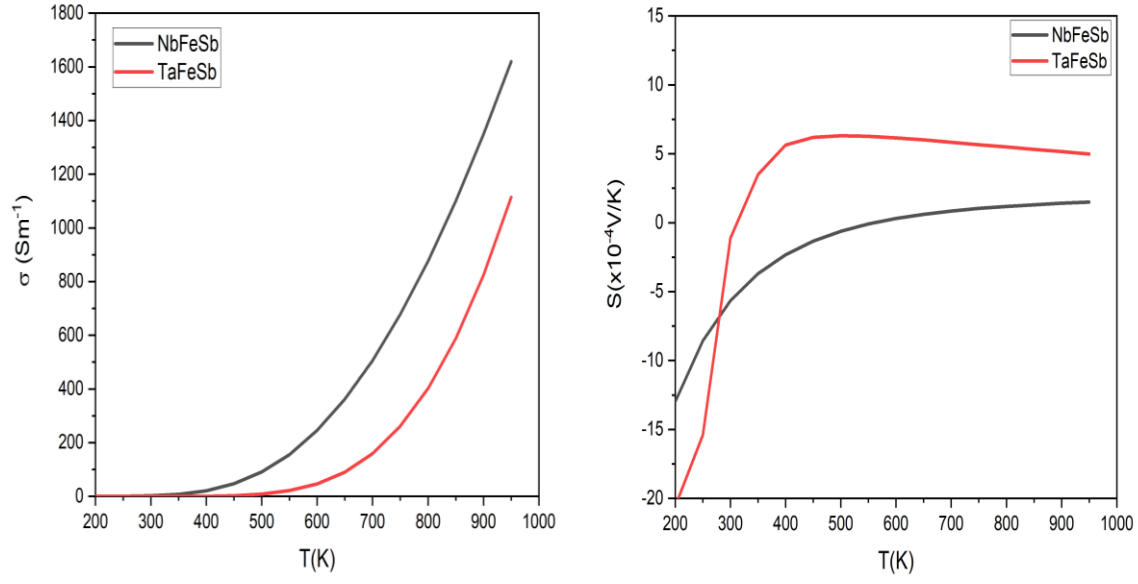


Figure 20: left -Conductivity (Sm^{-1}) vs T (K), right- Seebeck coefficient (V/K) vs T (K) for TaFeSb and NbFeSb

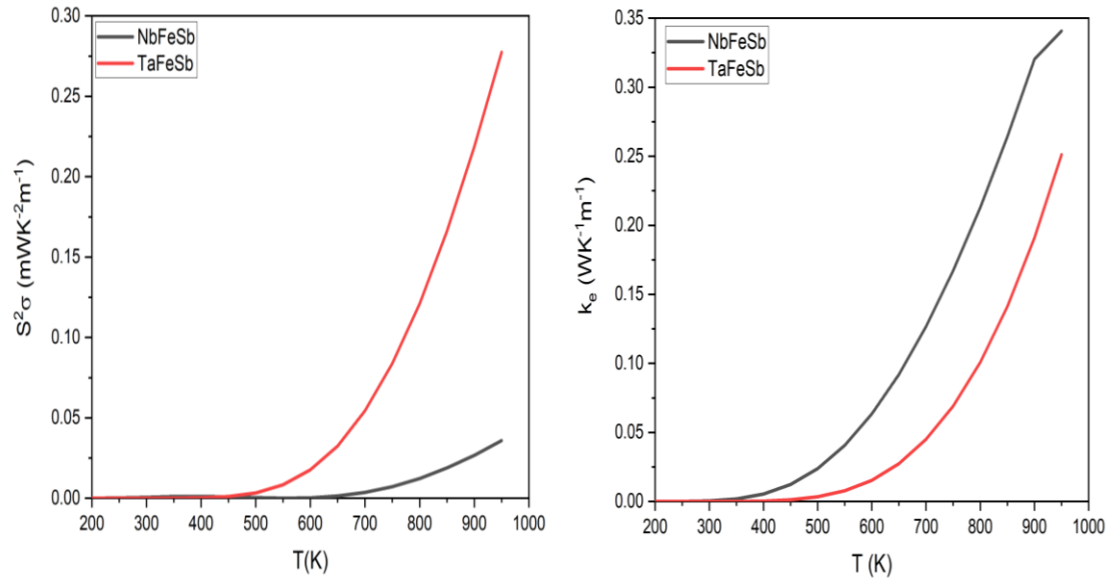


Figure 21. Power factor ($\text{WK}^{-2}\text{m}^{-1}$) vs T (K) right- Electronic thermal conductivity ($\text{WK}^{-1}\text{m}^{-1}$) vs T (K)

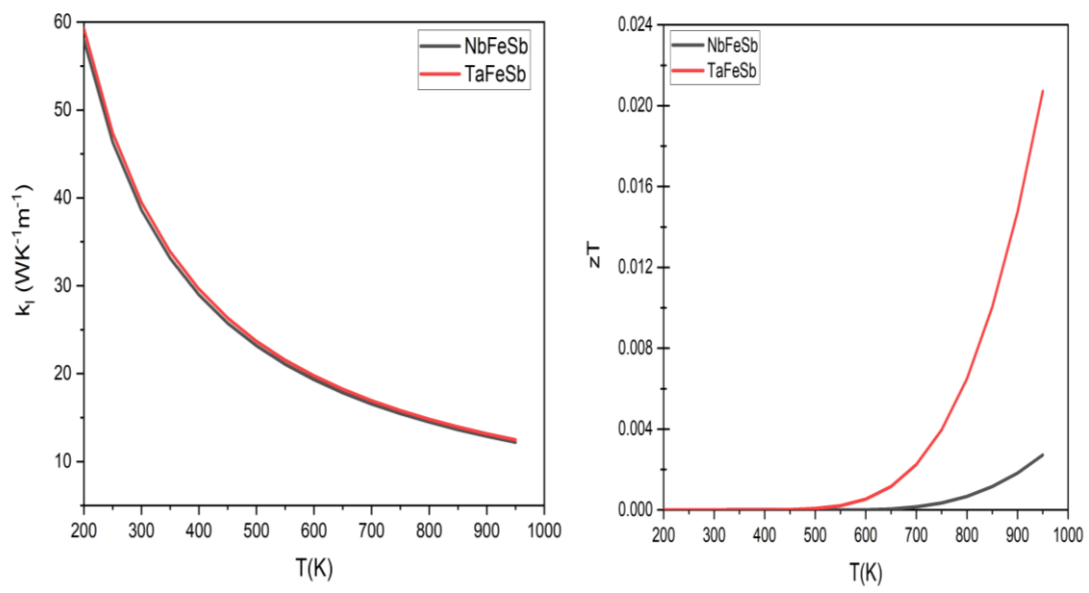


Figure 22. Lattice thermal conductivity ($\text{WK}^{-1}\text{m}^{-1}$) vs T (K), right- Figure of Merit (zT) vs T (K)

Table V below show the power factor obtained for the two compounds at 300K. Even though the values of Power factor for the two compounds are extremely low, we can still infer from these results that pure NbFeSb possess higher Power factor at room temperature as compared to pure TaFeSb. This was because at room temperature the Seebeck coefficient for both compounds are almost the same while the electrical conductivity of NbFeSb at room temperature is about 70 times that of TaFeSb.

Table 5 Transport properties of pure NbFeSb and TaFeSb at room temperature.

XFeSb	S(V/K)	σ ($\Omega^{-1}\text{m}^{-1}$)	$S^2 \sigma$ ($\text{WK}^{-2}\text{m}^{-1}$)
X=Ta,	-0.00112715	0.0284	3.6×10^{-8}
X=Nb	-0.000564575	1.89821789	6.05×10^{-7}

4.2 Electronic Thermoelectric Properties of Doped TaFeSb

This subsection presents the results obtained for doped TaFeSb from RBA and Supercell. Firstly, the results obtained for p-type and n-type TaFeSb is discussed, this is then followed by the discussion on the thermoelectric properties of Mn-doped and Co-doped TaFeSb.

4.2.1 Electronic Thermoelectric Properties of p-type and n-type TaFeSb

For the purpose of comparison, the thermoelectric properties of p-type and n-type XFeSb were evaluated by employing rigid band approximation (RBA) in BoltzTraP2 where the dopant atoms only caused a shift in the fermi level but no effect on the band structure. Based on this, the following graphs were obtained for TaFeSb:

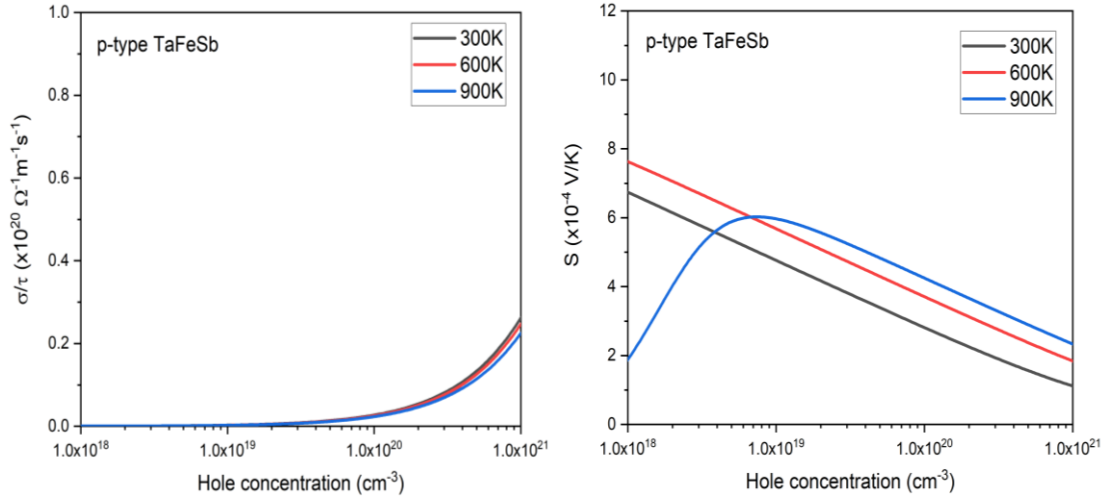


Figure 23. σ/τ ($\times 10^{20} \Omega^{-1} \text{m}^{-1} \text{s}^{-1}$) vs Hole concentration(cm^{-3}) Right: S ($\times 10^{-4} \text{ V/K}$) vs Hole concentration (cm^{-3})

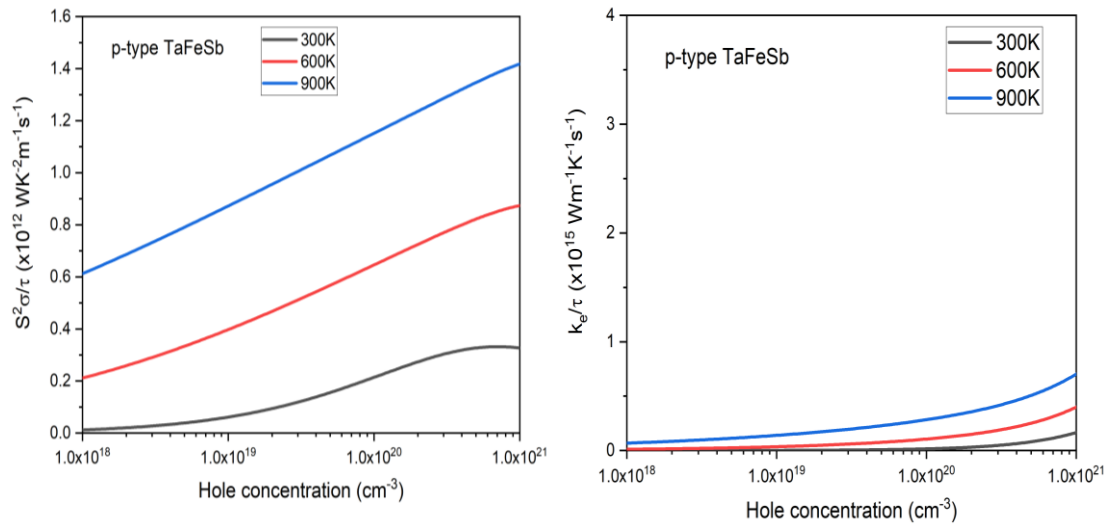


Figure 24. Left: $S^2\sigma/\tau$ ($\times 10^{11} \text{ WK}^{-2} \text{m}^{-1} \text{s}^{-1}$) vs Hole concentration(cm^{-3}) Right: k_e/τ ($\times 10^{15} \text{ WK}^{-1} \text{m}^{-1} \text{s}^{-1}$) vs Hole concentration (cm^{-3})

These graphs clearly show that Maximum Power Factor shift towards higher doping level as temperature increases from 300K to 900K for the p-type TaFeSb. By multiplying the maximum power factor divided by relaxation time (PF/τ) by the value of relaxation time at 300K, a maximum Power fact of 15.7mW/mK^2 was obtained for p-type TaFeSb at a hole concentration of $6.9 \times 10^{20}\text{cm}^{-3}$ ($x=0.036$), this was close to a value of 16.11mW/mK^2 ($x=0.037$) obtained by [52]. At the same doping concentration and temperature a value of 25.4 mW/mK^2 was obtained for the n-type TaFeSb.

To obtain the true dependence of Power Factor (PF) with temperature, the output of BoltzTrap2 were post processed by multiplying the σ/τ and PF/τ by temperature dependence τ ($\tau \propto T^{-3/2}$). The constant of proportionality was obtained by substituting the value for τ at 300K obtained by [52]. This yielded the results below for 600K and 900K:

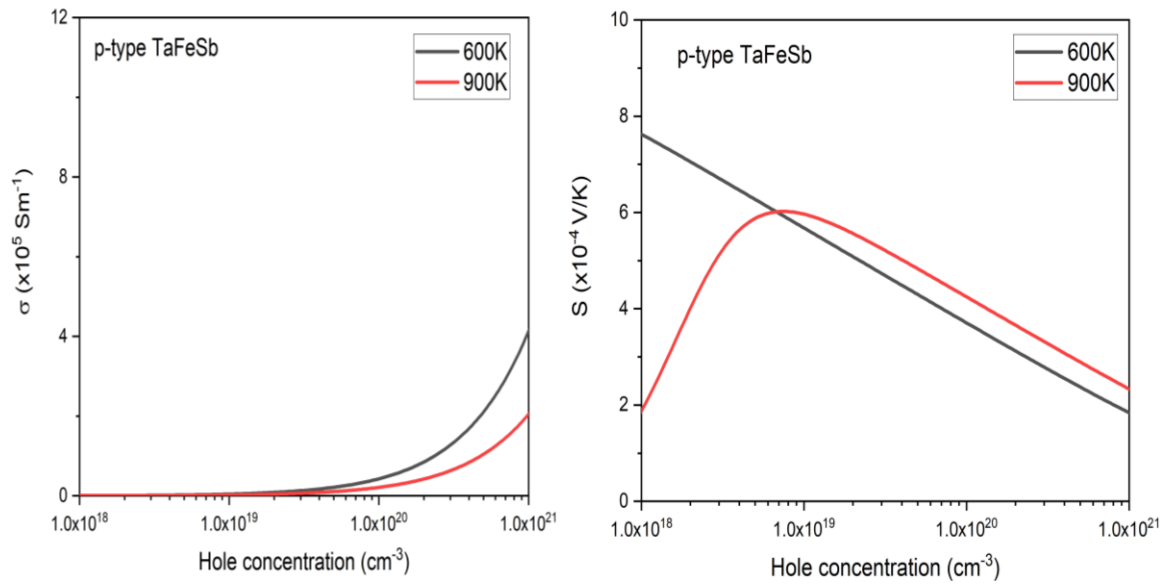


Figure 25. Left: σ (10^5 Sm^{-1}) vs Hole concentration(cm^{-3}) Right: S (10^{-4} V/K) vs Hole concentration(cm^{-3})

The graphs above show the extent to which doping can affect the electrical conductivity and the Seebeck Coefficient. In figure 27-left, it can be noted that p-type TaFeSb can yield a conductivity value as high as $\sim 4 \times 10^5 \text{Sm}^{-1}$ for a doping concentration of $1 \times 10^{21} \text{cm}^{-3}$ at 600K and a value of $\sim 3 \times 10^5 \text{Sm}^{-1}$ at 900K for the same carrier concentration. It is also obvious from this graph that the electrical conductivity decreases with increase in temperature due to charge carrier scattering but increases with increase in doping level. The significant increase in the electrical conductivity was due to the modification in the density of state by doping and the increased population density. Again, it is important to remind the reader that the results above were obtained by virtual doping in BOLTZTRAP2 software which did not consider the type of dopant atom, the doping site and its effect on the band structure and density of state. Figure 25-right shows the dependence of Seebeck coefficient on the hole concentration, this plot reveals that the Seebeck coefficient at moderate and high doping level, the S decreases with increase in charge carrier concentration as expected from equation (4) in section 1.3.1. At extremely low hole concentration, it can be seen on the graph that the S increases with increase in hole concentration at 900K. This may be due to the fact that concentration is very low (as it is close to the intrinsic concentration) has such has negligible effect on the S. It can then be inferred that at extremely low hole concentration, S increases with concentration until it reaches a threshold (temperature specific) where S begins to decrease with increase in hole concentration. From the graph, S at 900K is approximately $2.5 \times 10^{-4} \text{V/K}$ at a hole concentration $1 \times 10^{21} \text{cm}^{-3}$ while S approximately $2 \times 10^{-4} \text{V/K}$ at the same doping level.

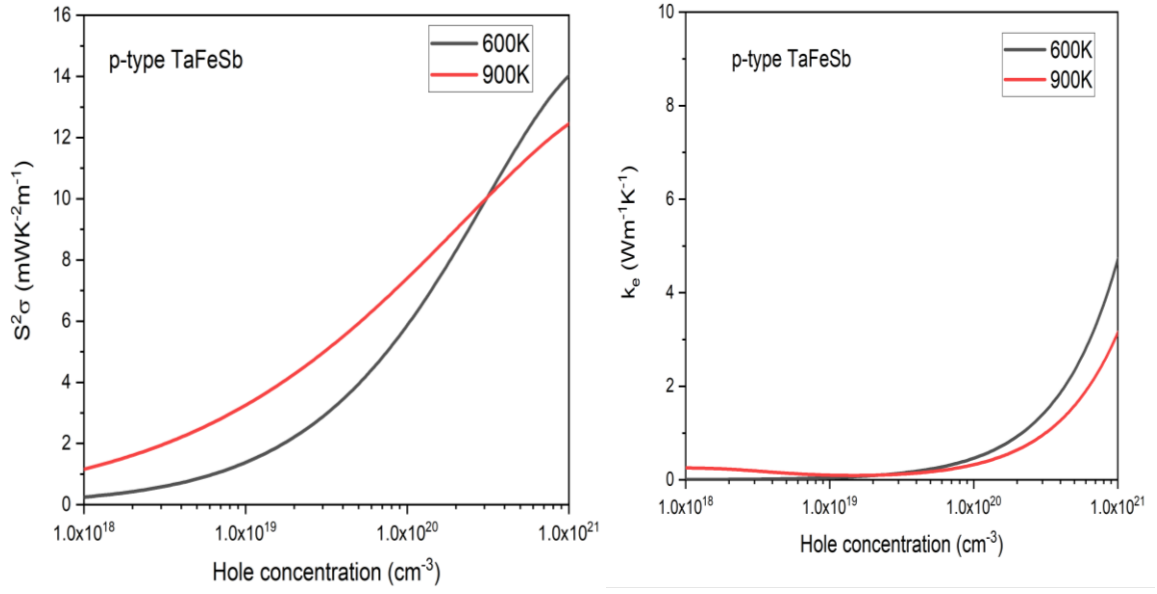


Figure 26. Left: $S^2\sigma$ ($\text{WK}^{-2}\text{m}^{-1}$) vs Hole concentration (cm^{-3}) Right: k_e ($\text{WK}^{-1}\text{m}^{-1}$) vs Hole concentration(cm^{-3})

Figure 26- show the dependence of power factor and electronic thermal conductivity on hole concentration or doping level. From these plots, we can observe that both power factor and electronic thermal conductivity increase with increase in hole concentration. Figure 26-left also reveals that a maximum power factor ($PF \sim 14 \text{mWK}^{-2}\text{m}^{-1}$) can be obtained for a p-type TaFeSb at 600K for a doping concentration of $1 \times 10^{21} \text{cm}^{-3}$. This value is 2 less than the value $\sim 16 \text{mWK}^{-2}\text{m}^{-1}$ obtained at 300K. At 900K., a maximum value of $\sim 12 \text{mWK}^{-2}\text{m}^{-1}$ was obtained for p-type TaFeSb for a doping concentration of $1 \times 10^{21} \text{cm}^{-3}$. However, the electronic conductivity can go as high as $3 \text{WK}^{-1}\text{m}^{-1}$ at this hole concentration as shown in figure 26-right.

The figures below show the dependence of transport properties (σ/τ , S , $S^2\sigma/\tau$ k_e/τ) on the electron concentration for the n-type TaFeSb.

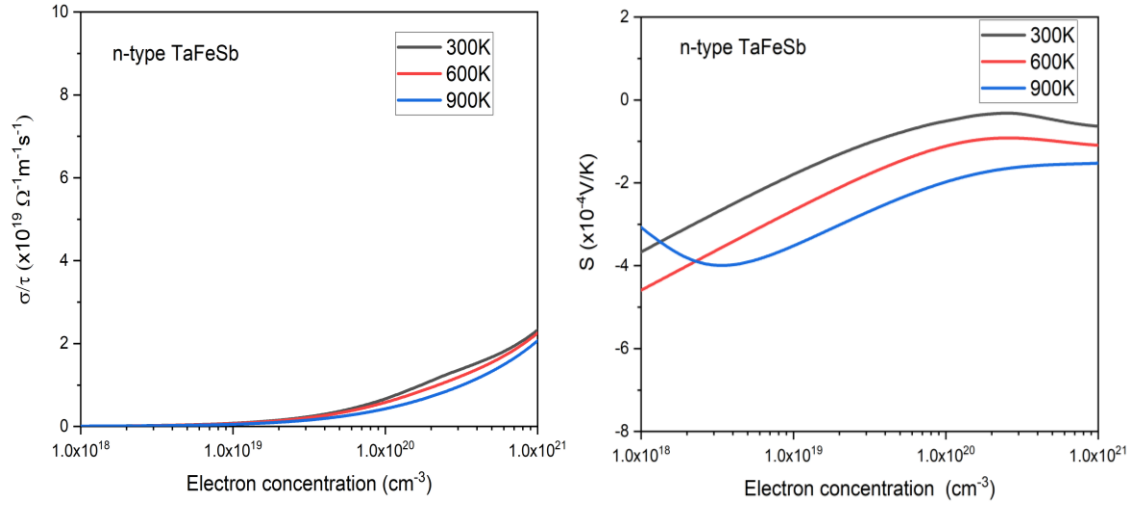


Figure 27. Left: σ/τ ($10^{19} \Omega^{-1} \text{m}^{-1} \text{s}^{-1}$) vs Electron concentration(cm^{-3}) Right: S (10^{-4}V/K) vs Electron concentration (cm^{-3})

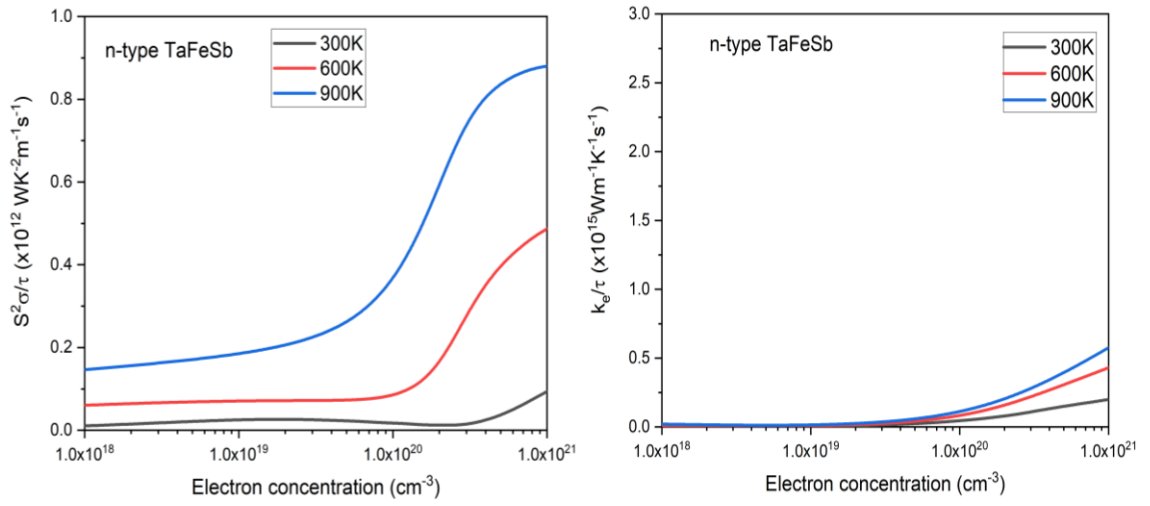


Figure 28. Left: $S^2\sigma/\tau$ ($10^{12} \text{WK}^{-2} \text{m}^{-1} \text{s}^{-1}$) vs Electron concentration(cm^{-3}) Right: k_e/τ ($10^{15} \text{WK}^{-1} \text{m}^{-1} \text{s}^{-1}$) vs Electron concentration (cm^{-3})

It is also apparent from these results that the transport properties increase with increase in carrier density. To be able to fully understand the true dependence of the transport properties on the electron concentration for n-type TaFeSb, the following graphs are presented:

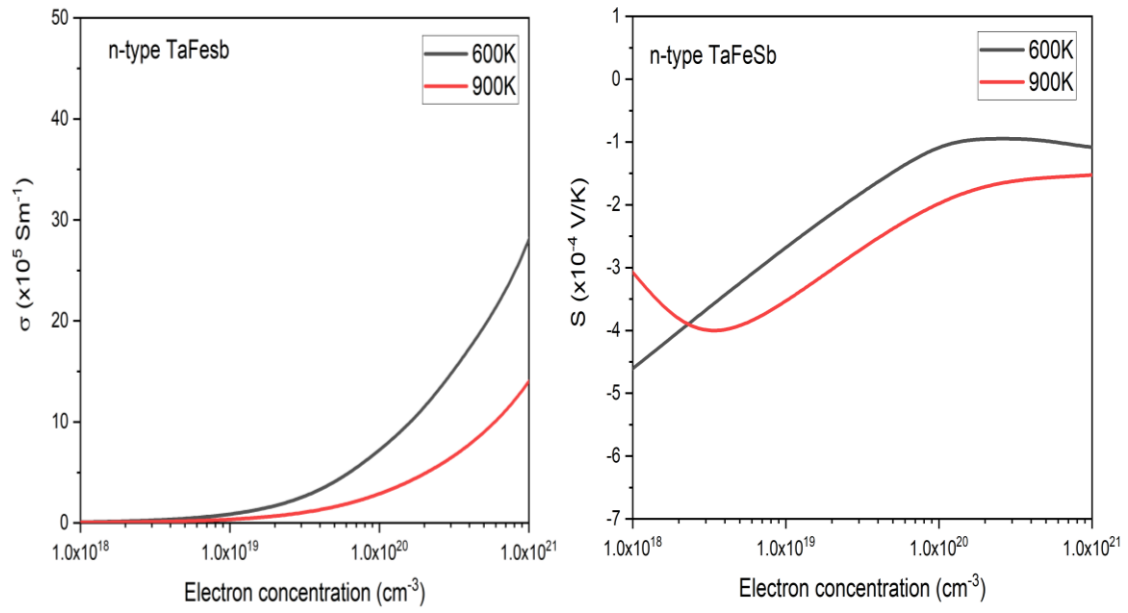


Figure 29. Left: σ ($\times 10^5 \text{ Sm}^{-1}$) vs Electron concentration (cm^{-3}) Right: S ($\times 10^{-4} \text{ V/K}$) vs Electron concentration (cm^{-3})

Figure 29-left shows electrical conductivity versus electron concentration or doping level plot for n-type TaFeSb, also as expected electrical conductivity increases with increase in electron concentration due to modification of DOS and an increase in the population density. For both temperatures maximum Seebeck Coefficient at 600K and 900K from the graph are approximately $28 \times 10^5 \text{Sm}^{-1}$ and $13 \times 10^5 \text{Sm}^{-1}$ for a doping concentration of $1 \times 10^{21} \text{cm}^{-3}$. High electrical conductivity observed in this case may be due higher electron mobility and high relaxation time as compared to p-type TaFeSb. Also, as observed in figure xxix-right for both $T=600\text{K}$ and $T=900\text{K}$, the absolute value of Seebeck coefficient ‘S’ first increases with concentration but at this time for a long concentration range before it reaches a maximum at $\sim 1 \times 10^{20} \text{cm}^{-3}$ and then decreases with increase in concentration.

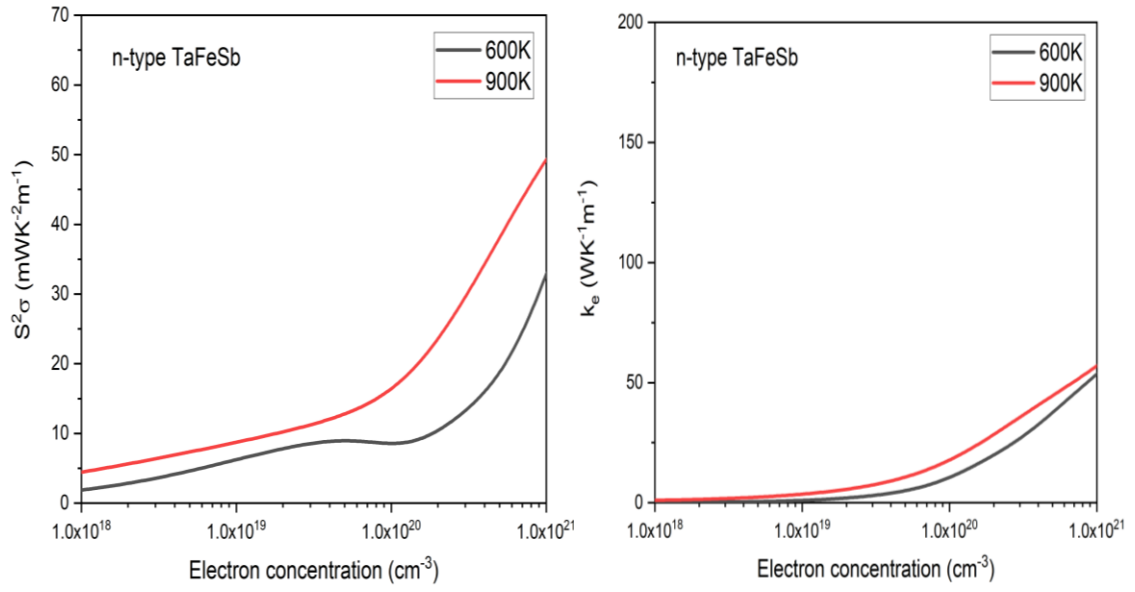


Figure 30. Left: $S^2\sigma$ (mWK⁻²m⁻¹) vs Electron concentration (cm⁻³) Right: k_e (WK⁻¹m⁻¹) vs Electron concentration (cm⁻³)

Figure 30 left shows the power factor versus concentration for n-type TaFeSb, from this graph we can see that no significant increase in the power factor was observed for both temperatures until when concentration is approximately $n \sim 1 \times 10^{20} \text{cm}^{-3}$. The power factor then increases from this point up to a value of $\sim 50 \text{mWK}^{-2} \text{m}^{-1}$ at 900K and $\sim 33 \text{mWK}^{-2} \text{m}^{-1}$ at 600K for $n \sim 1 \times 10^{21} \text{cm}^{-3}$. Due to high electrical conductivity of n-type TaFeSb, the electronic thermal conductivity is also high as seen in figure 30-right, where it is apparent that electronic thermal conductivity can go as high as $\sim 50 \text{WK}^{-1} \text{m}^{-1}$ for both $T=600\text{K}$ and $T=900\text{K}$ at $n \sim 1 \times 10^{21} \text{cm}^{-3}$.

4.2.2 Electronic Structure of Mn and Co-doped TaFeSb

Having verified the effect of virtual doping of TaFeSb using Rigid Band Approximation (RBA) approach, the dopant atoms were then explicitly introduced at the Fe site to be able to compare with RBA results, a high concentration of $2.38 \times 10^{21} \text{cm}^{-3}$ ($x=0.125$) was chosen for the supercell method. First the effects of the dopants on the density of state were studied and these are shown in figure 31 and 32 below. It is apparent from these graphs that the addition of Mn and Co considerably contributed to the DOS in the conduction and valence bands. Since the transport properties are dependent on the electronic density of states, the contribution to the DOS will eventually result to a significance increase in electrical conductivity in both cases. This of course is expected to increase the power factor in both cases as compared to the intrinsic.

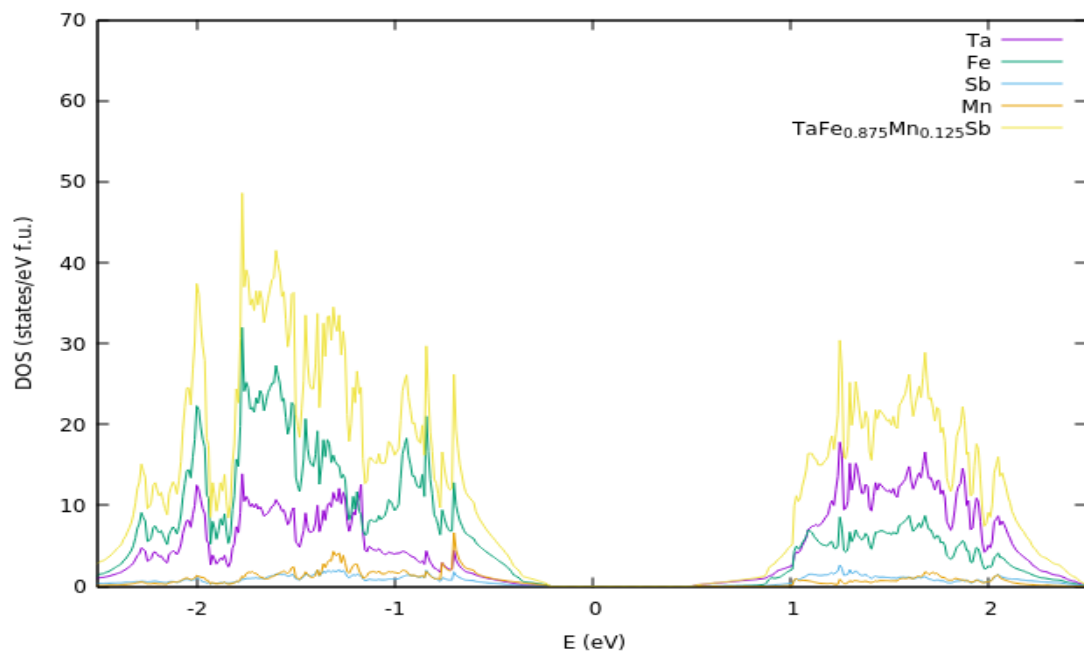


Figure 31. DOS of TaFe_{0.875} Mn_{0.125}Sb

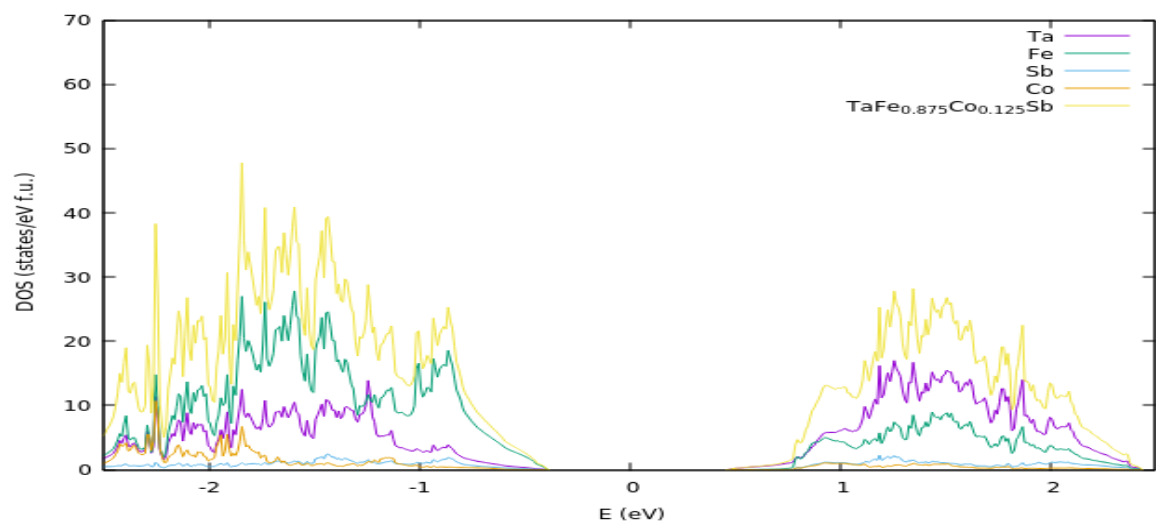


Figure 32. DOS of TaFe_{0.875} Co_{0.125}Sb

4.2.3 Electronic Thermoelectric Properties of Mn and Co-doped TaFeSb

Introducing Mn and Co dopants at the Fe lattice site are expected to have significant effects on the electronic thermoelectric properties. This is because, Mn replacing Fe at its lattice site introduces a hole due to one electron deficiency of Mn with respect to the parent atom Fe. As a result, Mn doped at Fe site produces a p-type material. While Co doped at the Fe site introduces an electron which makes the material to be n-type. As expected, this respective doping results in change in fermi level which causes a significant change in the electronic thermoelectric properties. The introduction of foreign atoms is also expected to cause a point scattering of phonons which in turn will lead to reduction of lattice thermal conductivity. Figure 33 left and right give the electrical conductivity versus temperature plot and the Seebeck coefficient versus temperature plot for Mn doped TaFeSb respectively. From these plots, the electrical conductivity decreases with increasing temperature as shown in figure 33 left as a result of the scattering of charge carriers as temperature increases an indication of heavy doping. From this plot, the value of electrical conductivity at 600K is approximately $8 \times 10^5 \text{Sm}^{-1}$ and $\sim 6 \times 10^5 \text{Sm}^{-1}$ at 900K. Also from the Seebeck versus temperature plot in figure 33 right, the S increases with increase in Temperature as expected. From this graph a value of $11.5 \times 10^{-5} \text{V/K}$ was obtained at 600K and $\sim 13 \times 10^{-5} \text{V/K}$ at 900K.

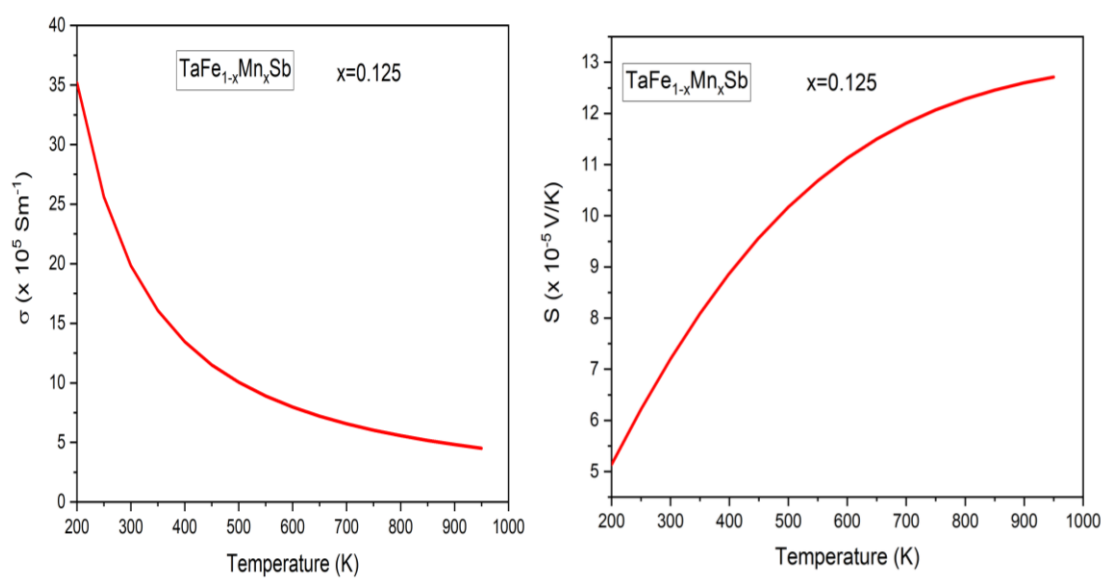


Figure 33. Left: σ ($\times 10^5 \text{ Sm}^{-1}$) vs T(K) Right: S ($\times 10^{-5} \text{ V/K}$) vs T(K)

Reduction in electrical conductivity as temperature increases (in figure 33-left) which is attributed to high charge carrier scattering causes a significant decrease in the power factor as shown in figure 34-left below. From this figure , the power factor at 900K can be approximated to be $7.5\text{mWK}^{-2}\text{m}^{-1}$ while at 600K is $\sim 10\text{mWK}^{-2}\text{m}^{-1}$. Figure 34-right shows the dependence of the electronic thermal conductivity on temperature and as expected the electronic thermal conductivity decreases from a value of $\sim 18\text{WK}^{-1}\text{m}^{-1}$ at 600K to a value of $\sim 15\text{WK}^{-1}\text{m}^{-1}$ at 900K.

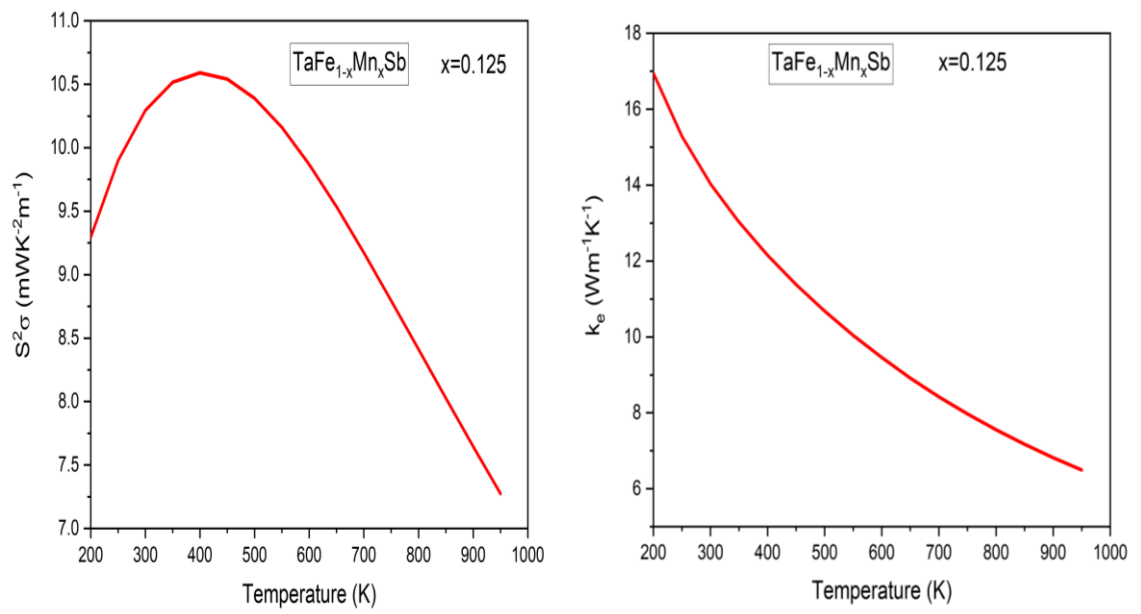


Figure 34. Left: $S^2\sigma$ ($\text{mWK}^{-2}\text{m}^{-1}$) vs T(K) Right: k_e ($\text{Wm}^{-1}\text{K}^{-1}$) vs T(K)

Figure 35-left below shows the lattice thermal conductivities for both pure and Mn doped TaFeSb versus temperature plot. From this graph, it can be noted that there is no noticeable difference between the lattice thermal conductivity for pure and the doped sample, this may be due to the small mass difference between the parent atom Fe and the dopant atom Mn which implies small strain induced within the lattice and less phonon scattering. It can also be noted from this figure that the value of lattice thermal conductivities for both pure and Mn-doped compounds are $\sim 15 \text{WK}^{-1}\text{m}^{-1}$ and $\sim 18 \text{WK}^{-1}\text{m}^{-1}$ at 900K and 600K respectively.

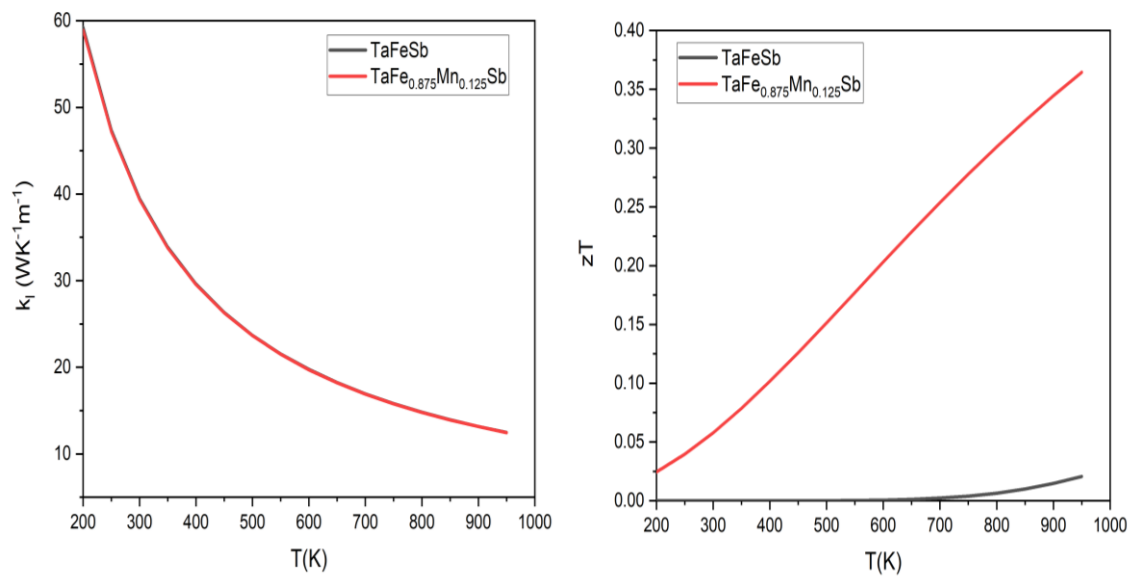


Figure 35. Left: k_l ($\text{WK}^{-1}\text{m}^{-1}$) vs T(K) Right: Figure of merit (zT) vs T(K)

The following figures show the results obtained for the Co-doped TaFeSb; figure 36 left gives the electrical conductivity versus temperature plot while figure 36 -right shows the dependence of Seebeck coefficient on Temperature. From the conductivity versus temperature plot, the conductivity was found to decrease from a value of $50 \times 10^5 \text{Sm}^{-1}$ at 600K to a value $25 \times 10^5 \text{Sm}^{-1}$ the huge electrical conductivity predicted for Co-doped TaFeSb here is consistent with the electrical conductivity predicted for n-type TaFeSb using RBA method. As mentioned in the previous section, the huge electrical conductivity is as a result of the high relaxation time for electron. However, in the S versus T plot, negative increase from a value of $\sim -8 \times 10^{-5} \text{V/K}$ at 600K to a value of $\sim -10 \times 10^{-5} \text{V/K}$ at 900K for the Co-doped TaFeSb was observed.

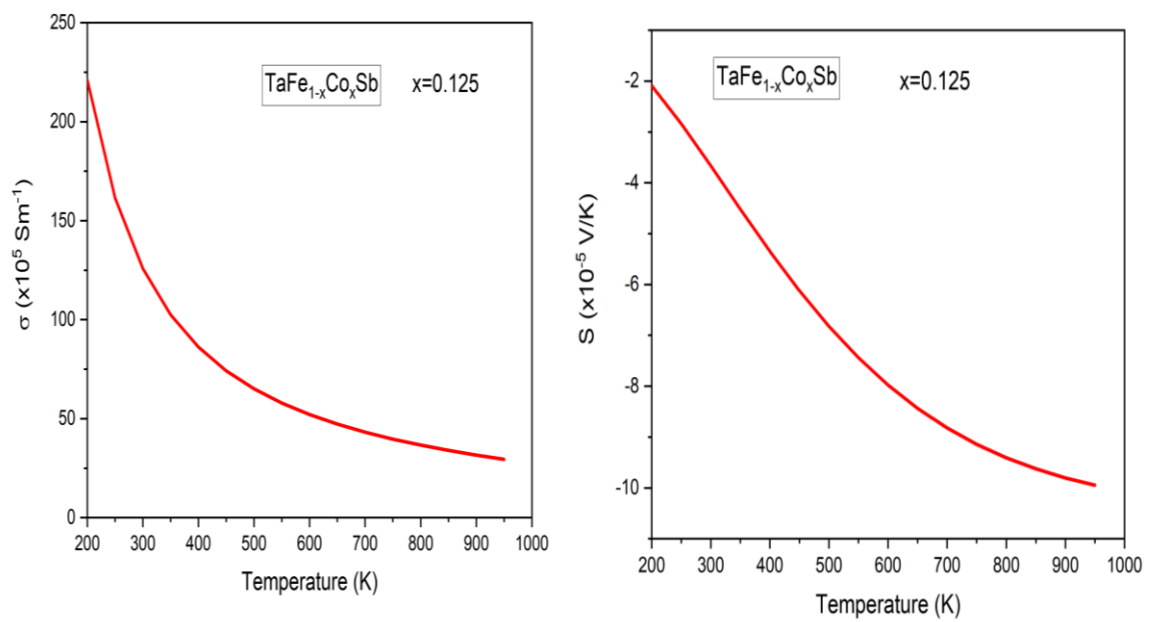


Figure 36. Left: σ ($\times 10^5 \text{ Sm}^{-1}$) vs T(K) Right: S ($\times 10^{-5} \text{ V/K}$) vs T(K)

Due to very high electrical conductivity and relatively moderate Seebeck coefficient values, high power factor values were obtained and the dependence of this power factor on temperature is shown in figure 37-left below. From this figure, we see a value of $\sim 300 \text{mWK}^{-2}\text{m}^{-1}$ at 600K and $\sim 260 \text{mWK}^{-2}\text{m}^{-1}$ at 900K. Figure 37- right shows the dependence of electronic thermal conductivity on temperature, as expected this graph shows a decrease in electronic thermal conductivity with increase in temperature. From the graph, electronic thermal conductivity decreases from a value of $\sim 80 \text{Wm}^{-1}\text{K}^{-1}$ at 600K to a value of $\sim 55 \text{Wm}^{-1}\text{K}^{-1}$ at 900K.

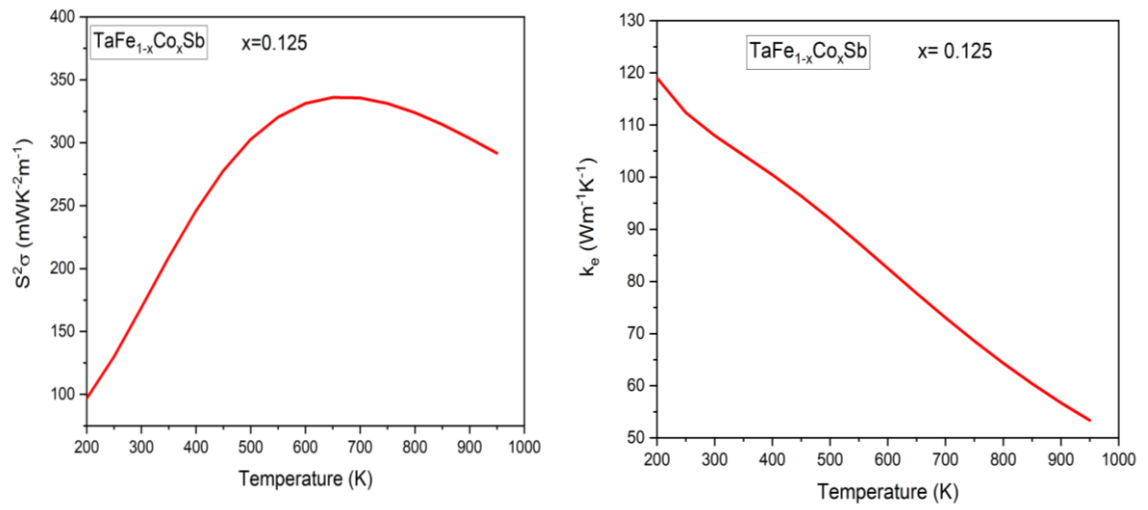


Figure 37. Left: $S^2\sigma$ ($\text{mWK}^{-2}\text{m}^{-1}$) vs T(K) Right: k_e ($\text{Wm}^{-1}\text{K}^{-1}$) vs T(K)

To summarize all, as temperature increases the S becomes more negative, this leads to an initial increase in PF up to a temperature of about 650K. Beyond this temperature the PF gradually decreases with temperature because of low electrical conductivity which further decreases with increase in temperature and slight change of S with temperature. Though the Co-doped TaFeSb produces relatively larger power factor as compared to Mn doped, it is worth noting that this huge PF is coming from the electrical conductivity which also implies huge k_e as seen in k_e vs temperature graph. This is not desirable as larger k_e will decrease the zT .

The dependence of the lattice thermal conductivity and zT on temperature for pure and Co-doped TaFeSb is shown below; from figure 38 left we can see a small difference between the lattice thermal conductivity for the pure sample and that of the Co-doped compound where the k_l of the doped TaFeSb can be seen to be slightly below the lattice thermal conductivity for pure TaFeSb at low temperature regime ($\sim 200\text{K}$ to 600K) above this temperature range the lattice thermal conductivity for both cases are approximately the same. The small difference observed in this case is due to relatively large mass difference between Co and Fe as compared to Mn and Fe where no difference was observed.

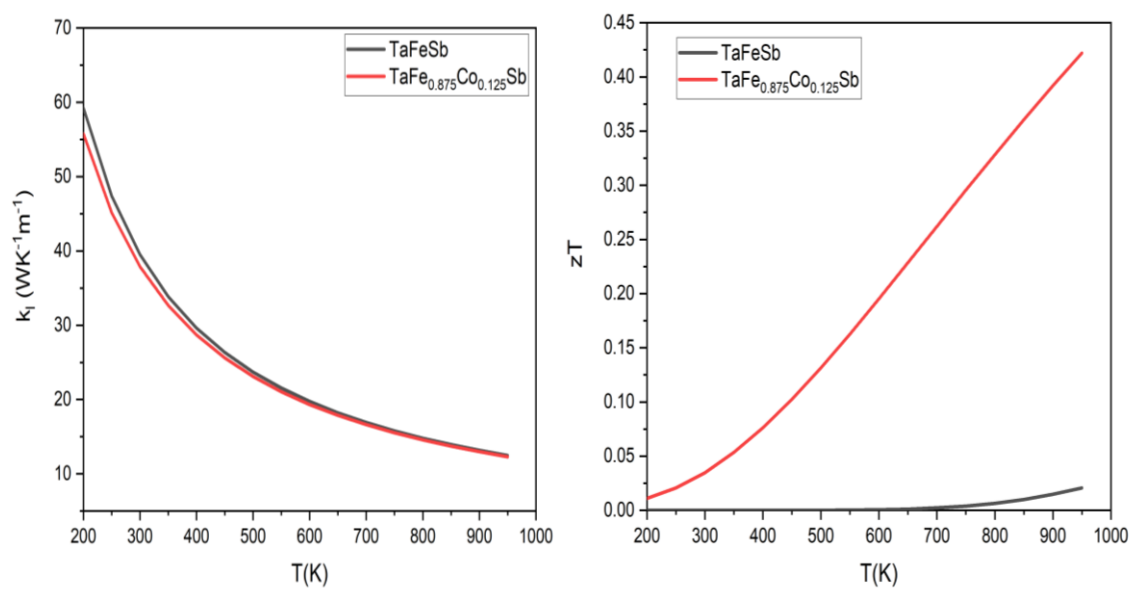


Figure 38. k_l ($\text{WK}^{-1}\text{m}^{-1}$) vs T (K) Right- Figure of merit vs T (K)

The table below, shows the results for the p and n-type TaFeSb at different temperatures for a doping concentration of $2.38 \times 10^{21} \text{ cm}^{-3}$, the p-type and n-type TaFeSb in the table refer to the results obtained by RBA while Mn and Co-doped are respective results for p-type and n-type TaFeSb by supercell approach.

Table 6 Electronic thermoelectric properties of n-type, p-type, Mn-doped and Co-doped TaFeSb at 300K, 600K and 900K.

N=2.38x10²¹cm⁻³	T(K)	$\sigma \times 10^5(\text{Sm}^{-1})$	$S \times 10^{-5}(\text{V/K})$	$S^2 \sigma (\text{mWK}^{-2}\text{m}^{-1})$
p-type TaFeSb	300	27.90	6.90	13.28
	600	9.34	12.52	14.64
	900	4.62	16.81	13.06
Mn-doped TaFeSb	300	19.82	7.2	10.27
	600	7.97	11.13	9.87
	900	4.82	12.59	7.64
n-type TaFeSb	300	145	-5.78	48.44
	600	49.4	-10.56	55.09
	900	25.4	14.01	49.86
Co-doped TaFeSb	300	126	-3.67	16.97
	600	52.1	-7.98	33.18
	900	31.6	-9.8	30.35

From table VI, it is apparent that, RBA overestimated the Seebeck coefficient for both p-type and n-type at 300K, 600K and 900K, this is consistent to the conclusion reached by Mal-Soon et. al. [56] where they claimed that introducing dopant into the lattice of half Heusler tend to affect the hole band structure considerably which lowers the Seebeck coefficient predicted by virtual doping method in BoltzTraP. Also, at 300K, the electrical conductivity obtained from the supercell Mn and Co-doped TaFeSb were found to be lower than those predicted for p and n-type TaFeSb by RBA. However, it is difficult to assign a particle trend to electrical conductivity difference at higher temperature (600K and 900K). This may be due to the approximation which considers only temperature dependent relaxation time used to obtain the electrical conductivities at higher temperature. Nonetheless, it can be inferred from this table that virtual doping in BoltzTraP2 overestimated electrical conductivity, Seebeck coefficient and hence the power factor for both p-type and n-type TaFeSb. Consequently, it can be concluded that TaFeSb does not show rigid band behavior for Co and Mn dopants.

4.3 Thermoelectric Properties of Doped NbFeSb

This subsection presents the results obtained for doped NbFeSb from RBA and Supercell. Firstly, the results obtained for p-type and n-type NbFeSb is discussed, this is then followed by the discussion on the thermoelectric properties of Mn-doped and Co-doped NbFeSb.

4.3.1 Electronic Thermoelectric Properties of p-type and n-type NbFeSb

Similar to TaFeSb, the electronic thermoelectric properties were plotted against hole doping concentration and these results are shown in the figures below;

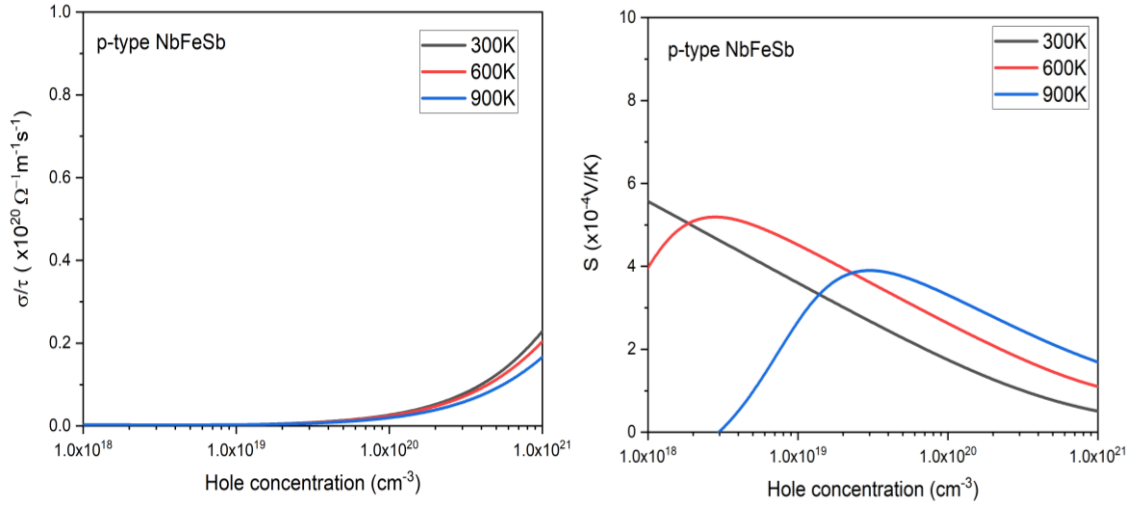


Figure 39. Left: σ/τ ($\times 10^{20} \Omega^{-1} \text{m}^{-1} \text{s}^{-1}$) vs Hole concentration(cm^{-3}) Right: S ($\times 10^{-4} \text{V/K}$) vs Hole concentration (cm^{-3})

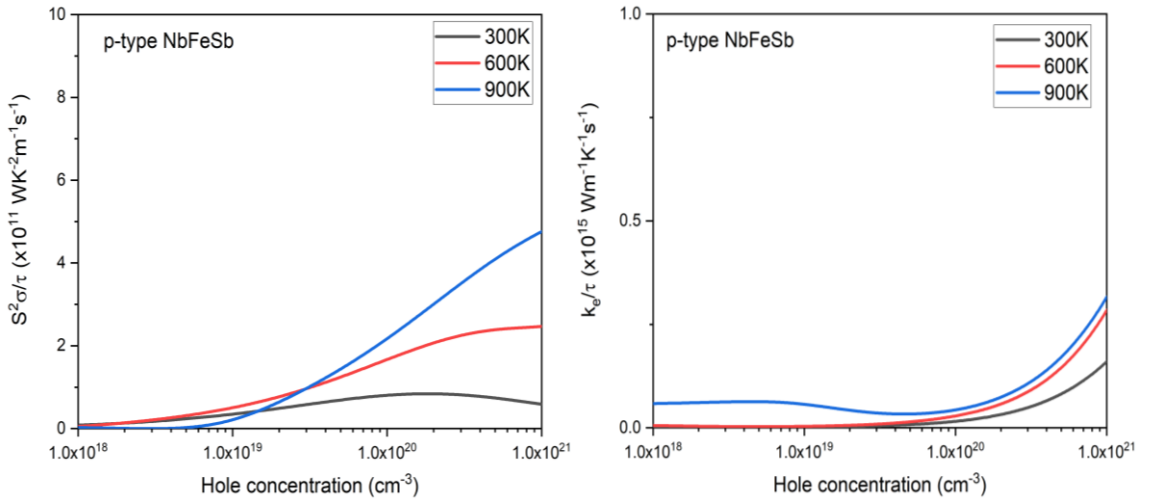


Figure 40. $S^2\sigma/\tau$ ($\times 10^{11} \text{WK}^{-2} \text{m}^{-1} \text{s}^{-1}$) vs Hole concentration(cm^{-3}) Right: κ_e/τ ($\times 10^{15} \text{WK}^{-1} \text{m}^{-1} \text{s}^{-1}$) vs Hole concentration (cm^{-3})

From the graphs above, it is apparent that increase in hole concentration results to improvement in σ/τ , ke/τ and power factor at each temperature. The true dependence of transport properties was obtained by multiplying σ/τ , ke/τ and $S^2\sigma/\tau$ by the value of relaxation time at each temperature, and the results obtained are shown in the graphs below:

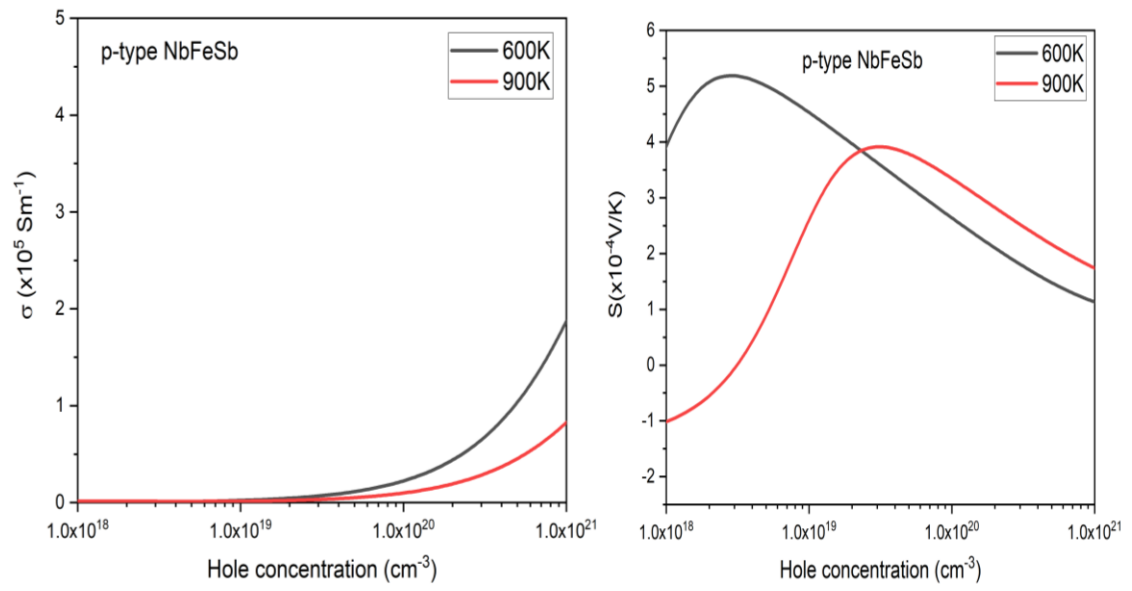


Figure 41. Left- σ (10^5 Sm^{-1}) vs Hole concentration(cm^{-3}) Right- S (10^{-4} V/K) vs Hole concentration(cm^{-3})

In figure 41-left, It is obvious that the electrical conductivity decreases with increase in temperature due to charge carrier scattering but increases with increase in doping level, in this case the value of electrical conductivity can go as high as $1.8 \times 10^5 \text{Sm}^{-1}$ at 600K for a doping concentration of $1 \times 10^{21} \text{cm}^{-3}$ and a value $\sim 0.8 \text{Sm}^{-1}$ for a doping concentration of $1 \times 10^{21} \text{cm}^{-3}$, these values are lower than $4 \times 10^5 \text{Sm}^{-1}$ and $3 \times 10^5 \text{Sm}^{-1}$ at 600K and 900K respectively obtained for TaFeSb, The increase in the electrical conductivity was due to the modification in the density of state by doping and the increased population density. Figure 41-right shows the dependence of Seebeck coefficient on the hole concentration, this plot reveals that the Seebeck coefficient at moderate and high doping level, the S decreases with increase in charge carrier concentration as expected from equation (4) in section 1.3.1. At extremely low hole concentration, it can be seen on the graph that the S increases with increase in hole concentration at 900K. This may be due to the fact that concentration is very low (as it is close to the intrinsic concentration) as such hole doping concentration has negligible effect on the S while other factors such as the mobility of the charge carriers present may be responsible for the increase in S. It can then be inferred that at extremely low hole concentration, S increases with concentration until it reaches a threshold (temperature specific) where S begins to decrease with increase in hole concentration. From the graph, S at 900K is approximately $1.9 \times 10^{-4} \text{V/K}$ at a hole concentration $1 \times 10^{21} \text{cm}^{-3}$ while S is approximately $1.2 \times 10^{-4} \text{V/K}$, these values are also low as compared to $\sim 2.5 \times 10^{-4} \text{V/K}$ and $\sim 2 \times 10^{-4} \text{V/K}$ obtained for TaFeSb at 900K and 600K respectively at the same doping level.

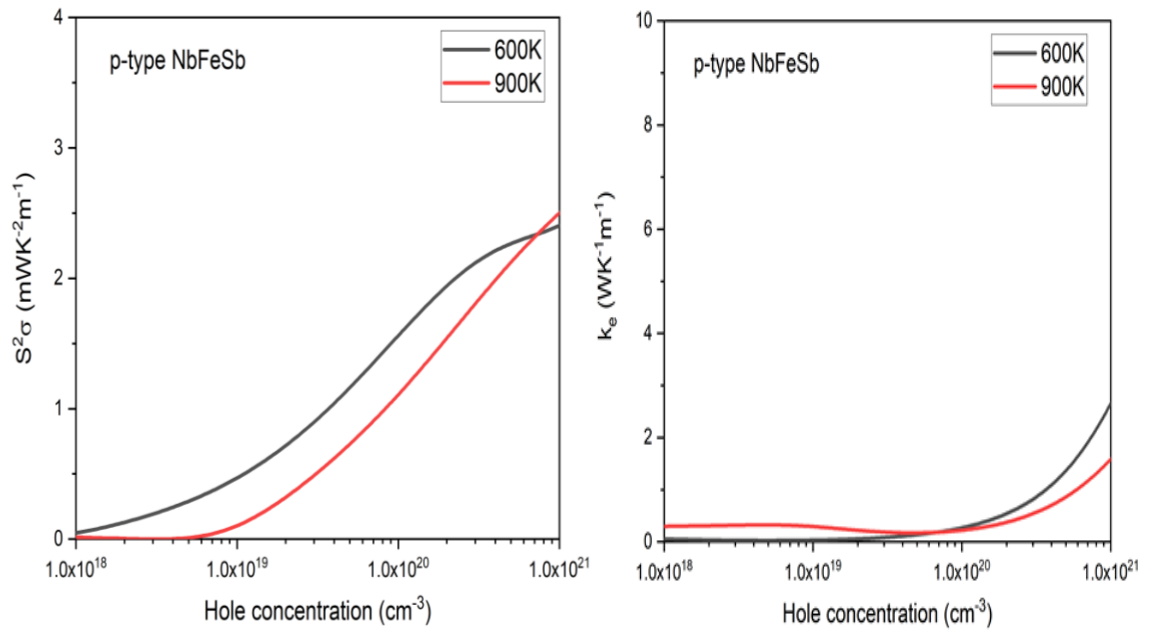


Figure 42. $S^2\sigma$ (mWK⁻²m⁻¹) vs Hole concentration(cm⁻³) Right- k_e (WK⁻¹m⁻¹) vs Hole concentration(cm⁻³)

Figure 42-left and right above show the dependence of power factor and electronic thermal conductivity on hole concentration or doping level. From these plots we can see that both power factor and electronic thermal conductivity increase with increase in hole concentration. Figure 42-left also reveals that a maximum power factor at 600K and 900K are respectively $\sim 2.5 \text{ mWK}^{-2} \text{ m}^{-1}$ and $2.6 \text{ mWK}^{-2} \text{ m}^{-1}$ these values are very much less than $\text{PF} \sim 14 \text{ mWK}^{-2} \text{ m}^{-1}$ at 600K and $12 \text{ mWK}^{-2} \text{ m}^{-1}$ at 900K for p-type TaFeSb at a doping concentration of $1 \times 10^{21} \text{ cm}^{-3}$ confirming p-type TaFeSb as a better p-type material. However, the electronic conductivity can go up to $2.3 \text{ WK}^{-1} \text{ m}^{-1}$ at 600K and $1.8 \text{ WK}^{-1} \text{ m}^{-1}$ at 900K for this hole concentration as shown in figure 42-right.

The dependence of transport properties on electron concentration for NbFeSb are given in the following figures:

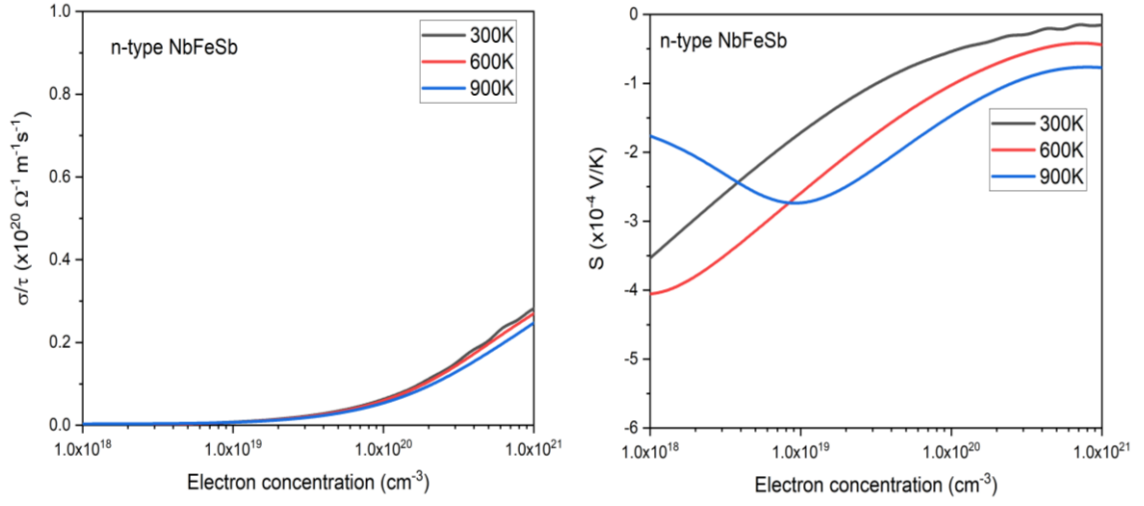


Figure 43. Left- σ ($\times 10^5 \text{Sm}^{-1}$) vs Electron concentration(cm^{-3}) Right- S ($\times 10^{-4} \text{V/K}$) vs Electron concentration(cm^{-3})

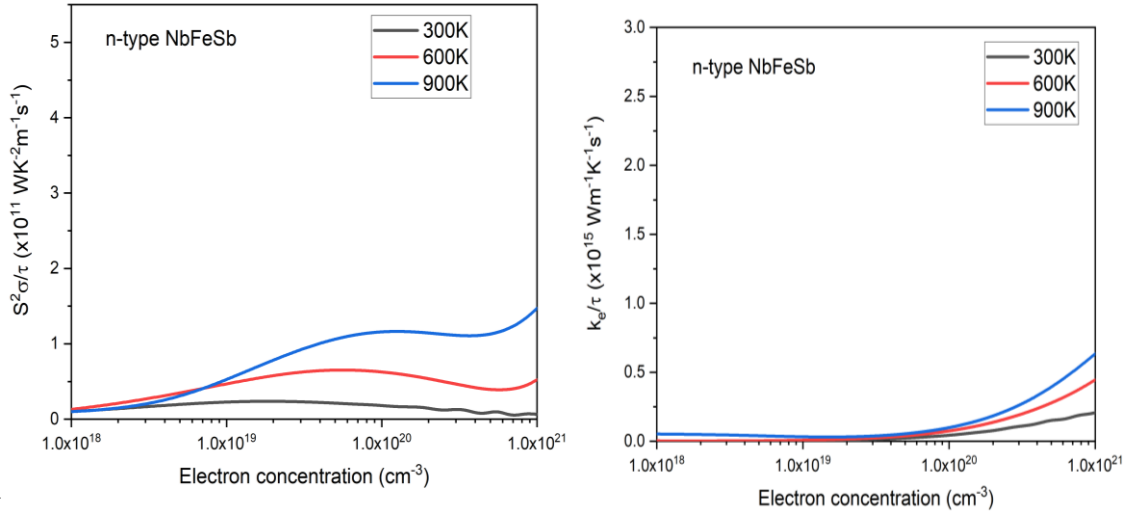


Figure 44. Left: $S^2\sigma$ ($\text{mWK}^{-2} \text{m}^{-1}$) vs Electron concentration(cm^{-3}) Right: k_e ($\text{WK}^{-1} \text{m}^{-1}$) vs Electron concentration(cm^{-3})

the graphs above follow similar trend with the ones obtained for the p-type NbFeSb, as expected, increase in electron concentration results to improvement in σ/τ , k_e/τ and power factor at each temperature.

4.3.2 Electronic Structure of Mn and Co-doped NbFeSb

The electronic structure of Mn and Co-doped TaFeSb are shown in figure 45 and 46 below. Similar to the results obtained for TaFeSb, it is apparent from figure 45 and 46 that the addition of Mn and Co into the lattice of NbFeSb considerably contributed to the Density of states (DOS) in the conduction and valence bands. Since the transport properties are dependent on the electronic density of states, the contribution to the DOS will eventually result to a significance increase in electrical conductivity in both cases. This of course is expected to increase the power factor in both cases as compared to the intrinsic.

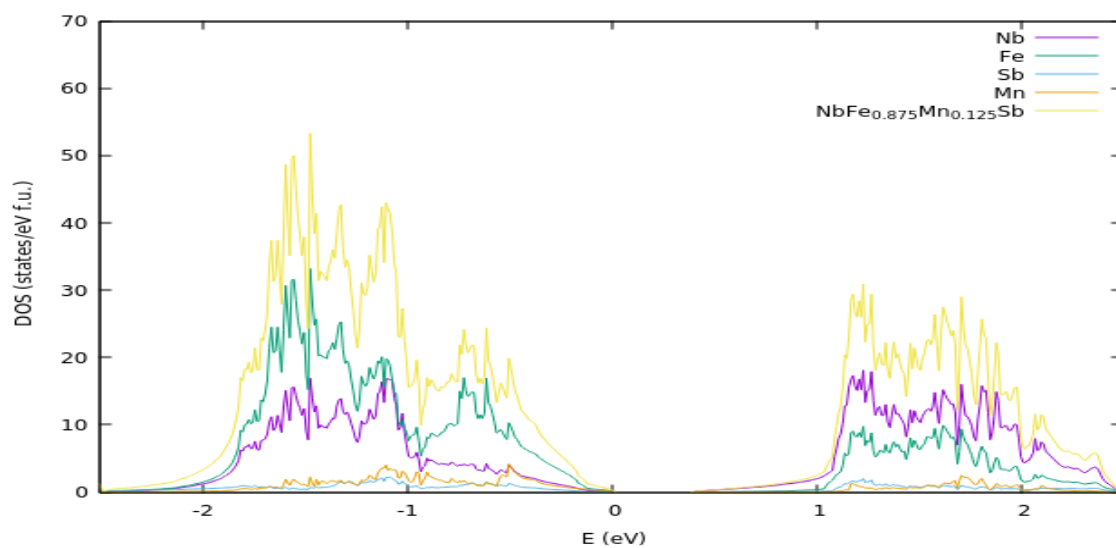


Figure 45. DOS of NbFe_{0.875} Mn_{0.125}Sb

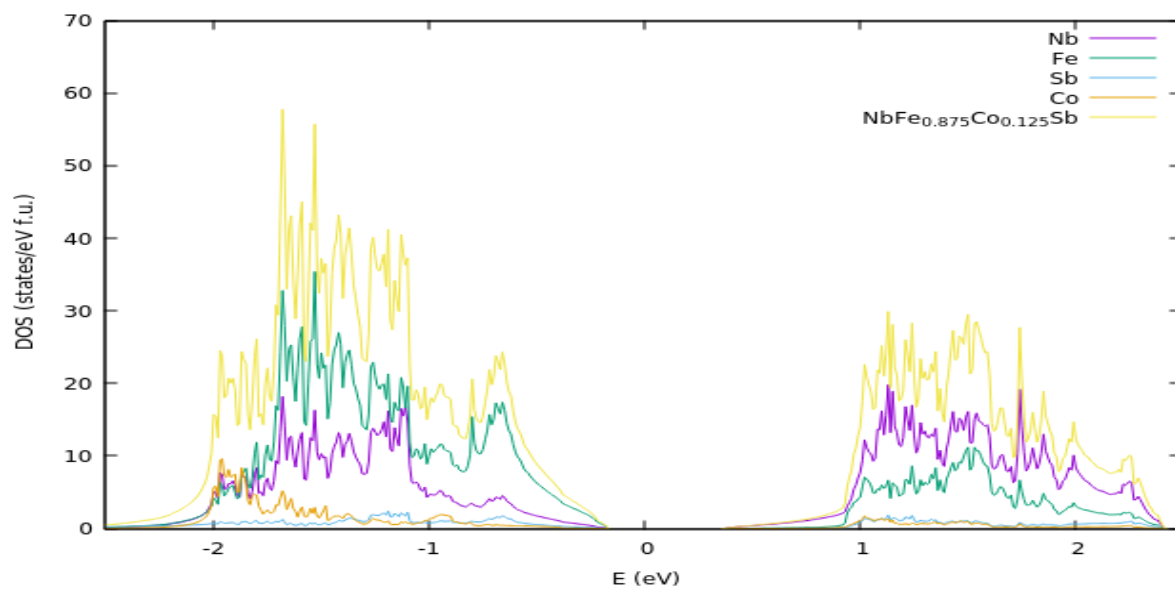


Figure 46. DOS of NbFe_{0.875} Co_{0.125}Sb

4.3.3 Electronic Thermoelectric Properties of Mn-doped and Co-doped NbFeSb

The results obtained for Mn-doped NbFeSb are shown in the figures below, figure 47 shows the electrical conductivity vs temperature and Seebeck coefficient vs temperature plots for Mn-doped NbFeSb. We can see from these graphs that the electrical conductivity decreases from a value of $\sim 19 \times 10^5 \text{Sm}^{-1}$ at 200K to a value of $\sim 3 \times 10^5 \text{Sm}^{-1}$ at 900K. However, S increases from $0.53 \times 10^{-4} \text{V/K}$ at 200K to $\sim 13 \times 10^{-4} \text{V/K}$ at 900K.

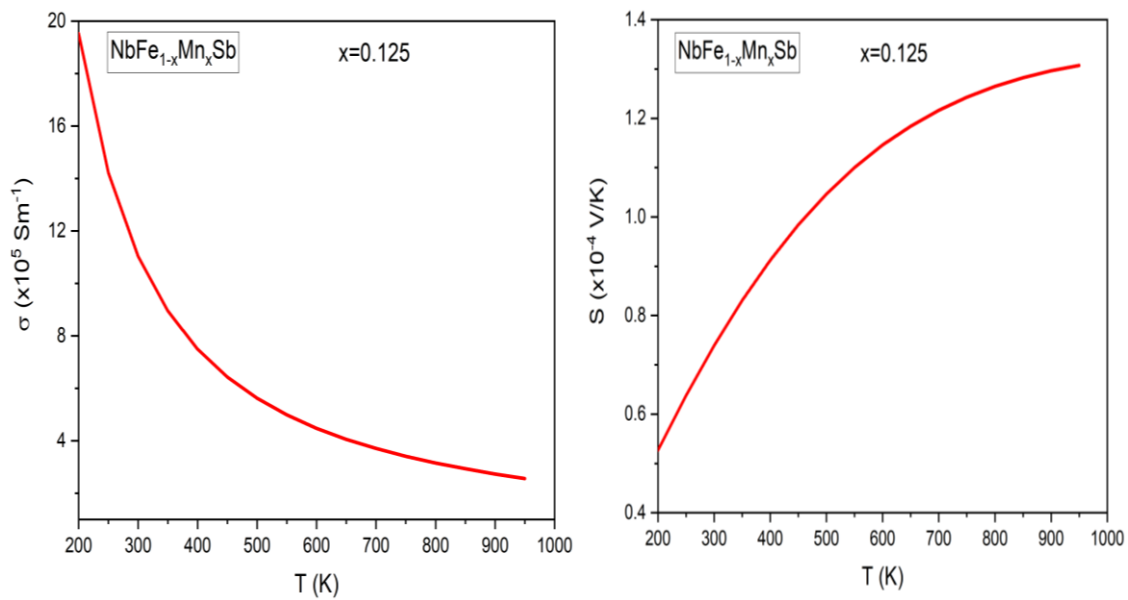


Figure 47. Left: $\sigma (\times 10^5 \text{ Sm}^{-1})$ vs $T(\text{K})$ Right: $S(\times 10^{-5} \text{ V/K})$ vs $T(\text{K})$

Figure 48 shows the dependence of power factor and ke on temperature for the Mn-doped NbFeSb, a maximum power factor $\sim 6.3 \text{ mWK}^{-2} \text{ m}^{-1}$ was obtained at $T=450\text{K}$ as seen in figure 48 left. As expected, ke decreases with increase in temperature.

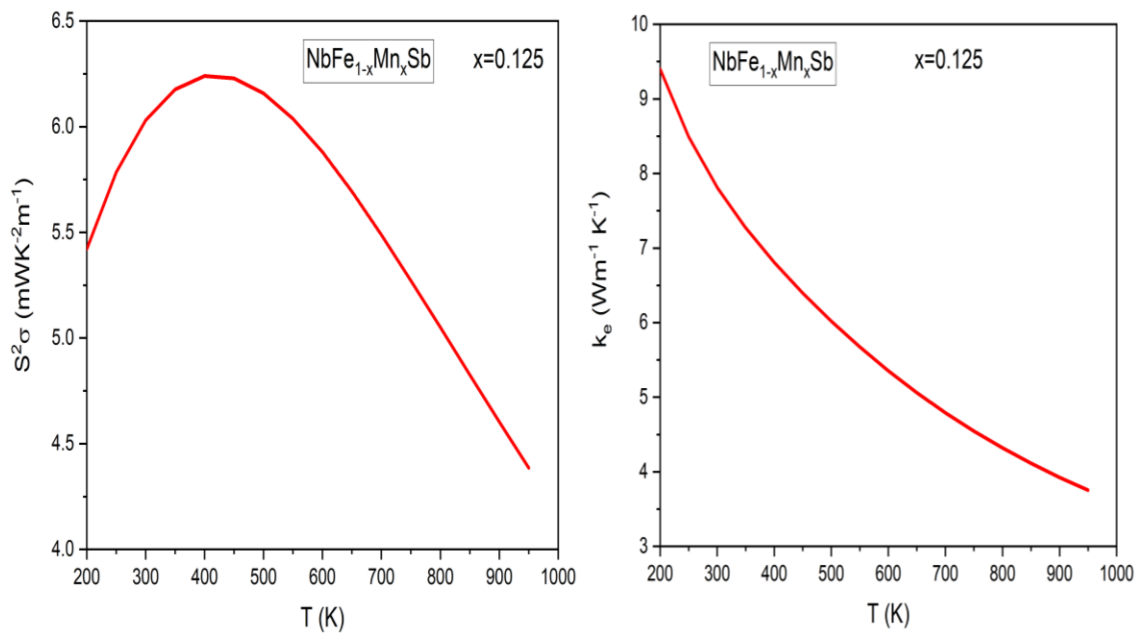


Figure 48. Left: $S^2\sigma$ ($\text{mWK}^{-2}\text{m}^{-1}$) vs T (K) Right: k_e ($\text{Wm}^{-1}\text{K}^{-1}$) vs T (K)

A plot of kl vs temperature and a plot of figure of merit vs temperature for both pure and doped NbFeSb are shown in figure 49. There is no significant difference observed between kl for pure and doped because of small mass difference between Mn and Fe. However, the zT of Mn-doped NbFeSb was found to be very much larger than that of the pure NbFeSb as seen in figure xlix-right. A maximum zT of ~ 0.28 was obtained for Mn-doped NbFeSb at 950K.

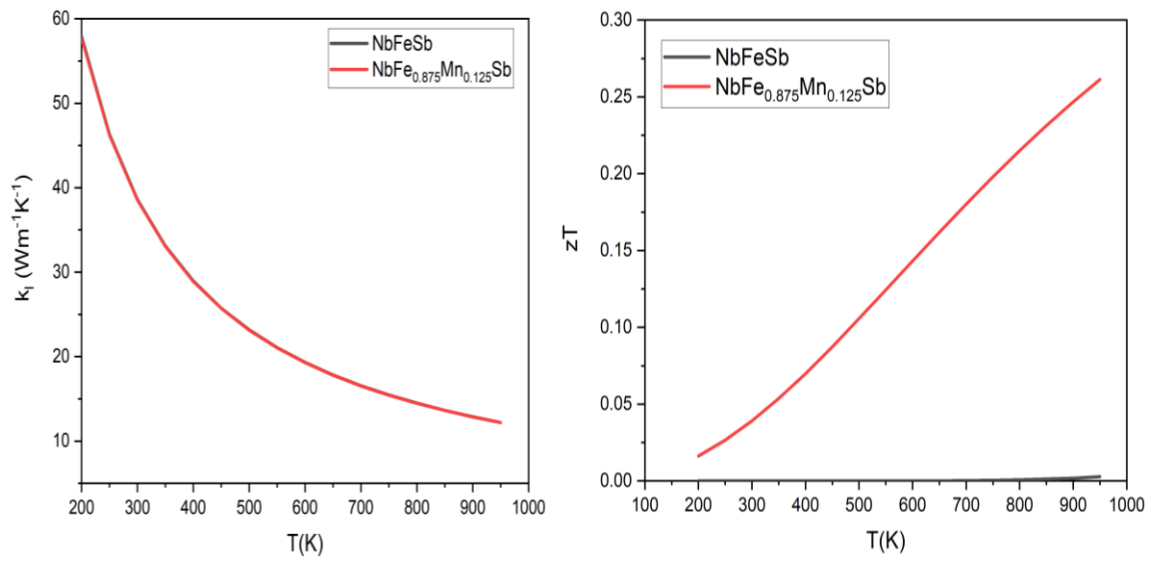


Figure 49. Left- k_l ($\text{WK}^{-1}\text{m}^{-1}$) vs $T(\text{K})$ Right: Figure of merit zT vs $T(\text{K})$

The results obtained for Co-doped NbFeSb are shown in the figures below, figure 1 shows the electrical conductivity vs temperature and Seebeck coefficient vs temperature plots for Mn-doped NbFeSb. We can see from these graphs that the electrical conductivity is about 10 order of magnitude higher than that of Mn-doped NbFeSb, this is as a result of the value of relaxation for electron which is higher than that of the hole. The electrical conductivity decreases from a value of $\sim 300 \times 10^5 \text{ Sm}^{-1}$ at 200K to a value of $\sim 30 \times 10^5 \text{ Sm}^{-1}$ at 900K. However, smaller values of S were recorded as compared to the Mn-doped case. We can see from the graph a negative increase from $\sim -0.025 \times 10^{-4} \text{ V/K}$ at 200K to $\sim -0.3 \times 10^{-4} \text{ V/K}$ at 900K.

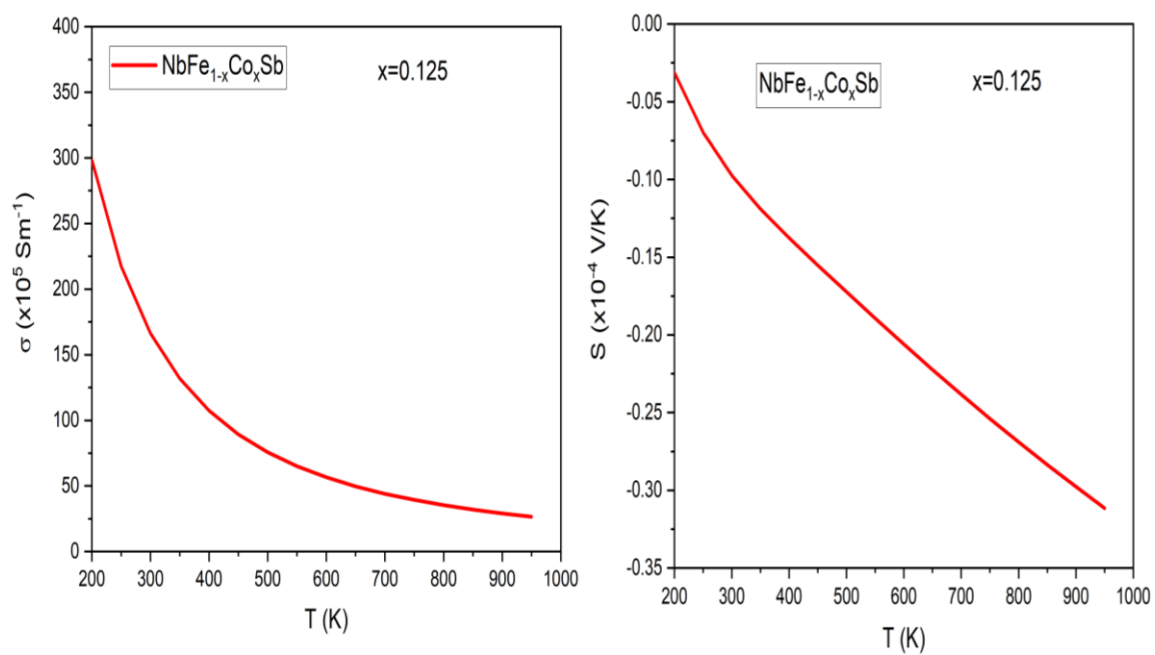


Figure 50. Left: σ ($\times 10^5 \text{ Sm}^{-1}$) vs $T(\text{K})$ Right: $S(\times 10^{-5} \text{ V/K})$ vs $T(\text{K})$

Figure 51 shows the dependence of power factor and ke on temperature for the Co-doped NbFeSb, a maximum power factor $\sim 2.5 \text{ mWK}^{-2} \text{ m}^{-1}$ was obtained at $T=900\text{K}$, a value lower than maximum power factor obtained for the Mn-doped case at 450K . As expected, ke decreases with increase in temperature.

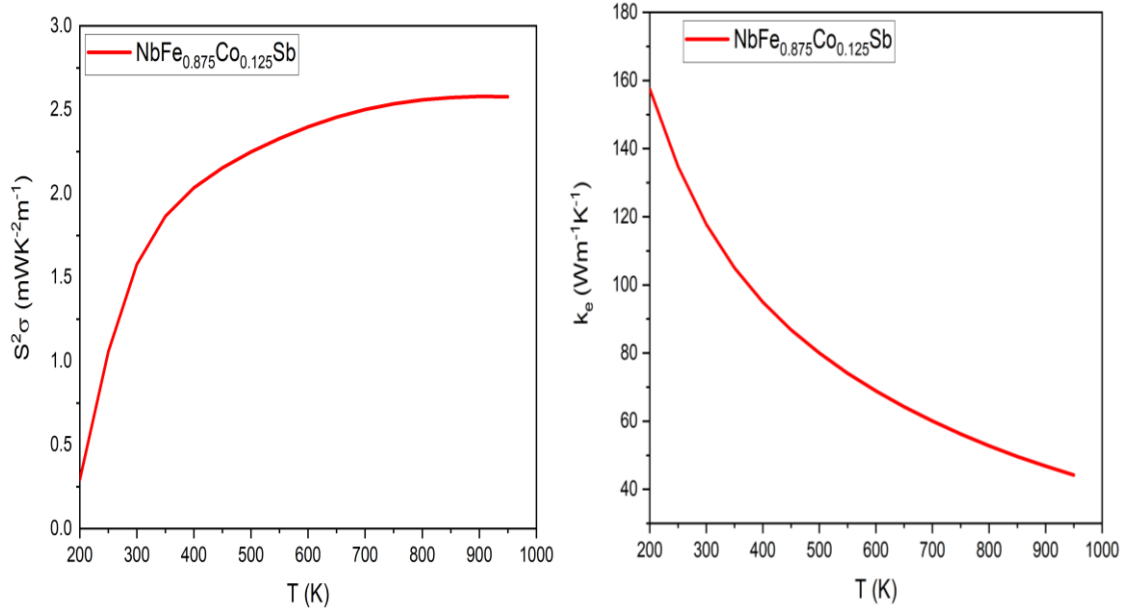


Figure 51. Left $S^2\sigma$ ($\text{mWK}^{-2}\text{m}^{-1}$) vs T (K) Right: κ_e ($\text{Wm}^{-1}\text{K}^{-1}$) vs T (K)

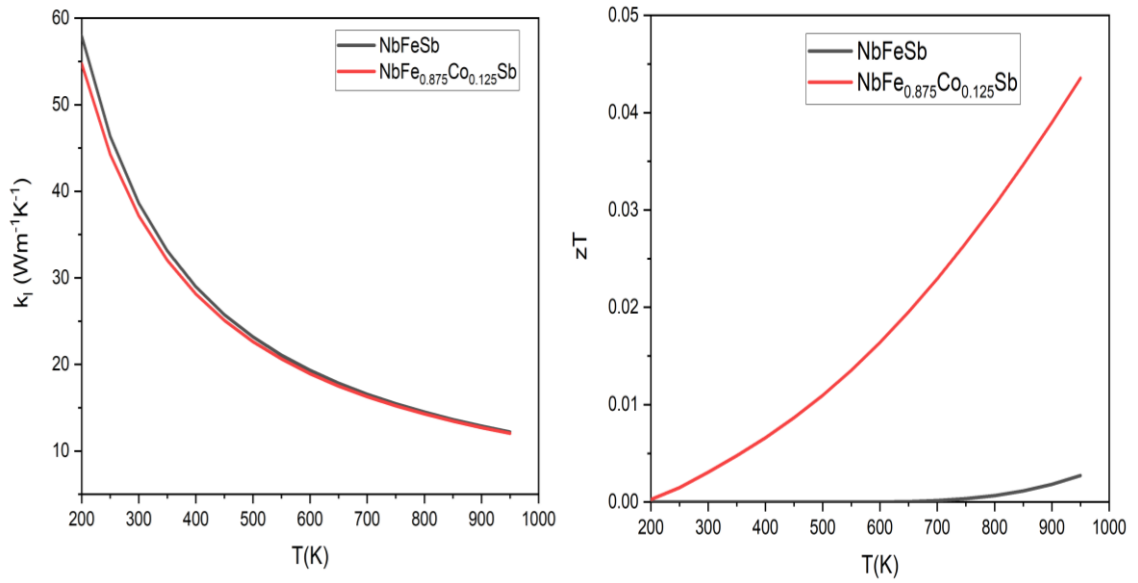


Figure 52. Left- κ_l ($\text{Wm}^{-1}\text{K}^{-1}$) vs T (K) Right: Figure of merit zT vs T (K)

A plot of kl vs temperature and a plot of figure of merit vs temperature for both pure and Co-doped NbFeSb are shown in figure 52 above. In this case there is a noticeable slight difference observed between kl for pure and doped because of the mass difference between Co and Fe is relatively larger than that between Mn and Fe. However, the zT of Co-doped NbFeSb was found to be very much larger than that of the pure NbFeSb as seen in figure lii-right. A maximum zT of ~ 0.045 was obtained for Co-doped NbFeSb at 950K. However, this value of zT was much smaller than the value of 0.28 obtained for the Mn-doped case. The smaller value of zT in Co-doped NbFeSb can be attributed to the high thermal conductivity and very much lower Seebeck coefficient.

The table below, shows the results for the p and n-type NbFeSb at different temperatures for a doping concentration of $2.38 \times 10^{21} \text{ cm}^{-3}$, the p-type and n-type NbFeSb in the table refer to the results obtained by RBA while Mn and Co-doped are respective results for p-type and n-type NbFeSb by supercell approach.

Table 7 Electronic thermoelectric properties of n-type, p-type, Mn-doped and Co-doped NbFeSb at 300K, 600K and 900K.

N=2.38x10²¹cm⁻³	T(K)	$\sigma \times 10^5(\text{Sm}^{-1})$	$S \times 10^{-5}(\text{V/K})$	$S^2 \sigma(\text{mWK}^{-2}\text{m}^{-2})$
p-type NbFeSb	300	11.38	3.99	1.81
	600	3.53	8.71	2.67
	900	1.63	12.9	2.71
Mn-doped NbFeSb	300	11.10	7.39	6.06
	600	4.48	11.45	5.86
	900	2.74	12.95	4.59
n-type NbFeSb	300	96.50	-3.76	13.64
	600	33.50	-6.52	14.24
	900	17.20	-8.79	13.28
Co-doped NbFeSb	300	166.00	-1.09	1.97
	600	56.50	-2.03	2.32
	900	29.10	-2.93	2.49

From table VII above we can infer that RBA underestimated the power factor for p-type and overestimated the power fact for the n-type.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In this work, the thermoelectric properties of pure and doped XFeSb (where X=Ta, Nb) compounds were studied from first principle using Density Functional Theory (DFT) and Boltzmann Transport Theory. Both Rigid Band Approximation (RBA) method and Supercell approach were used to study the thermoelectric behavior of the doped compounds under the Constant Relaxation Time Approximation (CRTA) as implemented in BOLTZTRAP2. The results obtained showed that NbFeSb has a relatively higher power factor at room temperature as compared to the TaFeSb in the intrinsic case due to its relatively higher electrical conductivity. Above this temperature, the Power factor of TaFeSb was found to be higher than that of NbFeSb due to relatively larger Seebeck coefficient of TaFeSb. TaFeSb in the intrinsic case was found to behave as n-type at low temperature but behave as p-type at higher temperature. Very low figure of merit values of ~ 0.021 and ~ 0.002 were recorded at 950K for pure TaFeSb and NbFeSb respectively. These values increased to ~ 0.355 and ~ 0.454 for the Mn-doped TaFeSb and Co-doped TaFeSb respectively. Also, the zT values for NbFeSb increased to ~ 0.254 and ~ 0.04 for the Mn-doped NbFeSb and Co-doped NbFeSb respectively all at 950K. As expected, the lattice thermal conductivity was found to decrease with temperature due to

phonon scattering in both cases. I have also used RBA approach to also calculate the thermoelectric properties of the compounds by virtual doping at different doping levels and by the use of supercell approach. This was to verify the validity of RBA for Mn and Co doped XFeSb. The results obtained showed that virtual doping in BoltztraP2 overestimated electrical conductivity, Seebeck coefficient and hence the power factor for both p-type and n-type TaFeSb. Consequently, it can be concluded that TaFeSb does not show rigid band behavior for Co and Mn dopants. Similar conclusion can be reached for n-type and p-type NbFeSb where the RBA results were inconsistent with the supercell results. Slack's equation was used to evaluate the lattice thermal conductivity which only included point phonon scattering but did not account for effect of grain boundary and other defects. Consequently, k_l can be thought of as being overestimated by this method. Thus, including these factors will further reduce k_l and result to much higher zT for these doped compounds. Future work will include looking for a more appropriate method for the calculation of the lattice thermal conductivity and co-doping with other dopants which will further enhance the figure of merit.

5.2 RECOMMENDATION

It is recommended that a more accurate method like SHENGBTE code which allows determination of lattice thermal conductivity from 2nd order and 3rd order force constants should be employed to calculate the phonon contribution to thermal conductivity. Co-doping at the X and Fe sites is also recommended as this is expected to further increase the power factor and decreases the phonon contribution to thermal conductivity which is expected to yield very high figure of merit.

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CURRICULUM VITAE

AHMED RIDWAN ADESOYE

FLAT 3 DICON QUARTERS, BARNAWA 800281, KADUNA NIGERIA.

ahmedridwan@rocketmail.com, rahmed@aust.edu.ng

☎ +2348035062193,

+966556784795

EDUCATION

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS – SAUDI ARABIA

MSC – MATERIALS SCIENCE AND ENGINEERING (**GPA: 3.92/4.0**)

IN VIEW

AFRICAN UNIVERSITY OF SCIENCE AND TECHNOLOGY – GALADIMAWA ABUJA, NIGERIA

MSC – MATERIALS SCIENCE AND ENGINEERING (**GPA: 3.9/4.0**)

2017

AHMADU BELLO UNIVERSITY – SAMARU ZARIA KADUNA, NIGERIA

2014

BSC – PHYSICS (**4.6/5.0**)

ANSAR-UD-DEEN COLLEGE – OFFA KWARA STATE, NIGERIA

2009

SENIOR SECONDARY CERTIFICATE EXAMINATION (SSCE)

ANSAR-UD-DEEN PRIMARY SCHOOL– OFFA KWARA STATE, NIGERIA

2003

FIRST SCHOOL LEAVING CERTIFICATE

HONOURS AND AWARDS

- 2017 African University of Science and Technology Abuja Best Graduating Student

Award

- 2017 Second Best Innovator Award, African University of Science and Technology Abuja
- 2014 Ahmadu Bello University Academic Excellence Award
- 2009 Certificate of honor, Ansar-ud-deen College Offa Kwara State Nigeria
- 2009 Best Audience Award, Offa Student Union, Offa Kwara State Nigeria

MEMBERSHIP, CONFERENCES, TRAINING & CERTIFICATION

- 9th International Conference of the African Materials Research Society Gaborone, 2017.

- Pan African School of Materials (PASMAT) Energy Workshop, 2017.

- Pan African Materials Institute (PAMI), 2016.

(Student Member)

- African Materials Research Society (AMRS), 2016.

(Student member)

- Pan African School of Materials (PASMAT) Biomaterials Workshop, 2016.

- National Youth Service Corps (NYSC), 2015

- Ahmadu Bello University (ABU) Alumni Association, 2014.

(Member)

- National Association of Physics Students (ABU Chapter), 2013.

(Director of Education)

SELECTED PRESENTATIONS

- Characterization of Nanocomposite Polymer Electrolyte for Solid State Electrochemical Application, December 11, 2017, 9th International Conference of the African Materials Research Society Gaborone Botswana

- Characterization of doped Graphene for Organic Light Emitting Diodes (OLEDs),
December 13, 2017, 9th International Conference of the African Materials Research
Society Gaborone Botswana