Report on

# THERMOELECTRIC MATERIALS AND THEIR PROPERTIES

*submitted towards the partial fulfilment*
*of the requirement for the award of the*
*degree of*

Master of Science

*in*

Physics

*Submitted by*

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# DECLARATION

We hereby certify that the work, which is presented in the report entitled "Thermoelectric materials and their properties" in fulfilment of the requirement for the award of the Degree of Master of Science in Physics and submitted to the Department of Applied Physics, Delhi Technological University ,Delhi. It's an authentic record of our own, carried out under the supervision of Dr. Mukhtiyar Singh.

The work presented in this report has not been submitted and is not considered for the award for any other course/degree of this or any other Institute/University.

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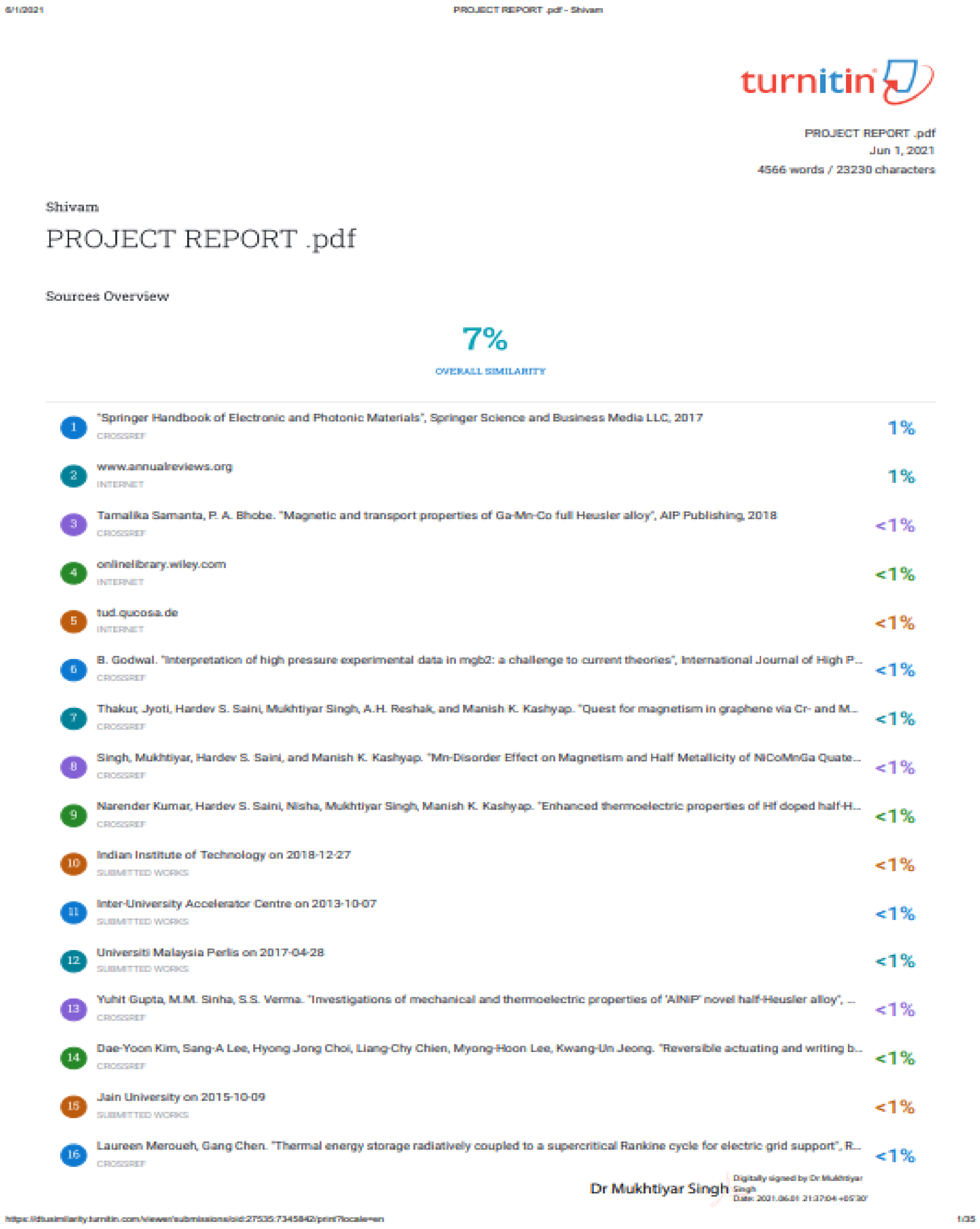

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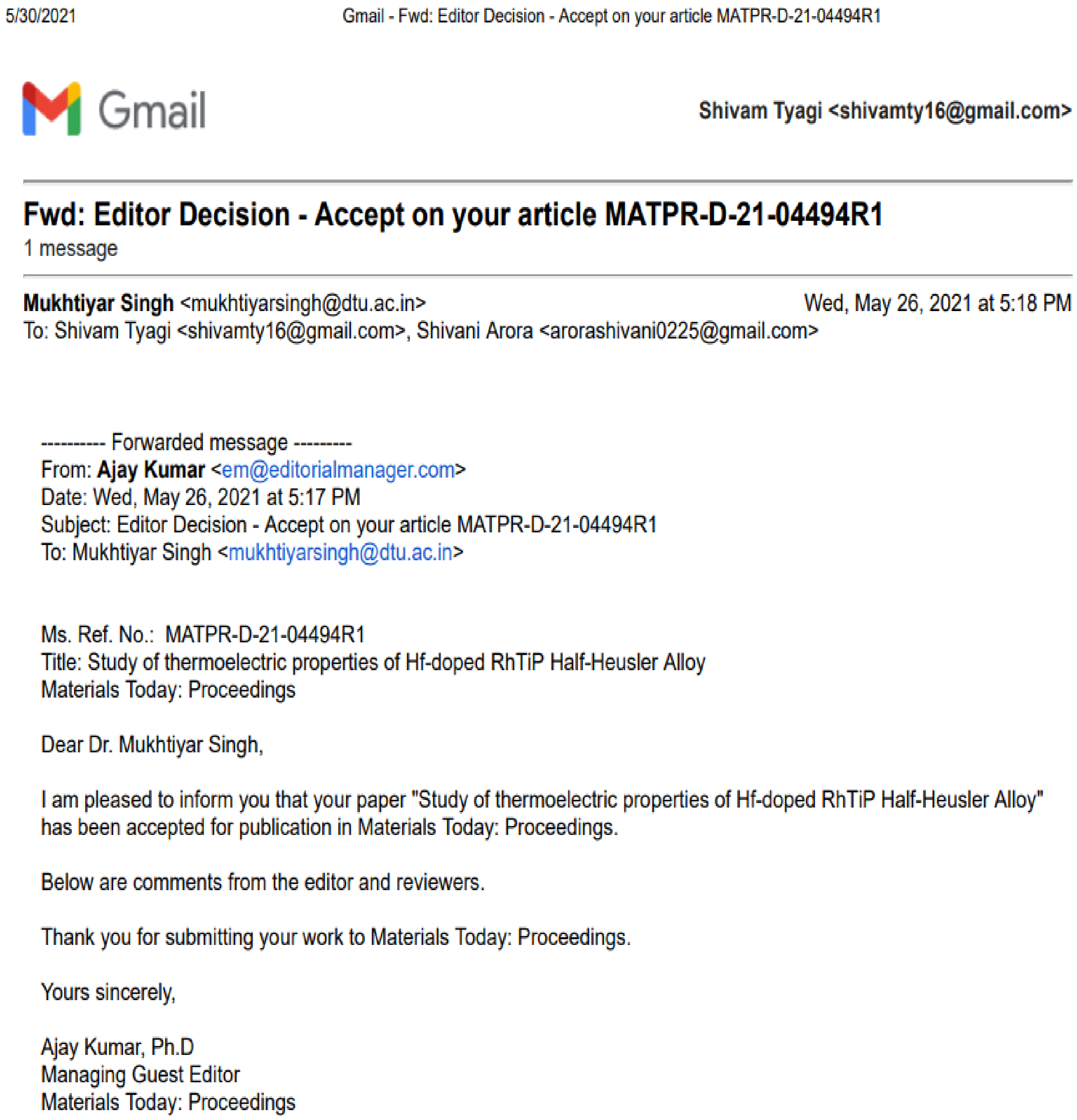

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I am pleased to inform you that your paper "Study of thermoelectric properties of Hf-doped RhTiP Half-Heusler Alloy" has been accepted for publication in Materials Today: Proceedings.

Below are comments from the editor and reviewers.

Thank you for submitting your work to Materials Today: Proceedings.

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We, Shivam Tyagi and Shivani Arora would like to express our greatest gratitude to the people who have helped and supported us throughout our report. We are very grateful to our teacher Dr. Mukhtiyar Singh for his continuous support for the early stages of conceptual inception and ongoing advice and encouragement.

THANK YOU

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# LIST OF SYMBOLS AND ABBREVIATIONS

1. ZT- FIGURE OF MERIT
2. S- SEEBECK COEFFICIENT
3. T- ABSOLUTE TEMPERATURE
4. $\sigma$- ELECTRICAL CONDUCTIVITY
5. $\kappa$- THERMAL CONDUCTIVITY
6. $\kappa_e$ – ELECTRICAL THERMAL CONDUCTIVITY
7. $\kappa_l$ – LATTICE THERMAL CONDUCTIVITY
8. V- VOLTAGE
9. µ - MOBILITY

# ABSTRACT

Seeing today’s scenario, it can easily be depicted that the time will come when the human race will witness the shortage and extinction of non-renewable natural resources due to their abundance use in today’s time. So, to keep this thing in mind, many scientists turn their focus towards some promising alternatives of fossil fuels, and thermoelectric material is one of them.

This work presented a first-principles-based investigation pertaining to the analysis of the effect of Hf doping on thermoelectric properties of half Heusler alloy RhTiP. The energy bandgap of RhTiP is 0.810 eV. With increase in the concentration, the bandgap became less for $RhTi_{0.75}Hf_{0.25}P$ and increased for all other doping concentrations, the energy bandgap rise linearly with doping concentration. At 100% doping of Hf, i.e., for RhHfP, it is observed to be 1.464 eV. Here the material showed the highest thermoelectric performance at 100% doping of Hf in place of Ti (RhHfP) at room temperature, while other resultant compounds after the doping were also showing good thermoelectric behaviour. The maximum value of power factor and electrical conductivity at room temperature were $0.19688\text{x}10^{12}\ WK^{-2}m^{-1}s^{-1}$ and $3.2058*10^{18}\Omega^{-1}m^{-1}s^{-1}$which belong to RhHfP. The maximum $ZT$ value came out to be 0.7950 at room temperature, which is again of RhHfP.

# CHAPTER-01

# INTRODUCTION

## 1.1) Thermoelectricity:

In semiconductors, the phenomenon of thermoelectricity was first observed by Estonian physicist Thomas Seebeck [1], in which the conversion of heat to electricity took place. In this effect, the generation of a voltage in a circuit comprised of two different conductors due to a temperature difference was observed, and later on, William Thomson, also known as Lord Kelvin, discovered that when we pass an electric current through the circuit, the absorption and production of heat energy took place. These two phenomena combined are known as thermoelectricity.

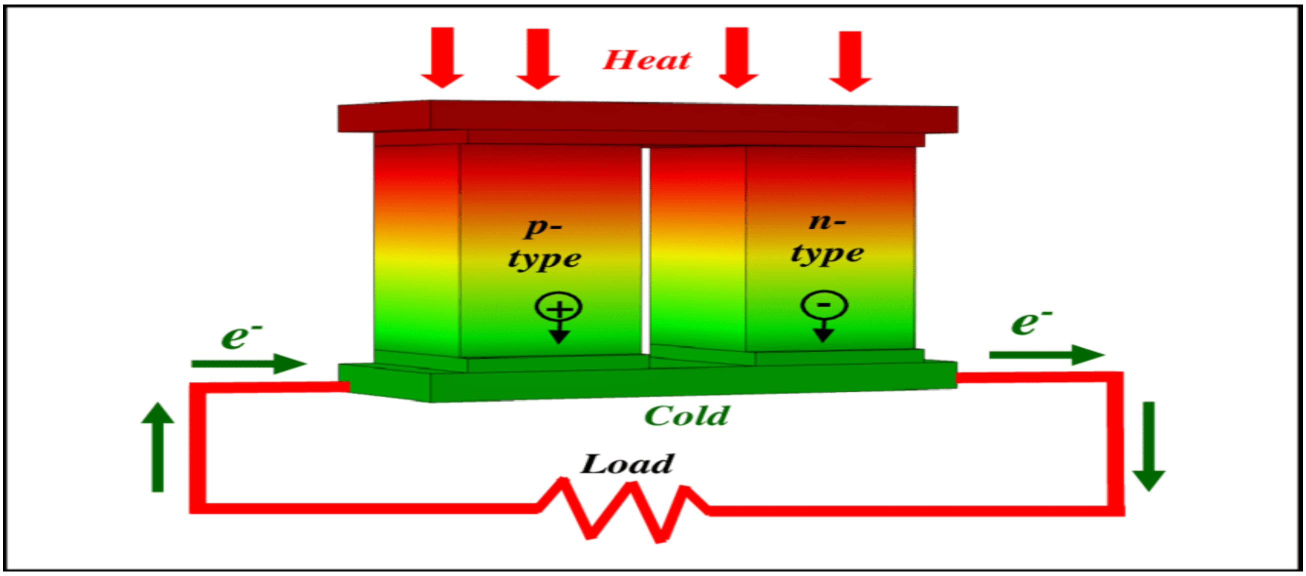

Figure 1: Schematic diagram of Thermoelectricity [1]

The thermoelectric process is fundamentally a microscopic one involving the transport and exchange of energy by and between electrons and lattice vibrations, or phonon in solids.

For a thermoelectric device operating between the Heat source and Heat sink temperature. Different electrons are excited to different energy levels, leading to the generation of electricity.[2]

## 1.2) Figure of merit, an important parameter:

The thermoelectric performance of a specific material can be determined using a certain parameter/constant given as ZT (figure of merit) [3].

The formula of ZT is given by:

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

where

$$S = -\Delta V / \Delta T$$

$$\sigma = ne\mu$$

The quantity $S^2 ne$ is determined by electronic band structure. For S to be large, we want the carrier density i,e, number of electrons per unit volume, to be small, both are contradictory situation, so instead, we take $S^2\sigma$ to be large. We want the ratio $\mu/k$ to be large and this quantity is determined by the nature of electron and phonon scattering [2]. Also electrical conductivity and smaller thermal conductivity are not possible together. So, a good thermoelectric is one which maintains the balance between the two quantity.

## 1.3) Heusler alloys:

Dr. Friedrich Heusler discovered this new class of intermetallic materials in 1903[18]. They are composed of mainly metals that are in the pure state and are not magnetic. Their basic composition is two parts of copper, one part of manganese, and aluminium, which possesses strong ferromagnetic properties [4]. The composition Cu2MnAl behaves like a ferromagnet, although none of its constituents element is magnetic by itself. Further study determined that Cu2MnAL crystallizes in FCC structure (space group F-m3m, 225)[2].

Half-Heusler alloys have gained considerable interest in the present era due to their high-temperature stability, comparatively high Seebeck coefficient, and relatively high $ZT$ value. The half heusler alloys have a bandgap between 0.1-1 eV. The various ways to increase the thermoelectricity is to tune the band structure by applying the strain or pressure and by doping of suitable elements, by increasing the ZT value of the compound (which is done by either decreasing the value of lattice thermal conductivity or by increasing electrical conductivity).

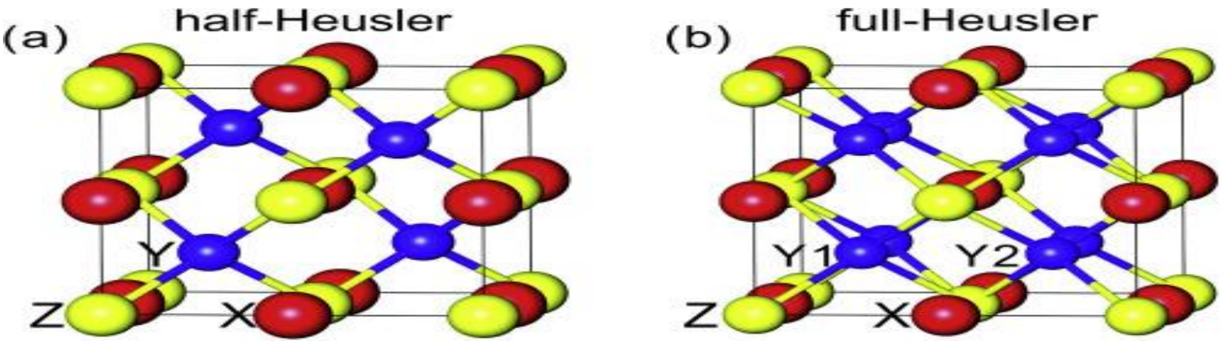

FIGURE 2 Half –Heusler and Full-Heusler . [4]

By filling the 4th sub-lattice, a series of compounds can be formed between half and full Heuslers, which can be described as XYZ and $X_2YZ$, respectively, where X,Y are transition Metal elements and Z is the main group element. The full Heusler compounds have other variants, including inverse structure in which X is interchanged with Y, and quarternary Heusler [5] in which one of the X is replaced by 4th distinct elements.

# CHAPTER-02

# THERMOELECTRIC properties of solids.

## 2.1 Thermal Properties of Solid:

### Specific heat a determining parameter:

If we supply heat energy to a system, its internal energy changes, as well as some work, has also been done on it, which is observed by the change in its volume, this is the first law of thermodynamics. Now let us now suppose that there is no change in volume, then all the heat energy will be stored as internal energy of the system [6].

$$C_v = (\frac{\partial U}{\partial T})_V$$

So, heat capacity is the external heat required to raise the temperature of the system by 1 degree at constant volume. This value depends upon the size, volume, and mass of the system. If we consider finite unit mass, it is called specific heat capacity, and if we consider Avogadro number of atoms, it is called molar heat capacity.

Specific heat is the most important parameter in determining the thermal properties of any system. If we give some amount of heat to a system, we will observe that atom in a lattice will vibrate, so its kinetic energy and potential energy will change as a result, its internal energy get changed, which manifests as a specific heat [2]. So for determining the variation of specific heat with temperature, several models were proposed:

- Dulong – Petit model
- Einstein model
- Debye model

**Debye model**, **the answer to many questions**:

Till now, Dulong-Petit Model was able to explain the variation of specific heat capacity at high temperature but failed to explain the variations at low temperature. Now, Debye came forward, he considered that atoms and molecules at lattice points are not independent of each other[7], infact, they are coupled. They do not vibrate with the same frequency but the range of frequency, so we can have different modes of vibrations. When elastic waves propagate through the lattice, it will see the crystal has a continuum medium[2]. He considered the string is fixed at one end then we have travelling waves and when both ends are fixed, we get standing waves

$$u_n(x,t) = Asink_n x \cos w_n x$$

This wave function is a solution of wave equation in nth mode of of one dimension where

$$k_n = \frac{2\pi}{\lambda_n}$$

And n is mode of vibrations and n>=1

$$\nu_n = \frac{nv}{2L}$$

Where $\nu_n$ is frequency and v be the velocity of wave.

We observed that different mode of vibrations have different mode of frequency.

Number of modes in the frequency range $\vartheta$ is evaluated and it is found to be proportional to square of frequency [2]. Also each mode has a possibility to go in higher energy state and each mode is considered to be harmonic oscillate and the higher energy states will be nh$\upsilon$.

Defining a Debye temperature $T_D$,

When temperature is higher comparable to debye temperature we get:

$$C_v = 3Nk = 3R$$

When temperature is lower comparable to debye temperature:

$$C_v \, \alpha \, T^3$$

Which is the experimentally correct estimation of variation of specific

at low temperature.

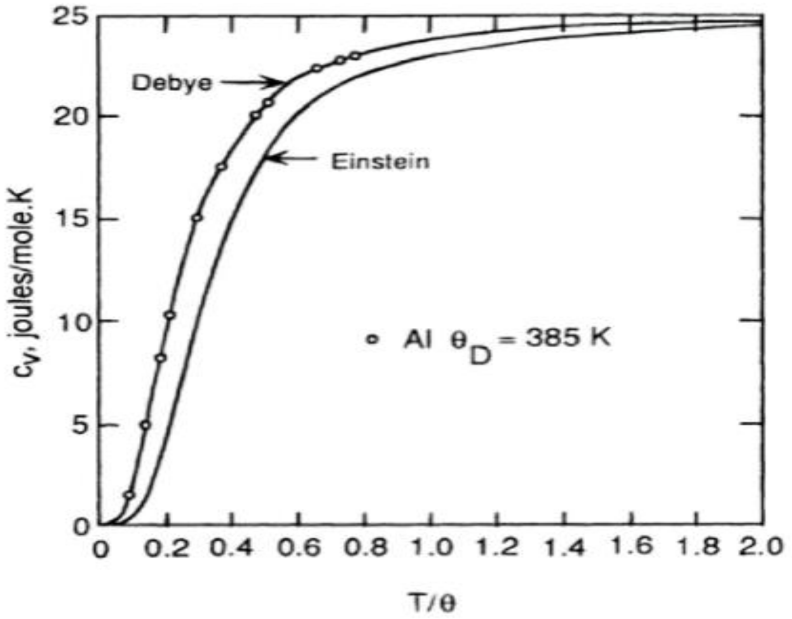

Figure 3 : Specific Heat capacity Debye MODEL [21]

## 2.2 Electrical properties of solids:

In Classical theory and quantum theory, we have ignored the ions in the crystal. The ions will have potential. Now the question arises of which type of potential will exist there. It was suggested that potential will be periodic [8].

And wave function was proposed by Bloch according to this theorem.

BLOCH THEOREM [2]:

It states that plane wave, when modulated with another function will follow the periodicity of potential

$$\psi_k = e^{ikx}\mathrm{u(x)}$$

POTENIAL:

V(x)=0 0< x<a

V(x) = $V_0$ 0>x>-b

On solving this system by applying the required boundary conditions we get [9],

$$P\frac{\sin(\alpha a)}{(\alpha a)} + \cos(\alpha a) = cosk(a+b)$$

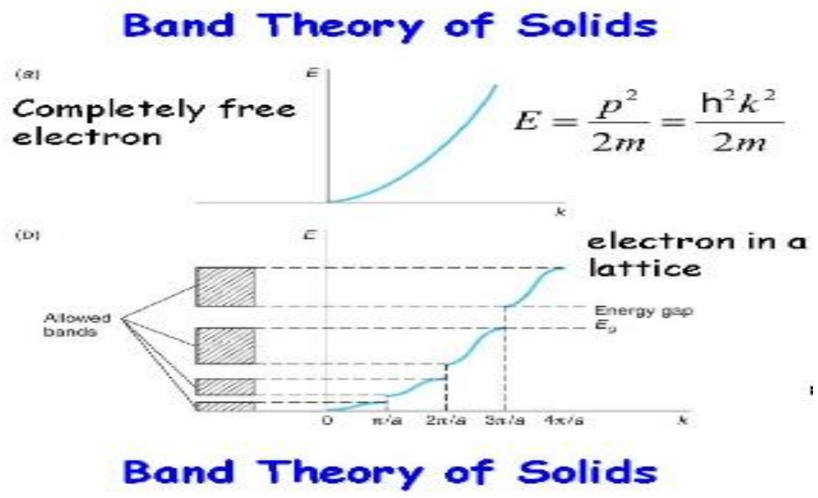

Figure 3: Band theory of solids [9]

# CHAPTER- 03

# *Study of thermoelectric properties of Hf doped RhTiP

## 3.1 Motivation Behind the paper

In the 21st century, it is quite difficult to imagine our single day without electrical energy. For machine work and in day-to-day life, we need energy for the fulfilment of different tasks. The exponential rise in demand for energy is a significant area of concern because a high portion of this energy comes from burning fossil fuels. These resources are present in the limited quantity on earth.  Scientists are trying to find different environment-friendly and efficient ways to generate electricity that can be extracted from the waste heat.  One of such ways is efficient thermoelectric materials that can convert waste heat into electricity.

So, it becomes crucial to use these possible resources to turn waste heat into useful applications. And the role of researchers become too great in this contribution to find and synthesize such materials, which can lead to the reduction of dependence on fossil fuels, resulting in reduction of pollution and global warming level.

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*** Accepted in Material's Today Proceedings**

## 3.2 Building of idea

Now, the biggest question that arises in front of us is how to know which material is a good thermoelectric material and which one is not?

For, that there exists a constant/parameter whose value can tell us about the thermoelectric performance of a specific material if the value of that constant is somewhere around 1 or a little less than 1 also then it is considered as a good thermoelectric material, that constant is known as the figure of merit denoted by $ZT$.

The formula of ZT is given by

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

And the last question is why we choose the material RHTiP?

We tried some more materials, but unfortunately we were unable to find desired results from them. In the family of ABX type Half heusler alloy, RhTiP is a newly found material that is proven to be stable in previous studies [10]*, and it is yet to be developed experimentally. It can be used as an excellent thermoelectric material since it has a pretty highpower factor and Seebeck coefficient [10]. RhTiP is a ductile material with a bonding nature to be weakly ionic [10], so the property of the material to withhold external pressure and strain is relatively low in this case. Due to the presence of weak ionic bond, its disassociation energy should also be low; hence it is not on the problematic side to replace a specific atom from the sample experimentally. And there are already many good thermoelectric materials with the same configuration TaCoSn [11], ScPtSb [12]. This motivates us to work on the possibility of enhancing the $ZT$ value of RhTiP half-heusler alloy, which eventually increases its thermoelectric performance.

Why we choose Hf for doping?

In the present work, the doping of Hf is done on alloy RhTiP to study the effect of this doping on electronic and thermoelectric. The main reason for using Hf as a doping agent is because of its chemical stability and pretty high boiling and melting point so that it can withstand high temperatures. Our aim of this study is to get high stable material with good thermoelectric properties at different concentrations of Hf.

# CHAPTER-04 –

# METHODOLOGIES AND RESULTS

## 4.1 Theoretical Methodology

The structural, electronic, and thermal transport properties of RhTiP pristine and doped samples were investigated using Density Functional Theory (DFT) [13, 14] based on the Full Potential Linear Augmented Plane Wave (FPLAPW) method as implemented in Wein2K code [15]. Generalized gradient approximation (GGA) formalism within the Perdew-Burke-Ernzerhof (PBE) parametrization was used to handle the exchange-correlation potentials [16].Plane wave cut-off parameters were decided by $R_{MT}K_{max}$=7. A uniform K-mesh of $20 \times 20 \times 20$ has been used for 8000 irreducible Brillouin zone integration which was completed byusing the original Monkhorst-Pack's scheme in the irreducible Brillouin zone (IBZ). The energy convergence criterion was fixed to 0.00001, and charge convergence was monitored accordingly. The transport properties were obtained using the BoltzTrap code [17]**,** which solved the semiclassical Boltzmann transport equation while having a constant relaxation time $\tau$. This code was used to determine factors like power factor, Seebeck coefficient, electrical conductivity, etc. The power factor $S^2\sigma$ was presented in units of $\tau$, where $\tau$ is relaxation time. We constructed a 1x1x1 supercell of 12 atoms in order to simulate the various doping concentration.

## 4.2 RESULTS AND DISCUSSION

First of all, this work performed the structural optimization of RhTiP, and it is found to be stable in the cubic semiconducting phase with a lattice constant of 5.76 Å. This value of lattice constant is in good agreement with what is available in the literature. The positions of the atoms inside crystal are (0.25, 0.25, 0.25) for Rh atom, (0.5, 0.5, 0.5) for Ti atom and (0, 0, 0) for P atom. The rest of the calculations are perform on the optimized lattice constant.

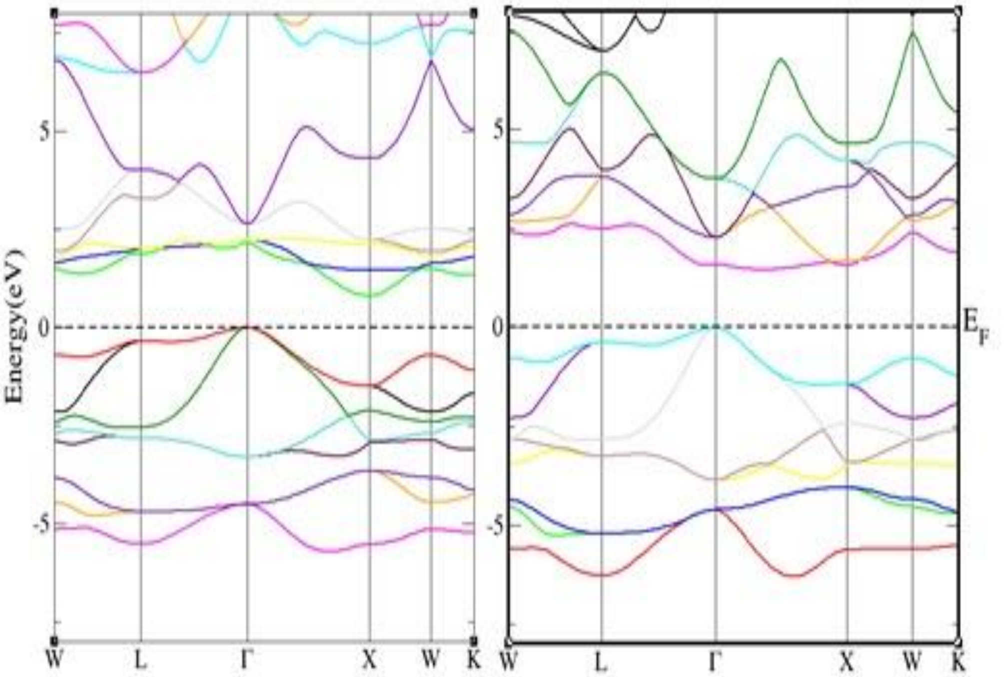

Fig. 5. (a) Bandstructure of RhTiP; and of (b) RhHfP

The semiconducting nature of all the concentrations in$RhTi_{1-x}Hf_xP$ (x = 0.25, 0.50, 0.75, 1) have found to be intact. The bandgap value for RhTiP is 0.81 eV, which is in fair agreement with the previous study, 0.83 eV [10]. The energy dispersion shown in Fig. 5, along with high symmetry, points W$\rightarrow L \rightarrow \Gamma \rightarrow X \rightarrow W \rightarrow K$. The observation was that pure RhTiP has an indirect bandgap whose valence maxima were at Γ and the conduction minima were at X high-symmetry point, while during the process of doping, the nature of the bandgap was tuned.

The values of the bandgap for all the concentrations being study are listed in Table -1.

Table 1. Resultant alloys after doping and their respective bandgap values.

| Alloys | Bandgap (in eV) |
|---|---|
| RhTip | 0.815 (0.830) * |
| RhTiP | 0.810 |
| $RhTi_{0.75}Hf_{0.25}P$ | 0.797 |
| $RhTi_{0.5}Hf_{0.5}P$ | 0.877 |
| $RhTi_{0.25}Hf_{0.75}P$ | 1.078 |
| RhHfP | 1.464 |

* Other's work [5].

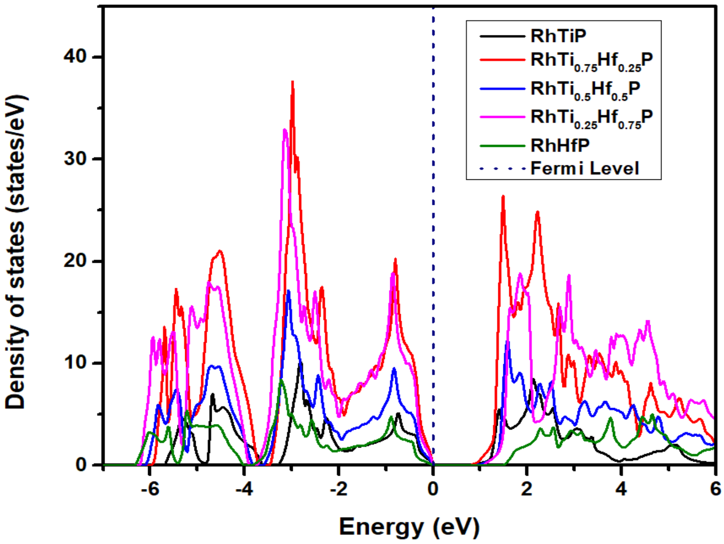

Fig. 6. Density of states plot of $RhTi_{1-x}Hf_xP$ (x = 0.25, 0.50, 0.75, 1).

As shown in Fig.6, the density of states (DOS) shows that for $RhTi_{0.75}Hf_{0.25}P$, the DOSattainsmaximum value for energy approx. -3 eVat valence band and in conduction band peak occur at approx 1.5 eV. Still, all these peaks are pretty steep as in a minor variation in energy, the value of DOS falls very sharply, the minimum value of DOS is coming out to be in the case of RhHfP. Here both 25% and 75% doping concentrations possess the highest DOS value in both valence and conduction band, while both RhTIP and RhHfP have the minimum value amongst them. The young's (E), shear (G), and bulk modulus (B) of this material were found in earlier studies [10] and are 177.72, 66.21, 188.58, respectively, which prove the stability of the material.

The value of the Seebeck coefficient of RhTiP comes out to be 247.1 $\mu V/K$ at room temperature, and this value approaches up to 247.7 $\mu V/K$ at 1200 K (as depicted in Fig. 7(a). The maximum power factor of the parent system is 1.44 x $10^{12}\ WK^{-2}m^{-1}s^{-1}$ at 1200 K temperature and at room temperature, its value is 1.823 x $10^{11}\ WK^{-2}m^{-1}s^{-1}$ . And finally, the ZT value of pure RhTiP is maximum at room temperature, that is, 0.77479. After that, we dope this pure RhTiP with Hf, which leads to a chemically stable compound, as discussed in previous studies [18, 19]. It has been studied by researchers that the alloys doped with an impurity such as Hf and Zr are found to be chemically stable [18, 19]. Doping of Hf is done such as we got four different concentrations $RhTi_{0.75}Hf_{0.25}P$, $RhTi_{0.5}Hf_{0.5}P$, $RhTi_{0.25}Hf_{0.75}P$, and finally RhHfP.

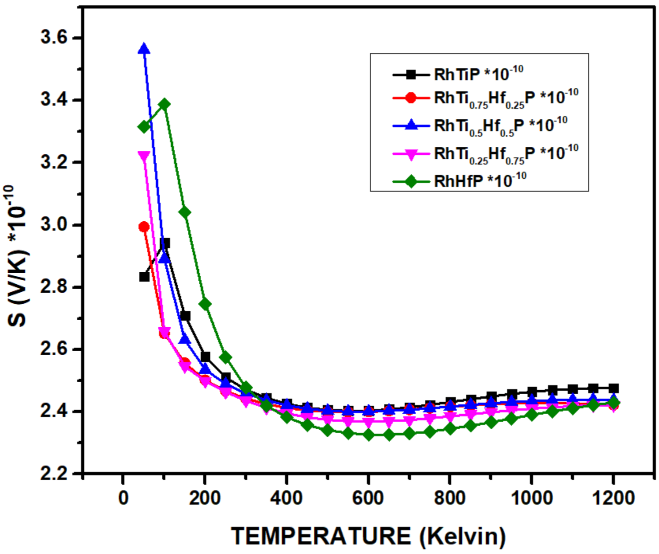

Fig-7(a)- Plot of seebeck coefficient with respect to temperature.

The Seebeck coefficient's value decreases with an increase in doping percentage. As shown in Fig.7(a), we can clearly see that it first decreases in all cases and then increases with respect to temperature. The maximum value of the Seebeck coefficient is 356.407 $\mu V/K$ of RhTi$_{0.5}$Hf$_{0.5}$P at 50 K, and the minimum for alloy RhTi$_{0.25}$Hf$_{0.75}$P at 650 K (232.712$\mu V/K$). ). Interestingly the value of electrical conductivity increases with the increase in temperature (as shown in Fig.7(b)) but here also the maximum value of electrical conductivity belongs to pure RhTiP at 1200 K (2.34x$10^{19}\Omega^{-1}m^{-1}s^{-1}$).

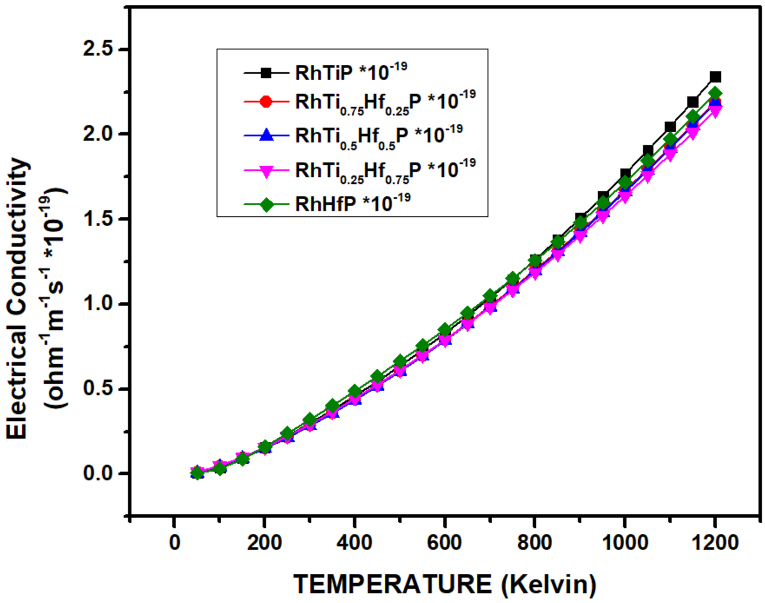

Fig-7(b)- Plot of electrical conductivity with respect to temperature.

As in Fig.7(c), it is visible the power factor also increases with the increase in temperature (as the formula suggests PF=$S^2\sigma$ ) just like the electrical conductivity (also electrical conductivity of pure alloy is maximum at almost all temperature range that might be because of the fact that radius of Ti is smaller than that of doping element Hf so charge carriers have a lesser space to move around and that may result in decreasing its electrical conductivity), the maximum value of power factor belongs to pure alloy RhTiP (Fig. 7(c)) that is, approx. 1.44 x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$ at 1200 K and in the doped systems, the maximum value of the power factor belongs to RhHfP, which is 1.321x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$.

The calculated maximum values of power factor for other doped concentrations such as $RhTi_{0.5}Hf_{0.5}P$, $RhTi_{0.75}Hf_{0.25}P$, and $RhTi_{0.25}Hf_{0.75}P$ are 1.300 x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$, 1.285 x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$and 1.25704 x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$, respectively.

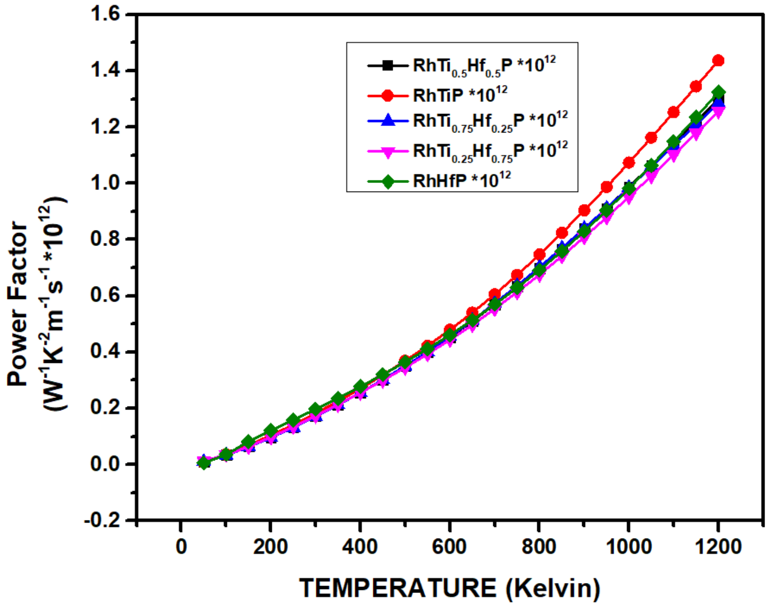

Fig-7(c)- Plot of power factor of different doping percentages versus temperature.

At room temperature, the power factor for RhHfP is maximum (0.19688x$10^{12}$ $WK^{-2}m^{-1}s^{-1}$) while on the other hand, at room temperature $RhTi_{0.75}Hf_{0.25}P$ have a minimum power factor (0.17152 x$10^{12}$ $WK^{-2}m^{-1}s^{-1}$) which is still not that much low but on the higher side, so even at the minimum value, we can say that this material can work as a good thermoelectric material.

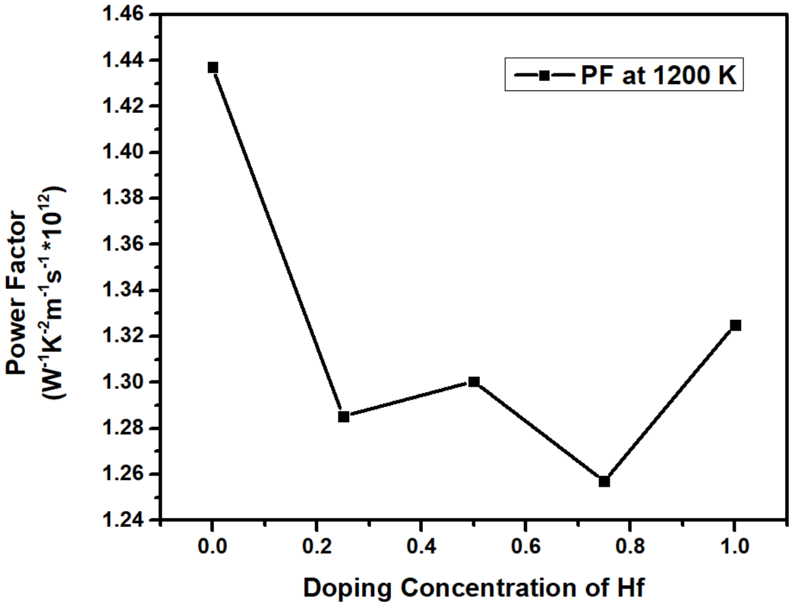

Fig-8- plot of the maximum value of PF versus doping percentage.

The variation of the power factor with doping percentage of Hf is shown in Fig. 8. The figure of merit (*ZT*) is maximum at 50 K for all doping concentrations (as shown in Fig.9(a)), and amongst them, the highest *ZT* value is 0.87327, which is of $RhTi_{0.5}Hf_{0.5}P$. The ZT values for RhTiP, $RhTi_{0.75}Hf_{0.25}P$, $RhTi_{0.25}Hf_{0.75}P$ and RhHfP are 0.75406, 0.84247, 0.86763, 0.80341, respectively.

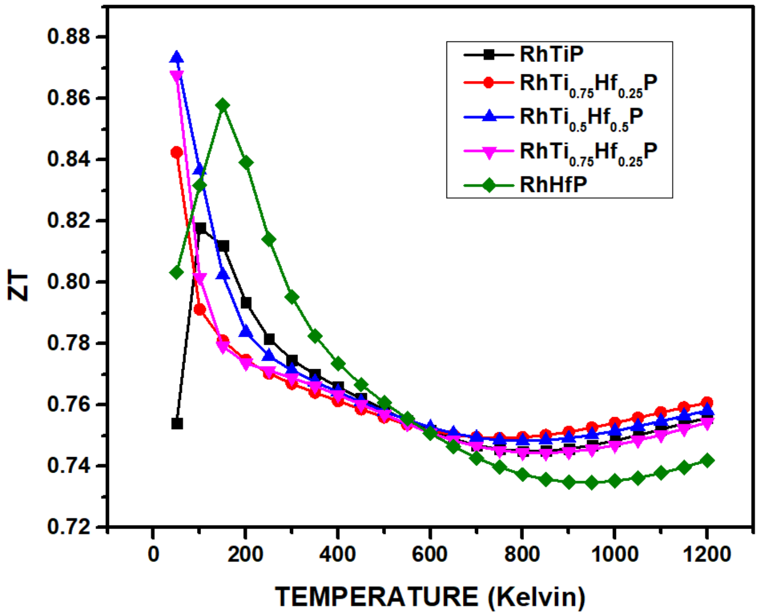

Fig-9(a)- Plot of ZT value of different temperature.

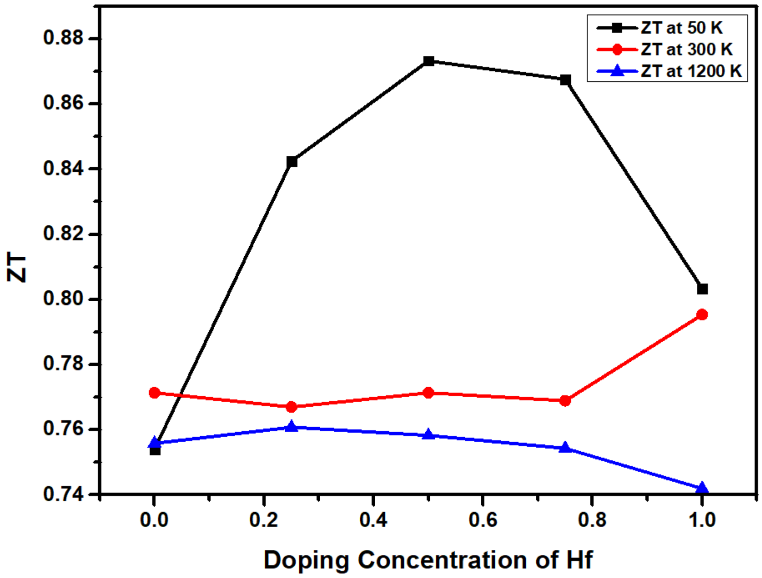

Fig-9(b)- Plot of ZT at 50 K, 300 K, and 1200 K versus the doping concentration.

We also find that the maximum value of $ZT$ is 0.87327 at 50 K of 50% doping concentration, but 50 K is a very low temperature that is almost no use. So having a high value on that temperature couldn't quite help us. Hence, if we look towards a more realistic one, then at around 250 K, we observe that RhHfP acquires the maximum $ZT$ value, which is approx. 0.81. All the variations in ZT value at different temperatures can be seen in Fig.9(b). The increase in $ZT$ value of parent alloy attains a peak at somewhere about 100 K, and then again, it decreases slowly. All the other alloys also have their respective peaks at different temperatures. At room temperature, the $ZT$ values are 0.77479, 0.76701, 0.77137, 0.76892, and 0.79534 for 0%, 25%, 50%, 75% and 100% doping concentrations of Hf, respectively. In this case, it is quite easy to observe that at room temperature, RhHfP possesses the maximum ZT value amongst all other compounds. The variation of the maximum value of $ZT$ is not linear with doping concentration, unlike in the case of TaFeSb [20], which is quite linear; it decreased for 25% doping, increase for 50%, then again decrease to 75%, and finally attain the highest peak at 100% doping of Hf in place of Ti at 300K.

## 4.3 CONCLUSION

We have carefully calculated the thermoelectric properties of half-Heusler alloy RhTiP by doping different Hf concentrations using first-principles calculations. We have found that the bandgap of RhTiP increases with the effect of doping except for $RhTi_{0.5}Hf_{0.5}P$, where it decreased than the parent value and reached its maximum value of 1.464 eV for 100% doping of Hf in place of Ti. At room temperature, the power factor of RhHfP is maximum amongst all, which is 1.9688 $*10^{11}$, and the maximum $ZT$ value at room temperature is of again RhHfP which is 0.79534. The $RhTi_{1-x}Hf_xP$has a maximum power factor of 1.43712 $* 10^{12}\ WK^{-2}m^{-1}s^{-1}$ which is relatively high, which makes it a very promising alloy deserving experimental synthesis. Also, the maximum value of ZT is 0.87327 for $RhTi_{0.5}Hf_{0.5}P$ at 50 K. Other values are not very much less than 1, which proves that all these resultant compounds are promising thermoelectric materials. However, a detail investigation of their lattice thermal conductivity is still lacking, and it will be quite interesting to work on it.

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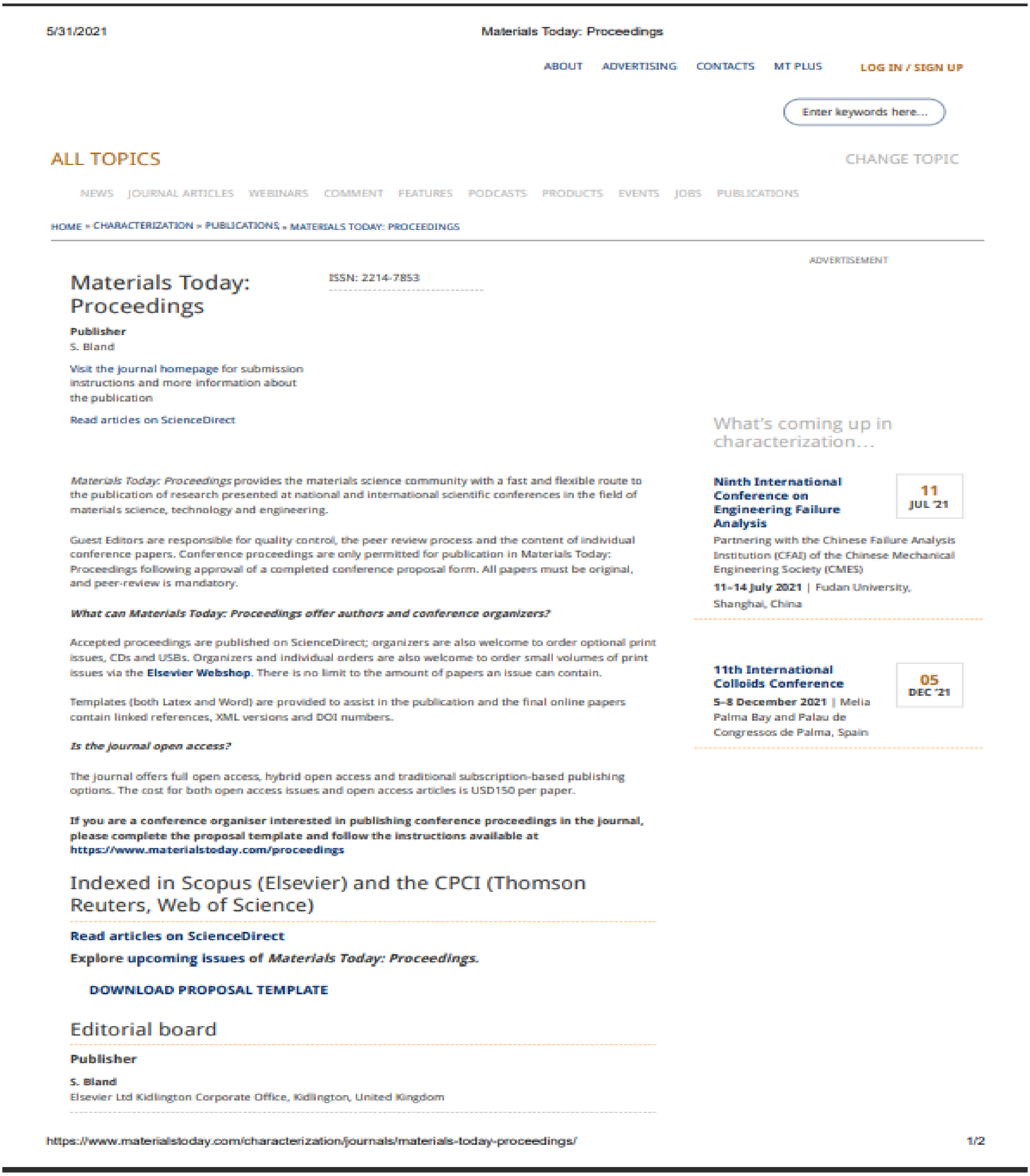

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# Study of thermoelectric properties of Hf-doped RhTiP Half-Heusler Alloy

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*Department of Applied Physics, Delhi Technological University, Delhi-110042, India.*

## Abstract

This work presented a first-principles based investigation pertaining to the analysis of the effect of Hf doping on thermoelectric properties of half Heusler alloy RhTiP. The energy bandgap of RhTiP is 0.810 eV. With increase in the concentration, the bandgap become less for $RhTi_{0.75}Hf_{0.25}P$ and increased for all other doping concentrations, the energy bandgap rise linearly with doping cocncentration. At 100% doping of Hf, i.e., for RhHfP, it is observed to be 1.464 eV. Here the material showed the highest thermoelectric performance at 100% doping of Hf in place of Ti (RhHfP) at room temperature, while other resultant compounds after the doping were also showing good thermoelectric behaviour. The maximum value of power factor and electrical conductivity at room temperature were $0.19688 \text{x}\, 10^{12}\ WK^{-2}m^{-1}s^{-1}$ and $3.2058 {*} 10^{18} \Omega^{-1}m^{-1}s^{-1}$which belong to RhHfP . The maximum $ZT$ value came out to be 0.7950 at room temperature, which is again of RhHfP. So, it was estimated that RhHfP could become a good thermoelectric material amongst all the studied concentrations.

*Keywords: Heusler thermoelectric; DFT; Boltztrap; RhTiP; GGA.*

## 1. Introduction

In the 21st century, we cannot imagine our single day without electrical energy. For machine work and in day-to-day life, we need energy for the fulfillment of different tasks. The exponential rise in demand for energy is a significant area of concern because a high portion of this energy comes from burning fossil fuels. These resources are present in the limited quantity on earth. Scientists are trying to find different environment-friendly and efficient ways to generate electricity that can be extracted from the waste heat. One of such ways is efficient thermoelectric materials that can convert waste heat into electricity. The thermoelectric performance of a material can be determined using a parameter known as the figure of merit denoted by $ZT$ and given as

$$ZT = \frac{S^2\sigma T}{\kappa}, \qquad \text{.......(1)}$$

where $S$ is the Seeback coefficient, σ is the electrical conductivity, $T$ is the absolute temperature, and κ is known as the thermal conductivity given as

$$\kappa = \kappa_e + \kappa_l,$$

where $\kappa_e$is the electronic thermal conductivity and $\kappa_l$ is the lattice thermal conductivity. A material having a high figure of merit $(ZT)$ has good thermoelectric properties. The dependence of $ZT$ on various parameters can be easily determined from equation (1). The electronic thermal conductivity given by the Wiedemann-

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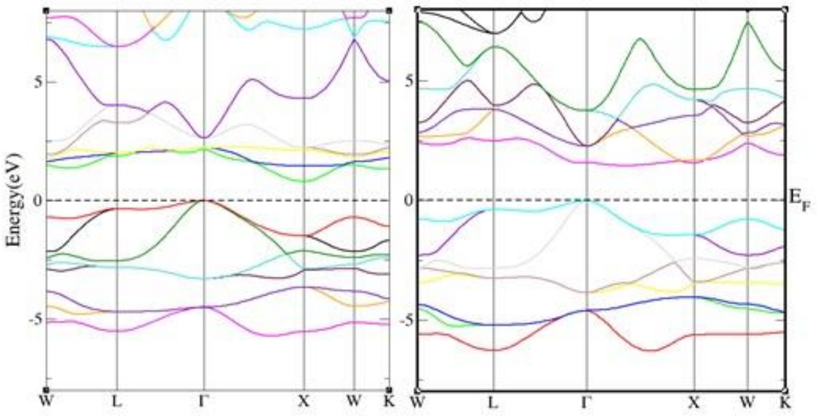
Franz Law [1], that is, $\kappa_e = L\sigma T,$ where, L is the Lorentz constant ($\approx 2.4 * 10^{-8} J^2 K^2 C^{-2}$ ).
Half-Heusler alloys have gained considerable interest in the present era due to their high-temperature stability, comparatively high Seebeck coefficient, and relatively high $ZT$ value. The half heusler alloys have a bandgap between 0.1-1 eV [2-3]. The various ways to increase the thermoelectricity is to tune the band structure by applying the strain or pressure and by doping of suitable elements [4], by increasing the ZT value of the compound (which is done by either decreasing the value of lattice thermal conductivity or by increasing electrical conductivity).
In the family of ABX type Half heusler alloy, RhTiP is a newly found material that is proven to be stable in previous studies [5], and it is yet to be developed experimentally. It can be used as an excellent thermoelectric material since it has a pretty high-power factor and Seebeck coefficient [5]. RhTiP is a ductile material with a bonding nature to be weakly ionic [5], so the property of the material to withhold external pressure and strain is relatively low in this case. Due to the presence of weak ionic bond, its disassociation energy should also be low; hence it is not on the problematic side to replace a specific atom from the sample experimentally. And there are already many good thermoelectric materials with the same configuration TaCoSn [6], ScPtSb [7]. This motivates us to work on the possibility of enhancing the $ZT$ value of RhTiP half-heusler alloy, which eventually increases its thermoelectric performance.

In the present work, the doping of Hf is done on alloy RhTiP to study the effect of this doping on electronic and thermoelectric. The main reason for using Hf as a doping agent is because of its chemical stability and pretty high boiling and melting point so that it can withstand high temperatures. Our aim of this study is to get high stable material with good thermoelectric properties at different concentrations of Hf.

## 2. Computational details

The structural, electronic, and thermal transport properties of RhTiP pristine and doped samples were investigated using Density Functional Theory (DFT) [8,9] based on the Full Potential Linear Augmented Plane Wave (FPLAPW) method as implemented in Wein2K code [10]. Generalized gradient approximation (GGA) formalism within the Perdew-Burke-Ernzerhof (PBE) parametrization was used to handle the exchange-correlation potentials [11]. Plane wave cut-off parameters were decided by $R_{MT}K_{max}$=7. A uniform K-mesh of $20 \times 20 \times 20$ has been used for 8000 irreducible Brillouin zone integration which was completed by using the original Monkhorst-Pack's scheme in the irreducible Brillouin zone (IBZ). The energy convergence criterion was fixed to 0.00001, and charge convergence was monitored accordingly. The transport properties were obtained using the BoltzTrap code [12], which solved the semiclassical Boltzmann transport equation while having a constant relaxation time $\tau$. This code was used to determine factors like power factor, Seebeck coefficient, electrical conductivity, etc. The power factor $S^2\sigma$ was presented in units of $\tau$, where $\tau$ is relaxation time . We constructed a 1x1x1 supercell of 12 atoms in order to simulate the various doping concentration.

## 3. Results and discussion



(a) (b)

Fig. 1. (a) Bandstructure of RhTiP; and of (b) RhHfP

First of all, this work performed the structural optimization of RhTiP, and it is found to be stable in the cubic semiconducting phase with a lattice constant of 5.76 Å. This value of lattice constant is in good agreement with what is available in the literature. The positions of the atoms inside crystal are (0.25, 0.25, 0.25) for Rh atom, (0.5, 0.5, 0.5) for Ti atom and (0, 0, 0) for P atom. The rest of the calculations are perform on the optimized lattice constant.

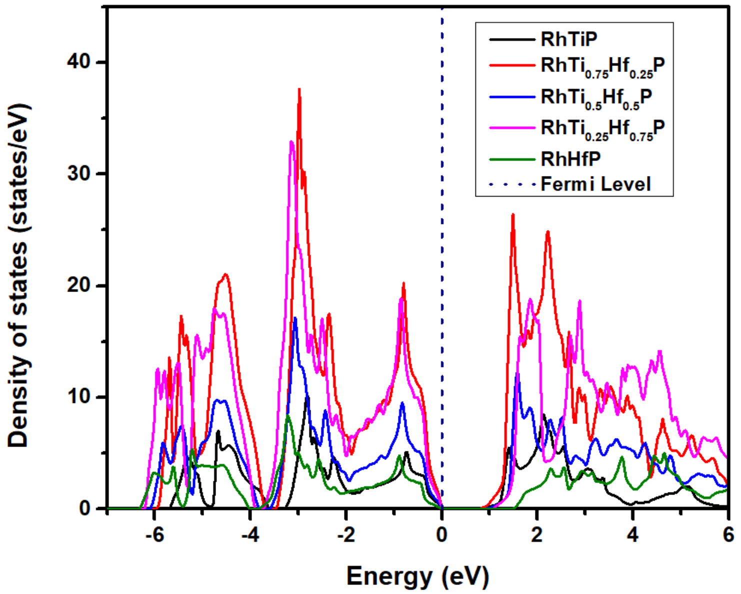


Fig. 2. Density of states plot of RhTi$_{1-x}$Hf$_x$P (x = 0.25, 0.50, 0.75, 1).

The semiconducting nature of all the concentrations in RhTi$_{1-x}$Hf$_x$P (x = 0.25, 0.50, 0.75, 1) have found to be intact. The bandgap value for RhTiP is 0.81 eV, which is in fair agreement with the previous study, 0.83 eV [5]. The energy dispersion shown in Fig. 1, along with high symmetry, points W$\rightarrow L \rightarrow \Gamma \rightarrow X \rightarrow W \rightarrow K$. The observation was that pure RhTiP has an indirect bandgap whose valence maxima were at $\Gamma$ and the conduction minima were at X high-symmetry point, while during the process of doping, the nature of the bandgap was tuned. The values of the bandgap for all the concentrations being study are listed in Table -1.

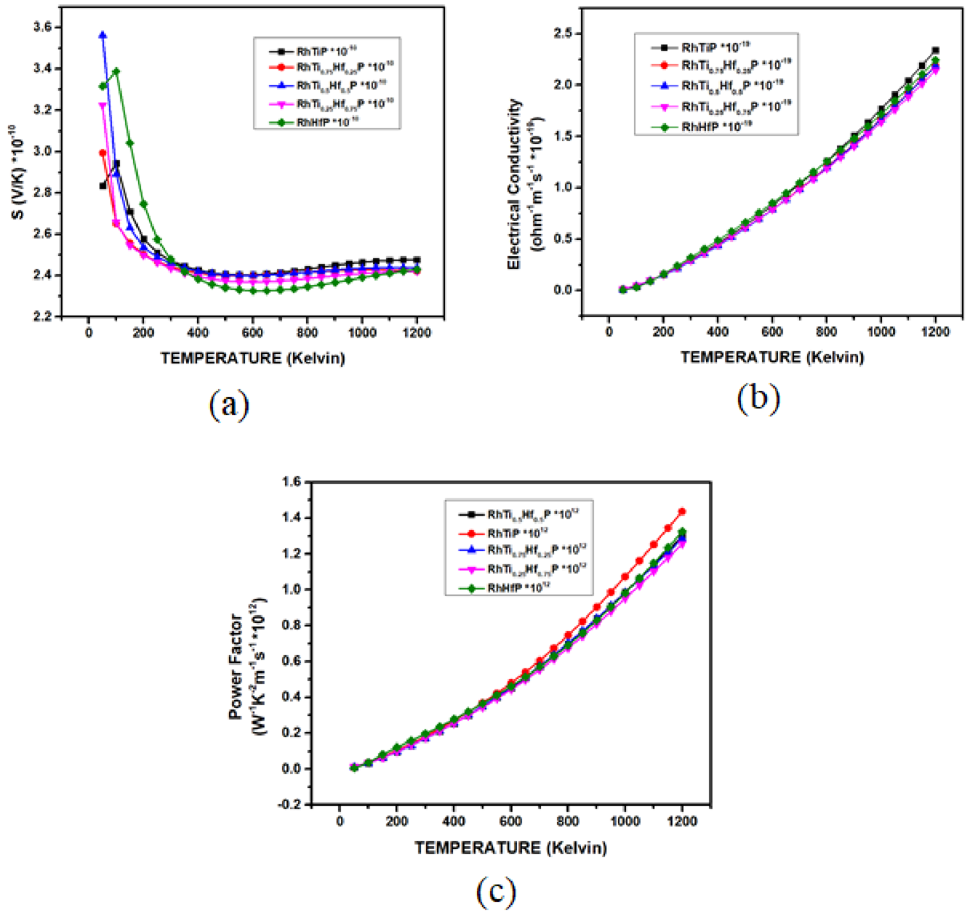
Table 1. Resultant alloys after doping and their respective bandgap values.

| Alloys | Bandgap (in eV) |
|---|---|
| RhTip | 0.815 (0.830) * |
| RhTiP | 0.810 |
| RhTi$_{0.75}$Hf$_{0.25}$P | 0.797 |
| RhTi$_{0.5}$Hf$_{0.5}$P | 0.877 |
| RhTi$_{0.25}$Hf$_{0.75}$P | 1.078 |
| RhHfP | 1.464 |

* Other's work [5].

As shown in Fig.2, the density of states (DOS) shows that for $RhTi_{0.75}Hf_{0.25}P$, the DOS attains maximum value for energy approx. -3 eV at valence band and in conduction band peak occur at approx 1.5 eV. Still, all these peaks are pretty steep as in a minor variation in energy, the value of DOS falls very sharply, the minimum value of DOS is coming out to be in the case of RhHfP. Here both 25% and 75% doping concentrations possess the highest DOS value in both valence and conduction band, while both RhTIP and RhHfP have the minimum value amongst them. The young's (E), shear (G), and bulk modulus (B) of this material were found in earlier studies [5] and are 177.72, 66.21, 188.58, respectively, which prove the stability of the material.

Let us first summarize the transport properties of pure RhTiP half-heusler alloy. The value of the Seebeck coefficient of RhTiP comes out to be 247.1 $\mu V/K$ at room temperature, and this value approaches up to 247.7 $\mu V/K$ at 1200 K (as depicted in Fig. 3(a)). The maximum power factor of the parent system is 1.44 x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$ at 1200 K temperature and at room temperature, its value is 1.823 x $10^{11}$ $WK^{-2}m^{-1}s^{-1}$. And finally, the ZT value of pure RhTiP is maximum at room temperature, that is, 0.77479. After that, we dope this pure RhTiP with Hf, which leads to a chemically stable compound, as discussed in previous studies [13] [14]. It has been studied by researchers that the alloys doped with an impurity such as Hf and Zr are found to be chemically stable [13-14]. Doping of Hf is done such as we got four different concentrations $RhTi_{0.75}Hf_{0.25}P$, $RhTi_{0.5}Hf_{0.5}P$, $RhTi_{0.25}Hf_{0.75}P$, and finally RhHfP.



(a)

(b)

(c)

Fig. 3. (a) Plot of Seebeck coefficient for different doping concentrations with respect to temperature, (b) Plot of electrical conductivity for different doping concentrations with respect to temperature, (c) Plot of power factor of different doping concentrations versus temperature.

The Seebeck coefficient's value decreases with an increase in doping percentage. As shown in Fig.3(a), we can clearly see that it first decreases in all cases and then increases with respect to temperature. The maximum value of the Seebeck coefficient is 356.407 $\mu V/K$ of $RhTi_{0.5}Hf_{0.5}P$ at 50 K, and the minimum for alloy $RhTi_{0.25}Hf_{0.75}P$ at 650 K (232.712$\mu V/K$). Interestingly the value of electrical conductivity increases with the increase in temperature (as shown in Fig.3(b)) but here also the maximum value of electrical conductivity belongs to pure RhTiP at 1200 K (2.34x$10^{19}\Omega^{-1}m^{-1}s^{-1}$). As in Fig.3(c), it is visible the power factor also increases with the increase in temperature (as the formula suggests PF=$S^2\sigma$ ) just like the electrical conductivity (also electrical conductivity of pure alloy is maximum at almost all temperature range that might be because of the fact that radius of Ti is smaller than that of doping element Hf so charge carriers have a lesser space to move around and that may result in decreasing its electrical conductivity), the maximum value of power factor belongs to pure alloy RhTiP (Fig. 3(c)) that is, approx. 1.44 x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$ at 1200 K and in the doped systems, the maximum value of the power factor belongs to RhHfP, which is 1.321x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$. The calculated maximum values of power factor for other doped concentrations such as $RhTi_{0.5}Hf_{0.5}P$, $RhTi_{0.75}Hf_{0.25}P$, and $RhTi_{0.25}Hf_{0.75}P$ are 1.300 x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$, 1.285 x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$and 1.25704 x $10^{12}$ $WK^{-2}m^{-1}s^{-1}$, respectively.

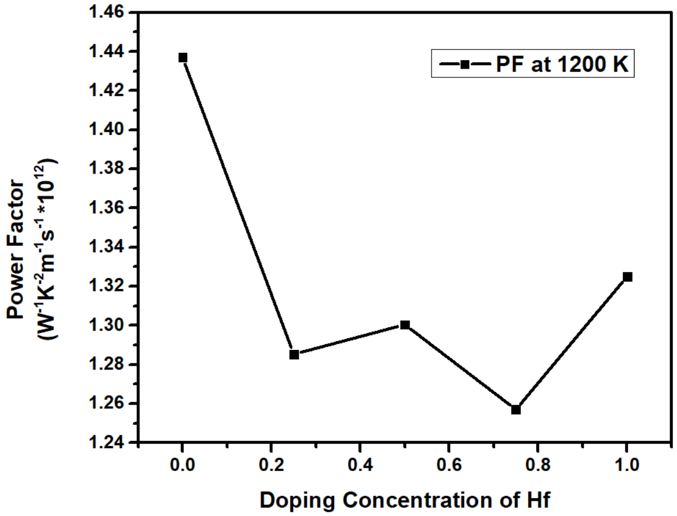
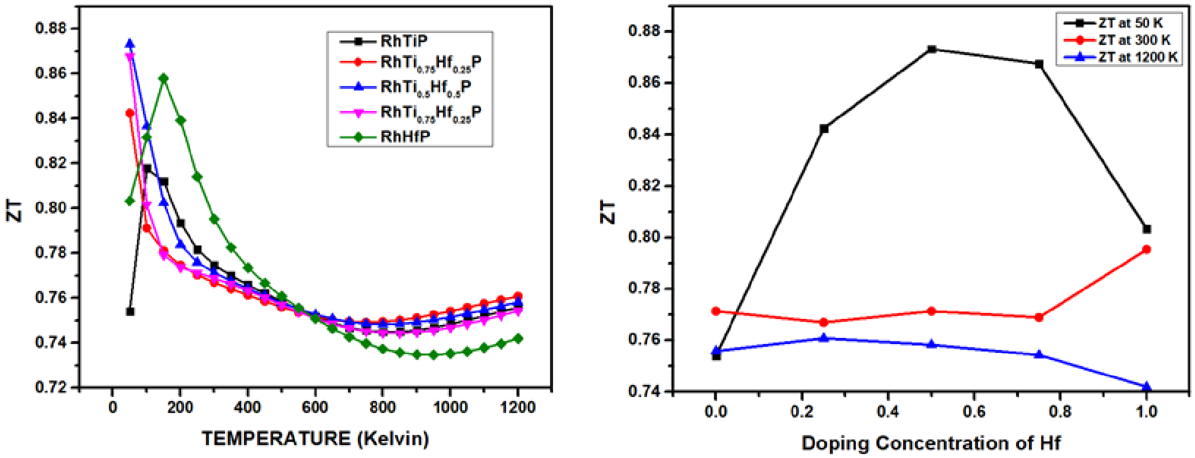


Fig. 4. Plot of the maximum value of PF versus doping concentration



(a)

(b)

Fig. 5. (a) Plot of ZT value at different temperatures, (b) Plot of ZT at 50 K, 300 K, and 1200 K versus the doping concentration.

At room temperature, the power factor for RhHfP is maximum (0.19688x$10^{12}$ $WK^{-2}m^{-1}s^{-1}$) while on the other hand, at room temperature $RhTi_{0.75}Hf_{0.25}P$ have a minimum power factor (0.17152 x$10^{12}$ $WK^{-2}m^{-1}s^{-1}$) which is still not that much low but on the higher side, so even at the minimum value, we can say that this material can work as a good thermoelectric material.

The variation of the power factor with doping percentage of Hf is shown in Fig. 4. The figure of merit (*ZT*) is maximum at 50 K for all doping concentrations (as shown in Fig.5(a)), and amongst them, the highest *ZT* value is 0.87327, which is of $\mathrm{RhTi_{0.5}Hf_{0.5}P}$. The ZT values for RhTiP, $RhTi_{0.75}Hf_{0.25}P$, $RhTi_{0.25}Hf_{0.75}P$ and RhHfP are 0.75406, 0.84247, 0.86763, 0.80341, respectively. We also find that the maximum value of *ZT* is 0.87327 at 50 K of 50% doping concentration, but 50 K is a very low temperature that is almost no use. So having a high value on that temperature couldn't quite help us. Hence, if we look towards a more realistic one, then at around 250 K, we observe that RhHfP acquires the maximum *ZT* value, which is approx. 0.81. All the variations in ZT value at different temperatures can be seen in Fig.5(b). The increase in *ZT* value of parent alloy attains a peak at somewhere about 100 K, and then again, it decreases slowly. All the other alloys also have their respective peaks at different temperatures. At room temperature, the *ZT* values are 0.77479, 0.76701, 0.77137, 0.76892, and 0.79534 for 0%, 25%, 50%, 75% and 100% doping concentrations of Hf, respectively. In this case, it is quite easy to observe that at room temperature, RhHfP possesses the maximum ZT value amongst all other compounds. The variation of the maximum value of *ZT* is not linear with doping concentration, unlike in the case of TaFeSb [15], which is quite linear; it decreased for 25% doping, increase for 50%, then again decrease to 75%, and finally attain the highest peak at 100% doping of Hf in place of Ti at 300K.

## 4. Conclusion

We have carefully calculated the thermoelectric properties of half-Heusler alloy RhTiP by doping different Hf concentrations using first-principles calculations. We have found that the bandgap of RhTiP increases with the effect of doping except for $RhTi_{0.5}Hf_{0.5}P$, where it decreased than the parent value and reached its maximum value of 1.464 eV for 100% doping of Hf in place of Ti. At room temperature, the power factor of RhHfP is maximum amongst all, which is 1.9688 *$10^{11}$, and the maximum ZT value at room temperature is of again RhHfP which is 0.79534. The $RhTi_{1-x}Hf_xP$ has a maximum power factor of 1.43712 * $10^{12}$ $WK^{-2}m^{-1}s^{-1}$ which is relatively high, which makes it a very promising alloy deserving experimental synthesis. Also, the maximum value of ZT is 0.87327 for $RhTi_{0.5}Hf_{0.5}P$ at 50 K. Other values are not very much less than 1, which proves that all these resultant compounds are promising thermoelectric materials. However, a detail investigation of their lattice thermal conductivity is still lacking, and it will be quite interesting to work on it.

## Acknowledgments

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