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Survey of Possible Thermoelectricity in α, β and γ Phases of HfNiPb Half-Heusler Compound by First Principle Approach.

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Abstract The three phases of half-Heusler alloys were examined via density functional and Boltzmann transport approach. Perdew-Burke-Ernzhof Projector Augmented Wave (PBE-PAW) within the Generalized Gradient Approximation (GGA) technique was employed in this study. The quantum simulations affirmed β phase as the most stable phase with least total energy and direct band gap energy of 0.1eV at points $X \rightarrow X$. Transport properties such as: electrical conductivity, Seebeck coefficient, figure of merit and power factor as function of holes concentrations were analysed at temperature range of 300K to 1000K for α, β and γ Phases of HfNiPb half-Heusler alloys. Little variation was recorded in the lattice parameter for the three phases. The figure of merit revealed p-type semiconductor systems. We observed high value of figure of merits at temperature 800K (0.65), at 1000K (0.58) and average value at 300K(0.45) for beta(β) phase. This study revealed HfNiPb is a promising thermoelectric material with the computed Seebeck, and dimensionless figure of merit's data.

Keywords: Density functional theory, Boltzmann transport approach, Power factor, Figure of merit, Half-Heusler

I. Introduction

The trend in global population growth with ever increasing social amenities such as automobiles, industries, hospitals, schools and other organizations call for alternative source of energy. Half-Heusler alloys are drawing more attention because of its high thermoelectric properties, affordability, non-existence of green house emission and massive harvesting of energy. Half-Heusler atoms are ternary systems comprising XYZ face centre cubic crystal structure. X and Y belong to transition or rare-earth metal while Z is an element from the main group [1].

Half-Heusler (HH) alloys which find usage in supercomputing, spintronics, magnetic shape memory effects, topological surface states and power generation [2, 3, 4, 5, 6] are known by the number of valence electrons. HH alloys' stability and creation of new properties of materials centre's on the number of valence electrons. Though there exist materials with outer valence electron count (VEC) of 17, 18 and 19. The most stable ones have 18 VEC. Some subgroups of 18 electrons are: III-X-V, IV-X-IV, IV-IX-V and V-IX-IV. Thermoelectric materials with more or lesser value of 18 VEC are metallic and magnetic respectively [7]. Sizable numbers of materials with 18VEC have been examined [8, 9, 10]. The unit cell of full- Heusler (FH) alloy comprises of $L2_1$ and that of HH alloy contains Cl_b structure which is categorized into three phases: α (alpha), β(beta) and γ(gamma), that is with atomic positions XYZ, YZX and XYZ respectively. The atomic arrangement in α

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phase can further be arranged by interchanging positions of X and Z as XYZ or ZYX with minute difference in lattice parameter and equal value of ground total energy.

Boltzmann transport theory (BTT) is a useful tool for assessing transport of neutrons, photons, electrons, mass, charge, momentum and current in a medium due to temperature change. Electrical conductivity is made possible with BTT via theoretical system detailed by temperature gradient of particles in a medium and the crystal lattice defects. Density functional theory methodology and Boltzmann transport theory as provided in Quantum Espresso and Boltzmann Transport Properties (BoltzTrap) packages were used in this study.

Figure of merit (FOM) is an algorithm design in form of numerical value in order to measure the effectiveness, performance, suitability and quality of a material. FOM finds functionality in measuring properties such as half metallicity, spintronics, polarization, magnetoresistance and thermoelectric utilization. It is dimensionless, unit less and can be expressed as seen in equation (1).

$$zT = \frac{S^2 \sigma}{K} T \qquad (1)$$

Power Factor (PF) as a vital parameter for an improved renewable energy enhances the efficiency of energy conversion through Seebeck effect. It showcases capacity of material to produce high voltage at a given temperature gradient and reduced electrical resistance losses. PF is written as in equation (2):

$$\mathrm{PF} = S^2 \sigma \qquad (2)$$

Seebeck coefficient evaluates temperature gradient ratio of an induced thermoelectric voltage of material and it is a function of productive performance of thermoelectric generators and coolers. Seebeck coefficient is either positively charged (electron holes) or negatively charged (electrons). It is expressed as written in equation (3):

$$S_{\alpha\beta}(T,\mu) = \frac{1}{eT\Omega\sigma_{\alpha\beta}(T\mu)} \int \overline{\sigma}_{\alpha\beta}\, (\varepsilon - \mu) \left[\frac{\partial f_0(T,\varepsilon,\mu)}{\partial \varepsilon}\right] d\varepsilon \qquad (3)$$

The Electrical conductivity (σ) connotes capacity of material to allow passage of electric current and this is determined by variation of carrier concentration or the carrier mobility.

Electrical conductivity of materials is functional of temperature and this is enhanced in semiconductor materials. Material composition and its properties are highly significant for an improved conductivity and also the presence of numerous free electrons in metal unlike insulator increases electrical conductivity. Existence impurities and pressure contributes to conductivity. It thus finds applications in biomedical sector, environmental science, material science and electronic and as well in electronic and wiring. This is state in equation (4).

$$\sigma_{\alpha\beta}(T,\mu) = \frac{1}{\Omega} \int \vec{\sigma}_{\alpha\beta}(\varepsilon) \left[\frac{-\partial f_o(T,\varepsilon,\mu)}{\partial \varepsilon}\right] \qquad (4)$$

And the transport distribution function ($\bar{\alpha}$) is expressed as written in equation (5):

$$\bar{\alpha}_{\alpha\beta}(\varepsilon) = \frac{e^2}{N} \sum \tau_i V_\alpha(i,\vec{k}) . \frac{\delta(\varepsilon - \varepsilon_{i,\vec{k}})}{d\varepsilon} \qquad (5)$$

In the recent past, some researchers examined some properties of HH HfNiPb using various approaches such as Tran-Blaha modified Becke-Johnson (TB-mBJ) and TB-mBJ plus spin-orbit coupling, full-potential linearized augmented plane-wave [11] and full-potential linearized augmented plane-wave plus local orbits methods

[12]. This work examines structural, electronic and thermoelectric properties of three phases of HfNiPb compounds.

II. Materials and Method

Quantum simulation and First principles computations in this survey were accomplished by making use of Perdew-Burke-Ernzhof – Projector Augmented Wave (PBE-PAW) within the Generalized Gradient Approximation (GGA). The nonlinear core correction scalar relativistic pseudopotentials were made use of as supplied in Quantum Espresso code [13]. PBE-PAW is preferred since its computational efficient, it inculcates efficient examination of core and valence electrons and its cost and time effective. Integration over the Brillouin zone which is crucial in assessing electronic band structures, density of states, effective masses, transport properties were carried out. The Monkhorst-Pack [14] k-mesh were equally optimized and the K-point sampling 7x7x7 were used for $\alpha-$phase$(XYZ)$with Wycoff positionsHf 4b (0.5, 0.5, 0.5), Ni 4c (0.25, 0.25, 0.25) and Pb 4a (0, 0, 0). 8x8x8 k-point mesh were employed for both $\alpha-$phase$(ZYX)$and γ phase. Grid of 6x6x6 k-point mesh was set for β phase. And 32x32x32 k-points mesh was applied for Density of states (DOS) assessment.

Boltzmann Transport Theory which is a nonlinear integral-differential equation as found in BoltTrap code was used to solve the transport equation for electrons and phonons. Transport coefficients as a function of holes concentration like Figure of Merit, power factor, Electronic fitness function, electrical conductivity and Seebeck coefficient at temperatures 300K, 500K and 800K were solved.

III. Results and Discussion

A. Structural and Electronic Properties

The self-consistency relaxation calculation of the optimized lattice constants ofα, β and γ phases of HfNiPb were carried out within convergence of 0.1mRy. The minimized lattice constants were obtained as shown in Table 1. The calculated lattice constant for α phase was in close agreement with the existing data [11]. The minute variation is due to artifact in GGA. There was little variation in the values of lattice parameters of α phase of ternary HfNiPb, although, they have equal total ground energy. The β phase has the highest lattice constant and the least total energy and so, the most stable phase. The details of volume (V)-energy (E) were fixed in the third–order Birch-Murnaghan equation of state[15] which is expressed in equation (6), both bulk modulus (B) pressure and its derivative (B') were examined at room temperature as shown in Table 1 and Table 2 respectively.

$$\delta E(V) = E - E_0 = BV_0\left[\frac{V_n}{B'}\right] + \left(\frac{1}{(1-B')}\right) + \left(\frac{V_n}{B'(B'-1)}\right) \tag{6}$$

Table 1: Optimised lattice parameter (a) in (Å) and total energy in (Ry) of *α, β and γ* phases of HfNiPb

Types of Phases	Present Value of Lattice Parameter	Previous Theoretical Data	Ground Total Energy
$\alpha-$phase(XYZ)	6.178	6.252[16], 6.125[12]	-1996.01
$\alpha-$phase(ZYX)	6.208		-1996.01
$\beta-$phase	6.214		-1995.82
$\gamma-$phase	6.209		-1995.83

Table 2: Estimated Bulk Modulus (B) and Pressure (B') Derivatives of α, β and γ phases of HfNiPb from 3rd Order Birch-Murnaghan

Material	This Work		Other Works	
	B (GPa)	B'	B (GPa)	B'
$\alpha-$ phase(XYZ)	39.6	3.79	129.94[12]	4.91[12]
$\alpha-$ phase(ZYX)	39.9	3.80		
$\beta-$ phase	42.9	4.81		
$\gamma-$ phase	44.1	4.77		

This structure crystallized into Face-centered cubic (FCC) structure and of the type MgSrSi with space group $F\vec{4}3m$. Xcrysden, [17] was used in visualizing and analyzing stable structure of β phase which is shown in Figure 1. The total energy as a function of volume of β phase was also examined. The band structure of β phase of HfNiPb alloys with direct band gap of 0.1eV at points $W \rightarrow W$ is revealed is in Figure 2.

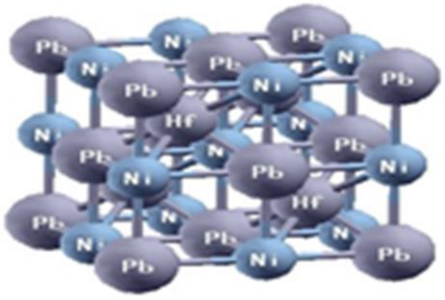

Figure 1: Crystal Structure of HfNiPb (β–phase)

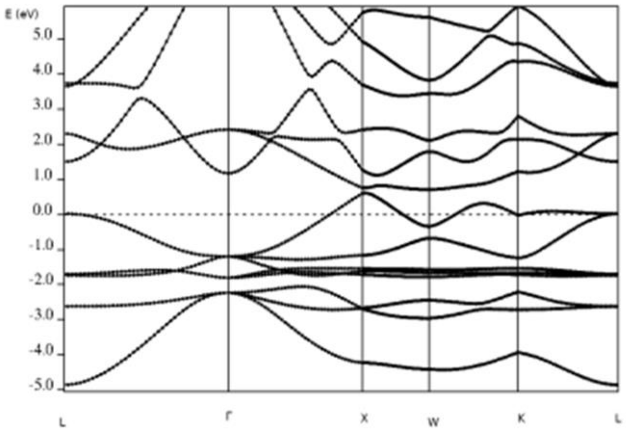

Figure 2: Band Structure of HfNiPb (β–phase)

B. Density of State, Partial Density of State and Energy Band Structure

Dispersion relation along high symmetry k-points is vital in getting band gaps, band widths, effective masses and phonon frequencies. The direct energy band gap of α phase at point K is in excellent agreement with previous theoretical values as displayed in Table 3.

β –phase recorded the least energy band gap, direct energy 0.1eV at point K, enhances its electrical conductivity.

Types of Phases	Direct Path	Indirect Path	Band Energy Gap (Present Value)		Existing Theoretical Data
			Direct	Indirect	
$\alpha-$ phase(XYZ)	$K \rightarrow K$	$G \rightarrow K$	0.3	0.4	0.32[11], 0.256[11]
$\alpha-$ phase(ZYX)	$K \rightarrow K$	$G \rightarrow K$	0.3	0.4	
$\beta-$ phase	$W \rightarrow W$		0.1	-	
$\gamma-$ phase	$K \rightarrow K$	$G \rightarrow K$	0.3	0.2	

The estimated DOS and PDOS of β –phase of HfNiPb are made known in Figures 3 and 4. Estimated DOS and PDOS have two conspicuous peaks. The uppermost valence band is dominated by Hf- 5d states. Concurrently, the least conduction band is dominated by mixing of Ni-4d and Pb-6p states. At point X of band structure, energized electrons at upper valence band cross over Fermi level making the material a typical semiconductor for better thermoelectric response.

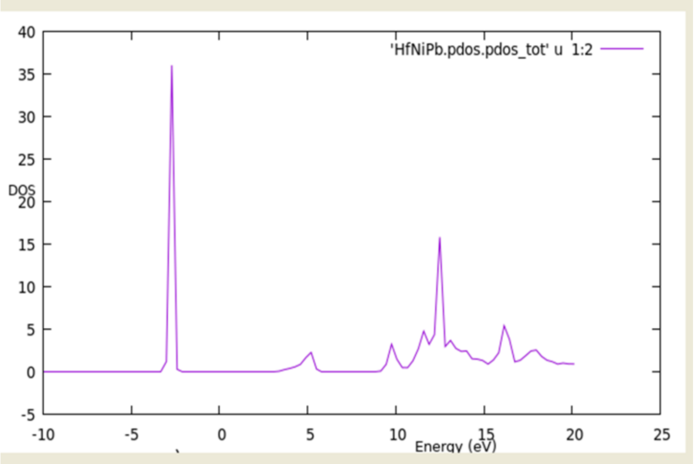

Figure 3: Total Density of States (TDOS) of HfNiPb (β–phase)

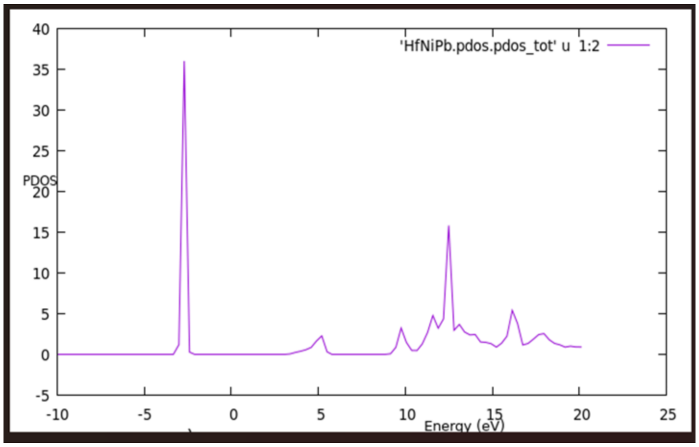

Figure 4: Total Partial Density of States (TPDOS) of HfNiPb (β –phase)

C. Thermoelectric Property

Ability of material to adequately deliver thermoelectrically centre on its dimensionless figure of merit(ZT), power factor, electronic fitness function, electrical conductivity and Seebeck coefficient. This study showcased p-type semiconductor, beta phase of HfNiPb. The measured ZT for HfNiPb as a function of hole concentration is shown in Figure 5. The highest ZT of 0.65 observed at temperature 800K is higher than calculated ZT (0.43) at temperature of 1200K [12]. The power factor(PF)computation with varied hole concentrations at close range of [(37.10-37.49) x $10^{22}cm^{-3}$)] and various temperatures 300K, 500K and 800K were actualized as exhibited in Figure 6. PF at temperature 800K (27.0279 x $10^{10}W/msK^{2}$) is more pronounced than that of 500K (19.9129 x $10^{10}W/msK^{2}$) and 300K (11.17698 x $10^{10}W/msK^{2}$) respectfully. Electronic Fitness Function (EFF) which gives details of electronic feature of thermoelectric material is utmost at temperature 800K with value $0.558571x10^{-19}W^{5/3}ms^{-1/3}K^{-2}$ as demonstrated in Figure 7. A good electrical conductivity is enhanced in thermoelectric material with reduced temperature as evident at temperature of 300K (6.97705S/ms) in Figure 8. A higher value of Seebeck coefficient which imply a preferred semiconductor material was also evaluated at temperature of 800K as indicated in Figure 9.

IV. Conclusion

In this research work, structural, electronic and thermoelectric properties of three phases of cubic crystal half Heusler compounds of HfNiPb were examined using Perdew-Burke-Ernzhof –Projector Augmented Wave (PBE-PAW) within the Generalized Gradient Approximation (GGA) based on Density

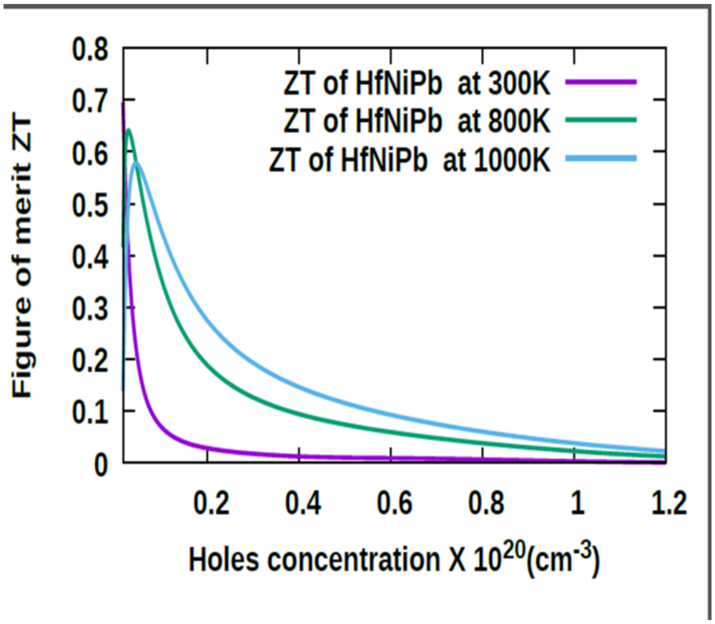

Figure 5: Figure of Merit HfNiPb (β –phase)

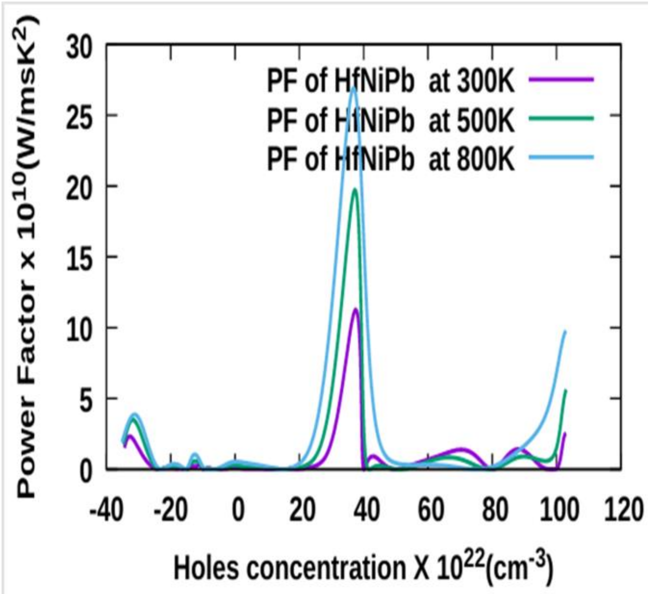

Figure 6: Power Factor of HfNiPb (β –phase)

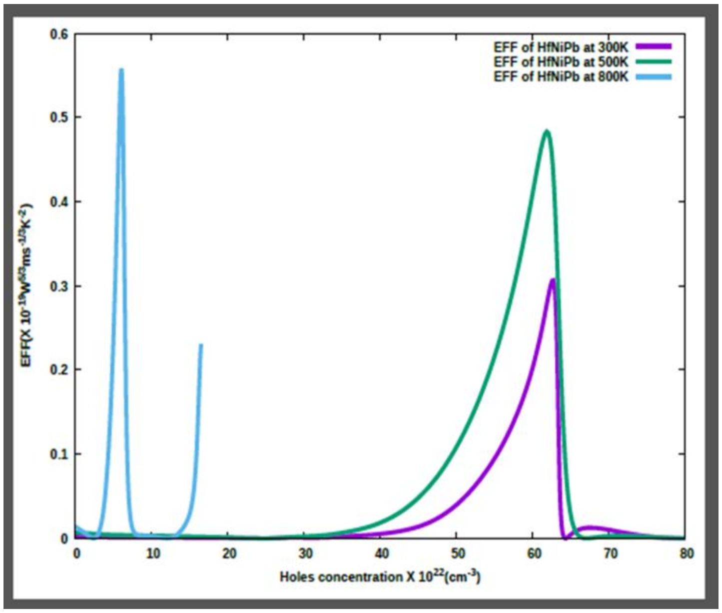

Figure 7: Electronic Fitness Function of HfNiPb (β –phase)

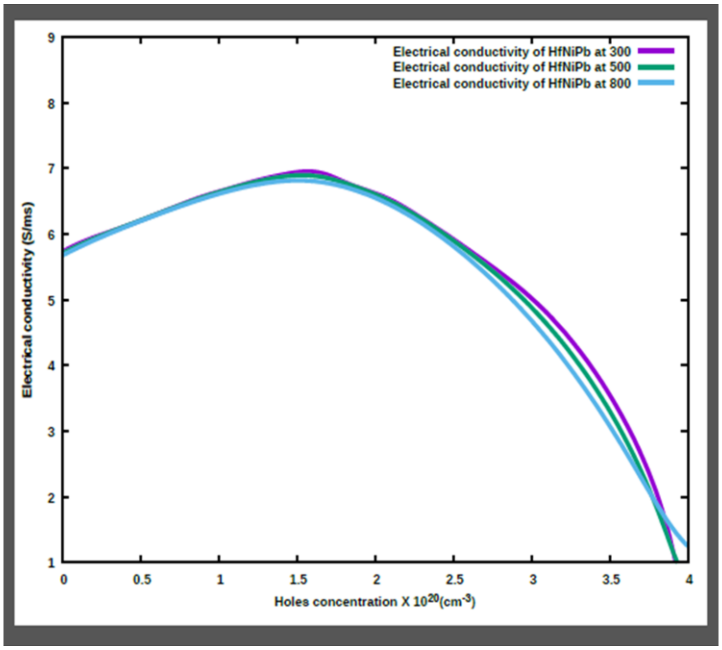

Figure 8: Electrical Conductivity of HfNiPb (β –phase)

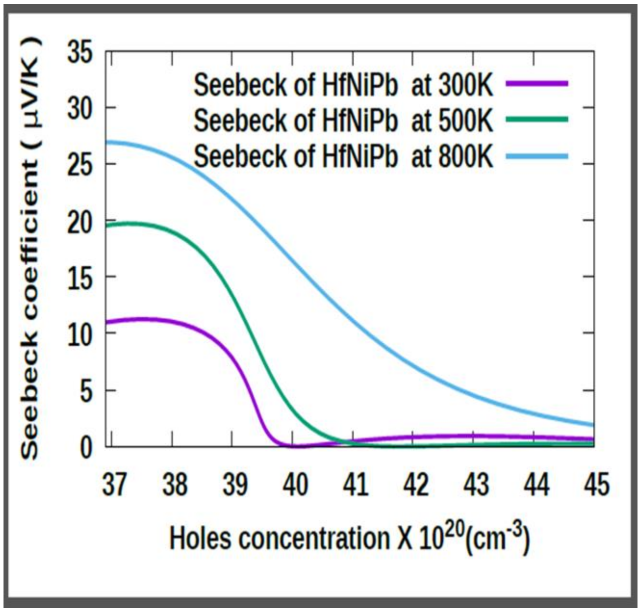

Figure 9: Seebeck Coefficient ofHfNiPb ($\beta-$ phase)

Functional Theory as well as Boltzmann theory provided in Quantum Espresso package and BoltzTrap code separately. There was little variation in optimized lattice parameter of the three phases considered in this study which is very close to the existing theoretical values. It was discovered that the total energy of two alpha phases were equal irrespective of change in the arrangement of their atomic positions. Beta phase emerged as the most stable phase with least direct energy gap of 0.1 eV. It was revealed that this p-type HfNiPb is a promising thermoelectric material with highest figure of merit (0.65) at temperature of 800K.The experimentalists are encouraged to examine possible means of high thermoelectricity of beta phase of HfNiPb.

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