

First- Principles Exploration of Structural, Electronic and Thermoelectric Properties of VRhSi Half-Heusler Compound .

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Abstract This study probed into theoretical analysis of structural, electronic and thermoelectric properties of half-Heusler VRhSi compound within the framework of Generalized Gradient Approximation (GGA) using Perdew-Burke-Ernzerhof for solids (PBEsol) based on Density Functional Theory (DFT). The optimized lattice parameter ($5.65\text{\AA}$), volume (6.67a.u^3), pressure (161KBar) and pressure derivative (3.99) were calculated using third order Birch-Munaghan Equation of State. This material has an indirect energy band gap of 0.28eV as expressed by electronic structure. Thermoelectric properties as a function of electrons and holes concentrations at various temperatures 300K, 500K and 800K were examined from the semi-classical Boltzmann Transport equation. This study revealed p-type semiconductor VRhSi half-Heusler compound with high power factor, Seebeck coefficient, electronic fitness function and figure of merit as a suitable material for thermoelectric functionalities.

Keywords: PBEsol, Density Functional Theory, Thermoelectric properties, Half-Heusler, Electronic Structure

I. Introduction

Quest for energy keeps soaring higher on a daily basis as it is the key thing to power industries, hospitals, institutions, organizations and so on. Strategies such as solar, wind, geothermal, hydropower, bio energy and ocean have been used. Heusler compound fits in the more in a search for a cost efficient, nonpolluting and unlimited supply of energy. Fact finding about Heusler compound is fascinating because of its applications such as sensors, actuators, energy harvesters, magnetic cooling devices and its various properties which include electricity production, spintronic applications, magnetic and structural properties [1, 2].

Heusler compounds came to know in 1903 [3]. The foremost Heusler compound surveyed crystallized into $L2_1$ structure and have four face

centred cubic sublattices and these are: Full Heusler ($XYXZ$), half-Heusler ($X Y Z$), Quaternary Heusler ($X Y X' Z$) and Inverse Heusler ($X Y Y Z$). X and Y elements are members of transition metal while Z is in the p-block which belongs to main group element. Thermoelectric functionality of Heusler compound enhances its increase probing and birth of innovative materials. Half Heusler compounds emerge as one of best materials to rely on for effective thermoelectric responses. This work conducts an investigation into a new half-Heusler compound VRhSi and considers its structural property like: lattice constant, optimized volume, pressure and pressure derivative, electronic and thermoelectric qualities.

Sizable research works, experimental and theoretical wise had been carried out on n-type and p-type half-Heusler (HH) compounds [4, 5, 6, 7]. But there is no investigation of n-type and

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p-type of VRhSi compound. VRhSi compound is an inorganic half-Heusler semiconductor. This study examines structure and electronic attributes from first-principle and thermoelectric responses of both n-type and p-type VRhSi materials using Boltzmann transport theory (BTT) as supplied in Boltzmann Transport Properties (BoltzTrap) packages.

II. Materials and Method

Quantum simulations were performed on ternary half-Heusler VRhSi compound within the Generalized Gradient Approximation rooted in Density Functional Theory. The exchange correlation functional applied is Perdew-Burke-Ernzerhof for solid (PBEsol) as obtained in Quantum Espresso Library [8]. The plane wave cutoff energy in the wave function was set at 80Ry. Convergence for self-consistent calculation was set at 0.1mRy. In the first Brillouin zone, k-point grid was established at 3x3x3 k-points mesh for electronic band structure computation [9], and 32 x 32 x 32 k-points grid was fixed for density of state calculation. Boltzmann Transport Theory as presented in Boltzmann Transport Properties (BoltzTrap) code was employed to search for thermoelectric influences, the likes of: Seebeck coefficients, electrical conductivity, power factor, figure of merit and electronic fitness function.

III. Results and Discussion

A. Structural and Electronic Properties

The Wyckoff positions of the atoms X (Vanadium), Y (Rhodium), and Z (Silicon) are: X (0.50, 0.50, 0.50), Y (0.25, 0.25, 0.25) and Z (0.00, 0.00, 0.00). VRhSi ternary Half-Heusler compound takes after MgAgAs structure type and crystallized into face-centred cubic structure with space group $F43m$ and Cl_b structure type.

The total ground lattice constant (a), bulk modulus (B) and pressure derivative (B') were calculated by fitting energy (E) and volume (V) into third order Birch – Munaghan Equation of state [10, 11] as expressed in equation (1). The optimized lattice constant (5.65Å), obtained in this work is in close agreement with β -phase of VRhSi compound of Ahmed et al., 2024 as shown in Table 1. But there is a variation in Wyckoff atomic position of their β -phase; X (0.50, 0.50, and 0.50), Y (0.00, 0.00, and 0.00) and Z (0.25, 0.25, and 0.25) and the one used in this work. Optimized lattice constant and volume (6.67a.u³) are displayed in Figures 1 and 2 respectively.

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

where E_0 is the equilibrium energy, V_0 is equilibrium volume, B is the bulk modulus and B' is the pressure derivative.

Table 1: Ground state lattice constant a (5.65Å), Bulk modulus, B(GPa), Pressure derivative, B', Minimum Energy, $E_{\min}$ (Ry) and Band Energy gap, E_g (eV)

Compound	(Å)	B (GPa)	B'	$E_{\min}$ (Ry)	E_g (eV)
Present work	5.65	1.61	3.99	- 1512.41035	0.28
Previous work	5.69 ^[12]				

B. Band Structure

The electronic band structure which is vital in estimating materials influences in designing and electronic devices optimization along the high symmetry k-points as evidenced in Figure 3 is a semiconductor type with small indirect energy

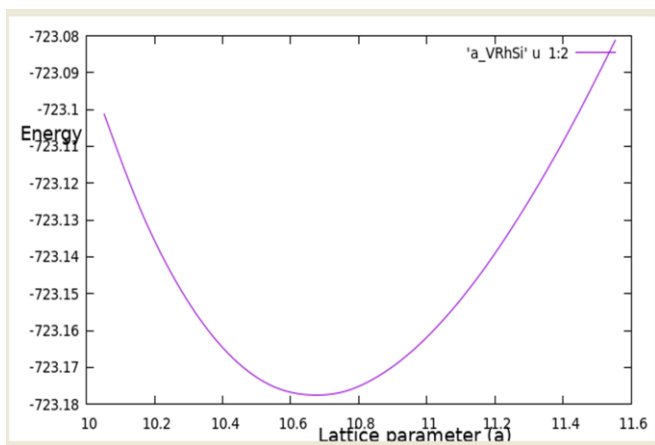


Figure 1: Optimized Lattice constant of VRhSi

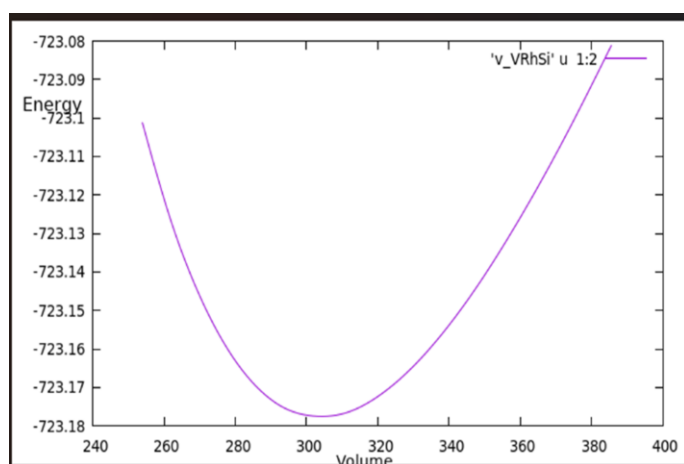


Figure 2: Equilibrium Volume of VRhSi

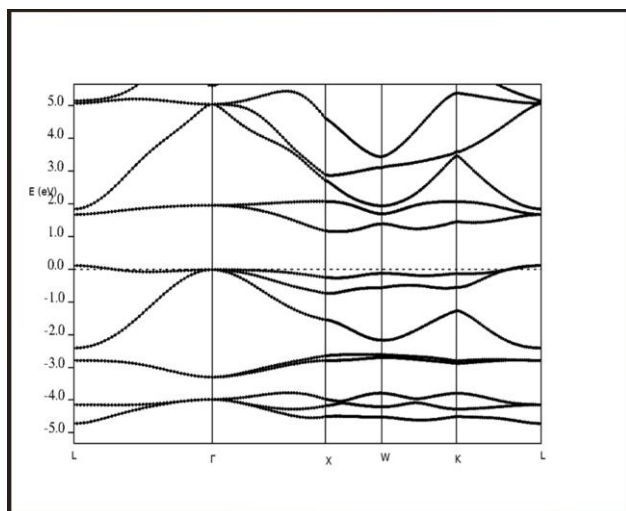


Figure 3: Band Structure of VRhSi

gap 0.28eV from the topmost valence band at point Γ and minimum conduction band at point X. The upper valence band is dominated by Rh-4d states and Si -3p states. The lowest conduction band emanated from V- 3d states.

Total Density of States (TDOS) determines the total number of available energy states per unit energy range in a material and taking into consideration all possible energy levels and degrees of freedom. TDOS is expressed mathematically as:

$$TDOS(E) = \int DOS(E') dE' \quad (2)$$

Here in, TDOS(E) is the total density of state at energy E, DOS(E') is the density of state at energy E' and $\int dE'$ is the integration over all energy levels.

Six peaks emanated above the Fermi level which measures the occupation of electron states in a material. There is hybridization of Rh-4d states to form covalent bond with Si – 3p state. And Vanadium which is recognized by his versatility, V- 3d states chemically bonded with Rh-4d states and Si – 3p state as represented in Figure 4. Total partial density of state (TPDOS) evaluates the addition of the partial density of state for all orbital, atoms or bands in a material as depicted in Figure 5.

Seebeck coefficient otherwise termed thermopower, thermoelectric power and thermoelectric sensitivity evaluates extent of a stimulated thermoelectric voltage with respect to temperature difference across the material triggered by the Seebeck effect [13]. A material with high Seebeck coefficient is essential for harnessing renewable energy. It is negative for negatively charged carriers for instance electrons and positive for positively charged carriers like electron holes as reflected in Figure 6. Seebeck

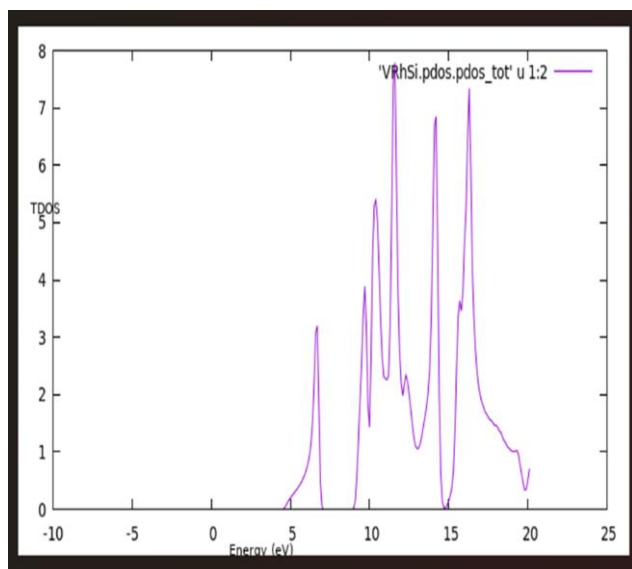


Figure 4: Total Density of State of VRhSi Compound

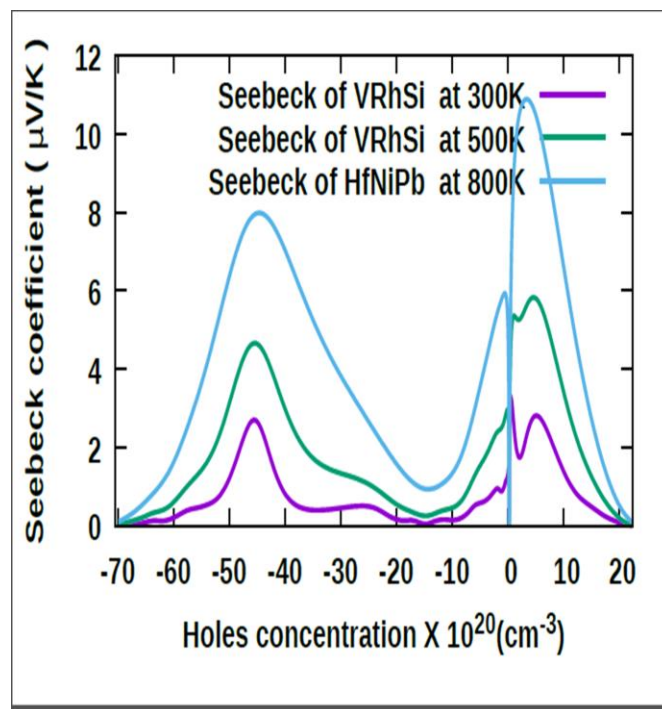


Figure 6: Seebeck Coefficient of VRhSi Compound

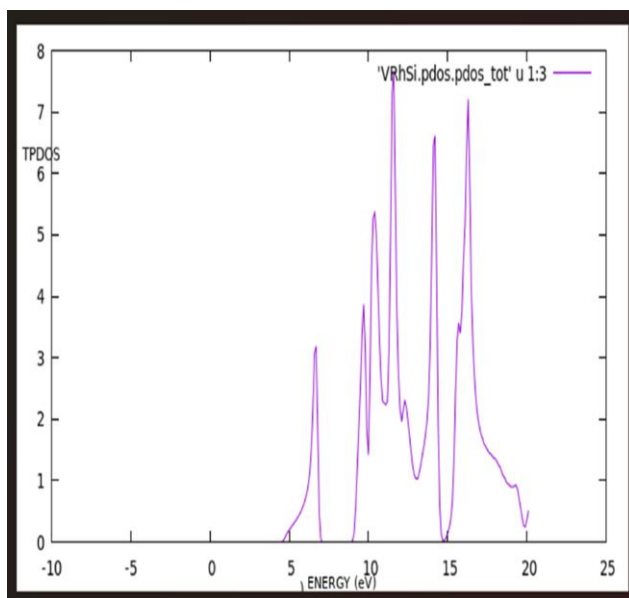


Figure 5: Total Partial Density of State of VRhSi Compound

coefficient as a function of charge carriers was scrutinized. It was discovered that Seebeck coefficient increase with varied temperature for both carriers, but the peak value is at $10.8472 \mu\text{V/K}$ at temperature 800K for p-type semiconductor VRhSi alloy.

Electronic fitness function (EFF) is important because of its capacity to measure and optimize the effectiveness and efficiency of electronic and thermoelectric devices. EFF uses simulations to appraise fitness and its inverse connection between Seebeck coefficient and electrical conductivity. Consequence of variation of EFF with charge carriers is indicated on Table 2 and unraveled in Figure 7. EFF is more pronounced ($0.517 \text{ W}^{7/3} \text{ ms}^{-1/3} \text{ K}^{-2}$) in p-type semiconductor HH VRhSi compound than its counterpart, n-type material. EFF increased with temperatures

with ranging from 300K to 800k for both types of HH semiconductor VRhSi.

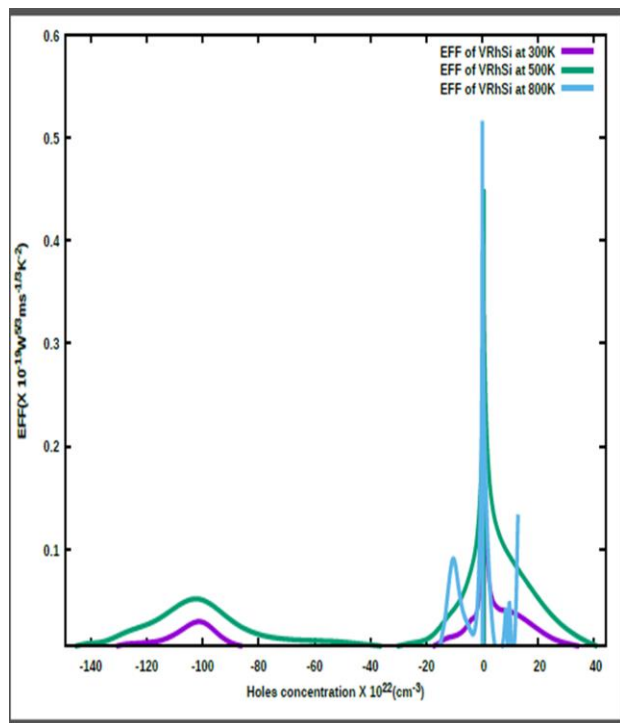


Figure 7: Electronic Fitness Function of VRhSi Compound

Electrical conductivity showcases ability of material to allow passage of electric current through it. Presence of free electrons in n-type domain enhanced greater level of conductivity at temperature 800K with maximum value of 11.9406 S/ms than p-type zone with 2.56S/ms at 300K as shown in Figure 8. N-type semiconductor finds application in power electronics, integrated circuits and optoelectronics.

Power factor and Figure of merit are germane in figuring out materials to be used in harvesting clean energy which thermoelectric depicts. In this study, PF of a p-type semiconductor HH VRhSi is much more feasible at temperature 800K (10.97W/msK^2) than n-type (7.98

W/msK^2) at same temperature. The figure of merit favours p-type HH semiconductor as well with highest value of 10.955 as presented in Table 2 and pictured in Figure 9 and 10 respectively.

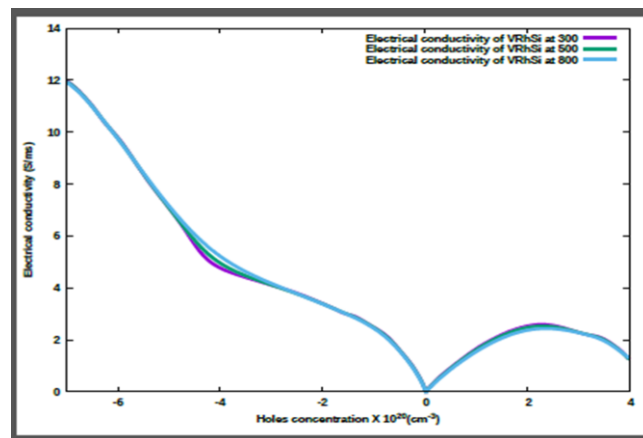


Figure 8: Electrical Conductivity of VRhSi Compound

Table 2: Calculated values of thermoelectric properties of n-type and p-type semiconductors of VRhSi compound: Seebeck coefficient (S in $\mu\text{V/K}$), Electrical conductivity (σ in S/ms), Power factor (PF in W/msK^2), Figure of Merit (ZT), Electronic fitness function (EFF in $\text{W}^{5/3}\text{ms}^{-1/3}\text{K}^{-2}$) at temperatures; 300K, 500K and 800 K (T in K).

T	Type	S	Σ	PF	ZT	EFF
n-type						
800		8.0012	11.9406	7.98	8.0370	0.09
500		4.6508		4.62	4.6868	0.052
300		2.74152		2.69	2.70	0.032
p-type						
800		10.8472		10.97	10.955	0.517
500		5.8036		5.84	5.8	0.18
300		3.2090	2.5680	3.19	3.1	0.052

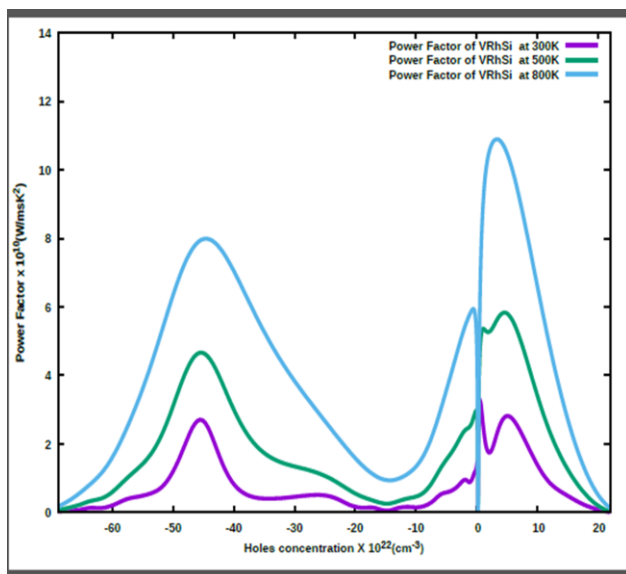


Figure 9: Power Factor of VRhSi Compound

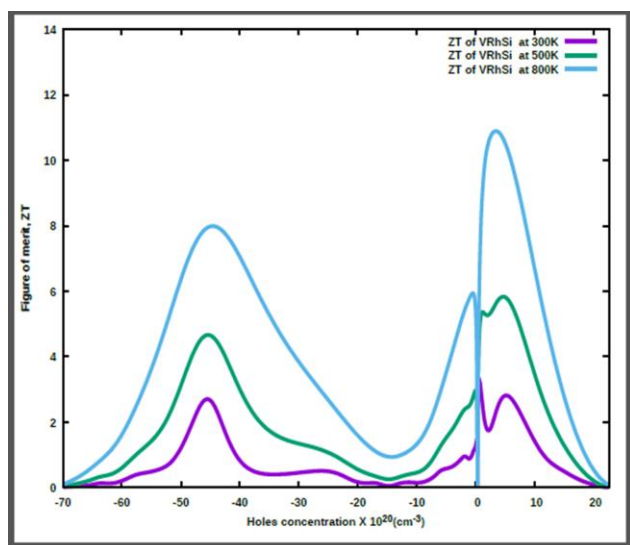


Figure 10: Figure of Merit of VRhSi Compound

IV. Conclusion

An investigation into the structural, electronic and thermoelectric properties of VRhSi compound was conducted in this study using first-principles approach and Boltzmann transport theory. An indirect energy gap of 0.28eV was recorded. Thermoelectric electric properties which included Seebeck coefficient, Electronic Fitness Function, electrical

Print ISSN 2714-2469; E- ISSN 2782-8425 UNIOSUN Journal of Engineering and Environmental Sciences (UJEES)

conductivity, power factor and figure of merit for both n-type and p-type semiconductor of VRhSi compound were appraised. It was discovered that p-type of VRhSi compound has the highest Seebeck, power factor, figure of merit and Electronic Fitness Function at temperature of 800K and this makes it a promising material for energy harvesting. The experimentalists are encouraged to look into this p-type VRhSi compound for production of clean and renewable energy.

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