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BAND STRUCTURE, THERMOELECTRIC FEATURES AND ELECTRONIC FITNESS FUNCTION OF P-TYPE SEMICONDUCTOR HALF-HEUSLER RhCrGe COMPOUND

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ABSTRACT
This work conducted an investigation of structural, electronic and thermoelectric reactions of the ternary half-Heusler RhCrGe compound utilising Perdew-Burke-Ernzerhof for solids within Generalised Gradient Approximation (PBEsol-GGA) rooted in Density Functional Theory (DFT) as implemented in Quantum Espresso software bundle. The material demonstrated a semiconductor type only with an indirect energy gap of 0.7eV. Electronic transport features were calculated using BoltzTrap code and TransM code. This study revealed p-type material with the thermoelectric properties suggesting better values of figure of merit, power factor, Seebeck coefficient and electronic fitness function as temperature increased from 300K to 800 K.

KEYWORDS: Half-Heusler, ternary compound, Density Functional Theory, Transport Theory, Semiconductor.

INTRODUCTION
The foremost source of energy such as biofuel, fossil fuel which served purposes before this century but expose the end users to dangers like climate change, global warming, green house effects and release of carbon (iv) oxide to the air. Inadequate supply and cost implication are making biomas hard to come by. Renewable energy such as solar energy, wind power, hydroelectric power, geothermal energy and tidal power are also sources of energy. The search for a sustainable energy which is cost effective, health-challenges- free, pave way to durable, ecofriendly, void of pollution of any kind and lack of acid rain to mention a few, result into Heusler alloys. Conrald, Friedrich and Otto Heusler alloys [Tavares *et al*., 2023] comprises of elements from transition metals and p-block elements and are further divided into Full Heusler (FH), half-Heusler (HH), inverse Heusler, binary and quartenary alloys.
Heusler compounds crystallized into face-centred cubic crystal structure; $L2_1$ for FH comprising X_2YZ and $C1_b$ structure and for HH containing XYZ. Other discoveries [Wolfgang *et al*., 2017, Naghibolashraf*i et al*., 2016] revealed further compositions namely; double HH composed of $X_2XY'Z_2$ [Anand *et al*., 2020] and triple HH constructed from $X_2X'Y_3Z_3$[Imasato *et al*., 2022]. Dong and co-researchers [Dong *et al*., 2022] discovered $TiRu_{1+x}Sb$ (x = 0.15 – 1.0) solid solution with continuous compositions and examined its tunable p – to n- type that bridge gap between HH and FH phases. Kawasaki and his research team [Kawasaki *et al*., 2022] established that there are other structures of Heusler compound which is due to structural distortions and change in atomic site ordering. Ternary HH compounds are unique since they compose of elements which are nontoxic, cost effective and with notable thermal stability. Some of their applications are: spintronics and magnetic sensors, topological insulators, potential materials for solar cells and photovoltaic usage, catalysis for different chemical reaction and energy storage, magnetic refrigeration, biosensors, bioimaging and cancer treatment and replenishable energy in thermoelectricity. Valence electrons determine the type of chemical bonding among the constituent atoms and affect properties of material for instance, electronic structure, structural stability, magnetic, thermoelectric properties and so on. Valence electron is fundamental in production of new HH compounds. There exist 18 valence electrons, seventeen valence electrons, nineteen or twenty two valence electrons. HH compounds with total valence of 8 and 18 counts form semiconductor [Kandpal *et al*., 2006]. RhCrGe material is a typical example of 18 valence electron counts.
The first ternary HH Cu_2MnAl was discovered in 1903 by Friedrich, Groot *et al*, (1983) explored NiMnSb, Mehmood *et al*, (2017) appraised structural, elastic, mechanical, electronic, magnetic and optical behaviours of RhCrSi and RhCrGe using full potential linearized augmented plane wave (FP-LAPW) approach. Amrani et al, (2020) delved into physical properties of RhCrSi, RhCrGe, RhCrP and RhCrAs. This study conducts a DFT investigation into the structure, electronic and thermoelectric qualities of RhCrGe using it to search for its structural, electronic and thermoelectric potentials.

MATERIALS AND METHODS
Ultrasoft pseudopotential (USSP), nonlinear core correction scalar relativistic and exchange functional type of PBEsol-GGA [Perdew *et al*, 1996] as found in Quantum Espresso pseudopotential library [Scandolo *et al*, 2005, Giannozi *et al*, 2009, Giannozi *et al*, 2017] based on DFT was employed in the quantum simulation for calculation of structural and electronic features. USSP provides accurate, time and computational efficiency in DFT estimation as it permits lower energy cutoffs and smoother pseudo-wavefunctions. The k-point mesh, lattice constants, volume, and cutoff kinetic energy were optimized through self consistent calculation with convergence fix at 0.01mRy. A fine k-point sampling is set at 5x5x5 [Monkhorst-Pack, 1976] in the first Brillouin zone. The cutoff kinetic energy for wavefunctions and its charge densities are put in 100Ry and 600Ry respectively. A denser k-point mesh 30x30x30 was fixed to calculate Density of State (DOS) and Partial Density of State

(PDOS). Thermoelectric responses are derived by solving the equations of transport theory in Semi-classical Boltzmann Transport theory as established in BoltzTrap code. Equations in TransM package were solved to examine Electronic Fitness Function (EFF) [Madsen and Singh, 2006].

RESULTS AND DISCUSSION

Structural and Electronics Properties

Materials crystallized into various structure type, the likes of AlLiSi- type, Cu_2MnAl- type, NaTi –type to mention a few. RhCrGe compound is an example of MgAgAs structure type and crystallized into face centred cubic structure F43m space with space group number 216. Wyckoff positions of atoms in crystals describe the arrangement of atoms within a crystal structure. Rh inhabited the Wyckoff position 4b (0.5, 0.5, 0.5), Cr occupied 4c (0.25, 0.25, 0.25), Ge is situated at 4a (0.0, 0.0, 0.0) and position 4d (0.75, 0.75, 0.75) is left unoccupied [Solola *et al*, 2023]. The equilibrium lattice constant, bulk modulus B, pressure derivative, B' are attained by imputing total ground energy and its corresponding volume's values obtained into third order Birch-Murnaghan equation of state by applying equation (1). The diagram of relaxed ground energy plotted against volume is presented in Figure 1. The minimized volume from the curve (parabola) of energy versus volume is 305 au^3. The examined lattice constant is 5.651Å, bulk modulus is 127KBar and pressure derivative is 4.05 as indicated in Table 1. The calculated lattice constant obtained is in close agreement to that of experimental and existing theoretical data. The measured pressure derivative is also in close agreement with previous theoretical data [Zhang and Xu, 2020],
the difference is due to artefact which is in GGA pseudopotential which lead to little underestimation of values [Ayedun et al, 2017].

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

Where Vo is the equilibrium volume, B is the bulk modulus and B' is pressure derivative.

Table 1: Optimized lattice constant, a (Å), Minimum Volume V $(Å)^3$, Bulk modulus, B (GPa), Pressure derivative, B', Band Energy gap, E_g (eV) and Method used.

RhCrGe Compound	a (Å)	V $(Å)^3$	B (KBar)	B' (GPa)	E_g	Method
Present Study	5.651	305	127	4.05	0.70	PBEsol-GGA
Previous Experimental Work	5. 75					Gaussian process regression Model
Existing Theoretical Values	5.76[a]	325[a]	173.04	5.00	0.82[a], 0.35[b]	FP-LAPW FP-LAPW

[a]Mehmood *et al*, 2017, [b]Amrani *et al*, 2020.

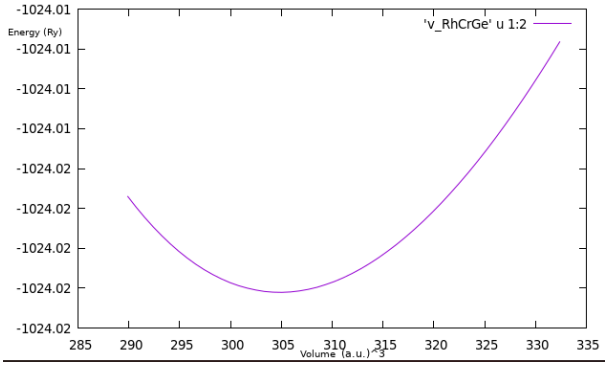

Fig.1: Total energy (Ry) versus volume of RhCrGe

The band structure of RhCrGe material investigated in this study is plotted along the path of high symmetry direction L→Γ→X→W→K→L in first Brillouin zone as illustrated in Fig. 2a. This compound exhibit semiconductor type with a small indirect band energy gap of 0.7eV. The uppermost valence band is located at W k-vector and lowest conduction band is situated at L k-vector of the first irreducible Brillouin zone. The calculated energy gap is in good agreement with the existing theoretical report [Mehmood *et al*, 2017]. The difference is due to different methodologies embarked upon. Previous theoretical studies [Mehmood *et al*, 2017, Amrani *et al*, 2020] reported half-metallic existence of RhCrGe. There is no existing experimental value to compare the energy gap with and this is the first time that semiconductor nature of RhCrGe material is reported in literature.

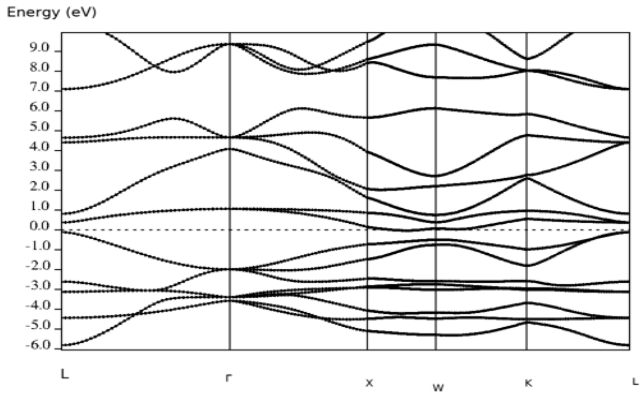

Figure 2(a): Electronic Band Structure of RhCrGe

Density of states (DOS) is of help in estimating the performance of charge carriers in semiconductor, material science and in describing the energy levels in quantum systems. Partial Density of States (PDOS) measure density of state for a given subset of energy levels. It is applied in orbital decomposition and finds usefulness in probing DOS for a particular energy band. The outer valence electrons of RhCrGe are: Rh ($4d^8$, $5s^1$), Cr ($3d^5$, $4s^1$) and Ge ($4s^2$ $4p^2$). The Fermi level is positioned at zero energy. There is a prominent peak of 41.48states/eV at -8.10 eV at valence band and at the conduction band, there is a peak after 5eV along the Energy axis and there are more peaks between 10 to 20eV. The peaks at the valence band are contributions from Rh d-orbital, Rh s-orbital, Cr d-orbital, Cr s-orbital and Ge p-orbital while peaks at conduction bands are due to Rh

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4d-state, Cr 3d-state and Ge 4p-state. Analyzed DOS and PDOS are presented in Fig. 2(b-c).

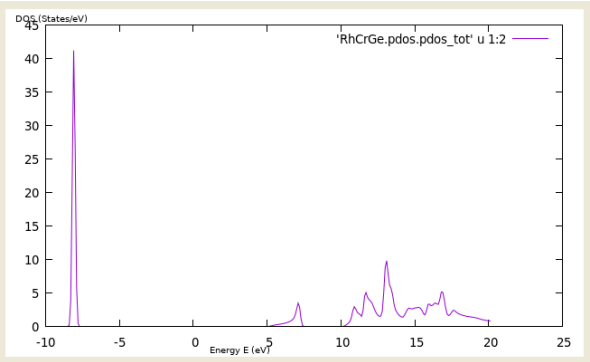

Figure 2(b): Density of State of RhCrGe

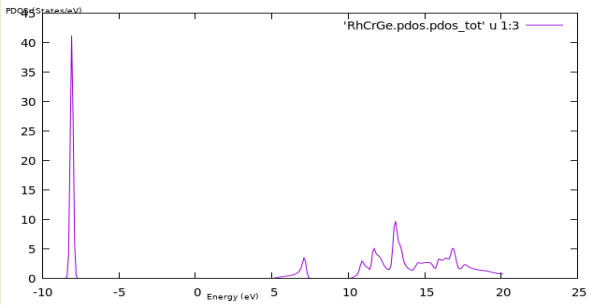

Figure 2(c): Partial Density of State of RhCrGe.

Thermoelectric Property

Thermoelectric properties zero in on the capacity of a material to convert heat into electricity or electricity to heat. Semi-classical Boltztrap code was engaged in this section to determine the electronic transport properties of RhCrGe. The following determinants of electronic transport responses as a function of hole concentration at different temperatures were investigated; Seebeck coefficient (S), Figure of merit (ZT), electrical conductivity (σ), electronic fitness function (EFF) and power factor (PF).

PF considers the functionality of material by showcasing the maximum power the material can generate. The higher the PF, the better the conversion of heat into electricity. PF rises with increase in temperature as demonstrated in Fig. 3a for a p-type RhCrGe material. PF values increase with temperature, at 300K (4.16 x10^{10}W/msK^2), 500K (9.19 x10^{10}W/msK^2) and reach its peak at 800K (15.73 x10^{10}W/msK^2) at constant hole concentration of 13.00 x 10^{22}cm^{-3}.

High PF is required for an extreme ZT value and this is a measure of the overall performance of a thermoelectric material. Variation of RhCrGe n-type and p-type as a functional of holes concentration were studied as ZT increased with risen temperature. Least ZT was recorded at temperature 300K (purple colour), next to it is 500K (green colour) and the highest at temperature 800K (blue colour) as shown in Fig. 3b which indicates the plot of ZT as a function of holes concentration but the p-type is more favoured

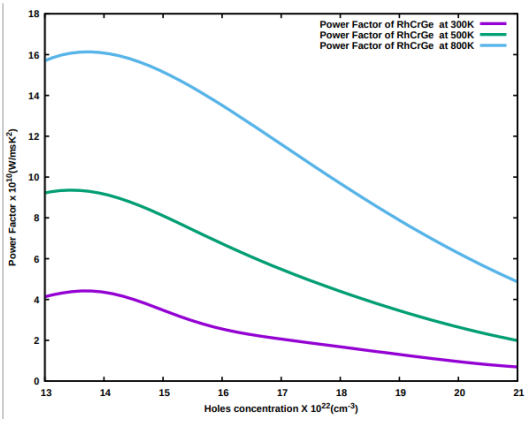

Figure 3(a): Power Factor of RhCrGe with respect to carrier concentration

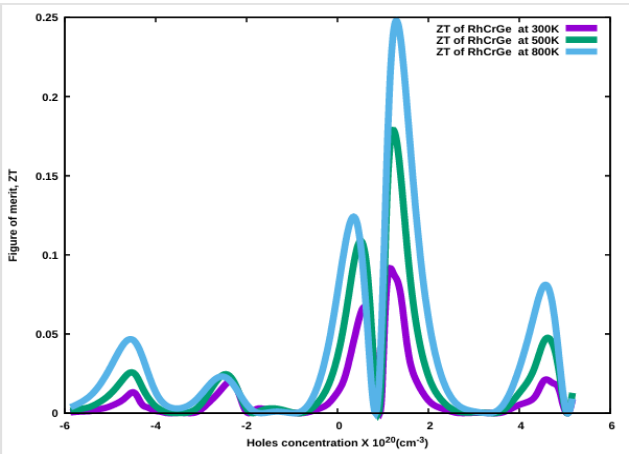

Figure 3(b): Figure of merit of RhCrGe as a function of carrier concentration

Electronic transport properties were plotted with reference to charge carriers for n-type and p-type semiconductor in order to determine the dominant carrier (electrons or hole). Temperature, nature of material involved and presence of impurity affect electrical conductivity. Conductivity reduces with rise in temperature because of increased vibrations that scatter electrons. N-type has highest concentrations of electrons at -5.91x 10^{20}cm^{-3} with maximum electrical conductivity of 11.96 S/ms, at minimal temperature of 300K before Fermi level than holes as shown in Fig. contrarily for a semiconductor, conductivity increases with rise in temperature as more charge carriers become available [Iyasara *et al*, 2023]. A good thermoelectric material has highest possible electrical conductivity and a Seebeck coefficient with low thermal conductivity.

Fig.3 (d) describes p-type semiconductor with varied values of Seebeck coefficient with hole concentration and temperatures.

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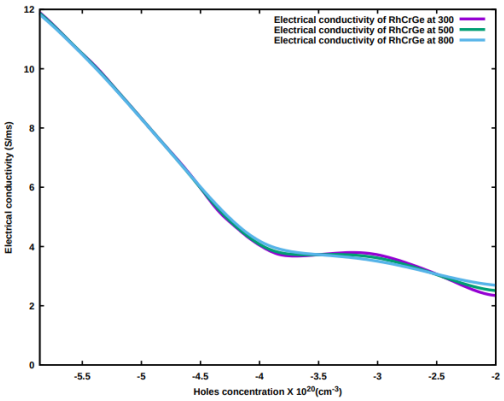

Figure 3(c): Electrical conductivity of RhCrGe as a function of carrier concentration (electrons)

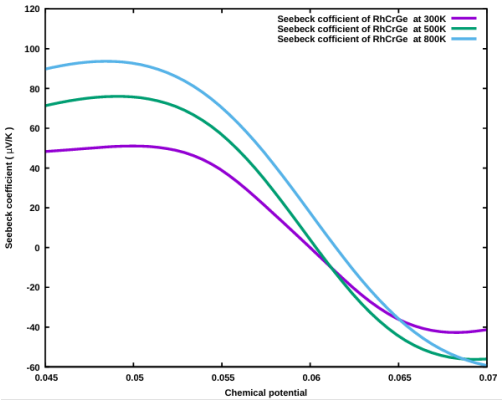

Figure 3(d): Seebeck coefficient of RhCrGe as a function of carrier concentration (holes).

EFF was computed by solving equations in BoltzTrap code and MTrans code under the constant relaxation time [Xing *et al*, 2017]. EFF looks into efficiency of electronic transport and finds out materials which deal with inverse relationship between electrical conductivity and Seebeck coefficient as shown in Fig. 3e. It was noticed that EFF varies with change in temperature and the peak is pronounced at temperature 800K.

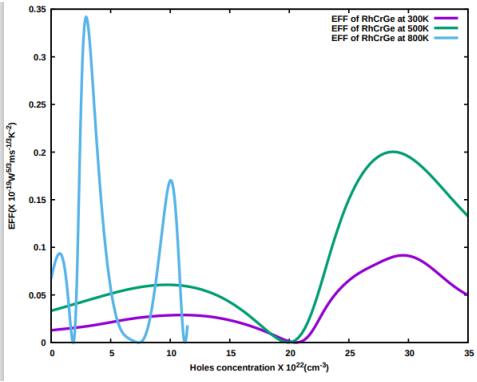

Figure 3(e): Electronic fitness function of RhCrGe versus holes concentration

CONCLUSION

This study used PBEsol-GGA based on DFT to determine the structural, electronic and thermoelectric reactions of ternary RhCrGe compound which exhibited semiconductor property only with an indirect energy gap 0.70eV between W-L. P-type of RhCrGe produced high power factor, Figure of merit Seebeck coefficient and EFF improved as the temperature increased from 300K to 800K. This makes p-type RhCrGe material to have edge over its counterpart n-type and make it to be a favourable and an oncoming thermoelectric candidate.

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