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Energy Gap and Impact of Change in Temperature as Core Determinant of Transport Property of the Ternary NbNiBi Half-Heusler Compound

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Abstract: This study used Perdew-Burke-Ernzehof-projected augmented wave (PBE-PAW) based on Generalized Gradient Approximation (GGA) to examine the structural and electronic qualities of a new ternary half-Heusler NbNiBi compound. Thermoelectric properties were measured by solving transport theory in BoltzTrap software bundles. The findings revealed optimized lattice constant of 5.96Å, bulk modulus 500kbar, and pressure derivative of 5.00. An indirect energy gap of 2.0eV showcases this material to be a semiconductor type. The energy gap was maintained, the temperature dependence of this compound was calculated from 50^0K through 350^0K in step of 50^0K. Highest values of Seebeck coefficient (2801.86 μV/K), Figure of merit (1.01) and electrical conductivity of 3.26 S/ms were recorded at lowest temperature of 50^0K. The outcome of this work illustrates the potential of NbNiBi material in electronic, engineering, thermoelectricity and its possible innovative uses for further experimental and theoretical considerations.

Keywords: *Intrinsic semiconductor, Density Functional Theory, ternary compound, temperature, energy gap.*

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1.0 Introduction

The global pursuit of clean and sustainable energy sources has led to extensive exploration of technologies such as solar, wind, hydroelectric, and bioenergy. However, their intermittent nature and high storage costs have limited their standalone applications. This has driven a parallel interest in energy conversion materials that can harvest and convert waste heat into electricity, especially for powering low-energy devices and enhancing energy efficiency in industrial systems. Thermoelectric materials, which convert temperature gradients directly into electrical voltage, have thus attracted growing attention for applications in power generation and refrigeration.

Among various thermoelectric materials, half-Heusler (HH) alloys have emerged as promising candidates due to their mechanical strength, thermal stability, and tunable electronic properties. These ternary intermetallic compounds, typically represented as XYZ (where X and Y are transition or rare-earth metals and Z is a p-block element), crystallize in a face-centered cubic MgAgAs-type structure and often obey the 18-valence-electron rule for semiconductor behavior (Graf et al., 2011). Previous studies have demonstrated that several half-Heusler compounds exhibit high Seebeck coefficients and desirable electrical conductivity, making them suitable for thermoelectric applications (Bhattacharya & Maiti, 2023).

Research has focused extensively on improving the thermoelectric performance of HH compounds such as ZrNiSn, TiCoSb, and NbFeSb through doping, nanostructuring, and defect engineering (Min et al., 2024; Naydenov et al., 2019,). However, there is a noticeable scarcity of computational or experimental studies on the NbNiBi system, especially regarding its temperature-dependent transport properties and electronic structure. While some bismuth-containing half-Heuslers have shown favorable thermoelectric behavior, NbNiBi remains

underexplored despite its potential advantages such as non-toxicity, elemental abundance, and favorable cost profile.

In solid-state physics, the energy gap (E_g), defined as the difference between the conduction band minimum (E_c) and the valence band maximum (E_v), is a fundamental parameter that governs a material's electronic and thermal transport properties. A material's classification as a metal, semiconductor, or insulator is largely determined by the size of this band gap. Semiconductors with narrow energy gaps (0.2–3.0 eV) are particularly important for thermoelectric and optoelectronic applications, whereas materials with larger gaps (3–7 eV) are typically insulating. The temperature dependence of the energy gap further affects carrier mobility, Seebeck coefficient, and electrical conductivity, all of which are critical to thermoelectric performance.

$$E_g = E_c - E_v \quad (1)$$

This study aims to investigate the structural, electronic, and thermoelectric properties of a novel ternary NbNiBi half-Heusler compound using Density Functional Theory (DFT) within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation and Boltzmann transport theory via the BoltzTrap code. Special focus is placed on evaluating how temperature variations affect the energy gap and transport properties of the material over a broad temperature range (50^0K to 350^0 K).

The significance of this work lies in its contribution to the discovery and understanding of previously uncharacterized half-Heusler compounds with potential applications in energy harvesting. The findings are expected to provide theoretical insights into the band gap engineering and thermoelectric optimization of NbNiBi and related systems, potentially guiding future experimental synthesis and device integration efforts.

2.0 Materials and Methods

The structural and electronic qualities of NbNiBi material were quantified using Perdew-Burke- Ernzehof-projected augmented wave (PBE-PAW) in accordance with density functional theory (Mourik et al., 2024) as observed in Quantum Espresso software package (Giannozi et al., 2009, Giannozi et al., 2017). The nonlinear core correction scalar relativistic and PBE functional type (Perdew et al., 1996) was processed by Generalized Gradient Approximation. Self-consistent calculations were made and convergence set at 0.01mRy. K-mesh was optimised and the k-point sampling in the first Brillouin zone was fixed at 7x7x7 (Monkhorst-Park, 1976). The cut off kinetic energy was self-consistently calculated in step of 10Ry up to 120 Ry and plane wave energy cut off was set at 90Ry. Denser k-point was set at 32x32x32 for estimations of density and partial density of states. Transport equations were solved using semi-classical Boltzmann software code (Madsen and Singh, 2006).

3.0 Results and Discussion

3.1 Structural and Electronic Properties

The structural, electronic, and density of states properties of the newly investigated NbNiBi half-Heusler compound were systematically studied using first-principles density functional theory (DFT). The results obtained provide insights into the stability, electronic behavior, and bonding characteristics of the material.

Structural Properties

The structural optimization of the NbNiBi compound was carried out to determine its equilibrium geometry. Fig. 1 illustrates the variation of the total energy with respect to the lattice constant. The curve shows a smooth decrease in energy until a minimum is reached, indicating the equilibrium state of the material. The minimum point on the curve corresponds to a lattice constant of 11.264 Bohr (5.96 Å)**.** This value represents the optimized lattice parameter at which the system is most stable. The steep slope observed before reaching the minimum suggests strong atomic interactions and a well-defined equilibrium configuration. The corresponding structural parameters are

summarized in Table 1. The bulk modulus (B) of the material is calculated to be 500 kbar, with a pressure derivative (B′) of 5.00. The high value of the bulk modulus reflects the mechanical rigidity of the compound, implying that it is resistant to volume compression under external pressure. The calculated minimum energy (E_{min}) of the system is −1675.26046 Ry, which further confirms the thermodynamic stability of the optimized structure. Additionally, the Fermi energy was computed to be 18.0862 eV, and the band gap (Eg) was found to be 2.00 eV, signifying a semiconducting nature.

Table 1: Equilibrium lattice parameter, a (Å), bulk modulus (B), pressure derivative (B'), minimum energy (emin), Fermi Energy (E_F) in eV and Band Energy gap, E_g (eV) of a new NbNiBi compound

NbNiBi	a (Å)	B(kbar)	B'	E_{min} (Ry)	Fermi Energy	Energy gap (eV)
Present work	5.96	500	5.00	-1675.26046	18.0862	2.00

3.1.1 Electronic Band Structure

The electronic band structure of NbNiBi was calculated and is displayed in Fig. 2. The band dispersion was plotted along high-symmetry directions in the Brillouin zone (L–Γ–X–W–K–L). The band structure clearly reveals that the valence band maximum (VBM) and conduction band minimum (CBM) do not intersect the Fermi level, confirming that NbNiBi is a semiconductor. The dispersion curve above the Fermi energy in the conduction band is more concentrated than the valence band below the Fermi energy level. The energy band gap is estimated to be 2.00 eV, in agreement with the value listed in Table 1. This moderate band gap is desirable for applications in thermoelectric devices and optoelectronic systems where thermal stability and sufficient carrier separation are required.

The shape and curvature of the bands around the conduction and valence band edges suggest relatively light effective masses for both electrons and holes, which may facilitate good charge carrier mobility—an essential characteristic for high thermoelectric performance. Furthermore, the absence of band crossings at the Fermi level rules out any metallic behavior in the compound.

Density of States and Partial Density of States

The total and projected densities of states (DOS and PDOS) are shown in Figs. 3 and 4 The total DOS, shown in Fig. 3, displays a prominent peak of 13.70 States/eV at -3.28eV. The outer valence electrons of NbNiBi compound are: Nb($5s^1$ $4d^4$), Ni($3d^8$ $4s^2$) and Bi ($6s^2$ $6p^3$). The major contribution of electrons at valence band are Ni 4d-orbital and Bi 3d-orbital. In Fig. 4, the partial density of states reveals the orbital contributions from individual atoms. The Bi and Nb atoms predominantly contribute to the conduction band, as indicated by the significant density in the energy range above the Fermi level. This division of roles among the constituent atoms implies strong hybridization, especially between the Nb d-orbitals and Bi d-orbitals, which is characteristic of covalent bonding with metallic interaction tendencies in half-Heusler structures.

The asymmetry in the DOS across the Fermi level, with more states above than below, suggests a favorable Seebeck coefficient for thermoelectric applications. Furthermore, the sharp DOS peaks imply the presence of flat bands, which may contribute to a high density of states effective mass, enhancing thermoelectric performance via improved power factor.

Significance and Implications

Overall, the NbNiBi compound exhibits structural stability, mechanical rigidity, and a suitable semiconducting band gap, all of which are essential for materials intended for energy conversion devices. The moderate band gap of 2.00 eV situates it in an ideal

range for thermoelectric applications, providing a balance between carrier concentration and thermal excitation. The electronic and density of states analyses confirm its semiconducting nature and reveal valuable insights into orbital interactions and bonding characteristics.

These findings suggest that NbNiBi, as a half-Heusler compound, holds promise for future applications in thermoelectric and electronic devices.

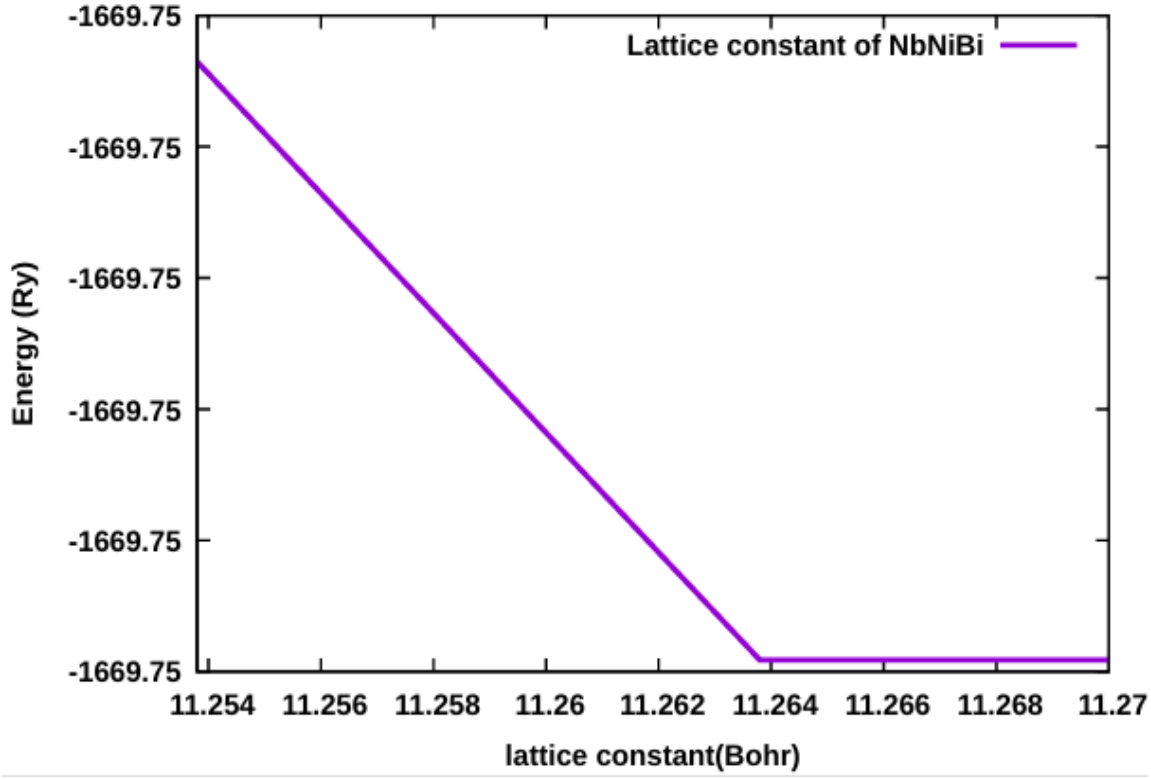

Fig. 1: Lattice parameter optimization curve of MnNiP

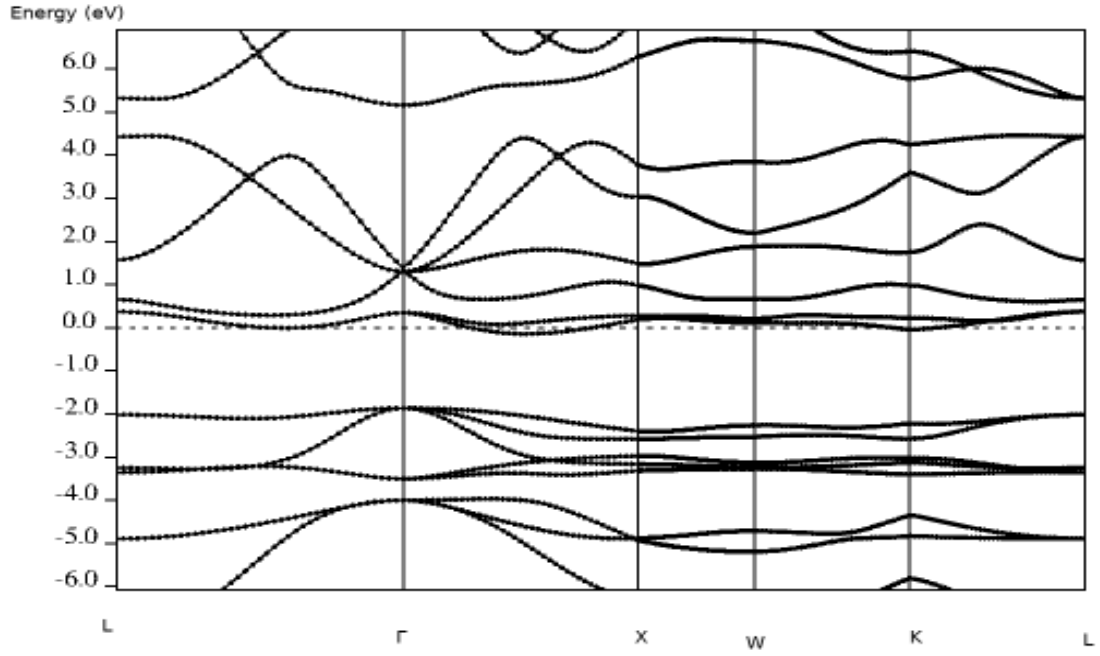

Fig. 2: Band energy of NbNiBi

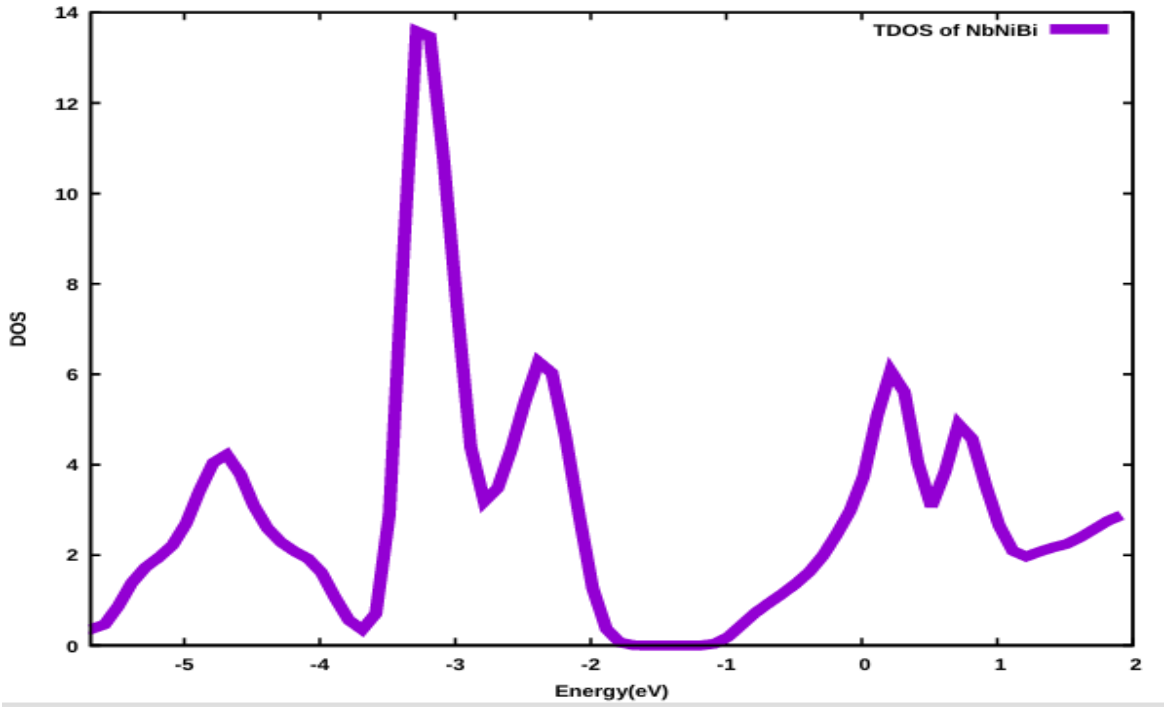

Fig. 3: Density of State of NbNiBi

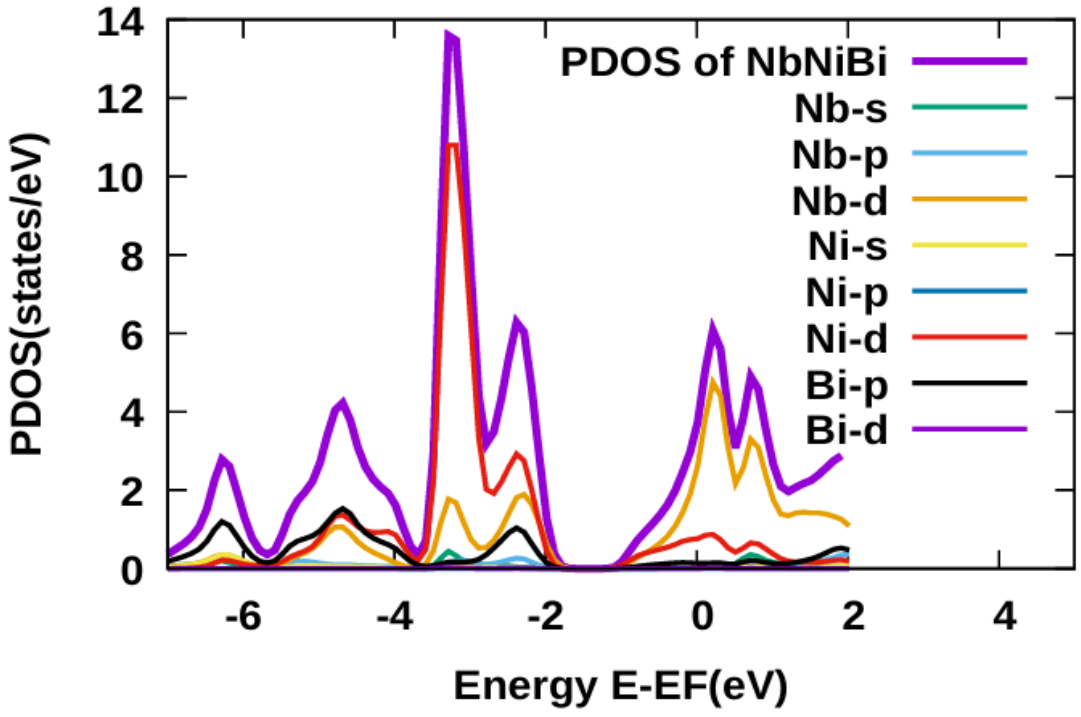

Fig. 4: Partial Density of State of NbNiBi

3.2 Thermoelectric Properties

This study investigates the thermoelectric properties of the NbNiBi compound across a broad temperature range from 50 K to 350 K. The performance of thermoelectric materials is typically evaluated using key parameters such as the Seebeck coefficient, figure of merit (ZT), power factor (PF), electrical conductivity (σ), and electronic fitness function (EFF). These parameters are temperature-dependent and help determine the material's potential for efficient energy conversion. The results for these parameters are summarized in Table 2.

Table 2: Thermoelectric Parameters of NbNiBi at Varying Temperatures

Temperature (K)	Seebeck Coefficient (μV/K)	Figure of Merit (ZT)	Power Factor (W/m·s·K²)	Electrical Conductivity (S/m·s)	Electronic Fitness Function (W^5/3·m⁻¹/³·K⁻²)
50	2801.86	1.01	0.25	3.26	0.012
100	2801.86	0.09	0.94	3.26	0.13
150	2747.82	0.03	2.01	2.22	0.17
200	2244.82	1.00	3.38	3.22	0.274
250	1793.16	0.57	4.68	3.16	0.272
300	1486.94	0.98	6.09	3.12	0.32
350	1270.79	0.95	7.59	3.08	0.375

From Table 2, several significant trends can be observed. The Seebeck coefficient is notably high at lower temperatures, remaining constant at 2801.86 μV/K between 50 K and 100 K, and then gradually decreasing to 1270.79 μV/K at 350 K. This decline reflects a typical semiconducting behavior, where the enhancement in thermal energy leads to reduced energy filtering of the charge carriers. The reduction in Seebeck values with increasing temperature is further visualized in Fig. 5, which plots the Seebeck coefficient against chemical potential at 200 K, 250 K, and 300 K. In this figure, the highest Seebeck value occurs at 200 K, corroborating the trend presented in Table 2. Seebeck coefficient recorded in this work is by far greater than the golden rule one which exists between 150 μV/K and 200μV/K for half-Heusler compounds (Feng et al., 2019).

The figure of merit (ZT) (Fig. 6) demonstrates exceptional thermoelectric performance at specific temperature points, with peaks at 50 K (ZT = 1.01), 200 K (ZT = 1.00), and 300 K (ZT = 0.98). These values signify the potential efficiency of NbNiBi in converting heat into electrical energy. A significant local minimum is observed at 150 K (ZT = 0.03), likely due to increased phonon-electron scattering or reduced carrier mobility, which hampers energy transport. The variation of ZT with carrier concentration is illustrated in Fig. 6, where it is evident that ZT tends to decrease as hole concentration increases, particularly beyond 2.2×10^{20} cm^{-3}. Notably, at 300 K, the ZT remains relatively high across moderate doping levels, reinforcing the data in Table 2. The power factor (PF), which combines the effects of Seebeck coefficient and electrical conductivity, increases steadily with temperature. It rises from 0.25 W/m·s·K² at 50 K to a maximum of 7.59 W/m·s·K² at 350 K, highlighting the material's improving thermoelectric conversion capability with temperature. This trend is graphically supported by Fig. 7, which shows the PF as a function of hole concentration. In this figure, the PF increases with doping up to a critical level and then declines, with the 300 K curve showing dominance—consistent with the high PF values reported in Table 2.

Electrical conductivity (σ) remains relatively stable across the temperature range, with slight fluctuations between 3.08 and 3.26 S/m·s, except for a noticeable dip at 150 K (2.22 S/m·s), which corresponds to the minimum ZT observed. This stability in conductivity suggests that NbNiBi possesses good electronic transport resilience over a wide temperature spectrum. The trend in conductivity with increasing hole concentration is further depicted in Fig. 8, which shows a slight decrease in conductivity at higher doping levels, possibly due to increased temperatures (Solola et al., 2023).

Lastly, the electronic fitness function (EFF) steadily increases with temperature, reaching its highest value of 0.375 W^5/3·m⁻¹/³·K⁻² at 350 K. The EFF is a composite parameter that integrates carrier mobility, Seebeck coefficient, and the effective mass, serving as

an indicator of the overall suitability of the material for thermoelectric applications. The variation in EFF with carrier concentration is plotted in **Fig. 9**, which reveals several local peaks, with the most prominent one appearing at 300 K. This observation aligns well with Table 2, reinforcing the interpretation that high-temperature regimes offer the best optimization for thermoelectric performance in NbNiBi. Finally,thermoelectric parameters of NbNiBi presented in Table 2 and supported by Figures 5 through 9 reveal a promising thermoelectric behavior, particularly in the temperature range of 200 K to 300 K. The material exhibits high Seebeck coefficients, near-unity ZT values, steadily increasing power factor, stable conductivity, and a rising electronic fitness function. These characteristics strongly indicate that NbNiBi is a viable candidate for low- to mid-temperature thermoelectric energy conversion applications, particularly in cryogenic and ambient temperature regimes where performance and stability are critical.

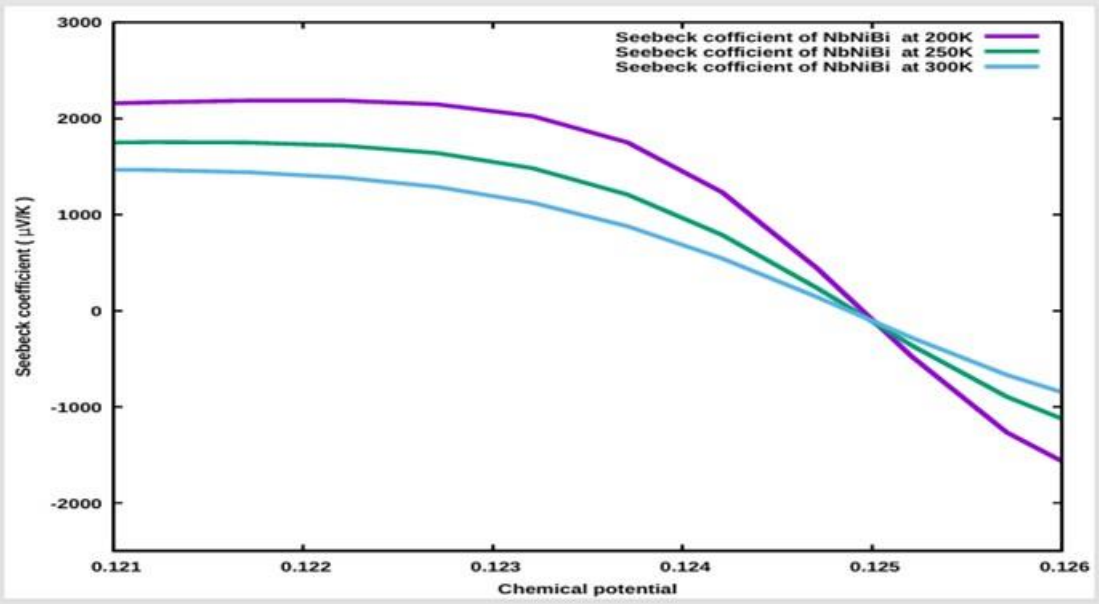

Fig. 5: Seebeck Coefficient of NbNiBi

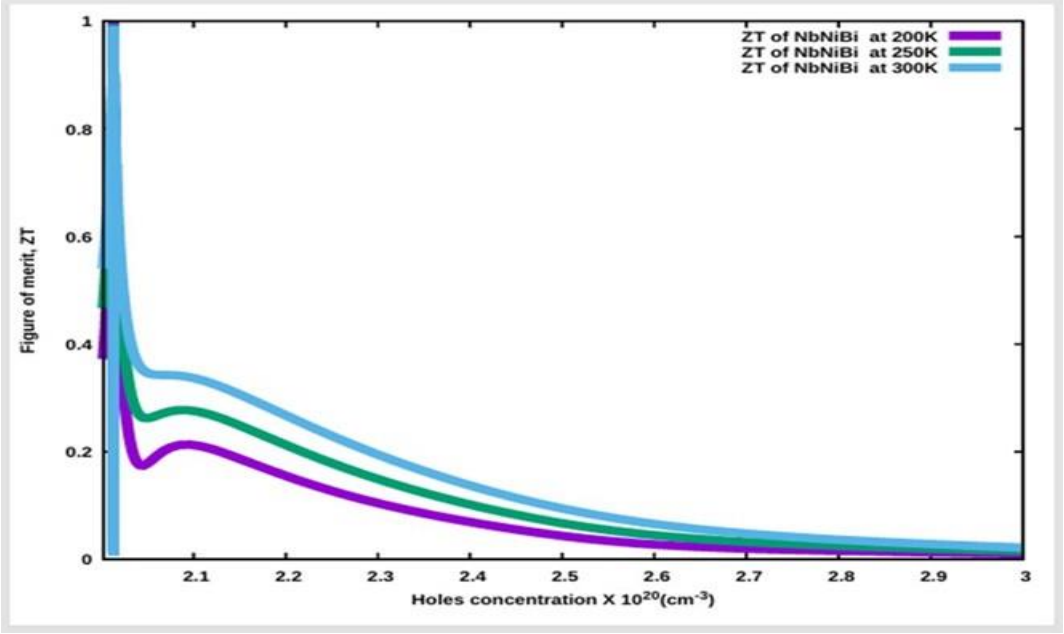

Fig. 6: Figure of merit of NbNiBi

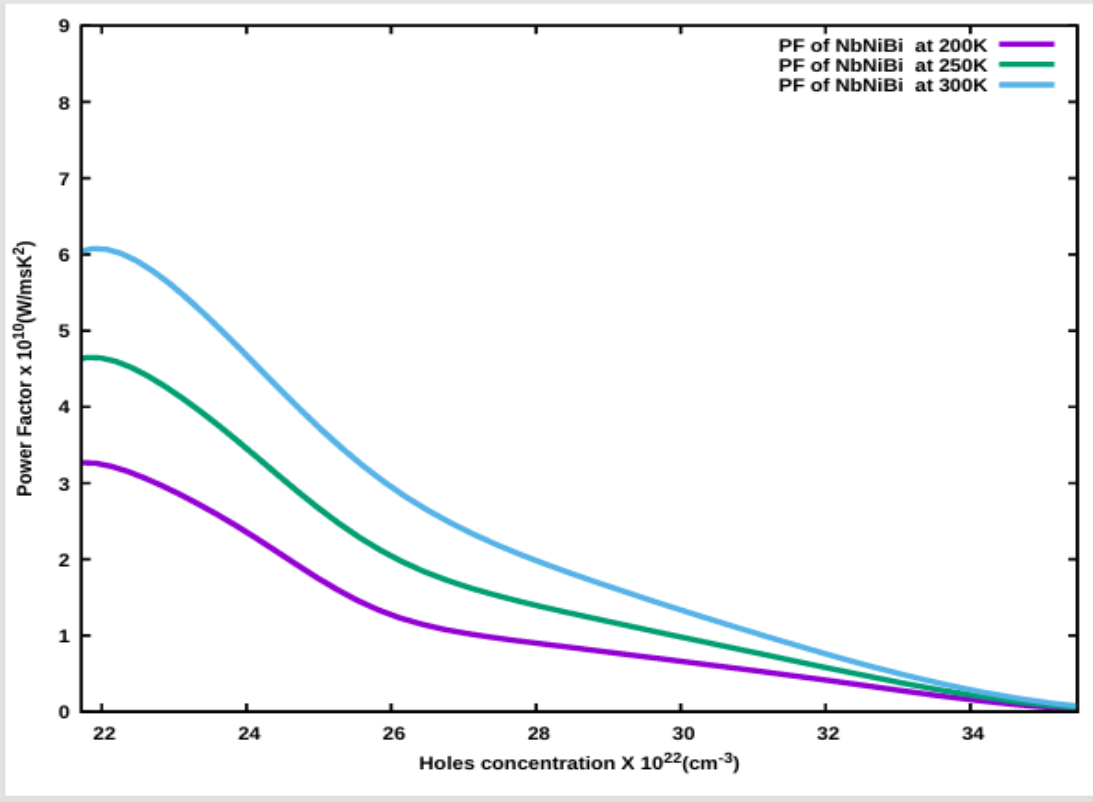

Fig. 7: Power Factor of NbNiBi

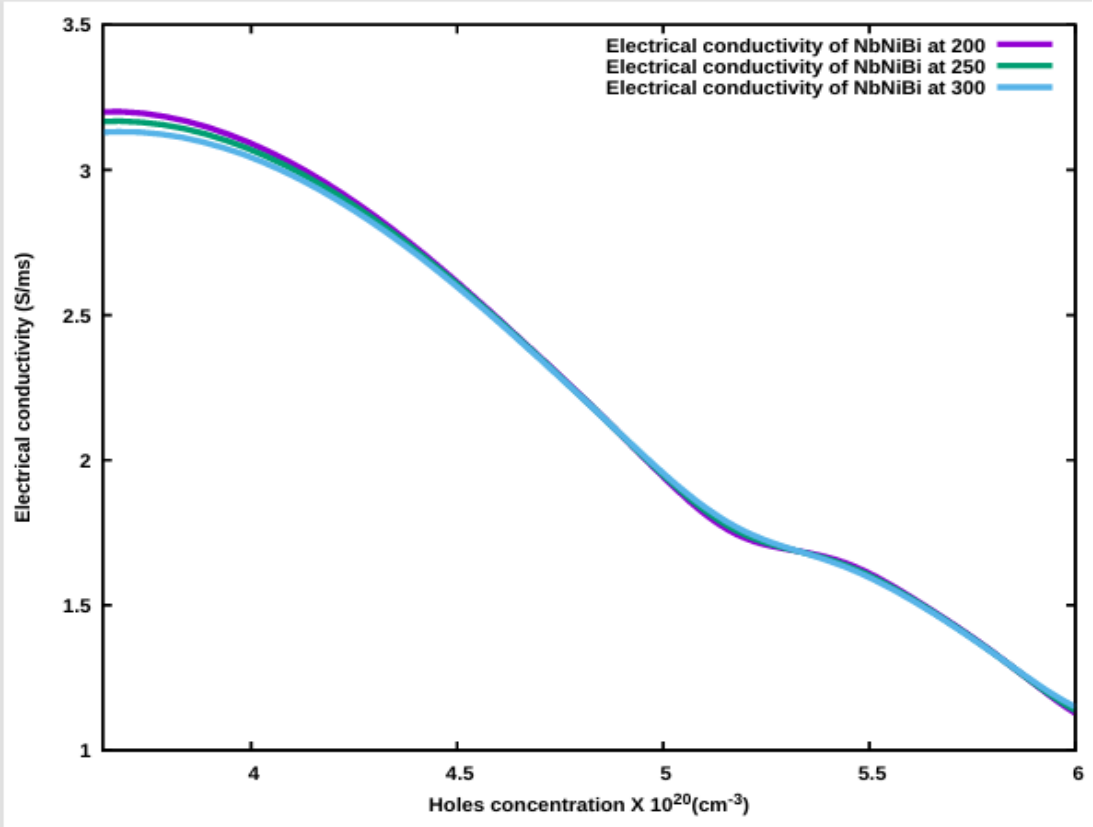

Fig. 8: Electrical conductivity of NbNiBi

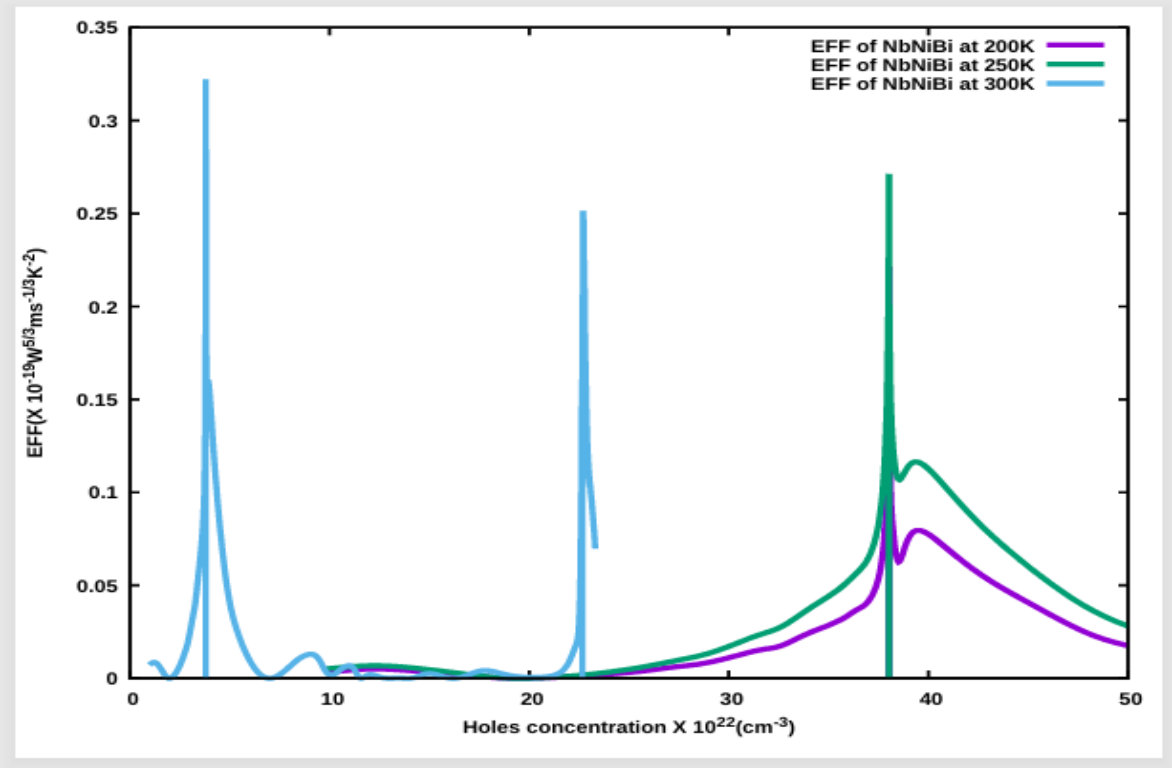

Fig. 9: Electronic Fitness Function of NbNiBi

4.0 Conclusion

The study employed first-principles density functional theory (DFT) with Perdew–Burke–Ernzerhof (PBE) functional and Boltzmann transport theory to investigate the structural, electronic, and thermoelectric properties of a novel NbNiBi half-Heusler compound. The equilibrium lattice parameter was found to be 5.96 Å, with a high bulk modulus of 500 kbar and a pressure derivative of 5.00, indicating excellent mechanical rigidity and structural stability. The optimized structure yielded a minimum energy of –1675.26046 Ry, and the Fermi energy was computed as 18.0862 eV. The compound exhibits a moderate indirect band gap of 2.00 eV, which was consistently observed in both the electronic band structure (Fig. 2) and total density of states (Fig. 3), with partial density of states (Fig. 4) indicating orbital hybridization between Nb d-orbitals and Bi p-orbitals.

The band structure confirms the semiconducting nature of NbNiBi, showing no overlap of conduction and valence bands, and the curvature around the band edges suggests favorable carrier mobility. The projected density of states further reveals that conduction and valence bands are largely dominated by d-orbitals of Bi and Nb, as well as Bi and Ni atoms respectively, underscoring the role of these atoms in shaping the material's electronic properties. The presence of localized Bi 6p states and the asymmetric distribution of DOS across the Fermi level implies potential for a high Seebeck coefficient, making this material a viable thermoelectric candidate.

Conclusively, the results affirm that NbNiBi possesses the necessary physical and electronic attributes for thermoelectric applications, particularly in energy harvesting systems operating across moderate to high temperatures. The compound combines thermodynamic and mechanical stability with a tunable band gap and favorable electronic structure, making it a strong candidate for integration into next-generation thermoelectric devices.

To advance these findings, it is recommended that experimental synthesis and characterization of NbNiBi be undertaken to validate the theoretical predictions, particularly the semiconducting nature and thermal transport performance. Additionally, doping and alloying strategies should be

explored to further optimize its thermoelectric efficiency. The integration of NbNiBi in thermoelectric modules should also be evaluated under operational conditions to assess long-term performance and device compatibility.

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Compliance with Ethical Standards Declaration

Ethical Approval

Not Applicable

Competing interests

The author declared no compositing interest

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Author's Contribution

The work was designed and written by the author, SEU