*Communication in Physical Sciences, 2024,* 11(2): 288-298

# Exploring the Thermoelectric Potential of Trigonal $MgS_2$: A Computational Investigation Using DFT and Boltzmann Transport Theory

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***Received: 18 January 2024/Accepted: 02 May 2024 /Published: 06 May 20***

***Abstract:*** *There has been a shift toward the development of cost-effective and environmentally friendly technologies, due to increased energy demand and attendant environmental degradations. Among these technologies, significant progress has been made in the field of thermoelectricity. Thermoelectric materials are recognized for their proficiency in converting waste heat energy into electricity, with their efficiency commonly assessed using the ZT (Fig. of merit) value.. This study investigates the thermoelectric properties of chalcogenide magnesium sulfide ($MgS_2$), with trigonal lattice structure, using Density Functional Theory (DFT) in conjunction with the Boltzmann Transport Theory. The initial assessment of structural and thermoelectric properties employs the Generalized Gradient Approximation (GGA) based on the Perdew–Burke–Ernzerhof approximation (GGA-PBE).*

*The results indicate that the studied compounds exhibit characteristics of a p-type semiconductor. The structural confirmation of $MgS_2$ reveals a trigonal configuration. The absolute value of the Seebeck coefficient demonstrates an increase with rising temperature across the measured range (100-400K). Simultaneously, the electrical conductivity exhibits a monotonically decreasing trend with increasing temperature, indicative of degenerating conduction behaviour. The power factor exhibits an upward trajectory with increasing temperature, consequently leading to an augmented dimensionless Fig. of merit ZT. The maximum ZT value observed for $MgS_2$ is 0.057.*

***keywords:*** *thermoelectric properties, chalcogenide, DFT calculations, BoltzTrap, Quantum Espresso*

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## 1.0 Introduction

The challenges of the global energy crisis, such as excessive energy consumption, pollution, and the depletion of energy sources, are

intricately linked to global warming (Ismail & Ahmed, 2010). Simultaneously, the detrimental emissions associated with fossil fuels pose a significant threat to ecological equilibrium(Jaziri et al., 2020). To address these issues, there is a pressing need for affordable, efficient, and environmentally friendly alternative energy sources, including gas biofuels, solar energy, and devices for electrical energy conversion (Blaha, Maafa, Chahed, Boukli, & Sayade, 2021)

In industrial processes, substantial amounts of waste heat are generated, representing a hitherto untapped resource. The conversion of waste heat to electricity presents a viable solution to the emerging global energy crisis. Traditional thermal energy conversion systems like Rankine engines, characterized by moving parts and maintenance demands, prove impractical for deployment in remote locations. Conversely, thermoelectric energy conversion utilizing thermoelectric materials offers a maintenance-free alternative, as it involves no moving parts (Nag, 2023).

Thermoelectricity, denoting the direct conversion of thermal energy (waste heat) into electrical energy, encompasses three key effects: the Seebeck effect, which induces stress in a material exposed to a temperature gradient, the Peltier effect, which governs heat absorption or release rates, and the Thompson effect, which characterizes changes in heat flux density under an electric current, allowing for the flow of density. The Seebeck effect is harnessed in simple devices like thermocouples for capturing thermal energy (Weera, 2014).

Devices built on the Seebeck effect within thermoelectric systems play a pivotal role in mitigating energy waste by converting waste heat into electrical energy. These established devices offer economic viability and align with modern energy system requirements. Materials such as chalcogenides have garnered significant attention for their versatility and have consequently gained popularity. Extensive research has been conducted on this class of compounds, focusing on their physical and chemical properties (Blaha et al., 2021)(Tesfaye & Moroz, 2018)(Shi et al., 2019).

There have been experiments carried out to confirm the theoretical predictions of these materials (Gupta, Kumar, Kaur, & Bera, 2020). It is difficult to directly improve the basic materials to enhance thermoelectric efficiency due to the complex and conflicting relationships of these parameters (Nag, 2023).

The primary objective of this investigation is to examine both the structural and thermoelectric characteristics of $MgS_2$. Notably, and to the best of our knowledge, the thermoelectric properties of this chalcogenide with a trigonal structure have not been explored (Bousnina, Giovannelli, Perrière, Guegan, & Delorme, 2019) These elements are considered less toxic than the commonly used alternatives such as lead (Pb), contributing to a more environmentally friendly condition (Alowa, 2021).

## 3.0 Materials and Methods

Density functional theory (DFT) calculations have been performed [25, 26] utilizing the whole plane wave approach implemented in the Quantum Espresso tool [27]. The generalized gradient approximation of Perdew-Burke-Ernzehof PBE-GGA) approximates the correlation-exchange interaction potential and energy [28, 29]. Also, to get beyond the restrictions of GGA, we have employed the modified Becke-Jonhson (mBJ) technique [30]. The wave function was enlarged to $l_{max}$ = 10 in the harmonic spherical basis set for the non-overlapping muffin-tin spheres. The wave function was enlarged in the interstitial areas using a plane wave basis set with a cut-off parameter of $RMTK_{max}$ = 8, where $K_{max}$ denotes the biggest K-vector in the first Brillouin zone and RMT is the smallest muffin-tin radius. We set the muffin-sphere radius to 2.0, 2.2, 2.4 a.u for S and Mg atoms

respectively. To separate the core states from valence ones, cut-off energy is set to be 60.0 Ry. The Brillouin zone integration is completed over a Monkhorst-Package [31, 32] with 12 × 12 × 12 k-mesh. The convergence criterion of the self-consistent total energy is taken to be $10^{-4}$ Ry. The dense k-mesh of 15 × 15 × 15 was used to obtain accurate thermoelectric properties, which are calculated with semi-classical Boltzmann theory and constant relaxation time approximation asset in BoltzTrap code [33], Next, the thermoelectric properties are studied using DFT in conjunction with the Boltzmann equation. This involves figuring out the power factor, electrical conductivity, and Seebeck coefficient. Additionally, the study aims to investigate the relationship between the electrical and thermoelectric characteristics of $MgS_2$'s chemical structure.

## 4.0 Results and Discussion

The results of the computational studies are presented and discussed as follows:

### *4.1 Structural properties*

The analyzed material exhibits a trigonal structure within the space group $R\bar{3}m$, as illustrated in Fig. 1. This crystal structure was modelled and observed using the Burai software within the Quantum Espresso framework. The calculated structural parameters align with experimental reports and other previous findings, confirming the reliability of the results (Sahnoun, Bouhani-Benziane, Sahnoun, & Driz, 2017) $MgS_2$ demonstrates stability with a lattice constant of 6.8 Å. Our calculations show good agreement with prior research (Blaha et al, 2021).

### *4.2 Thermoelectric properties*

The thermoelectric properties were investigated using the BoltzTraP code (Berri, 2022). The performance of thermoelectric materials is characterized by a dimensionless parameter known as the Fig. of merit ZT = $S^2\sigma T/k$. In this context, the electrical conductivity, thermal conductivity, Seebeck coefficient, and temperature are denoted by σ, k, S and T, respectively.

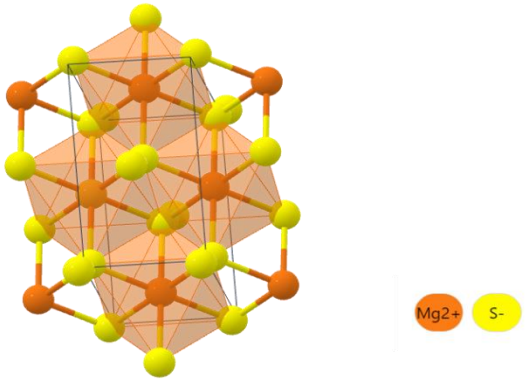


**Fig. 1: Trigonal lattice structure of $MgS_2$ (Materials Project, n.d.)**

These parameters were calculated based on the Boltzmann transport theory (Saidi et al., 2023). The relationship between atomic composition and thermoelectric properties is depicted, and Fig. 3 illustrates the variation of ZT with the chemical potential at different temperatures. Positive and negative values of the chemical potential represent concentrations of holes and electrons.

The relationship depicted in Fig. 3 illustrates that the Fig. of merit is temperature-dependent, indicating an increase with temperature. Moreover, a ZT value less than 1 imposes limitations on the accuracy of applications. Generally, improved ZT values are essential to enhance thermoelectric performance (Chang et al., 2020). In Fig. 4, the plot of $MgS_2$ versus Seebeck (S) at different chemical potentials is presented. Notably, there are both negative and positive values of S, with magnitudes exceeding 20 μV/K. This is beneficial for enhancing the performance of both p-type and n-type carriers. As evident from the graph, the dominant charge carrier type is p-type (since $S > 0$ at $\mu = 0$) (Ramanathan & Khalifeh, 2018)

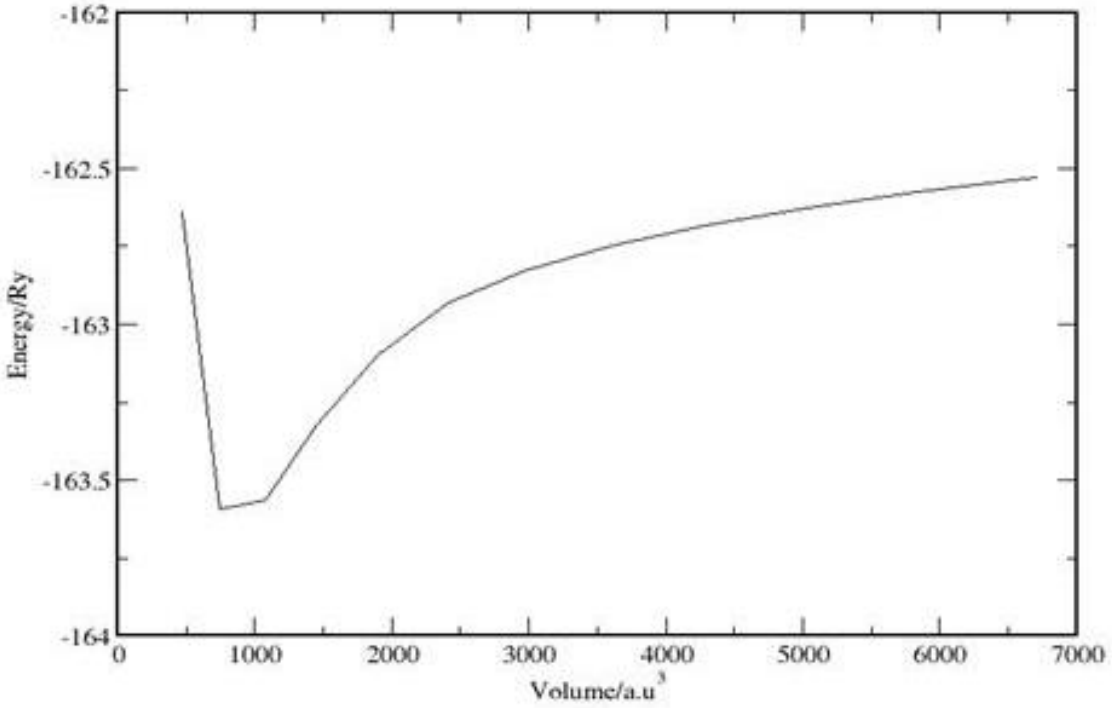


**Fig 2: Optimization plot of $MgS_2$ (Volume)**

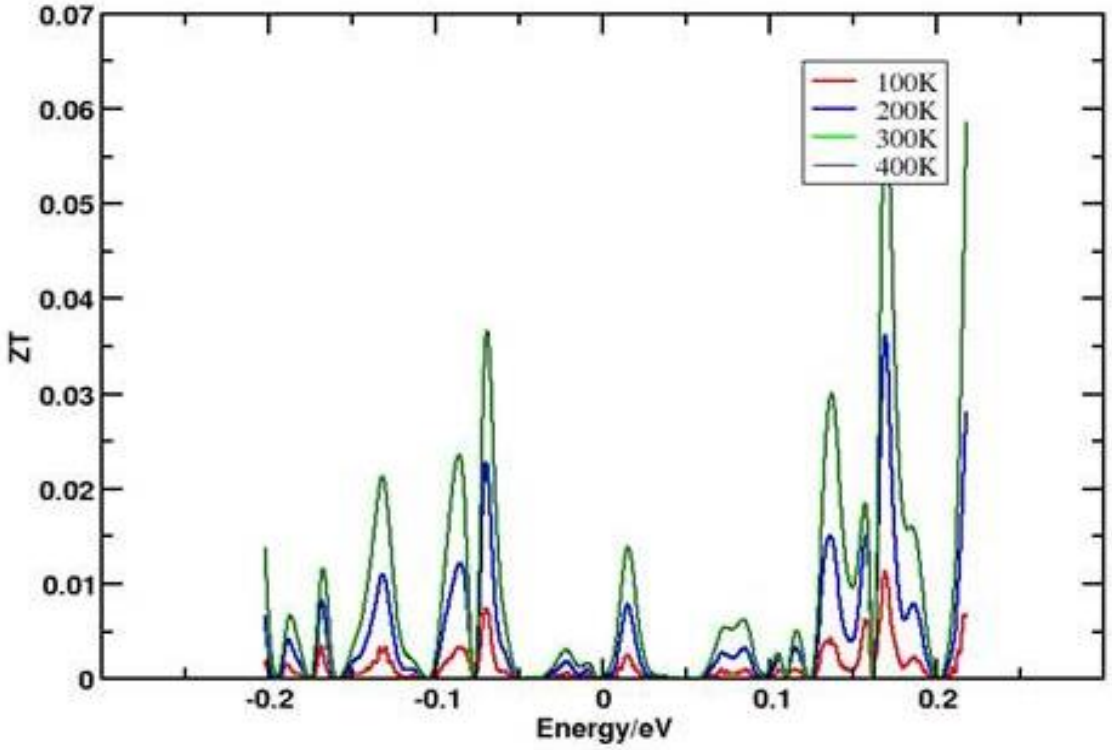


**Fig. 3: Plots of figure . of merit against Energy.**

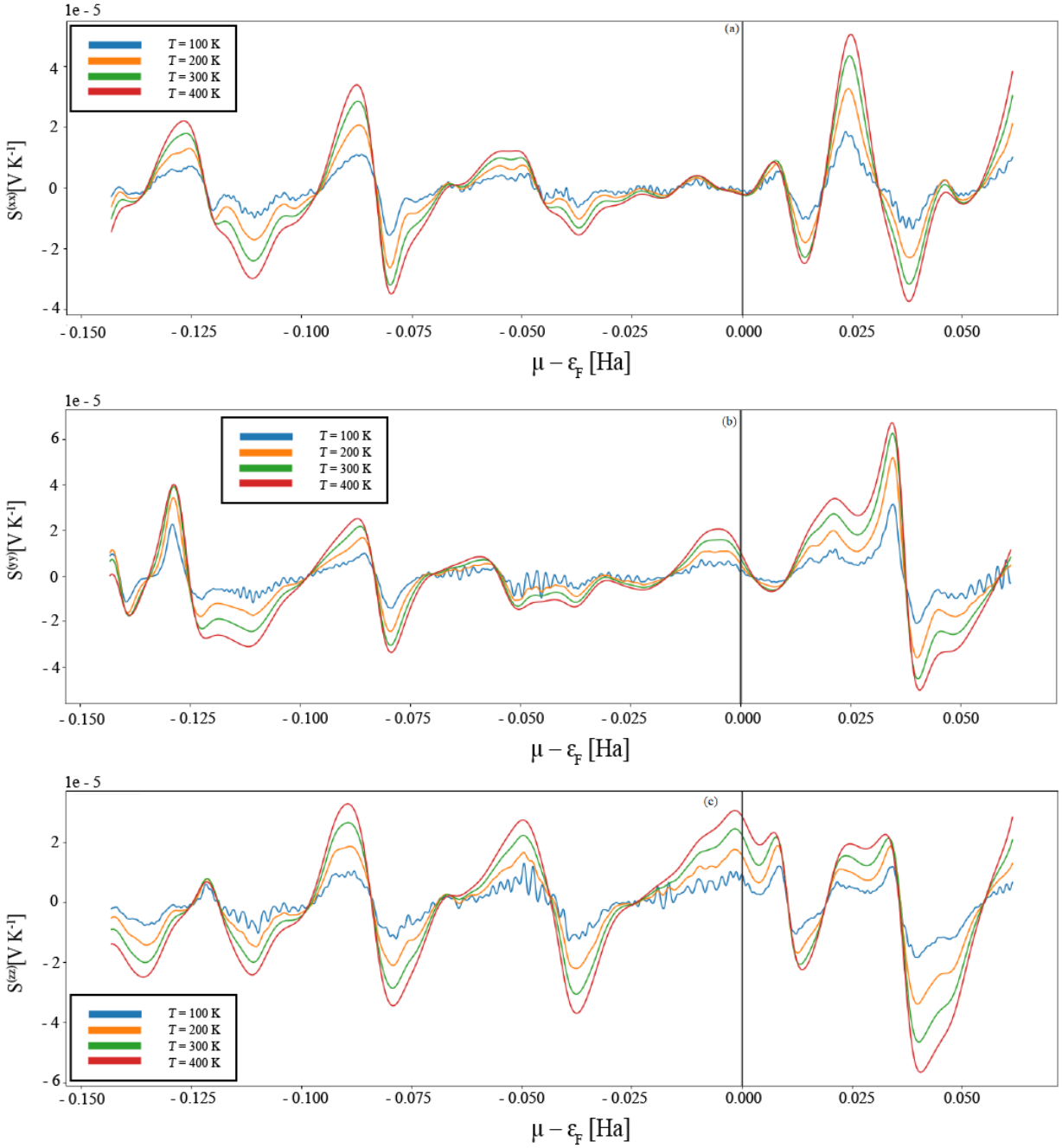


**Fig. 4: Calculated Seebeck of $MgS_2$ for (a) xx component (b) yy component and (c) zz component**

In Fig. 4, Seebeck S increases with temperature for $MgS_2$ compound across the entire range from 100 to 400 K. Understanding the electrical properties of various functional materials, including chalcogenides, poses challenges. However, our theoretical research, employing Density Functional Theory (DFT) combined with Boltzmann theory, enables us to comprehend the relationship between electrical conductivity and chemical structure. Electrical conductivity refers to the measure of a material's ability to conduct an electric current (Khan & Ur, 2018).

The curves depicted in Fig. 5 reveal that at lower temperatures (100 K), the material exhibits enhanced electrical conductivity

compared to higher temperatures. Notably, at elevated temperatures, the compounds exhibit electrical conductivity variations distinct from $MgS_2$, particularly in the range of 200 to 400 K.

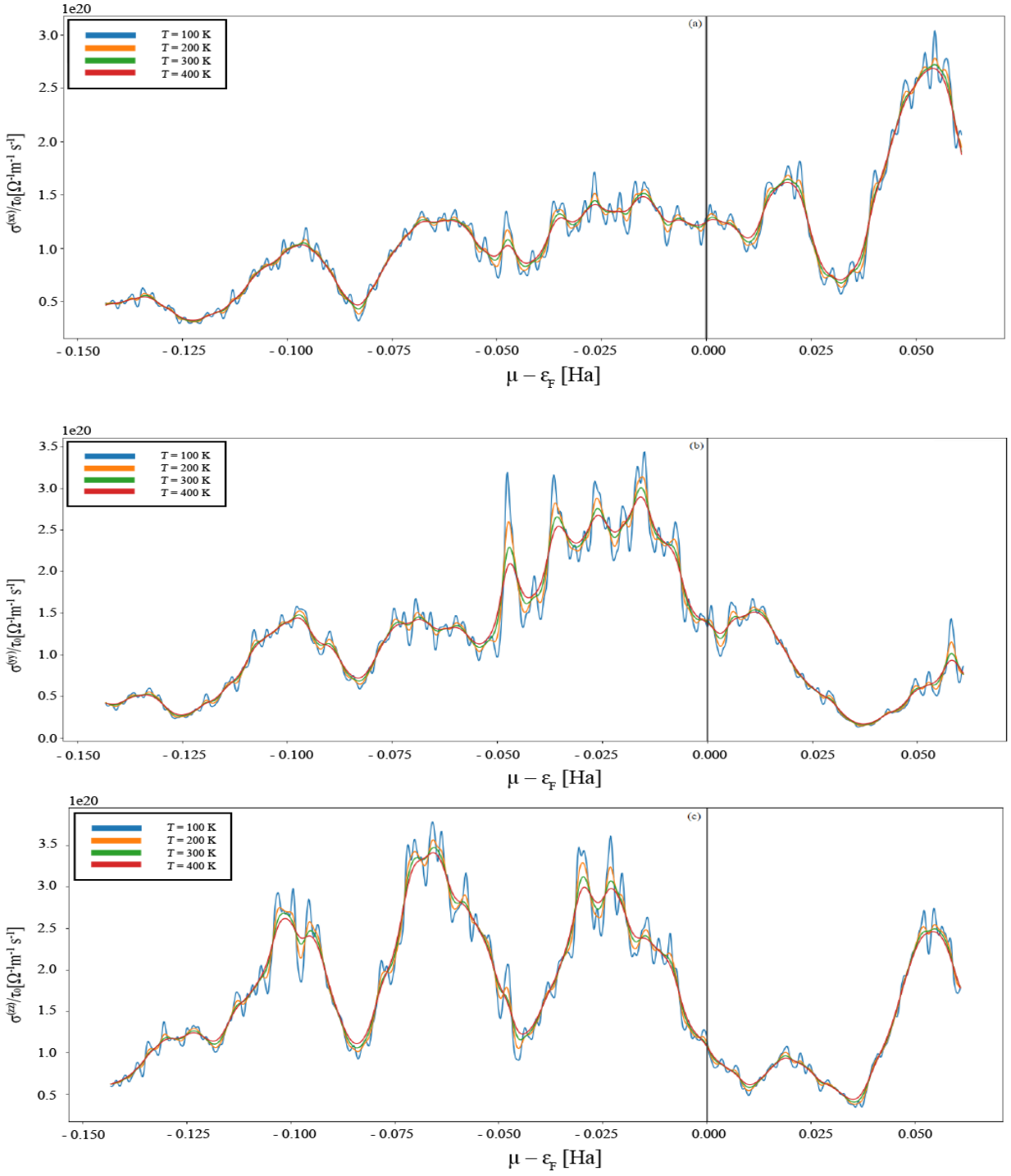


**Fig. 5: Calculated Electric conductivity of $MgS_2$ for (a) xx component, (b) yy component and (c) zz component.**

The performance of thermoelectric materials is assessed through the power factor (PF), a crucial thermoelectric parameter that correlates the Seebeck coefficient and electrical conductivity, expressed as $PF = S\sigma^2$. Fig. 6 illustrates the power factor of $MgS_2$ as a function of chemical strength (Khan & Ur, 2018).

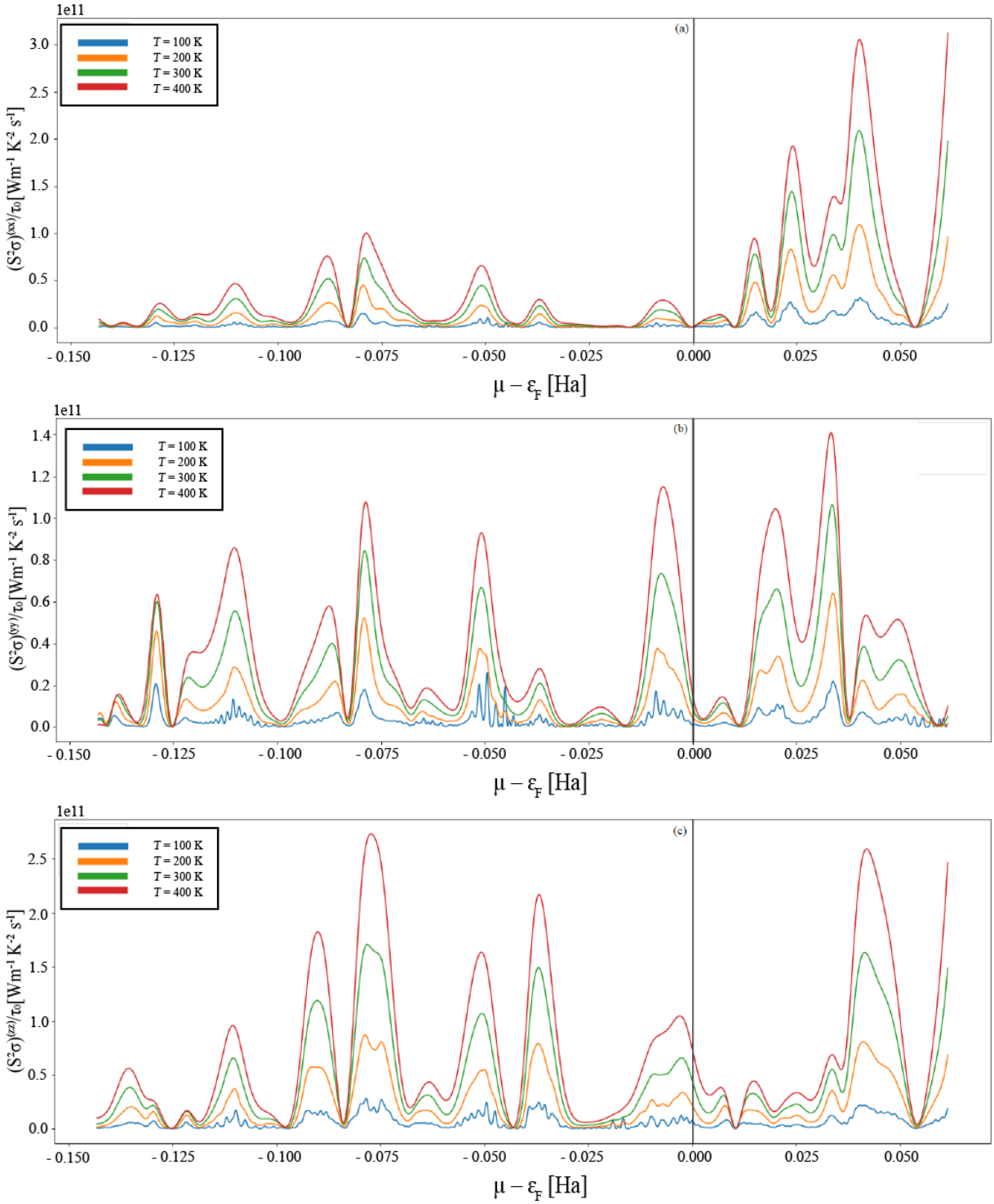


**Fig. 6: Calculated Power factor of $MgS_2$ for (a) xx component (b) yy component and (c) zz component.**

For $MgS_2$, the power factor demonstrates an increase with rising temperature, reaching its peak at 400 K. Below this temperature, a gradual decrease is observed (Zemzemi, 2023) The graph reveals that p-type $MgS_2$ exhibits a superior power factor compared to n-type variants, with the highest peaks at 3.06 x $10^{11}$ $Wm^{-1}$ $K^{-2}$ $s^{-1}$ at 0.0408 Ha, 1.409 x $10^{11}$ $Wm^{-1}$ $K^{-2}$ $s^{-1}$ at 0.0340 Ha, and 4.19 x $10^{11}$ $Wm^{-1}$ $K^{-2}$ $s^{-1}$ at 0.0654 Ha at 400 K for the xx, yy, and zz components of the plot, respectively (Jayaraman, Bhat Kademane, & Molli, 2016). The thermal conductivity diagrams presented in Fig. 7 indicate that the material exhibits high thermal conductivity, a characteristic that could potentially impact its efficacy as a thermoelectric material.

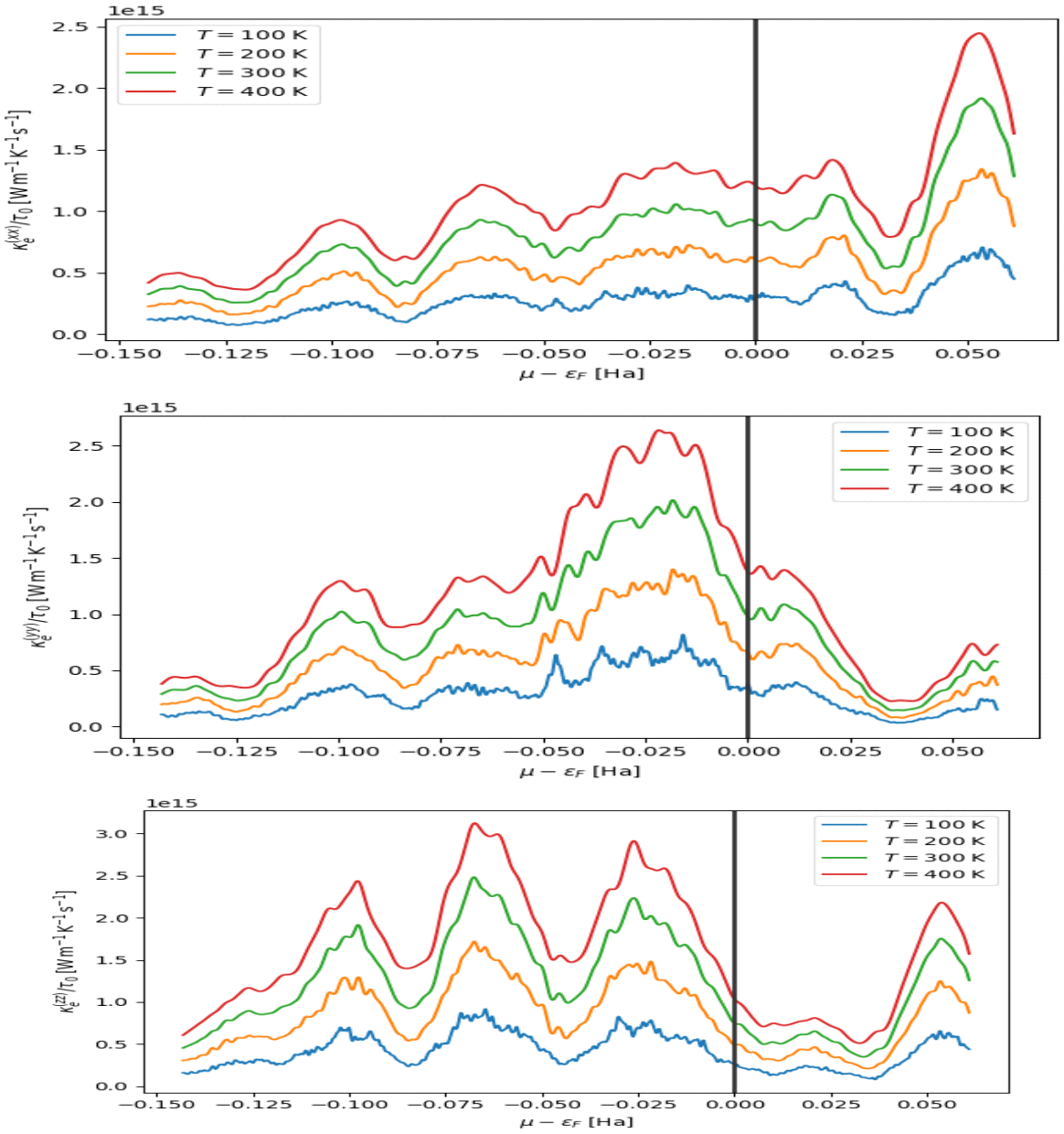


**Fig. 7: Calculated thermal conductivity of $MgS_2$ for (a) xx component (b) yy component and (c) zz component**

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## 4.0 Conclusion

In this study, we conducted a comprehensive investigation into the structural and thermoelectric properties of trigonal magnesium sulfide ($MgS_2$) using Density Functional Theory (DFT) in conjunction with Boltzmann Transport Theory. Our analysis revealed several key findings regarding the thermoelectric behaviour of $MgS_2$.

Firstly, our computational simulations confirmed the trigonal lattice structure of $MgS_2$, consistent with previous experimental reports. The calculated structural parameters aligned well with experimental data, validating the reliability of our computational approach.

Regarding thermoelectric properties, our results demonstrated that MgS2 exhibits characteristics of a p-type semiconductor. The Seebeck coefficient showed an increasing trend with temperature across the measured range (100-400K), indicating its proficiency in converting waste heat into electricity. However, the electrical conductivity exhibited a monotonically decreasing trend with increasing temperature, suggesting degenerating conduction behaviour.

Furthermore, the power factor, a crucial parameter in assessing thermoelectric materials, exhibited an upward trajectory with increasing temperature. This resulted in an augmented dimensionless Fig. of merit (ZT), reaching a maximum value of 0.057 for $MgS_2$. Although this ZT value is less than unity, indicating limitations for power generation applications, it may still find utility in certain applications where a lower ZT is acceptable, such as in refrigeration systems.

In conclusion, our study provides valuable insights into the thermoelectric properties of trigonal $MgS_2$, shedding light on its potential for waste heat recovery and energy conversion applications. Future research could focus on enhancing the thermoelectric efficiency of $MgS_2$ through doping or structural modifications to further optimize its performance.

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**Compliance with Ethical Standards**

**Declarations**:

The authors declare that they have no conflict of interest.

**Data availability**

All data used in this study will be readily available to the public.

**Consent for publication**

Not Applicable.

**Availability of data and materials**:

The publisher has the right to make the data public.

**Competing interests**

The authors declared no conflict of interest.

**Funding**

The authors declared no source of funding.

**Authors' Contributions**

**Dr. O.O. Oyebola** conceptualized the idea and proofreading, **Rilwan Balogun** prepared the methodology, assist in computation and manuscript editing, **Beelewu Damilola** prepared the manuscript and computation of the compound, **Oyebode Daniel** assists in computation while **Adegboyega Babajide** assists in computation and proofreading of manuscript.