

First-Principles Study of the Structural Stability and Electronic Structure of Bulk ZnS Using the SIESTA Code

Sandhya¹, Kusumanjali Deshmukh², Jagjeet Kaur Saluja³

^{1,2}Assistant Professor, Physics, Department of Physics, Govt.VYTPG Autonomous College, Durg, Chhattisgarh, India,

³Professor, Physics, Department of Physics, Govt.VYTPG Autonomous College, Durg, Chhattisgarh, India,

Abstract

In this study, density functional theory calculations based on first principles were performed using SIESTA 4.1.5 to explore the structural and electronic properties of zinc-blende ZnS. Specifically, the generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange-correlation functional, a double-zeta polarized basis set, and norm-conserving Troullier–Martins pseudopotentials were used. The former was applied to analyze the structure of the materials by means of lattice and bond parameters, cell volume, cohesive energy, and formation enthalpy. The authors predicted a Zn–S bond length equal to 2.4008 Å, a tetrahedral bond angle of 109.47°, and the cell volumes of 170.4283 Å³ for the primitive-cell model and 1363.4215 Å³ for the super cell model. The latter was used to determine the band-structure, density-of-states, and projected-density-of-states properties of ZnS. According to the researchers, the global band gaps of the material were 1.78 eV for both models, while the analysis of electronic states allowed characterizing the contributions of Zn and S orbitals to the valence and conduction bands. This description can be used to support further research on the structural and electronic properties of ZnS. However, verifying computational parameters, structural models, and band-gap energies is essential to compare the results with experimental data and evaluate the semiconductor's potential application in optoelectronic devices.

Keywords: Zinc sulfide, density functional theory, SIESTA, GGA-PBE, electronic band structure, density of states, semiconductor.

1. Introduction

Zinc sulphide (ZnS), a semiconductor with a large direct band gap in the near-UV range, is one of the most significant II-VI group semiconductors. Using it as an electro-optic modulator and as an anti-reflecting coating for solar cells, sensors, infrared windows, and lasers is an attractive option [1]. In solar cell applications, zinc sulfide offers several advantages over other semiconductor materials, chief among them being its special qualities and adaptability. ZnS increases efficiency and serves as a helpful buffer layer in multi-layer solar cell systems [2]. ZnS excellent light absorption and great transparency make it useful for a variety of purposes. Zinc sulphide (ZnS) has several advantages over other semiconductor materials that can harm the environment [3]. Because of its non-toxicity, the ZnS semiconductor

compound is regarded as one of the most exceptional useful materials [4]. This specific band gap range allows for optimal sunlight absorption, which is crucial for converting solar energy into electrical energy effectively. Furthermore, the efficiency of solar cells is closely tied to this band gap, as ZnS films can achieve higher performance metrics than conventional materials [5]. Density-functional theory (DFT) calculations have been shown to be a successful technique to better understand the structural, magnetic, optical, and electrical characteristics of semiconductors [6]. However, the electronic and magnetic structure of materials including 3d or 4f states is not suitably represented by DFT-based computations that use a generalized gradient approximation (GGA) or a local spin density approximation (LSDA) for the exchange and correlation potentials. By modeling band structure, density of states, and structural factors at the atomic scale, DFT simulations shed light on how dopants affect electrical and optical characteristics [7, 8]. The methodology employed in the study is based on computational techniques, specifically using density functional theory (DFT). The DFT code utilized for the analysis is WIEN2K, which is designed for calculating electronic properties [9]. In this work, we introduce a collaborative strategy to study the outcomes of pristine and super cell ZnS thin films by integrating theoretical DFT modeling.

2. Theoretical Methodology

Using the SIESTA (Spanish Initiative for electrical Simulations with Thousands of Atoms) simulation tool, Density Functional Theory (DFT) calculations were carried out to examine the structural, electrical, and optical characteristics of unit cell and super cell ZnS thin films at the atomic scale [10,11,12]. SIESTA provides accurate model for transition-metal and metal-doped systems using norm-conserving pseudopotentials and is suitable for large-scale simulations including thousands of atoms [13, 14, 15]. The Perdew–Burke–Ernzerhof (PBE) functional was used to handle the exchange–correlation effects inside the Generalized Gradient Approximation (GGA) framework [16]. All atomic species were represented using a double-zeta polarized (DZP) basis set. Norm-conserving Troullier–Martins pseudopotentials were used in place of the core electrons and 500 Ry selected as the real-space integration grid cutoff to guarantee precise total energy convergence [17].

Table -1: Input parameters of DFT studies.

System	Software	Functional	Basic Set	Energy Cutoff	K-point Grid
Primitive	SIESTA 4.1.5	GGA-PBE	DZP	300 Ry	$8 \times 8 \times 8$
Super cell	SIESTA 4.1.5	GGA-PBE	DZP	500 Ry	$4 \times 4 \times 4$

A zinc blende (sphalerite) or cubic unit cell consists of two zinc (Zn) and two sulfur (S) atoms were used to simulate the pristine ZnS structure. A $2 \times 2 \times 2$ supercell of 32 atoms was designed. The conjugate gradient method was used to achieve structural relaxation until all atoms' residual forces were less than 0.04 eV/Å. A $4 \times 4 \times 4$ Monkhorst–Pack k-point mesh was used to sample the Brillouin zone. The cohesive energy (E_p) and formation enthalpy (ΔH_p), computed as, were used to evaluate the thermodynamic stability of the improved structures [18].

$$E_C = \frac{1}{n} (E_{\text{bulk}} - N_A E_M - N_B E_N) \quad (1)$$

Where "n" indicates the number of atoms, E_{bulk} for the total energy of c-ZnS, p-ZnS, E_M and E_N for the energy of Zn and S single atoms, respectively, and N_A and N_B for the number of Zn and S atoms,

correspondingly. The total energy of Zn and S, and are denoted by E_{Mbulk} and E_{Nbulk} , respectively. Additionally, the enthalpy of formation ΔH can be computed as follows:

$$\Delta H = \Delta U = \frac{1}{n} (E_{\text{bulk}} - N_A E_{\text{Mbulk}} - N_B E_{\text{Nbulk}}) \quad (2)$$

where "n" stands for the number of atoms, E_{bulk} for the total energy of c-ZnS, p-ZnS, E_{Mbulk} , and E_{Nbulk} for the total energy of Zn and S respectively, and N_A and N_B for the corresponding numbers of Zn and S atoms. The formation enthalpy provides crucial information about the overall thermal stability of the system. Density of states (DOS), the projected density of states (PDOS) and band structure computations were used to analyze electronic characteristics.

3. Results and discussion

3.1. Structural analysis

The atomistic models created using the SIESTA software for density functional theory (DFT) calculations are shown in Fig. 3.1 Zn atoms are represented by the golden ball in the pictures, S atoms by the blue ball a feature of the zinc-blende cubic structure. The structural study of super cell ZnS and p-ZnS has been performed. Mesh cutoff, k-grid, and CG steps are among the input settings that are configured for this. The Monkhorst pack technique with a value of $(4 \times 4 \times 4)$ arbitrary units dispersed across all three axes was used to create the k-grid. In fig. (3.1) shows both unit cells and super cells are commonly used in Density Functional Theory (DFT) observations on zinc sulfide (ZnS) to investigate structural and electrical characteristics.

Unit Cell (4 atoms: 2 Zn, 2 S): Used to determine basic bulk ZnS parameters including lattice constants, equilibrium density, and band structure.

Table – 2: Input parameters of structures.

System Name	Cell Volume ($\text{\AA}^3$)	E_c (eV)	ΔH (eV)
Primitive cell	170.428308	-2.89038925	-0.824505125
Super cell	1363.421544	-2.921753	-0.824790

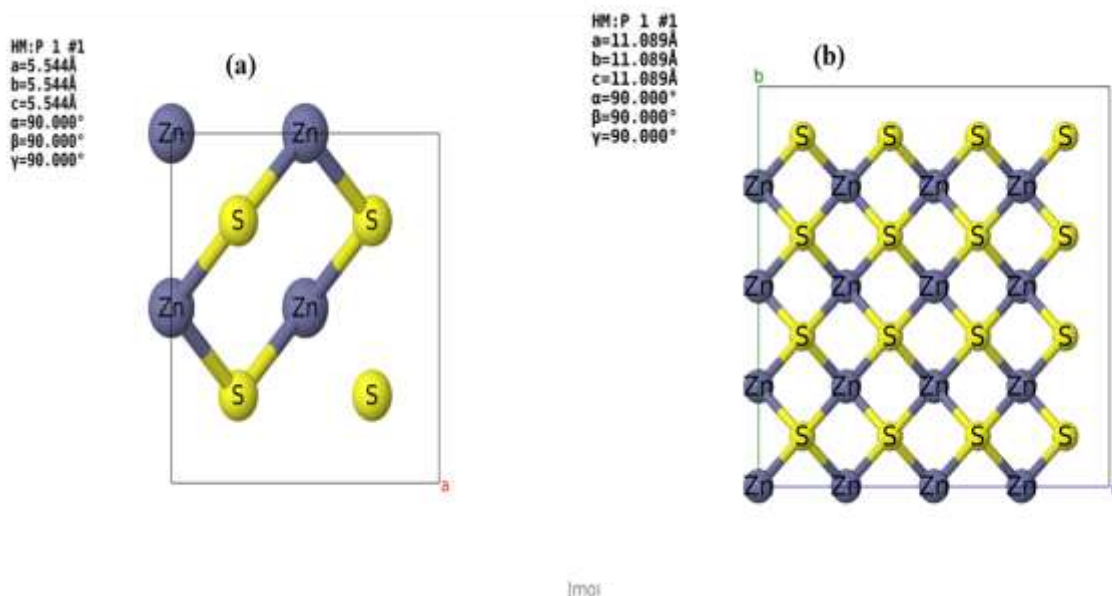


Fig. 3.1 ZnS (primitive cell and super cell) crystal structure.

Table – 3: Bond lengths and bond angles of various structures study.

System Name	Bond name	Bond Angle	Bond Length
Primitive cell	S-Zn	109.47	2.4008
Super cell	S-Zn	109.47	
S-Zn-S		109.47	2.4008
Zn-S-Zn		109.47	

3.2. Electronic Properties

Electronic structure calculations for primitive and super cell of ZnS were performed using Density Functional Theory (DFT) as implemented in the SIESTA package. The exchange-correlation functional used was GGA-PBE. A DZP basis set with a mesh cutoff of 500 Ry was employed. The Brillouin zone was sampled using a $8 \times 8 \times 8$ Monkhorst-Pack grid for unit cell and using a $4 \times 4 \times 4$ Monkhorst-Pack grid. The band structure was calculated along the high-symmetry path $\Gamma \rightarrow X \rightarrow W \rightarrow K \rightarrow \Gamma \rightarrow L \rightarrow U \rightarrow W \rightarrow L \rightarrow K \rightarrow U \rightarrow X$.

3.2 (i) Band Structure & Band Gap

Pure ZnS is a semiconductor with a broad bandgap. The band gap is frequently underestimated in theoretical calculations using normal DFT-GGA, necessitating the use of techniques like GGA+U (Hubbard U) or TB-mBJ

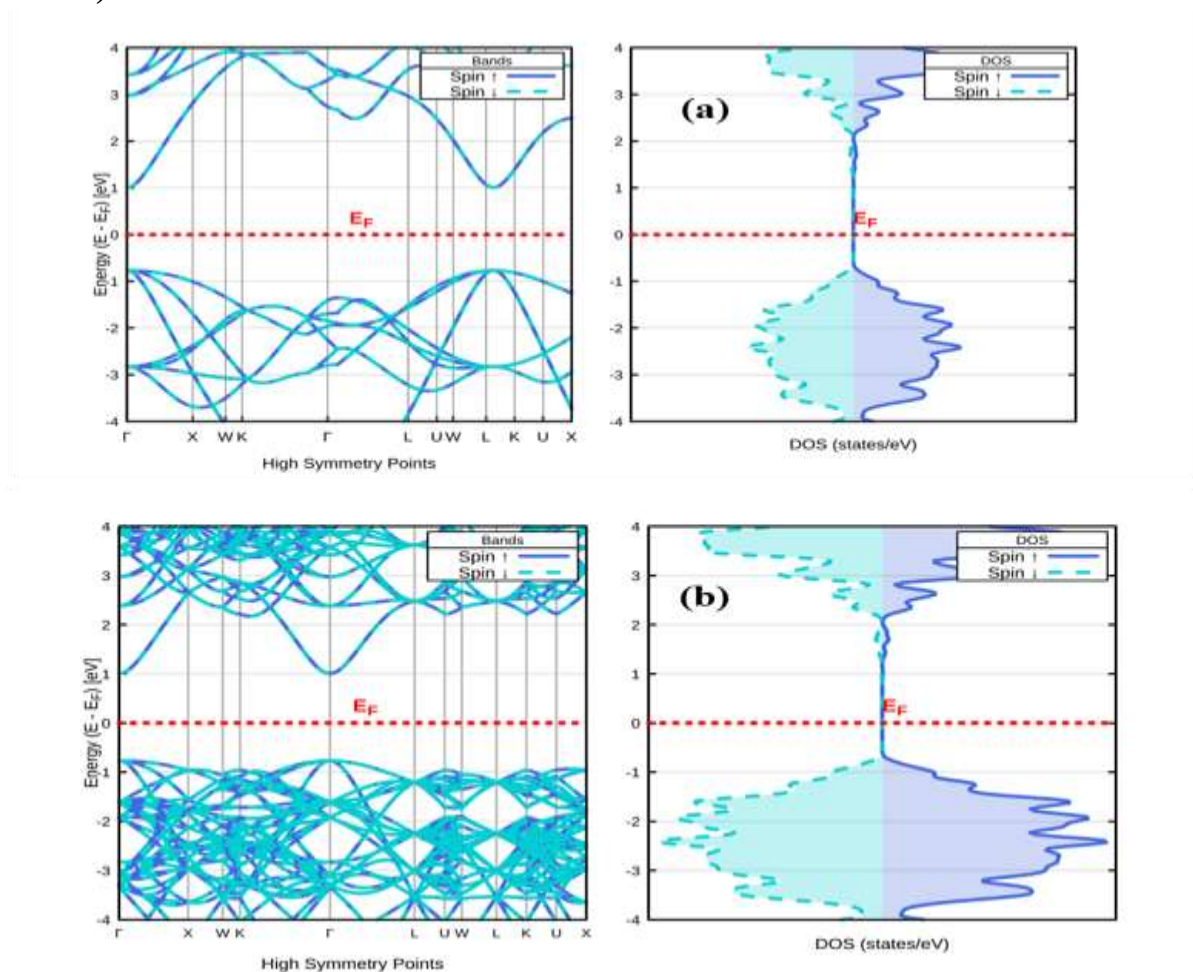


Fig. 3.2(i) Band Structure and DOS ZnS (Primitive cell and super cell).

3.2 (ii) Density of States (DOS)

The number of accessible quantum states per unit volume per unit energy is represented by the density of states (DOS). A DOS of zero denotes the band gap, or prohibited energy area, whereas a high DOS at a certain energy level suggests a high likelihood of electron occupancy. The DOS for ZnS primitive cell and super cell is shown in Figure 3.2 (i). The electron energy in relation to the Fermi level is represented by the X-axis ($E-E_f$), where positive values indicate the empty conduction band and negative values indicate the occupied valence band. The number of permitted electron states per unit of energy is represented by the Y-Axis. Zn-4s and Zn-4p states make up the conduction band, whilst S-3p states make up the valence band.

Table - 4: Electrical calculation such as Fermi energy, HOMO, LUMO, Gap, band gap and materials for ZnS (Unit cell and super cell).

Unit cell		Super cell	
Fermi Energ		-4.7970 eV	-4.7978 eV
Spin Up (1)	HOMO	5.5667 eV	-5.5667 eV
LUMO	-3.7899 eV		-3.7900 eV
Gap	1.7768 eV	1.7767	eV
Spin Down (2)	HOMO	-5.5659 eV	-5.5658 eV
LUMO	-3.7909 eV		-3.7910 eV
Gap	1.7750 eV	1.7748	eV
Global Band Gap	1.7768 eV	1.7767	eV
Material Type	Semiconductor	Semiconductor	

The forbidden energy gap of ZnS structure obtained in Figures 3.2 (i) and 3.2 (ii) is around 1.77 eV. Defect levels appear in the valence band region, which could be a variable in conductivity. The band gap is less than its bulk structure as a result of these defects. They show semiconductor characteristics because of this.

3.5.2 (iii) Projected Density of States (PDOS)

The projected density of states (PDOS) plot's notable, sharp peaks are characteristic of SIESTA's linear combination of atomic orbitals (LCAO) method. In contrast to plane-wave techniques, which have a propensity to delocalize electrons, tightly bound states are properly obtained by SIESTA's localized

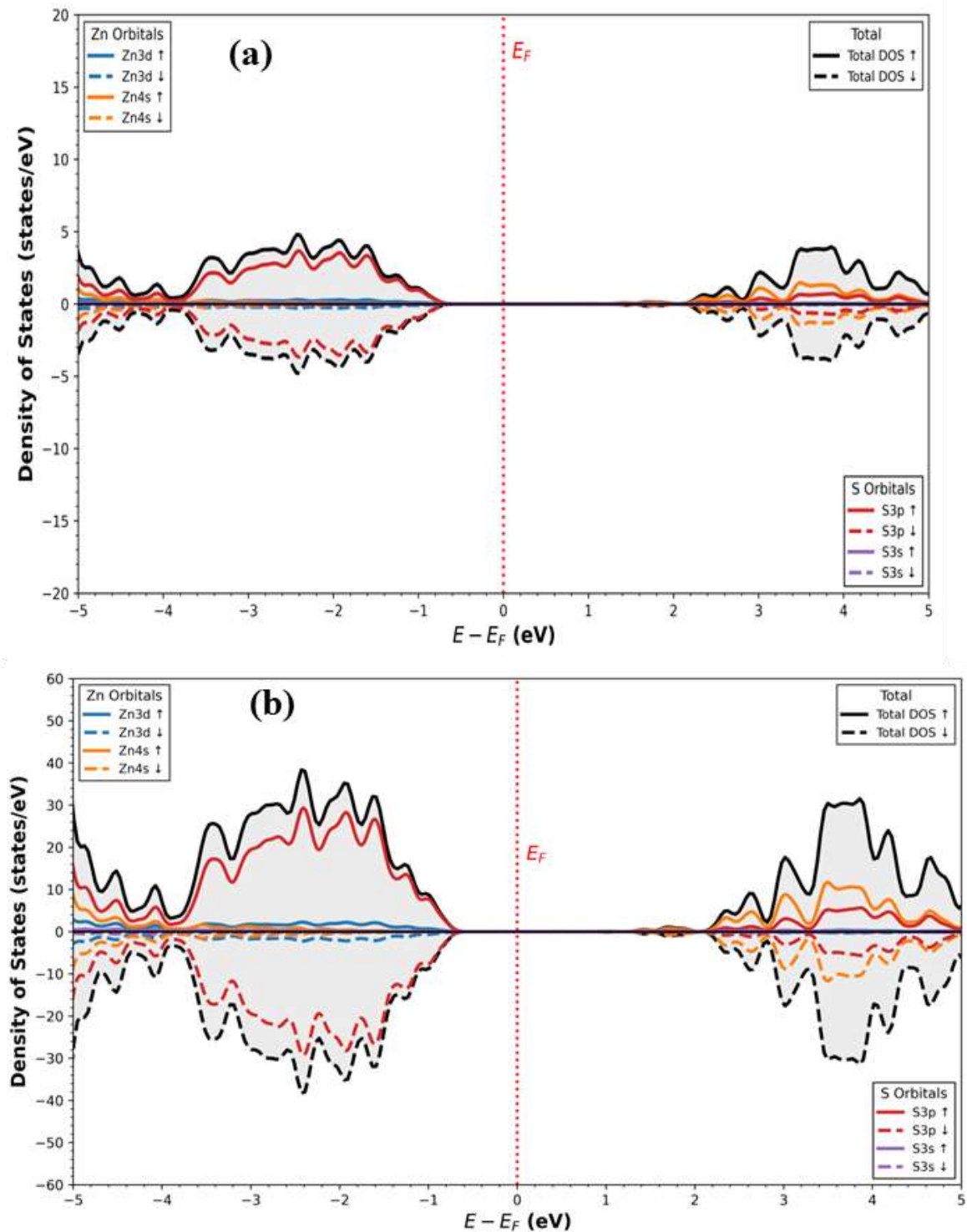


Fig. 3.2 (ii) Projected Density of States (PDOS) for ZnS (Primitive cell and super cell).

basis sets. The Zn atom's 3d orbital and the S atom's 3s orbital display the greatest contribution to the valence band in the case of ZnS, while the Zn atom's 4s orbital and the S atom's 3p orbital have the greatest contribution in the conduction band.

4. Conclusion

In this study, first-principles density functional theory calculations have been performed using the SIESTA simulation package to investigate the structural and electronic properties of zinc-blende ZnS. Calculations were done within the GGA-PBE framework using DZP basis set and norm-conserving pseudopotentials. This approach provided key insights into the structural and electronic properties of this semiconductor. Specifically, the analysis revealed that the calculated cell volume, Zn–S bond length (2.4008 Å), tetrahedral bond angle (109.47°), cohesive energy, and formation enthalpy of the considered structures were consistent with the tetrahedral coordination of the zinc-blende structure. Additionally, electronic structure was analyzed through band-structure, DOS, and PDOS calculations. The global band gap calculated for both primitive-cell and supercell approaches was found to be approximately 1.78 eV. Furthermore, calculations of optical properties, defect states, or dopant effects would be required to establish whether this material can be employed for a specific optoelectronic or solar-cell application.

5. References

1. Ozutok, F. Erturk K. and Bilgin, V (2012). Growth, Electrical, and Optical Study of ZnS:Mn Thin Film. *Acta Physica A*, 121, 221-223.
2. Zaniab Ahmed, Tareq Rahman, +7 more, Characterization and optimization of ZnS thin film properties synthesis via chemical bath deposition method for solar cell buffer layer,
3. Main Group Chemistry, (2022), 1, 22, 79-91.
4. X. Fang, T. Zhai, U.K. Gautam, L. Li, L. Wu, Y. Bando, ZnS nanostructures: From synthesis to applications, *Prog. Mater. Sci.* 56 (2011) 175–287.
5. Li, X.Y. He, M.H. Cao, Micro-emulsion-assisted synthesis of ZnS nanospheres and their photocatalytic activity, *Mater. Res. Bull.* 43 (2008) 3100-3110. H.F. Shi, X.K. Li, D.F.
6. Zhaomin Zhu, Tingyao Wu, Yanmei He, Efficiency Improvement of Ingan Solar Cell Based on Bayesian Optimization, (2025), 92-96.
7. A. ABBAD, H. A. BENTOUNES, W. BENSTAALI, S. BENTATA, B. BOUADJEMI, Influence of hubbard coefficient on the structural, electronic, magnetic and optical properties of Mn/fe codoped Zns, *Chalcogenide* , (2015), 12-6, 301-312.
8. Z.R. Khan, M. Shkir, A.S. Alshammari, I.M. Ashraf, S. AlFaify, J. Inorg. Organomet. Polym. Material , (2021), 31, 3880 .
9. V.D. Moreno-Regino, F.M. Castañeda-de-la-Hoya, C.G. Torres-Castanedo, J. Márquez-Marín, R. Castanedo-Pérez, G. Torres-Delgado, O. Zelaya-Ángel, *Results Phys.* (2019) , 13, 102238.
10. A. Kuzmin, Inga Pudza, Milena Dile, Katrina Laganovska, Aleksejs Zolotarjovs, Examining the Effect of Cu and Mn Dopants on the Structure of Zinc Blende ZnS Nanopowders. *Materials*, (2023), 16, 17.
11. N.K. Verma, B.S. Bhadoria, M.L. Verma, A. Tiwari, A DFT study on Armchair nanoribbon structures of TiN, ZrN, and HfN, *J. Electronic Materials*, (2024), 53(5), 2367-2381.
12. S.K. Nanda, A. Tiwari, V. Singh, M.L. Verma, N.K. Verma, K.H. Mahmoud, *J. Supercond. Nov. Magn.* (2025) , 38, 189.
13. A. Tiwari, R.H. Talwekar, M.L. Verma, *J. Electron. Mater.* (2021), 50, 3312.
14. N.K. Verma, S.K. Srivastava, M.L. Verma, A. Tiwari, *Mater. Chem. Phys.* (2023), 293, 126945.

15. N. Troullier, J.L. Martins, Efficient pseudopotentials for plane-wave calculations, (1991), Phys. Rev. B 43, 1993.
16. Javier Junquera, Oscar Paz, Daniel Sanchez Portal, Emilio Artacho, Numerical
17. Atomic Orbitals for Linear-Scaling Calculations, (2001), Physical Review B, 64, 235111.
18. A.S. Verma, B.K. Sarkar, V.K. Jindal, Cohesive energy of zinc blende (AIIIBV and AIIBVI) structured solids, journal of Physics (, 2010), 74(5), 0851-0855.