DFT Investigations of BeSnN₂ Chalcopyrite Compound for Optoelectronic Applications

Sanjay Lathwal¹, Aditi Gaur², Karina Khan³, Sunil Kumar Goyal⁴, Amit Soni*, Jagrati Sahariya*

¹Birla Institute of Technology & Science, Pilani-333031, Rajasthan, India
²,³,⁴Department of Electrical Engineering, Manipal University Jaipur, Jaipur-303007, Rajasthan, India
⁵Department of Physics, Manipal University Jaipur, Jaipur-303007, Rajasthan, India
⁶Department of Physics, National Institute of Technology, Srinagar (Garhwal)-246174, Uttarakhand, India

E-mail: *amitsoni_17@yahoo.co.in ; *jagrati.sahariya@gmail.com

Abstract. The ternary chalcopyrite compounds are a very renowned category to perform the theoretical investigation in order to find out a proper and apt compound for optoelectronic application. Solar cell is a very interesting field to compensate the energy supplying needs in place of other electricity generating sources. Several semiconductor compounds have been investigated and amongst them we have done a theoretical investigation of pure BeSnN₂ using DFT based computational tool i.e. Wien2k. The exchange correlation used for our study is Perdew Burke Ernzerhoff: Generalized Gradient Approximation (PBE-GGA). We have done electronic and optical investigation of the compound using the basic lattice parameters and other essential input parameters. The investigation has offered a bandgap of 1.005 eV which is suitable to quote for the optoelectronic applications. Optical properties like absorption, dielectric tensor (both real and imaginary), refraction and reflection have been investigated.

Keywords: Absorption, dielectric tensor, electronic, reflection, refraction, solar

1. Introduction

This work has been done to accomplish the investigation to know how successful BeSnN₂ is as an optoelectronic material. The compound is a ternary pnictide semiconductor with a chalcopyrite-based structure which belongs to the base compound of group II-A. The motivation of this work is the theoretical investigation of several such similar compounds and to analyze their electronic and optical nature. As we all know solar cells have seen tremendous growth to meet the energy requirement efficiently in comparison to other energy generating sources [1]. With time we require to get a solar cell compound that offers more efficiency and less economical investment.

Many ternary compounds based on group II-A and II-B primary compounds have been studied and their brief literature has been mentioned here. A theoretical investigation in which ZnSnN₂ has been found to provide a better solution as a solar cell or photovoltaic application [2]. This work talks about the work and development that has taken place on this sample. They have discussed and compared the computational and theoretical results based on this sample. ZnSiN₂ was another compound along with ZnGeN₂ that has been studied due to its wide-bandgap nature and giving us an insight into the bandgap engineering option. The experimental work has been presented in which growth of ZnSiN₂ on c-sapphire & silicon substrates is done using a low-pressure technique i.e.
MOVPE [3]. The effect of doping ZnSiP$_2$ with Ge and Sn at the Si site has been identified using the structural, electronic, and optical aspects through DFT-based wien2k. The different doping percentages have shown decrement in bandgap with Sn doping and not much change has been observed in the case of Ge doping [4]. The doping of Ge at si site in ZnSiP$_2$ has also been investigated showcasing the comparison with pure and 12.5% of Ge in ZNSiP$_2$ [5]. This work deals with the wideband material (more than 2 eV) i.e. MgSnN$_2$ to provide an alternative to the light-emitting diode and other optoelectronic device applications [6]. This work depicts the computational study of MgSnN$_2$ offering a bandgap of 2.69 eV. The material has been quoted aptly for short-wavelength absorber material for photovoltaic applications [7]. With the use of metathesis reaction under extreme pressure, MgSnN$_2$ a unique ternary nitride semiconductor compound is obtained [8]. In another work, optoelectronic investigation of V doped MgSnN$_2$ has been done using the first principle method. Basic plots like Density of states (DOS) and band structures present half-metallic characteristics for V-doped MgSnN$_2$ along with half-metallic-based bandgap of 0.74 eV and 0.36 eV for V$_{Mg}$ and V$_{Si}$ respectively [9]. The lattice parameters and structural features of MgSiN$_2$ and MgGeN$_2$ which are orthorhombic structured and wide bandgap based semiconductors are investigated using DFT. MgSiN$_2$ powder’s structural aspects and Raman spectra have been obtained [10]. The first principle calculation of 12.5 percent of Sr at the Mg site in the case of MgGeN$_2$ has been carried out to reveal the different features of the compound in optoelectronic applications [11]. Based on the first principle density functional calculations, the study of (BeSn, BeGe, MgGe)N$_2$ has been accomplished. The calculations depict that with BeSnN$_2$ and BeGeN$_2$, MnBe shows anti-ferromagnetism, whereas MnSn and MnGe show ferromagnetism [12]. Finally in one of the works, the band structures, equilibrium lattice inputs parameters and structural parameters, bulk moduli, and cohesive energies for chalcopyrite structure of BeCN$_2$, MgCN$_2$, BeSiN$_2$, MgSiN$_2$, and MgSiP$_2$ are calculated by the linear-muffin-tin-orbital method [13-15]. A theoretical study has been performed in one of the papers in which the FP-LAPW method has been adopted based on TB-mBJ approximations to investigate the chemical bond, structural aspect, electronic and optical features. The series undertook for investigation was BeMN$_2$$_{O2}$ (M = Si, Ge, Sn; N$_O$ = P, As) in which BeSiP$_2$ has yielded the maximum and direct in nature bandgap [16]. The mechanical aspects to study the stability along with other features like optical and electronic to investigate the behavior of BeSiP$_2$ and BeGeP$_2$ [17]. BeSiP$_2$ offers direct and BeGeP$_2$ offers indirect bandgap obtained using the FP-LMTO potential embedded in the VASP package.

The outline of the paper goes as follows: Section I discusses the Computational method, then in section II results & discussion are presented with a sub-section of electronic property analysis and optical property analysis each. This research aims to produce an investigation for the compound i.e. suitable in optoelectronic applications specifically solar cells.

2. Computational Method

This work has employed density functional theory for the computational method in the Perdew Burke Ernzerhoff: Generalized Gradient Approximation (PBE-GGA) exchange-correlation. The tool utilized for this purpose is wien2k following a DFT-based approach. The wien2k is based on Augmented Plane Wave (APW) method and performs all-electron calculation rather than pseudopotential [18]. The lattice parameters used in the calculations are a=b=4.689 Å & c=9.890 Å and the radius of muffin tin spheres for Be, Sn, and N being 1.89 a.u., 2.08 a.u. & 1.7 a.u. respectively. The lattice constant a (which belongs to the Zinc blende’s cubic lattice constant from where the chalcopyrite originates), q = c/a ratio, and the internal displacement parameter u are used as the structural parameters. With the use of 1000 k points in the irreducible part of the zone, well-converged results are produced. The k-mesh for the system consists of 10 x 10 x 10. The total energy’s meaningful behavior was obtained through MT correction and is obtained as a function of the internal structural value u and c/a ratio. The spacegroup of our system is tetragonal in structure, numbered 122 (I-42D). The body-centered tetragonal (BCT) lattice consists of eight atoms per unit cell in the case of
chalcopyrite structure ABC$_2$. The present compound belongs to the II-A group thus it has been compared with the compounds that contain other elements of this same group like Mg, Ca, etc.

3. Results & Discussion

a) Electronic Property Analysis

BeSnN$_2$ belongs to the tetragonal spacegroup and the crystal structure of the same briefly depicts the arrangement of Be, Sn, and N in the crystal cell. The top and bottom surface of the crystal is occupied by Be at all four corners along with their positions in the middle of the crystal as well. The Sn and N atoms are bonded together with a single bond. The representation of band structure comprises the high symmetrical and directional description of the Brillouin zone. The k points taken to plot the different bands ranged from -6.0 eV to 6.0 eV are Z, Γ, X, P, N & Γ. The Brillouin zone required to produce the band structure plot utilizes different positions of the k points and then presents the bandstructure representation. The Brillouin zone along with the crystal cell for BeSnN$_2$ is given here in figure 1 (a) and figure 1 (b). Bandstructure has provided a bandgap placed in between the maxima of the valence band and minima of the conduction band. The calculated bandgap for BeSnN$_2$ is 1.005 eV as shown in given figure 2 (a). In figure (b), the density of states for BeSnN$_2$ is depicted explaining the different orbital’s roles. The correlation between the band structure and DOS can be done to trace the band formation due to the orbital contribution [19]. The eigen-values were obtained from Kohn Sham and calculated over enough amount of fine k-grid existing in irreducible BZ. The density of states (DOS) is thus obtained by the modified tetrahedron method. The major contributions are as follows: in Be, the contribution is given by 2s orbitals, in Sn, the contribution is by 5p orbitals and 2p orbitals is the contributing orbital in N. The reduction of the bandgap is due to the major contribution by N – atom in BeSnX$_2$. In addition, Be and Sn form the covalent bond as in the second layer of DOS were total of Be, Sn, N represented. The formation energy of a compound is a crucial feature that intends to judge the stability of a compound through its chemical composition [20-21]. The formation energy for the given pure compound is calculated to be -45.91 eV. The more negative value of calculated formation energy the more stable is the compound in terms of its existence.

Figure 1. (a) Crystal structure and (b) Brillouin Zone for BeSnN$_2$ compound
b) Optical property analysis

The optical properties of a semiconductor compound are determined by its absorption, dielectric tensor, reflection, and refraction features [22-23]. The dielectric tensor’s real ($\varepsilon_1$) and imaginary part ($\varepsilon_2$) are determined by incident photon energy’s function. The imaginary dielectric tensor part offers transition peaks that point out to the interband transitions that take place in the band structure plot of our compound under investigation as can be seen in figure 2 (a). The mathematical equations for the optical properties have been deduced from the dielectric function [24]. The equation for dielectric tensor consists of real as well as imaginary parts and is given as:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega)$$

In the imaginary plot, these peaks are located at 4.74 eV and 5.56 eV as peak A and peak B respectively shown in figure 3 (b).

Also, the source of the different peaks is due to these interband transitions only. The static real dielectric tensor’s value i.e. $\varepsilon_1(0)$is 6.20. The real dielectric tensor component is shown in figure 3(a).
The absorption coefficient $\alpha$ is the processing of area under the curve for analysis. Tauc’s law states to determine the optical energy gap of a compound based on its absorption coefficient value. The absorption is determined by the expression:

$$\alpha(\omega) = \frac{4\pi}{\lambda} k(\omega)$$  \hspace{1cm} (2)

This is defined by the interband transitions that are nearer to the bandgap. The absorption curve is shown in figure 4 below explaining the perpendicular and parallel components of absorption. As per the figure, we can see that the components show an isotropic nature for the $(0 – 5)$ eV range, and the rest of the components show anisotropy.

![Absorption curve for BeSnN$_2$](image)

**Figure 4.** Absorption curve for the compound BeSnN$_2$

Refraction is the parameter that decides how a system behaves towards electromagnetic waves. The value of $n(\omega)$ i.e. refractive index is computed through the use of a real dielectric tensor [25]. It is given by the following equation:

$$n = \sqrt{\varepsilon_1}$$  \hspace{1cm} (3)

The reflection parameter decides the optical nature of a semiconductor in terms of the solar cell. It is found to react more sensitively towards the dielectric tensor’s real and imaginary parts [26]. The equation for reflection is given as follows:

$$R(\omega) = \frac{[n(\omega) - 1]^2 + k(\omega)^2}{[n(\omega) + 1]^2 + k(\omega)^2},$$  \hspace{1cm} (4)

The value of static reflectivity $R(0)$ is 18% and the value of static refractivity is calculated to be 2.47. In this manner, all the parameters show the anisotropic nature of this semiconductor as per the whole investigation.

![Reflection and Refraction plots for BeSnN$_2$](image)

**Figure 5.** (a) Reflection plot and (b) Refraction plot for BeSnN$_2$
Additional optical characteristics like optical conductivity can be calculated with the use of dielectric function in particular energy ranges. The curve of optical conductivity depicts many transition peaks that correspond to the excitations aroused by the bulk plasmon. This in brief is the movement or shift of electrons from the valence band to the conduction band. The equation defining the optical conductivity is given by:

$$\sigma(\omega) = -\frac{i\omega}{4\pi}\varepsilon(\omega)$$  \hspace{1cm} (5)

We have made use of compounds with elements that offer no or least toxicity in their composition. Therefore our compound has not reported any toxic nature during its past experimental and theoretical work. This can be stated in the literature review from [3-17].

4. Conclusion

The compound has achieved a positive response in terms of optoelectronic application. This sample with the PBE-GGA exchange-correlation functional offers a bandgap of 1.005 eV which is suitable for applications in solar cells and other optoelectronic fields. For a system to stand out as a suitable optoelectronic device especially photovoltaics the requirement to be fulfilled is to deliver direct bandgap and also the value of bandgap should be around and above 1.2 eV. The present system though offering 1.005 eV needs a very less amount of suitable doping either with a similar isoelectronic element or with a p-type or n-type dopant. The electronic and optical analysis has been done with features explored such as band structure, DOS, absorption curve, dielectric tensor plot, reflection, and refraction. The optical properties have presented the anisotropic nature of the compound between perpendicular and parallel components. The compound offers 18% reflection concluding it achieves the aim to be an apt solar cell compound with lesser reflectivity feature.

5. Acknowledgment

We would like to express our gratitude towards DST-SERB project grant no. EMR/2017/005534 for providing financial support in the completion of such computational work. Along with this, we would like to thank sincerely, Manipal University Jaipur for providing the appropriate platform to carry out the research. At last, we would like to thank all our research team members for the completion of the computational tasks with precision.

References

[1] Gul M, Kotak Y, Muneer T 2016 Review on recent trend of solar photovoltaic technology Energy Explor. Exploit. 34(4) 485-526.
[2] Khan I S et al 2020 Review of ZnSnN₂ semiconductor material J Phys Energy 2 032007.
[3] Cloitre T et al 2004 Epitaxial growth of ZnSiN₂ single-crystalline films on sapphire substrate Superlattices Microstruct. 36 377-383.
[4] Khan K et al 2020 Density functional investigations to study effect of M=(Ge, Sn) doping on optoelectronic response of ZnSi₁₋ₓMₓP₂ Optik 208.
[5] Khan K et al 2020 Investigation of structural and optoelectronic properties of ZnSi₁₋ₓGeₓP₂ (x = 0, 0125) compound using density functional theory AIP Conference Proceedings 2220.
[6] York K R 2018 MgSnN₂: A New Eco-friendly Wide Band Gap Semiconductor Western Michigan University 1-56.
[7] Dumre B et al 2021 Stability, and electronic and optical properties of ternary nitride phases of MgSnN₂: A first-principles study J. Phys. Chem. Solids 153, 110011.
[8] Kawamura F et al 2019 Synthesis of a Novel Rocksalt-Type Ternary Nitride Semiconductor MgSnN₂ Using the Metathesis Reaction under High Pressure Eur. J. Inorg. Chem. 1-17.
[9] Khan K et al 2021 Exploring Ab initio calculations of Mg₈₀₇₅Sr₀₁₂₅GeN₂ Alloy: A DFT Study theory IEEE In: Int. Conf. Adv Comp Inno Techno Engg.
[10] Huang H M et al 2013 First Principles Study of Half-Metallic and Magnetic Properties of V Doped MgSiN₂ Chalcoprite 27 257–261.
[11] Rasander M et al 2017 Structure and lattice dynamics of the wide band gap semiconductors MgSiN₂ and MgGeN₂ Int. J. Appl. Phys. 122 1-9.
[12] Rufinus J and DeWinter J L 2008 Magnetic properties of Mn-doped chalcopyrites: (BeSnBeGeMgGe)N₂ Journal of Applied Physics 103.
[13] Kocak B and Ciftci Y O 2016 Analysis of the structural electronic and optic properties of Ni doped MgSiP₂ semiconductor chalcopyrite compound AIP Conf Proc 1722 220013.
[14] Khan K et al 2020 Effect on structural and optoelectronic properties of Sn doping in MgSiP2-A DFT study J Phys: Conf Ser 1504 012013.
[15] Basalaev Y et al 2005 Electronic structure of triple phosphides MgSiP₂ ZnSiP₂ and CdsiP₂ Russian Physics Journal 48 78-83.
[16] Fahad S et al 2015 Structural elastic electronic bonding and optical properties of BeAZ₂ (A = Si Ge Sn; Z = P As) chalcopyrites J. Alloys Compd. 646 211-222.
[17] Gani Aa et al 2020 Mechanical stability and optoelectronic behavior of BeXP₂ (X=Si and Ge) chalcopyrite Chin. J. Phys. 64 174-182.
[18] Blaha P et al 2020 WIEN2k: An APW+lo program for calculating the properties of solids J Chem Phys 152 074101.
[19] Petukhov A G et al 1994 Electronic structure of wide-band-gap ternary pnictides with the chalcopyrite structure Phys Rev B 49 4549-4558.
[20] Agrawal A et al 2016 A Formation Energy Predictor for Crystalline Materials Using Ensemble Data Mining IEEE 16th Int .Conf. on Data Mining Workshops 1276-1279.
[21] http://docsquantumatkcom/tutorials/formation_energies/formation_energieshtml.
[22] Terzzas E Y et al 2009 Adv Mat Res. 68 89-95.
[23] Mousavi S J et al 2008 Calculation of the Structural Electrical and Optical Properties of κ-Al₂O₃ by Density Functional Theory Chin. J. Phys. 46 170-180.
[24] Bennacer H et al 2014 First Principal Calculations of Optical Properties of InGaN2 Using in Solar Cells Applications Conf on Multiphysics Modelling and Simulation for Systems Design and Monitoring. Applied Condition Monitoring 2 179-187.
[25] Berrah S et al 2009 Optical properties of the cubic alloy (In Ga) N Physica E 41 701–704.
[26] Ziane MI 2015 et al First principles study of structural electronic and optical properties of indium gallium nitride arsenide lattice matched to gallium arsenide Mater. Sci. Semicond. Process. 30 181–196.