The First Principle Investigation for the Structural and Optoelectronics Properties of Tetragonal Compound CaCN₂

K Khan¹, A Gaur², U Ahuja³, A Soni²* and J Sahariya⁴*

Corresponding author: amitsoni_17@yahoo.co.in; jagrati.sahariya@gmail.com

¹Department of Physics, Manipal University Jaipur, Jaipur-303007, Rajasthan, India
², ⁴Department of Electrical Engineering, Manipal University Jaipur, Jaipur-303007, Rajasthan, India
³Department of Electrical Engineering, NMIMS, Mukesh Patel School of Technology Management and Engineering, Mumbai-400056, Maharashtra, India
⁴Department of Physics, National Institute of Technology, Uttarakhand-246174 Srinagar (Garhwal), India

Abstract. The present study deals with the structural, electronic and optical properties of CaCN₂ ternary compound. For the computation of structural, electronic and optical properties of the CaCN₂, the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) exchange correlation within the framework of density functional theory as available in Wien2k code is used. Wien2k code is based on full potential linearized augmented plane wave method. The electronic properties are investigated in terms of energy band structure, partial and total density of states. Our investigation reveals the direct band gap nature of CaCN₂ with band gap of 1.66 eV. The optical behaviour CaCN₂ is explained through dielectric tensor, absorption, reflection and refraction spectra which show the utility of this compound in photovoltaic applications.

1. Introduction

Global increase in the population has drastically increased the energy consumption all over the world. The growing population need new technologies for development of the nation, resulting in soaring of energy demand in the last ten years. The energy requirement for present and future generation cannot be met solely through fossil fuels because they exist on Earth in straitened quantity. For sustainable development and to reduce the impacts of global warming, researchers are focusing on the renewable energy sources. Solar energy is one of the renewable energy that is the most bountiful, pollution free and is as capable as traditional energy sources to produce electricity [1-4]. To metamorphose the solar energy into its useful form, solar cells are required. A solar cell must exhibit some traits such as high efficiency, environmentally friendly, low fabrication cost, low installation cost and optimal band gap. All these characteristics make solar cells competitive for traditional solar cells [5-7]. The chalcopyrites
compounds of the group $A^{III}B^{II/IV}_{V/VI}C_{V/VI}$ are the crystal conform to the zinc blende structure have become the attractive compounds for the researchers due to their utility as the solar cell materials. These compounds exhibit almost all the features, needed for good solar cells. The ternary chalcopyrite II-IV-V$_2$ compounds are having the wide application in optoelectronic field. These compounds are used in many devices such as non-linear optical instruments, light emitting diode (LED), photo catalyst, photodetector and solar cells [8-12]. Most of the compounds such as II-IV-As$_2$ and II-IV-P$_2$ of the ternary group II-IV-V$_2$ are well investigated through practical and theoretical manner. But the nitride compounds of II-IV-N$_2$ are not explored much. The heterovalent ternary chalcopyrites of group II-IV-N$_2$ are similar to the III-N$_2$ in structure and opto-electronic properties. They are also showing the similar kind of semiconductor behaviour as III-N$_2$ compounds [13, 14]. The compounds of the group II-IV-N$_2$ exist in orthorhombic and tetragonal form. The tetragonal carbonitrides belongs to the group II-C-N$_2$ are well investigated due to their utility as solar cell materials which allow them to form in thin film and bulk solar cells. The carbonitrides samples of this group which are explored earlier and the band is reported up to 5 eV and the semiconductor behaviour [15]. The compound CaCN$_2$ is one of the candidate of this group having wide range of applications due to which it is synthesised in different manner for different purposes. The thermodynamic behaviour and densification action of the CaCN$_2$ have been analysed by experimental method [16-19]. Pang et al. [20] have been synthesized the carbon powder by using CaCN$_2$. Kim et al. [21] have been calculated the luminescence properties of the CaCN$_2$. Basalaev et al. [15] have been investigated the electronic properties of the group MCN$_2$ where $M$=Be, Mg, Ca, Zn, Cd, Hg, by using DFT-LDA within the framework of CRYSTAL code.

It is clear from above literature review that the optical properties of CaCN$_2$ is still not explored so we performed the structural and optoelectronic calculation of CaCN$_2$ by using DFT.

2. Computational Details

This work includes the calculations of the structural and optoelectronic properties of the CaCN$_2$ which is performed under the theoretical simulation that are executed in Wien2k code [21]. All these calculations are done by solving Kohn-Sham equations based in DFT, a frequently used theoretical tool for computing the physical properties of compounds [22,23]. These computations are underlying on the basis of full-potential linearized augmented plane wave (FP-LAPW) method. It is worth mentioning that in FP-LAPW method, the unit cell is divided in non-overlapping atomic sphere and interstitial region to obtain the different set of basis [24]. In order to gain the exactitude in calculation, we have used the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) for solving the exchange-correlation potential [25]. The electronic valence state of Ca, C and N are 3p$^3$4s$^2$, 2s$^2$2p$^2$, 2s$^2$2p$^3$ respectively and remaining energy states are taken at rest. The spherical harmonics inside the MT sphere for defining the electronic potential and density is taken up to, $l_{max}$=10 [24]. The radius of MT sphere of the atoms: Ca, C and N are 1.94, 1.65 and 1.74 respectively are used. The value of energy to separate the core and valence states is –6 Ry. The calculations are carried out with the mesh of 1000 k points and the charge density and potential in Fourier series are amplified up to $G_{max}$=12 (a.u.)$^{-1}$. The value of energy cut-off region, $R_{MT}$ $K_{MAX}$=7 is provided.

3. Result and Discussion

3.1 Structural Properties

The structure of CaCN$_2$ is obtained using PBE-GGA exchange correlation potential. The ternary chalcopyrite CaCN$_2$ compound crystallizes in the tetragonal structure with space group I4$\overline{3}$m (122). The structural optimization are performed to obtained the optimized lattice parameters which are $a = b = 4.498$ Å and $c = 8.370$ Å . The atomic positions for CaCN$_2$ is set as Ca (0,0,0); C (0,0,0.5) and N (0.29, 0.25, 0.125). The structure contains the three atoms having two positions of Ca and C and four positions of N. The tetragonal crystal structure of CaCN$_2$ along with the Brillouin zone synchronized with momentum points are presented in figure 1 (a-b).
3.2 Electronic Properties

The electronic properties of CaCN$_2$ are investigated using the PBE-GGA potential. The electronic properties are clearly understood by the energy band structure and total and partial density of states (DOS). Energy band and DOS for CaCN$_2$ are presented in figure 2 and 3 respectively. The band gap of any compound is an important parameter for finding the nature and electron transitions [26]. We have plotted the energy band structure in figure 2, along the high symmetry momentum points Z → Γ → X → P → N → Γ and their coordinates are as follow: (0.5,0.5,0.5); (0,0,0); (0,0,0.5); (0.25,0.25,0.25); (0,0.5,0); (0,0,0) respectively, for the first brillouin zone. The Fermi energy is set at 0 eV. From Fig. 2, it is clearly observed that CaCN$_2$ compound exhibits the direct energy band gap as its valence band maximum (VBM) and conduction band minimum (CBM) both lie at the same Z-Z momentum point. The calculated value of energy band gap is 1.66 eV which justify its semiconductor nature. The possible electronic transitions are also shown in figure 2.
For better understanding of the electronic properties and formation of energy bands, we have plotted the DOS spectra. The energy band gap calculated by band structure is also confirmed through the total DOS spectra. From figure 3, we can observe that the valence band just lie beneath the Fermi energy at 0 eV. The energy dispensation of all the energy states can be understood through the DOS spectra. It is visible from the DOS spectra that three bands are formed: core band (−6 to −8 eV); valence band (0 to −6 eV) and conduction band (0 to 6 eV) in CaCN₂. In valence band the major contribution of p-state of Ca and p-state of N while in the conduction band s-state of C and p-state of N. This arises due to the hybridisation of different energy states.

3.3 Optical Properties

In this section, we present the optical properties of the CaCN₂ which are related with the mobility of electrons and rate of their recombination. This property arises in a compound due to the interactivity between the photons and valence state electrons. We have plotted the spectra of complex dielectric tensor, absorption, refractivity and reflectivity for clear understanding the optical nature of CaCN₂. All these factors are frequency dependent and plotted up to 8 eV. The figure 4 (a) and (b) depicted the real and imaginary dielectric tensor spectra which are associated with the wave vector. When the light penetrates into the compound then its dispersion and polarisation is explained through the real dielectric tensor $\varepsilon_1(\omega)$ spectra [27] and its calculated absolute value for the studied compound is 6.94. The devitalization of light is described by the imaginary dielectric tensor $\varepsilon_2(\omega)$ spectra. The peaks A (2.6 eV), B (3.6 eV) and C (5.1 eV) in figure 4 (b) indicate the transition of electrons form valence to conduction bands which are as follow $I_{23}-I_{25}$, $I_{24}-I_{27}$ and $X_{19}-X_{30}$ as shown in figure 2. The absorption coefficient spectrum $\alpha(\omega)$ is presented in figure 5 (a) which is used to explain the absorption of light in the material. This compound shows the notable energy strength that lie in the range of 0–5 eV which is most suitable region for the absorption of visible light. The computed value of integrated absorption coefficient is $97.907 (\times10^4$ eV/cm). The spectra of reflectivity and refractivity are depicted in figure 5 (b) and (c) respectively.
Figure 4. (a) Real component of dielectric tensor (b) Imaginary component of dielectric tensor of CaCN$_2$ using PBE-GGA.

Figure 5. (a)Absorption Spectra (b) Reflectivity spectra and (c) refractivity spectra of CaCN$_2$ using PBE-GGA.

With the help of the reflectivity and refractivity spectra, we come to know about the transparency and roughness of the materials. The reflectivity is obtained through the reflection spectra is 20.4% at
absolute point. The absolute value refractivity spectrum of CaCN$_2$ is 2.6. It is clearly visible through all the optical spectra that parallel and perpendicular components are not coinciding with each other, which indicating the anisotropic nature of the CaCN$_2$.

4. Conclusion
The present study on the structural and opto-electronic properties of tetragonal chalcopyrite CaCN$_2$ has been investigated through the FP-LAPW method which is embodied in Wien2k code. Through the computed results we found that ternary chalcopyrite CaCN$_2$ have the suitable band gap for the photovoltaic activity. The electronic band structure and DOS spectra reveals the semiconductor behaviour of the compound having the direct band gap. The optical spectra confirm the utility of CaCN$_2$ for solar cell material and affirm the anisotropic nature of this compound.

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