Effect on structural and optoelectronic properties of Sn doping in MgSiP$_2$ - A DFT study

K Khan$^1$, A Gaur$^2$, U Ahuja$^3$, A Soni$^2$ and J Sahariya$^4$

Corresponding author: aditigaur075@gmail.com

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

Abstract. In the present paper, ab initio calculations of structural, band structure and optical properties of MgSi$_{0.94}$Sn$_{0.06}$P$_2$ are studied within the framework of Density Functional Theory (DFT). The exchange correlation used to carry out all the calculations is Perdew-Burke-Ernzerhof Generalized Gradient Approximation (PBE-GGA) which is embodied in Wien2k code using Full Potential-Linear Augmented Plane Wave (FP-LAPW) method. The band structure, partial and total density of states (DOS) are computed for the supercell structure of MgSi$_{0.94}$Sn$_{0.06}$P$_2$. The direct energy band gap ($E_g$) is found to be 1.36 eV which exhibits high optical absorption. It is observed that by adding a smaller percentage of Sn at Si Site in MgSiP$_2$ chalcopyrite increases the band gap thus making it suitable for photovoltaic applications.

1. Introduction

Solar energy is one of the renewable, inexhaustible and most abundant sources of energy available on earth. Many environmental issues can be resolved with the help of solar energy [1]. Solar cells are the devices which converts the solar energy into the electrical energy. This process of conversion of energy involves the photovoltaic module installation and has attracted the researchers in past few years [2]. The energy gap of ternary chalcopyrite compounds of group II-IV-V$_2$ lie in energy range 1.0 –2.4 eV [3,4]. This made these compounds more suitable for photovoltaic applications [3,4]. MgSiP$_2$ is one of the compounds belonging to this group and has attracted scientific community because of its structural, optical and electronic properties. Its strong anionic shift from tetrahedral position in chalcopyrite structure and strong tetragonal compression make this compound different from other semiconductors of group II-IV-V$_2$ [5]. Pseudodirect band gap nature of MgSiP$_2$ has been investigated.
by Ambrazevicius et al. [5] using the wavelength-modulated absorption spectra at different values of pressure and temperature. Using pseudopotential method Poplavnoi et al. [6] have computed the band structure of MgSiP2 and calculated band gap for the compound has reported as 1.65 eV. Trykozko [7] has crystallizes the MgSiP2 in antimony and has analysed its crystals through photomicrograph. On the theoretical side, Schilfgaarde et al. [8] have investigated the band structure by the quasiparticle self-consistent GW theory. Using density functional theory (DFT), optical characteristics of thin film of II-IV-V2 have been reported by Boukabrine et al. [4]. Ibrahim et al. [9] have reported the structural and optoelectronic properties of Mg-IV-V2 (IV=Si, Ge, Sn and V=P, As) compounds with DFT. Authors found that all of these semiconductors have direct band gap. Kocak et al. [10, 11] have incorporated Ni and Cu in MgSiP2 at Mg site and have performed structural, electronic and optical calculation of pure and doped compounds sing DFT. The above research on MgSiP2 have motivated us to undertake a systematic study on the electronic and optical properties for Sn doped and undoped MgSiP2.

2. Computational Details

All the computations for finding the crystal structure and optoelectronic behaviour of Sn-doped and undoped MgSiP2 are performed using the Kohn-Sham equation of the density functional theory (DFT) as embodied in Wien2k [12]. It is worth mentioning that DFT is widely used in theoretical technique to investigate the chemical and physical nature of crystal [13,14]. For obtaining the accuracy in the calculations exchange and correlation prescribed by Perdew et al. [15] is used. The energy cutoff parameter \( R_{\text{MT}} K_{\text{MAX}} \) was fixed to 7 to provide precision to the calculation [14]. The radius of the MT sphere in the compounds are 2.5, 2.07, 2.39 and 2.18 Å, for Mg, Si, Sn and P respectively. The computation is performed by taking the 100 k points, the value of \( G_{\text{MAX}} = 12 \) (a.u.)\(^{-1}\) and value angular momentum inside the sphere (\( l_{\text{max}} \)) is expanded upto =10 are used from the Wien manual [15].

3. Results and Discussion

3.1 Structural Properties

The tetragonal structure of MgSiP2 of space group \( \text{I4} \ 2d \ \text{(122)} \) is converted into supercell MgSi\(_{0.94}\)Sn\(_{0.06}\)P\(_2\) of dimension 2×2×2 of crystal structure monoclinic primitive and having space group 3(P2). The supercell produced contains 68 atoms. The lattice parameters of MgSiP\(_2\) are \( a=b=5.721 \) Å; \( c=10.23 \) Å. The crystal structure of both compounds are shown in figure 1. The Wyckoff positions for MgSiP\(_2\) are Mg (0,0,0); Si (0,0,0.5); P (0.29, 0.25, 0.125).

![Figure 1. Crystal structure of (a) MgSiP\(_2\) (b) MgSi\(_{0.94}\)Sn\(_{0.06}\)P\(_2\).](image)
3.2 Band Structure Properties

Both compounds MgSiP$_2$ and MgSi$_{0.94}$Sn$_{0.06}$P$_2$ possess the semiconductor nature reveals through the band spectra and DOS spectra, shown in figure 2. (a-b). From band structure, it is clear that valence band maximum (VBM) and conduction band minimum (CBM) for pure and undoped compounds exist at $\Gamma\Gamma$ momentum point hence exhibit direct band gap of 1.34 eV and 1.36 eV respectively. From the DOS, it is clearly observed that the upper most valence and lower most conduction bands are due to p-state of P and spd-states of Mg, Si/Sn, P, respectively. Therefore, only these states are responsible for the electronic properties of pure and Sn doped MgSiP$_2$ compound.

Figure 2. Band structure and density of states plotted using FP-LAPW PBE-GGA scheme for (a) MgSiP$_2$ (b) MgSi$_{0.94}$Sn$_{0.06}$P$_2$. 
3.3 Optical Properties

The optical behaviour of the MgSiP$_2$ and MgSi$_{0.94}$Sn$_{0.06}$P$_2$ are explained with the help of dielectric tensor, absorption coefficient, reflectivity and refractivity spectra. Real and imaginary component of dielectric tensor, $\varepsilon(\omega)$, for both the studied compounds are presented in figure 3 (a-b). The threshold energy obtained from the imaginary component, $\varepsilon_2(\omega)$, are found to be 1.30 eV which corresponds to the electronic transition between valence band maxima and conduction band minima. Further, to determine the photovoltaic application of these compounds, energy dependent absorption spectra, $\alpha(\omega)$, are shown in figure 4. It is clear from the absorption spectra in figure 4, that both compounds show the considerable intensity in the range of 0-5 eV where the most part of sun radiations gets absorbs. Reflectivity, $R(\omega)$, and refraction, $\eta(\omega)$, spectra for pure and Sn doped MgSiP$_2$ are shown in figure 5 (a, b). Through the reflectivity spectra we obtained the value of reflectivity 25.4% and 26.5 % for MgSiP$_2$ and MgSi$_{0.94}$Sn$_{0.06}$P$_2$ respectively.

Figure 3. (a) Real and (b) imaginary component of dielectric tensor for MgSiP$_2$ and MgSi$_{0.94}$Sn$_{0.06}$P$_2$ using PBE functional

Figure 4. Energy dependent absorption spectra for the studied compounds.
Figure 5. Parallel and perpendicular component of (a) reflectivity and (b) refraction for MgSiP$_2$ and MgSi$_{0.94}$Sn$_{0.06}$P$_2$ using PBE functional.

And by the combining effect of absorption and reflectivity we obtained the refractivity value at η(0) are 3.02 and 3.08 for MgSiP$_2$ and MgSi$_{0.94}$Sn$_{0.06}$P$_2$ respectively. For all the optical spectra shown in figure 3-5, parallel and perpendicular component coincide on each other for the energy range 0-3 eV and 10-12 eV and this depicts the isotropic nature of these compounds in this energy range.

4. Conclusion
The structural, electrical and optoelectronic properties of chalcopyrite ternary compounds MgSiP$_2$ and MgSi$_{0.94}$Sn$_{0.06}$P$_2$ compounds are investigated using FP-LAPW method. Through the study of the calculated band structure it is concluded that by 6% doping of Sn at Si site in MgSiP$_2$ decreases the band gap and both compounds are proved to be semiconductor. The results computed in present paper reveal that these compounds can be utilized solar cell material.

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6. References
[1] Sahariya J et al. 2017 Macromolecular Symposia 376 1-6.
[2] Yoshikawa K et al. 2017 Macmillian Publisher 2 1–8.
[3] Jaffe J E and Zunger A 1984 Phys. Rev. 2.
[4] Boukabrine F et al. 2016 Optical Materials 54 200–206.
[5] Ambrazevi G et al. 1981 Phys. Stat. Sol. 85.
[6] Poplavnoi A S and Polygalov Y I 1970 766-770.
[7] Trykozko R T 1975 Mat. Res. Bull 10 489-492.
[8] Schilfgaarde V et al. 2009 34th IEEE Photovoltaic Specialists Conference (PVSC).
[9] Ibrahim M et al. 2018 Surf. Rev. Let. 25 1850108 1-8.
[10] Kocak B and Ciftci Y O 2016 9th International Conf of the Balkan Physical Union 220013 1-4.
[11] Kocak B and Ciftci Y O anjala 2017 Journal of Alloys and Compound.
[12] Blaha P et al. 2019 1-287.
[13] Kumar P et al. 2017 86 131–138.
[14] Sahariya J et al. 2017 Material Chemistry and Physics 199 257-264.
[15] Perdew J P et al. 1992 Phys. Rev. 45 13244-13249.