Optoelectronic analysis of silicon doped ZnGa$_2$S$_4$: A first principle study

A Gaur$^1$, K Khan$^2$, A Soni$^1$, A Dashora$^3$, J Sahariya$^4$ and U Ahuja$^5$

$^1$Department of Electrical Engineering, Manipal University Jaipur, Jaipur-303007, Rajasthan India
$^2$Department of Physics, Manipal University Jaipur, Jaipur-303007, Rajasthan India
$^3$Department of Physics, Faculty of Science, The M.S. University of Baroda, Vadodra-390002, India
$^4$Department of Physics, National Institute of Technology, Uttarakhand, Srinagar (Garhwal)-246174, India
$^5$Department of Electrical Engineering, NMIMS, Mukesh Patel School of Technology Management and Engineering, Mumbai-400056, Maharashtra, India

Abstract. This paper depicts a comprehensive investigation of Si doping on the wide bandgap ternary semiconductor ZnGa$_2$S$_4$. The first principles Wien2k code is utilized by adopting the Perdew-Burkhe-Ernzerhof Generalized Gradient Approximation (PBE-GGA) method. Band engineering is done in order to get a suitable value of bandgap in the region of solar spectrum. For this purpose the doping of Si and its effect on ZnGa$_2$S$_4$ is investigated. The bandgap computed by the doping of Si atom has turned out to be 2.14 eV which has decreased in comparison to the bulk compound 2.38 eV. Electronic and optical properties of this doped material are studied. The integrated absorption curve offers a value of 61.205. The imaginary part of the dielectric tensor offers peaks which help in understanding the inter-band transitions. Also the values of reflection and refractive index are calculated exploring the feature of optical properties in the wien2k package.

1. Introduction
ZnGa$_2$S$_4$ belongs to the wideband X$^{II}$Y$_2^{III}$ Z$_4^{VI}$ semiconducting compound with a band gap reported higher than 3 eV [1]. These compounds find their utility in optoelectronic applications like infrared materials, LED, solar applications etc [2]. Hahn et al. in their work reported ZnGa$_2$S$_4$ as the ternary sulfide which is known to be having a defect sphalerite structure [3]. In a work by Lowe-Ma, X-ray powder diffraction data for ZnGa$_2$S$_4$ has been recorded [4]. Peng et al. in their work prepared nanostructured ZnGa$_2$S$_4$ by a simple method of thiourea reduction [5]. Significant stability and activity was also reported in the photocatalytic degradation of Methylene Blue. By the method of quasi-equilibrium deposition and pulsed laser deposition, new thin films of ZnGa$_2$S$_4$ has been formed [6]. ZnX$_2$Y$_4$ has been explored in different growth conditions which help in determining its structural properties [7]. Polycrystalline powders’ optical absorption study for ZnGa$_2$S$_4$ and Co2+ doped ZnGa$_2$S$_4$ has been done [8]. Obtaining single crystal for Mn and Ni doped ZnGa$_2$S$_4$ has been presented in the work by Park et al. by the process of Chemical vapour deposition technique [9]. Under the polarized radiations the optical absorption spectra was analyzed in the work of Joshi et al.
Photocatalytic activity for the evolution of hydrogen in the compound ZnGa$_2$S$_4$ has been observed with a bandgap of 3.4 eV present in the work by Kaga and Kudo [11]. Thus, investigation of the effect of Si doping in the compound ZnGa$_2$S$_4$ has been done in the ongoing work. The optical, electronic and structural properties of the system have been studied in order to decide the application field of the system. Bandgap engineering has been a tool in deciding the type of optoelectronic field of the system. Choosing a suitable doping element plays an important role in the bandgap engineering process.

2. Computational Details

The structural, electronic and optical properties of the tetragonal structured XY$_2$Z$_4$ (X=Zn; Y=Ga; Z=S) with the doping of Si have been investigated in this work. The work followed the first principle calculation basis with the utilization of Wien2k code. The exchange correlational functional used in this work is the Perdew-Burkhe-Ernzerhof (PBE) along with the Generalized Gradient Approximation (GGA). The entire self-consistent calculations termed as SCF were attained properly in the brillouin zone containing a k-point mesh of 3 x 3 x 1 grid. The cut-off energy was taken to be $10^{-6}$ Ry.

3. Results and Discussion

3.1 Structural Analysis

The initial crystal structure of the ternary compound used in this work is tetragonal in nature with the space group as 82 (I-4) [12]. This crystal structure has input lattice parameters in the following manner: a=b=5.26 Å and c=10.40Å. With the RMT values of Zn, Ga and S as 2.27 a.u., 2.26 a.u. and 1.86 a.u. respectively. The supercell of the compound with the dimensions of 2 x 2 x 2 is created along with the formation of 16 Zn, 32 Ga and 64 S atoms. The system after doping gets converted into 81-P4 space group. The provision of creating a supercell is undertaken in order to add an impurity atom in the already existing crystal structure. This in turn helps in altering the properties of a system for the beneficial use of it. Here 4 atoms of Ga have been replaced with Si which is acting as the doping element. Thus, at Ga site Si is located with its RMT value as 2.07 a.u. The crystal structure along with its coordinate axis is located in figure 1(a). The atoms denoting different colors are also depicted in the figure to differentiate from each other based on their specifications and brillouin zone of the system is given in figure 1(b).

![Figure 1](image.png)
3.2 Electronic Analysis

In this section of the work the Band structure and the DOS of the system is studied in detail. The energy gap between the valence and the conduction band is observed taking in account the maxima of valence band and minima of the conduction band. The analysis of band structure depicts that due to the doping of Si in ZnGa$_{2}$S$_{4}$ there is a shift in the fermi energy observed towards the conduction band. This means that the shifting towards the conduction band took place as being n-type semiconductor.

In this case the extrinsic semiconductor with donors as the doping element gives extra electrons to the system resulting in a shift towards Conduction band. The band structure plot is obtained by the use of k points - Gm, Z, X, M, A, Gm on the x axis and Energy values on the y-axis as per the respective supercell structure. The band structure of ZnGa$_{2-x}$Si$_{x}$S$_{4}$ is depicted in figure 2(a). The density of states along with the partial density of states is plotted in order to explain the total and partial effects of the individual atoms and their s, p and d hybridization. In our work, the major role in Zn atoms is played by the 4s, in Ga by 4p, in Si by 3p and in S by 3pis observed. The DOS and PDOS plot showing all these contributions is shown in figure 2 (b). The bandgap of 12.5% Si doped ZnGa$_{2}$S$_{4}$ has been reduced in comparison to the bulk compound [13]. The present bandgap recorded is 2.14 eV.

![Figure 2. (a) Band structure of the doped system; (b) DOS of the doped system](image)

3.3 Optical Analysis

Using the PBE-GGA functional, optical properties of ZnGa$_{1.875}$Si$_{0.125}$S$_{4}$ are investigated. The properties analyzed are absorption, reflection, refraction and dielectric tensor. Each with their own significance, establish a base for the study of optical properties which helps in concluding the utilization of compound in any of the optoelectronic application. The dielectric function is based on the Ehrenreich and Cohen’s equation i.e. $\varepsilon=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$ [14] where $\varepsilon_1(\omega)$ depicts the real part and $\varepsilon_2(\omega)$ depicts the imaginary part. The value of static dielectric constant of the real part $\varepsilon_1(0)$ is calculated to be 6.14.

The major peaks in the plot of $\varepsilon_2(\omega)$ lying in the visible spectrum can be observed at 1.16eV, 2.41eV and 3.86eV. The real and imaginary components of dielectric function has been shown in figure 3 (a).
and figure 3(b) respectively. From the dielectric components $\varepsilon_1(\omega)$ & $\varepsilon_2(\omega)$ the optical constants - absorption coefficient [15], reflectivity and refractive index are obtained. The system’s optical response is measured through the absorption coefficient. The integrated absorption coefficient (IAC) of the system is calculated to be 61.205. The absorption curve of the system is shown in figure 4(a). The static reflection constant $R(0)$ is calculated to be 0.18. Low value of reflectivity for a compound tends to be a good option for optoelectronic applications [16]. The reflectance spectra of the doped system is plotted in figure 4(b). The static refractive index constant $(0)$ is calculated to be 2.48. The refractive index curve of the doped system is plotted in figure 4(c).

![Figure 3. Dielectric tensor (a) real component and (b) imaginary component of ZnGa$_{1.875}$Si$_{0.125}$S$_4$](image)

![Figure 4(a) Absorption curve of ZnGa$_{1.875}$Si$_{0.125}$S$_4$; (b) Reflectivity spectra of ZnGa$_{1.875}$Si$_{0.125}$S$_4$; (c) Refractive index spectra of ZnGa$_{1.875}$Si$_{0.125}$S$_4$](image)

4. Conclusion

We have evaluated the properties in terms of structural, electronic and optical features of the Si doped ternary compound ZnGa$_2$S$_4$. In respect to the exchange correlation functional PBE-GGA has been used. There has been a decrement in bandgap observed which is valued 2.14 eV. The electronic structure of the system is analyzed by the band structure and DOS plots. The Integrated absorption coefficient (IAC) is recorded to be along with reflectivity and refractive index of the system. The absorption curve depicts an overlapping between its parallel and perpendicular components thus indicating isotropic nature of the compound. Low value of reflectivity means that the system can be
used as an optoelectronic device. In this manner we can say that these optical parameters decide the optoelectronic application field of the system.

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