Theoretical analysis of Sn-doped ZnS for optoelectronic applications

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Abstract. The wide band gap semiconductors like ZnS have gained tremendous response in the optoelectronic applications claiming their significant role in device operability at varied compositions and temperature. We have performed a detailed study of pure and Sn doped ZnS using Perdew-Burkhe-Ernzerhof (PBE) exchange correlation as embodied in Wien2k code. The doping of 6.25% Sn at Zn site, in ZnS has reduced the band gap (Eₐ) to 1.70 eV from 2.15 eV (Eₐ for bulk ZnS) thus making it more suitable for the applications of solar cell. Various properties such as band structure, density of states and integrated absorption coefficient depicting their electronic and optical nature are examined. The spectra of absorption curve states the possibility of material to be solar if it lies in the visible spectra range of 0-5 eV.

1. Introduction

The varied technological significance of wide band gap semiconductors has led to the cause of its research and study in the field of material science. The device operability feature of wide band semiconductor like ZnS [1], at high powder level and high temperature owns a unique position in the optoelectronic application field. Also the demand for materials which are optically active in blue-green spectral presents the need for such compounds [2]. The IIB-VIA family involves CdS, ZnS and the variants of S like Se and Te of group VIA. Amongst these, ZnS/ZnSe/ZnTe are the one which exists in the form of Zinc blend at room pressure. The three dimensional ZnS system crystallize in Wurtzite (WZ) and Zinc blend (ZB) at high and low temperatures/ambient temperatures, respectively [3]. Due to the wide range of applications such as short wavelength light emitting diodes (LEDs), the 3D structure of ZnS has been studied extensively. The stable wurtzite structure of ZnS exists in hexagonal form at high temperature. This hexagonal structure of ZnS offers a bandgap of 3.77 eV and its cubic structure offers a bandgap of 3.72 eV [4].

The doping of the different elements in ZnS provides a flexible range of bandgap to be utilized in different applications accordingly. Vaya et al. [5] has observed the effect of different transition metal
(TM) on the photo-catalytic bleaching of Y and the effect of Cr doping is noticeably more in comparison with other transition metal ions. The effect of TM on the pristine monolayer of ZnS has been reported by Chaurasiya and Dixit [6]. The authors have discussed the effect of doping in term of the conversion of the compound from nonmagnetic system to a magnetic system. Jeyakumari et al. [7] have discussed the doping effect of Ni, Co and some rare earth TMs on ZnS with its stability in applications of electroluminescent devices. The synthesis of Cu doped ZnS thin films and effect of the film thickness on the structural, electrical and optical properties has been observed by Goktas et al. [8]. Nagamani et al. [9] have synthesized the ZnS system with Al doping at different concentrations using the chemical bath deposition technique. Synthesis of ZnS doped with Sn is prepared by several methods like chemical bath deposition, Sol-gel method and powdered X-ray Diffraction etc. delivering different characterizations like structural, morphological and microstructural

3.1 Electronic Structural Analysis

To explain the system’s electronic structure appropriately we adopt the Density of states representation which is helpful in determining the number of states present in it. It is also used to determine the energy distributions of carriers and their concentration within a semiconductor [20].
The respective density of states around the bandgap and the band structure for both bulk and doped ZnS is represented in Figure 2 (a), 2 (b), 2 (c) and 2 (d).

The total density of states and the atomic projected density of states depict the combined effect of s, p and d orbitals in the configuration of the compound. Based on the DOS spectra and similar features help in deciding the position of upper valence band lying just underneath the fermi energy ($E_F = 0$). The major contribution is due to the 4s and 3p in case of Zn and S with the additional contribution of 5p in case of Sn. The bandstructure and DOS depicts that there has been a good agreement with its PBE calculation.

### 3.2 Optical Analysis

The optical parameters like real part dielectric function, imaginary part dielectric function, absorption, reflection and refraction. The absorption coefficient of pure ZnS and Sn doped ZnS is explained through the process of area under the curve analysis. Tauc’s law is used to define the optical bandgap based on the absorption coefficient and this study is defined on the basis of interband transitions near the bandgap.
Fig. 2. DOS representation of (a) ZnS and (c) Zn_{0.9375}Sn_{0.0625}S; band structure representation (b) ZnS and (d) Zn_{0.9375}Sn_{0.0625}S.

The value of IAC (Integrated absorption coefficient) is reported to be 50.12 for bulk ZnS and 61.77 for Zn_{0.9375}Sn_{0.0625}S by the insertion of doping element. Thus, the IAC has increased with doping and is represented in Fig. 3. The imaginary component offers the explanation of the transition peaks which in turn depicts the electronic transitions from valence to conduction band. The dielectric tensor’s real and imaginary part are represented in Fig. 4 (a) and 4 (b) respectively. The doping degree has an effect on framing the reflectivity parameter. The value of R (0) has been observed to increase from 0.169 to 0.246 and the reflectivity of both the compounds is shown in Fig. 5 (a). Fig. 5(b) shows refraction parameter.
giving an idea about the system’s response with respect to electromagnetic wave propagation. The value of $\eta(0)$ has seemed to increase with insertion of doping from 2.42 to 3.00.

Fig. 3. Absorption Spectra of ZnS and Zn$_{0.9375}$Sn$_{0.0625}$S using PBE functional

Fig. 4. Dielectric tensor (a) real component and (b) imaginary component of ZnS and Zn$_{0.9375}$Sn$_{0.0625}$S
4. Conclusion

The analytical data collected on the basis of structural, electronic and optical properties concludes the effect of Sn doping on ZnS. The first principle calculation is carried out using the WIEN2k package which is based on the FP-LAPW method. The exchange correlation method used is PBE-GGA providing bandgap of 2.14 eV for ZnS and the addition of impurity of Sn in ZnS yielded 1.69 eV. The calculated result depicts that the doping in ZnS offers a bandgap which lies in the optical range, thus being suitable for optoelectronic and solar applications. The dielectric tensor calculated considers the imaginary part through which the electronic transition is depicted from the valence band to conduction band. The optical constants namely: Absorption coefficient, reflection and refraction are also calculated.

5. Acknowledgement

We would like to thank Prof. P. Blaha for his commendable efforts in creating the Wien2k code making it possible for us to carry out efficient theoretical study. We would also like to express our gratitude towards DST-SERB, New Delhi under the project vide grant number EMR/2017/005534 along with Manipal University Jaipur to provide a platform and all the necessary facilities.

6. References

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