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The effect of In, Cu Co-doping on the electronic structure and optical properties of ZnS: First principal calculations

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Abstract

The effects of In and Cu co-doping ZnS on the structural, electronic and optical properties are investigated by using the full-potential linearized augmented plane wave method (FP-LAPW) with generalized gradient approximation plus Becke–Johnson potential as exchange-correlation potential, in a cubic structure. The calculated lattice parameter of Un-doped ZnS was in a good argument with the other theoretical calculations, and it was found to be increased by In, Cu co-doping. The electronic band structures are calculated and represented. The un-doped ZnS shows a semiconductor character with a direct band gap. Hence, it saves the semiconductor character with a direct band gap with some change in its value. It decreases by co-doping with In and Cu. Moreover, the real and imaginary part of the dielectric function as and the absorption coefficient attains its maximum in the near UV-Visible region. This theoretical study intensifies the understanding of the novel performances of In, Cu co-doped ZnS for optoelectronic applications.

Keywords: ZnS; doped, co-doped, FP-LAPW, GGA+mBJ

1. Introduction

Due to its potential applications in science and industry, semiconductor nanomaterials have received an immense amount of attention from researchers in recent years. Because of its chemical and physical characteristics, the II-VI group of semiconductors is widely used in a wide range of applications [1-2]. Zinc sulfide (ZnS) is widely recognized as a highly versatile and technologically significant II-VI compound smiconductor. Its large exciton binding energy (40 meV), abundance in nature, and lack of toxicity make it suitable for short-wavelength optoelectronic applications. As a result, it is frequently doped with a variety of dopants [3–7]. The potential use of zinc sulfide (ZnS) in many optoelectronic applications, such as photovoltaic cells, light-emitting diodes, and sensors, has drawn a lot of attention [8-15]. To create new materials for new applications in electronic, spintronics and optoelectronics, doping and co-doping with deferent ions is a useful technique for achieving tunable electronic, magnetic and optical properties. Zinc Sulfur (ZnS) is seen as a potentially useful host semi-conductor for a massive game of ions. ZnS was doped with various ions such as: Manganese (Mn) [16], Vanadium (V) [17] Nickel [18], cobalt [19], Iron (Fe) [20] and others [21-24] and co-doping with deferent ions [25-28]

In this present work, the first time we investigated structural and optoelectronic properties of undoped and In, Cu co-doped ZnS semiconductor using the full potential linear augmented plane wave FP-LAPW [29] method within the density functional theory (DFT)[30]. The electronic exchange-correlation energy is described by generalized gradient approximation. To our knowledge, no comprehensive literature has been provided regarding the structural and optoelectronic properties of In, Cu co-doped ZnS compounds

2. Method

As part of the density functional theory (DFT) [30], implemented in the Wien2k package [31], the full-potential linearized augmented plane wave (FP-LAPW) approach [29] is used for the current computations. The exchange and correlation effects are treated by the Perdew– Burke–Ernzerhof generalized gradient approximation (GGA) [31]. The GGA +mBJ [32], is applied to optimize the corresponding potential for calculating the electronic and optical properties.

We take a supercell of 8 atoms (Fig. 1b) The RMT (muffin-tin radii) are taken to be 2.54, 2.35, 2.56 and 1.8 atomic unit (a.u.) for Zn, Cu, In and S, respectively, where RMT is the minimum radius of the muffin-tin. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-5}Ryd. The integrals over the

Brillouin zone (BZ) are performed up to **136 k-points** (grid of **10 *10 *10)** meshes

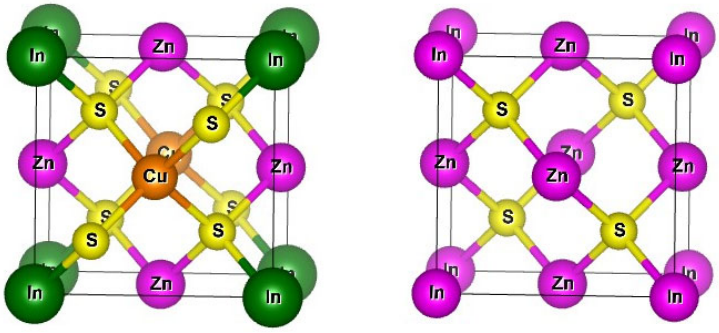

Fig.1. The crystalline structure of Un-doped ZnS and (In, Cu) co-doped ZnS.

3. Results and discussion

3.1. Structural properties

The lattice parameters are obtained by the calculation of the total energy as a function of the volume using Murnaghan's equation of states (EOS) [55]. The structural parameters are classified in Table1 In the case of un-doped ZnS, the lattice parameter is 5.44 Å. It is found to be very close with other calculations [2, 42]. However, the lattice parameter of ZnS is Increased by co-doping with In and Cu. This change in the values of the lattice parameters is due to the dimension of ionic radius of the Cu^{2+} (0.73Å) [1] and In^{2+} (0.80Å) [34] which are larger comparing to the ionic radius Zn^{2+}(0.74 Å) [26].

Table 1. The calculated equilibrium constant a (A°), bulk modulus B (GPa), first order pressure derivative of the bulk modulus B0 with others experimental and theoretical works

Compound		a(Ang)	B(GPa)	B'
Un-doped ZnS	Our work	5.45	76.04	4.95
	Other works	5.42[12]	89.22[12]	5.1[12]
(In, Cu) co-doped ZnS	Our work	5.56	66.25	4.95
	Other works	-	-	-

3.2.Electronic properties

Moreover, to understand the effect of In, Cu co-doping on the electronic properties of ZnS, the electronic band structures of Un-doped ZnS and (In, Cu) co-doped ZnS are calculated by the GGA and GGA+mBJ approximations.

These calculations indicate that the un-doped ZnS present a direct bandgap at $(\Gamma - \Gamma)$ point of the Brillouin zone it is seen that the minimum of the conduction band (CB) is situated at (Γ) point of the Brillouin zone and the maximum of the valence band (VB) is situated at (Γ) point. In the case of (In, Cu) co-doped ZnS. it is seen that the minimum of the conduction band (CB) is situated at (Σ) point of the Brillouin zone and the maximum of the valence band (VB) is situated at (Σ) point and this means that this system has also a direct bandgap at (Σ -Σ) point of the Brillouin zone. While, we noted a large decrease in its value from 1.51eV to 0.654 eV by GGA and from 3.56 eV to 0.654 eV by GGA . The change in the value and the nature of band gap energy is mainly due to the *sp–d* exchange interactions between the band electrons and the localized *d* electrons of the Cu, In ions [12].

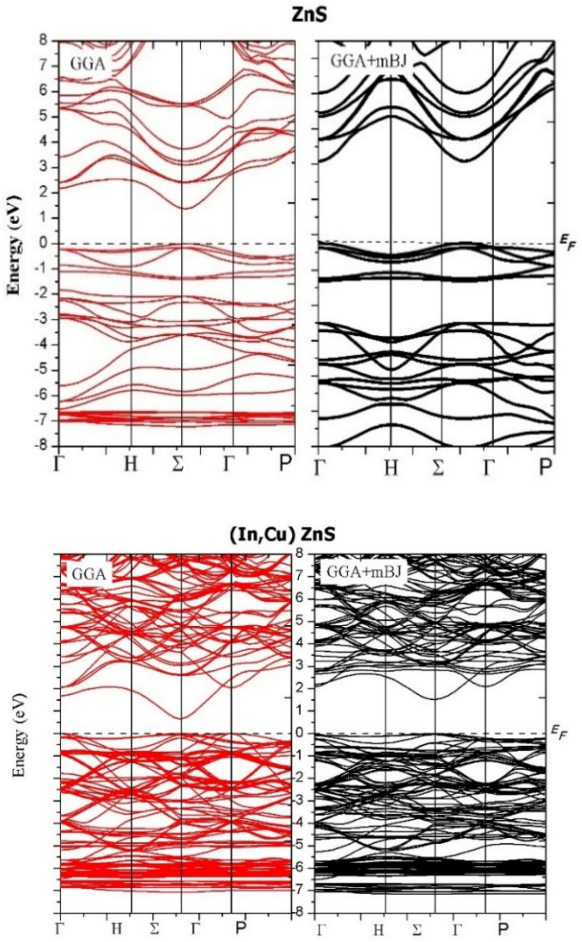

Fig.2. The band structures of Un-doped ZnS and (In, Cu) co-doped ZnS by GGA and GGA+mBJ approximation.

Table 2. The energy band gap of Un-doped ZnS and (In, Cu) co-doped ZnS by GGA and GGA+mBJ in comparison with others experimental ant theoretical works

Compound		E_g(eV)	
		GGA	GGA+mBJ
Un-doped ZnS	Our work	1.51	3.56
	Other works	[12]	[12]
(In, Cu) co-doped ZnS	Our work	0.654	
	Other works	-	-

3.3.Optical properties

The study of the optical properties of condensed matter has proven to be a important tool to understand the electronic properties of material. All the calculated optical parameters are getting from the dielectric function$\varepsilon(\omega)$. It is given by [35]:

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

ε_1 and $\varepsilon_2$are the real and imaginary part of the dielectric function and is the angular frequency. The real and imaginary parts of the dielectric function and the absorption coefficient as a function of the energy of Un-doped ZnS and (In, Cu) co-doped ZnS by GGA and GGA+mBJ approximation are plotted in **Fig.4 to Fig.6**.

Fig.4. presents the real part of the dielectric function. We can extract from the ε_1 curves the calculated static dielectric coefficient $\varepsilon_1(0)$. For un-doped ZnS, it is 3.5 and 3.65 by GGA and GGA+mBJ approximation. For (In, Cu) co-doped ZnS, we noted that $\varepsilon_1(0)$ increase in comparison to the un-doped ZnS and it is 4.70 and 6.5 by GGA and GGA+mBJ approximation , respectively

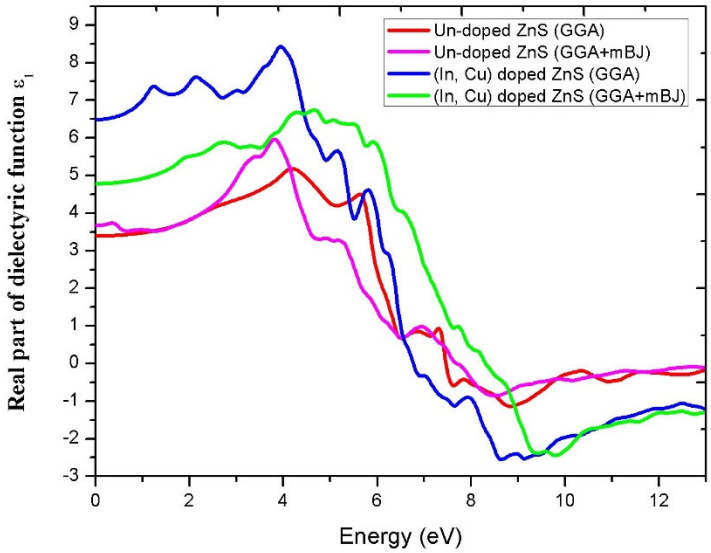

Fig.4. The real parts of dielectric function ε_1 as function of energy of Un-doped ZnS and (In, Cu) co-doped ZnS by GGA and GGA+mBJ approximation.

The imaginary part of dielectric function ε_2 as function of energy of Un-doped ZnS and (In, Cu) co-doped ZnS by GGA and GGA+mBJ approximation are presented in **Fig.6.** The most important value in these curves is the first transition which is considered by the band gap. The corresponding values of un-doped ZnS are 1.98 eV and 3 .00 eV by GGA and GGA+mBJ and 0.65 eV and 1.5 eV for (In, Cu) co-doped ZnS by GGA and GGA+mBJ approximation.We can see that all systems have a semiconducting character

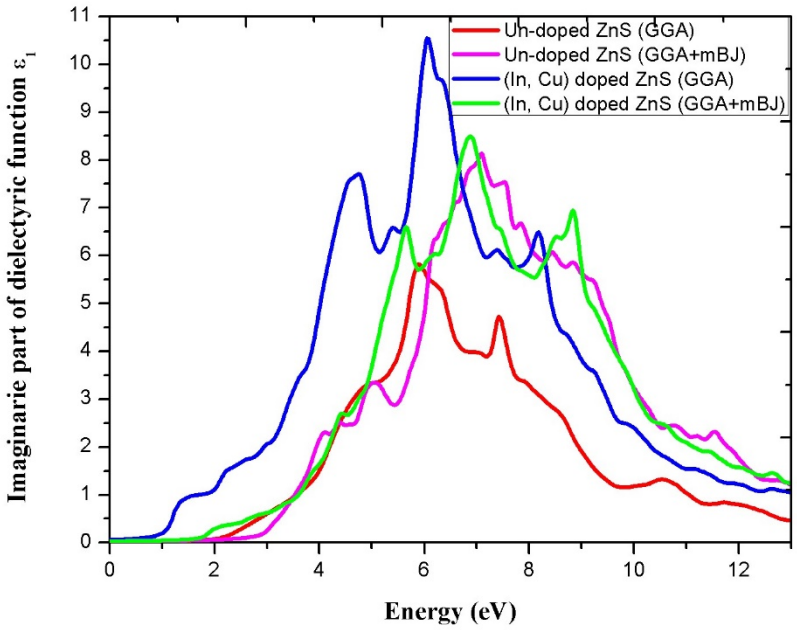

Fig.5. The imaginary parts of dielectric function $\varepsilon_1$as function of energy of Un-doped ZnS and (In, Cu) co-doped ZnS by GGA and GGA+mBJ approximation.

In Fig.6, we plotted the absorption coefficient as function of wave length for both systems by GGA and GGA+mBJ. the absorption coefficient is related to the imaginary part of dielectric function by:

$$\alpha(\omega) = \frac{1}{n(\omega)}\varepsilon_2(\omega)$$

We had noted that the two systems Un-doped ZnS and (In, Cu) co-doped have strong absorption in the range from 6 eV to 10 eV, corresponding to the UV region. Hence, the intensity of the absorption coefficient is decreased by co-doping with In and Cu ions.

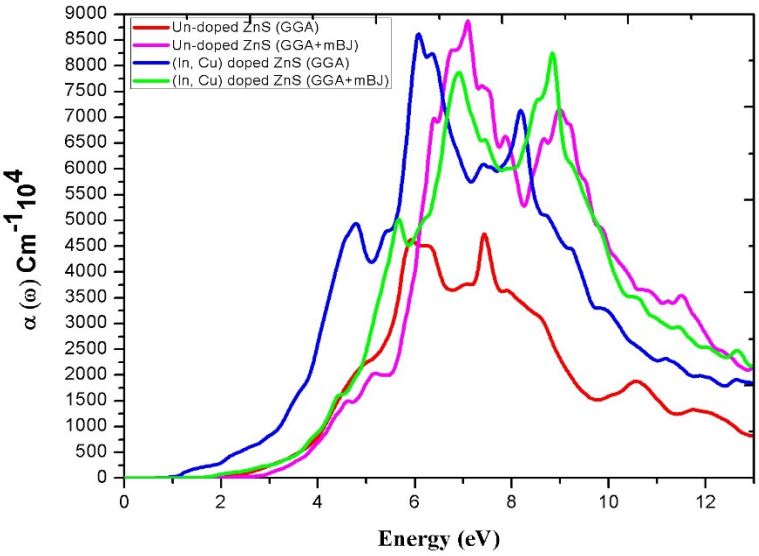

Fig.6. The absorption coefficient $\alpha(\omega)$as function of energy of Un-doped ZnS and (In, Cu) co-doped ZnS by GGA and GGA+mBJ approximation

4. Conclusion

In this study, we have investigated the effects of In and Cu co-doping ZnS on the structural, electronic and optical properties are investigated by using the full-potential linearized augmented plane wave method (FP-LAPW) with generalized gradient approximation plus Becke–Johnson potential as exchange-correlation potential, in a cubic structure. The calculated lattice parameter of Un-doped ZnS was in a good argument with the other theoretical calculation, and it was found to be increased by In, Cu co-doping. The electronic band structures are calculated and represented. The un-doped ZnS shows a semiconductor character with a direct band gap. Hence, it saves the semiconductor character with a direct band gap with some change in its value. It decreases by co-doping with In and Cu. Moreover, the real and imaginary part of the dielectric function as and the absorption coefficient attains its maximum in the near UV-Visible region. This theoretical study intensifies the understanding of the novel performances of In, Cu co-doped ZnS.

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