Optical Properties of ZnS and Effect of Doping with Transition Elements

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Abstract

By the help of density functional theory for a Cu doped ZnS compound the charge density, Fermi surface and electronic structure have been examined. We have used (FP-LAPW) method, to deal with interchange relationship potential for solving of kohn-sham equations. We apply generalized gradient approximation (GGA), local density approximation (LDA) and Engel-Vosko GGA (EVGGA). Cu doped ZnS compound confirms that nature of material is metallic and Fermi energy (EF) is obtained by the overlapping of Cu-p and Zn-d state. At Fermi energy (EF) calculated density of states is 51.932, 18.655 and 13.235 states/ev, and low-temperature electronic specific heat co-efficient ($\gamma$) is found to be 9.008mJ/mol-K\textsuperscript{2} for GGA, 3.236mJ/mol-K\textsuperscript{2} for LDA, and it was 2.295mJ/mol-K\textsuperscript{2} for EVGGA respectively. The thermal properties and optical constant were also discussed and calculated.

Keywords

ZnS, Charge Density, Fermi Surface, Electronic Structure.

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Introduction

One of the first discovered semi-conductors is zinc-sulphide ZnS [1] and it has generally shown strange ground laying properties versatility and a promise for novel distinct applications, which includes flat panel display, electroluminescence, light emitting diode (LED), bio devices, sensor, laser, infrared windows, etc.

Our concentration of this chapter is the formation of Nano particles of zinc sulphide in organic phase. To study the structure of ZnS nanoparticle we use XRD characterization and TEM measurement. To study the optical properties we used UV-vis absorption spectrum, FTIR and photoluminescence. To evaluate the size of synthesized nanoparticle we study Malvern’s particle size distribution. On doping phase transferred ZnS nanoparticle with various level of yttrium and manganese we analyzed various characteristics.

The bang gap of ZnS is large of about 3.77eV of Wurtzite (WZ) hexagonal form and 3.72eV (for cubic zinc blende) respectively and consequently it is more enough for visible-blind ultraviolet (UV) light-based devices for example photo detector/sensors. The ranges of energy level is describes by band structure of solid which tells that whether an electron is “allowed” or “forbidden” and it is useful to find optical and electronic properties of material.

In last ten years optical properties of nanocrystalline semiconductor have been study. [2-5]. The behavior of these material is different from bulk semiconductor. On decreasing the size of particle band composition of semiconductor also change. The band gap increase and at boundary of band divides into (different) level of energy called Quantum-confinement effect [7]. Due to quantum confinement of charge carrier present in particle the electronic and optical properties changes greatly [8, 9]. ZnS, has get much devotion due to its extensive band gap and has wide application in organic LEDs, UV light emitting diodes, flat panel display, efficient phosphors and photovoltaic devices etc [10].

The process of photoluminescence of ZnS when doped with further metal ions is not simple. The more accessible carrier for photoluminescence that have high surface to volume ratio when size of particle is small. [11].

The optical and physical properties of nanoparticles are very important for the surface states. Trapped and excitonic luminescence emission are observed from nanoparticles of semiconductor [12]. The trapped emission is stokes shifted and broad while the excitonic emission is located close to the absorption border of the particle and sharp. For ZnS nanoparticles only trapped luminescence that would arise from surface states is observed. [11].

For research in semiconductor nanocrystals doped ZnS nanoparticles transition metal ions are most popular. High luminescence yield for doped nanocrystals of semiconductor [12]. The doped semiconductor nanocrystal have a broad variety of application in sensors, spectacles and lasers. [13]. Bhargava et al [12] propose that for new events a well-built hybridization of d states of Mn2+ impurity and s-p states of ZnS host must occur as we decrease the size of particle. The energy transfer at a very fast rate between ZnS host and Mn2+ as a result of hybridization which yield higher quantum efficiency. In many luminescence materials Mn2+ ions are used as dopant, has a d5 configuration. Due to changes in crystal field strength with host Mn2+ ions shows wide emission peak. For a 4T1-6A1 transitions the color of emission changes from green to deep red.
Bulk ZnS in different electroluminescence Mn is commonly used. The transfer of electron and hole pairs into level of Mn2+ results in yellow-orange emission for 4T1-6A1 transitions.

**Methodology**

The compound ZnS crystal structure is shown in fig. 3.1. This compound shows monoclinic structure and a space group of P21/n. In Cu doped ZnS compound the lattice constant used are, 

\[
a=5.510(6) \, \text{Å}, \quad b=5.725(8) \, \text{Å}, \quad c=7.948(6) \, \text{Å}, \quad \beta=90.410(8) \quad [69].
\]

The experimental and enhanced atomic position [69] are given in Table 1. These values exactly match with our calculation. The calculations were done by using Wein2K [72] that is fully based on (FP-LAPW) method. To deal with exchange correlation potential for solving of Kohn-sham equations we use GGA, LDA and EVGGA approximation [73–75]. The value used for sphere radii are 1.88 au for Cu, 1.68 au for Zn, and 1.49 au for S, respectively. The well linked

![Crystal structure for ZnS compound](image)

3.1. Crystal structure for ZnS compound

Solutions find out with RMT \( K_{\text{max}} = 7.0 \) (where \( K_{\text{max}} \) is plane wave cut-off and RMT is smallest of the muffin-tin radii) and tested \( k \) point sampling. For calculating the optical properties which wants a heavy network of constantly scattered \( k \)-points, by the help of tetrahedron technique, with 1000\( k \)-points in the Brillouin zone integration was presented in the left part of the Brillouin zone without expanding. For optical comeback of medium at all photon energies we use dielectric function. In metals, for dielectric function there exist two contribution that is from intra band transition and inter band transition. The intra band as well as indirect interband transition require phonon for transfer of the momentum. The interband transition can be further divided into indirect and direct transition. The calculated direct interband connection to imaginary part of dielectric function is calculated by totaling transitions from occupied to unoccupied states (with \( k \) fixed).
above the Brillion region, satisfied free chance for the transition with suitable matrix element. Now imaginary part of dielectric function $\varepsilon(\omega)$ is written as 

$$
\varepsilon^{ij}_2(\omega) = \frac{4\pi^2e^2}{V m^2 \omega^2} \sum_{kn\sigma} \langle kn\sigma|p_i|kn'\sigma\rangle \langle kn'\sigma|p_j|kn\sigma\rangle \times f_{kn}(1 - f_{kn'})\sigma(E_{kn'} - E_{kn} - \hbar\omega)
$$

Here $m$ is the mass, $e$ is electron charge, $V$ is volume of unit cell, $\omega$ is frequency of incoming electromagnetic radiation, and $(px,py,pz)=p$ is momentum operator $knS$ is crystal wave function, having eigen value $E_{kn}$ with spin $\sigma$ and crystal momentum $k$. At last transitions from engaged to unoccupied states are count that is confirmed by fermi distribution function $f_{kn}$, and the term $\sigma(E_{kn'} - E_{kn} - \hbar\omega)$ represents situation for conservation of total energy. By using the relation, which is Kramer’s Kroning dispersion, the real part $\varepsilon_1(\omega)$ is obtained from imaginary part $\varepsilon_2(\omega)$ [80].

### 3.3 Results and discussion

#### 3.3.1 Electronic Structure

The Cu doped ZnS compound shows metallic nature because valence as well as conduction bands cross at Fermi energy and its electronic band structure is shown in fig.3.2. To make a meaningful contrast no experimental data neither complete work nor on band arrangement of this compound first principles calculations is appear in literature.

![Fig.3.2 Band structure of Cu doped ZnS compound](image)

At Fermi surface to understand nature of electronic state is important. At Fermi surface the DOS is obtained by overlapping of Cu-p state and Zn-d state, with a DOS which is at EF-N(EF) of about 18.655 for LDA, 51.932 GGA, and 13.235 for EVGGA states/eV. To draw attention to the overlap of bands around Fermi energy we expanded the band structure near Fermi energy. (see Fig3. 2).
3.3 (a) T

DOS
3.3 (b) PDOS for Cu

![Graph of PDOS for Cu](image)

Fig. 3.3 (c) PDOS for Zn

![Graph of PDOS for Zn](image)

Fig. 3.3 (d) PDOS for S

![Graph of PDOS for S](image)
In the supposition of free electron model for a Cu doped ZnS compound the obtained data permitted us to approximate the Sommer field constant \( \gamma \).

\[
\gamma = \frac{1}{3} \pi^2 N(E_F) k_B^2 \quad (3.3)
\]

Here \( k_B \) represents Boltzmann constant and \( N(E_F) \) is the DOS at Fermi energy. Fermi energy and the density of conditions allows us to compute uncovered electronic specific heat co-efficient, that is 9.008 mJ/mol-K2 for GGA, 3.236 mJ/mol-K2 for LDA and 2.295 mJ/mol-K2 for EVGGA respectively. For a Cu doped ZnS compound the partial density of situations as well as total density of states (TDOS) is plotted in Fig. 3.3. At lower energies i.e. -5.0 eV to -3.0 eV the Zn-s/p/d and Cu-s and S-s/p conditions are more important than the Cu-s and S-s/p states as shown by density of states. By overlapping of Zn-d and Cu-p state Fermi level is obtained. The Zn-s/p/d states are more significant than other atoms state at lower conduction band energies that is to say from 1.0 eV to 3.0 eV. At conduction band and valence band there be present a strong hybridization between Zn-s/p/d and Cu-s/p states.

### 3.3.2. Optical properties

For a Cu doped ZnS compound the real and imaginary part of dielectric function were calculated as a role of photon energy ranges from 0.0 eV to 14.0 eV as shown in fig:6. In a Cu doped ZnS compound the dielectric function \( \varepsilon = \varepsilon_1 + i \varepsilon_2 \) spectra will help in counting optical transitions. The imaginary part \( \varepsilon_2 \) of dielectric function is calculated from direct interband transitions. Now imaginary part of dielectric function there is a noticeable structure sketched by peaks from 4.0 eV to 8.0 eV as shown in fig. 6. At 1.0 eV the structure is related by direct interband transitions. From occupied Zn-d band to S-s state transitions originates which results in band structure. At less than 1.0 eV the real part of dielectric function is maximum and then decreases to region below 0.0 eV which shows reflectivity i.e. above 0.0 eV transmission of light is shown which show that nature of material is metallic. At 0.0 eV to 6.0 eV dielectric function’ real part has noticeable peaks and then sharply decreases and at about 9.0 eV passes through zero. From deeper valence bands to unoccupied band above Fermi level there is possibly strong interband transitions. The spectrum of reflectivity is displayed in Fig. 3.4. It has been observed that in this compound reflectivity is less than 50%. This shows that for visible region material is not good reflector. The spectra show zero reflectance at lower energies i.e. 2.0 eV to 5.0 eV and increase in energy a constant increase in reflectivity of compound and at high energies after increase in spectra at this point again decrease in spectra.
Fig. 3. 4 (a) imaginary and (b) real part of dielectric function.
In Figure 3.5 the spectra for the absorption effect $I(\omega)$ are displayed. The absorption coefficient catalogues decay of light intensity spreading in unit space within average. The calculated $I(\omega)$ for three incident radioactivity polarizations are showed in Fig.3.5. It is apparent, that the $I(\omega)$ spectra exhibit a clear absorption at high energy.

In Fig. 3.6 the computed electron energy-loss function $L(\omega)$ spectrum is exposed. $L(\omega)$, is an important representative for classifying the energy harm of a speedy electron short-lived during a material. The $L(\omega)$ spectra exhibit a wide peak at 11.0 to 14.0 eV for the investigated compound, relating to the plasma frequency $\omega_p$. This peak relay to the energy where $n(\omega)$ and $K(\omega)$ curves fractuals and with the zero passage of $\varepsilon_1(\omega)$.

The refractive index (see Fig. 3.7b), the refractive index, complex dielectric function is plotted in between 0.0 to 14.0 eV (arb. unit), at 0.0 eV the spectra shows the maximum value, and with increase in photon energy a decrease occur and at high energy graph almost vanish. The material loose transparency because the material absorbs high energy photon. At 8.0 eV, refractive index reduces to unity which specify that phase velocity of light is greater than velocity of light that is a contradiction to relativity. It looks like that signal must be transmit as a wave packet instead of monochromatic wave. A wave packet will propagate by a group velocity $v_g = \frac{d\omega}{dk}$, instead of phase velocity, $v = \frac{\omega}{k} = \frac{c}{n}$ in a dispersive medium. the relationship among $v_g$ and $v$ is given below

$$v_g = v \left(1 - \frac{k}{n} \frac{dn}{dk}\right)$$

![Fig.3.5. Absorption](image-url)
Fig. 3.6. Energy loss function

Reflectivity function and energy loss function are plotted against energy in eV. The plots show the variation of energy loss and reflectivity with energy across different energy levels.

Energy loss function 

Reflectivity function
Conclusion

In a survey of optoelectronic study of Cu doped ZnS compound that is based on full potential
calculation within frame of DFT displays that the nature of material is metallic. By the overlapping
of Cu-p and Zn-d state the Fermi level is accessed with DOS at Fermi energy $E_F$, $N(E_F)$, of 51.932
for GGA, 8.655 for LDA along with 13.235 sates/eV for EVGGA correspondingly. A low-
temperature electronic specific heat coefficient ($\gamma$) is chosen 9.008mJ/mol-K2 for GGA,
3.236mJ/mol-K2 for LDA and 2.295mJ/mol-K2 for EVGGA respectively. The real as well as
imaginary parts of dielectric functions were calculated. In between three components of real as
well as imaginary parts of dielectric functions a significant anisotropy was founded. We discover
that for a ZnS compound there occurs a loud rise below 1.0eV for real as well as imaginary parts
of dielectric functions.

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