CHAPTER V

5.1. Introduction:

Nanoparticles are effectively a bridge between bulk materials and atomic or molecular structures. Bulk materials possess constant physical properties regardless of its size, but at the nano-scale, the particles exhibit considerable quantum size approach which leads to interesting and sometimes unexpected size dependent optical and optoelectronic properties. Since the nanoparticles are finite in size, the continuous energy band of the bulk crystal transforms into a series of discrete states which results in widening of the band gap. When the diameters of the nanoparticles are comparable to or smaller than the bulk exciton Bohr radius of the material, the quantum confinement effect plays an important role. It modifies the electronic structure of the nanocrystals. There have been extensive studies on the fabrication and optical properties of nanocrystalline ZnS because of their characteristics different from the bulk crystal [1]. Much attention has been focussed in the synthesis of ZnS because they can become the new functional materials of the coming optoelectronic devices since the one-dimensional (1D) ZnS nanoparticles such as nanowires, nanorods exhibit special optical and electrical properties. Reductions of particle size influence the crystalline, melting point and structural stability [2]. Band gap of II-VI group semiconductors such as ZnS can be tuned by changing the particle size and hence they exhibit novel optical properties [3]. The nanosized crystallites can change optical properties which are different from bulk materials. Because of the wide band gap ZnS can be used as a host material for a variety of dopants which leads ZnS to use as electroluminescence devices,
Solar cells, optical switches and other optoelectronic devices [4]. In contrast to undoped materials, the doped materials play an important role in the electronic structure, transition probabilities and the optical properties [5]. For getting basic information on impurity states in quantum dots and their potential applications, doped semiconductors are extensively investigated. There are two different structures of ZnS. They are Zinc blende and Wurtzite both are direct band structure [6]. The size dependent optical properties of nanoparticles can be analysed by using absorption, transmittance and photoluminescence spectroscopy methods. Optical absorption and transmittance method can provide us the value as well as nature of direct and indirect band gap. Average particle size of the quantum dots and nanoparticles can be obtained by using UV-Visible absorption spectra. PL technique is a powerful and non-destructive tool to characterize variety material parameters. PL spectroscopy provides electrical characterization, surface identification, interface and impurity levels and surface roughness. Besides these, the band gap, doping type, composition, the size of the bulk materials can be observed through PL spectrum. For characterization of excitonic structure, impurity levels, structural properties of II-VI semiconductor PL has been used extensively. ZnS is a wide band gap semiconductor material of II-VI groups. Due to good optical absorbance and transmittance in the visible region it is widely used as window layer in various heterojunction solar cells and electroluminescent devices. The band gap of a material depends structure, composition and stoichiometry. The required band gap can be tailored by optimizing the growth conditions.

We have synthesized the doped and undoped ZnS nanoparticles by using CBD method since this method is relatively inexpensive, easy to handle and requires no sophisticated instrumentation.
In this chapter to study the optical properties of both doped and undoped nanoparticles UV-Vis absorption spectrum and photoluminescence measurements has been used.

5.2 Experimental:

The optical absorbance of ZnS was recorded at room temperature using a double beam automated spectrophotometer (HITACHI-U 3210) available at the Chemistry Department of Gauhati University. The spectrometer was maintained in dust free air cooled room. The absorption coefficient ($\alpha$) and absorbance of all the investigated samples were evaluated. The Photo luminescence studies of the nano particles were done at room temperature by using F-2500 FL Spectrophotometer.

5.3. Theoretical Considerations on Optical and Optoelectronic Measurements:

5.3.1. Quantum Confinement and size effects

Various reasons cause Quantum confinement effects. These effects play an important role on the electronic and optical properties of materials. This phenomenon occurs when the physical size of a particle i.e. the diameter of the particle becomes comparable to the de Broglie wavelength of the electrons and holes [7]. At this stage, the electronic and optical properties of the small particles deviate substantially from those of bulk materials [8]. In the crystal lattice of a bulk semiconductor material, an excited electron leaves behind a +ve charge called hole. The excited electron in the conduction band
attracted to the hole in the valence band by the electrostatic Coulomb force and an exciton i.e. a bound state of electron and hole is created. In condensed matter, exciton [9] can transport energy. But the net electric charge is not transported. If the size of the exciton exceeds the particle diameter, Quantum Confinement occurs.

The structure that satisfy the following de Broglie wavelength equation for a free electron, give rise to a series of discrete energy levels and will show the quantum confinement effect-

\[ \lambda = \frac{h}{mv} = \frac{h}{m_e v} \]  

Where, ‘h’ is the Plank’s constant.

\( m \) and \( v \) are the mass and velocity of the excited electron.

When the confining dimension of a particle is large compared to the wavelength of the particle, the particle behaves as a size independent free particle. Due to a continuous energy state, the band gap remains at its original state. But at nanoscale, due to a continuous energy state, the energy state becomes discrete and as a result the band gap becomes size tunable. For very very small size (typically less than 10 nm), the Quantum Confinement effects dominate the electronic and optical properties of the material. Quantum Confinement effect becomes visible when the crystal structure is less than the Bohr radius. As the crystal radius decreases, the optical spectrum decreases from red to blue [10].

The concept of band gap helps us to understand the characteristics of metals (conductors), semiconductors and insulators (non-metals). The outer shells electrons are responsible for most of the properties such as conductivity, absorption of light etc. According to Quantum Mechanics, there is a well defined gap called the electron band gap between the highest occupied state in the valence band and the lowest occupied
state in the conduction band. For larger band gap materials it is difficult for the valence electrons to jump to the conduction band. They show poor electrical conductivity (insulators) where as in conductors there is an overlap of valence and conduction bands. The electrons can move freely into the conduction band. In case of semiconductors since the band gap is narrow, the electrons can go to the conduction band with small amount of energy. For nanomaterials, band gap is an important concept because, in the nanoscale, there is an alternation in the band gap and the dependent properties.

For excitation from highest energy state in the valence band to the lowest energy state in the conduction band, an electron must absorb enough energy. The narrow band gap materials can absorb the high wave length visible range. This is because for transition of the electron into the conduction band, they require lower energy. But the valence electrons of large band gap materials absorb in the short wavelength UV region to jump to the conduction band.

The energy levels in atoms or molecules are not continuous but discrete. Electrons are excited only when the energy is discrete. Nanoparticles occupied the interval between the two i.e. between the discrete and continuous energy levels. With the reduction of number of particles, the potential energy bands split and shrink and then collapsed to the discrete atomic state.

Thus it is seen that electrons in Quantum dots may be excited by energies in discrete intervals rather than a continuum.

There are two approaches that can explain Quantum Confinement effect. These two methods are-

Effective Mass Approximation and Tight Binding Model.
5.3.1(a) Effective Mass Approximation (EMA)

This approach is used to calculate the size dependence of the band gap. It is based on assumption of parabolic relation between the electron energy $E$ and wave vector $K$. In this method the effective masses of an isolated electron and an isolated hole in a spherical potential are used. It is assumed that effective masses of carriers in the quantum dots are same as in a bulk semiconductor. This approach comes from the Schrodinger equation. Effective mass approximation treats the electron and hole independently, that’s why its interaction between them is ignored.

The sizes obtained from effective mass approximation that predicts the effective band gap due to three-dimensional confinement comparing to bulk as [11]-

$$E_{gn} = E_{gb} + \frac{\hbar^2}{8m^* r^2} - 1.8e^2/C_0Cr r - 0.124e^4/\hbar^2C^2[1/m_e^* + 1/m_h^*]^{-1} \quad \text{......(2)}$$

Where,

$E_{gn}$ is the band gap of nano particle

$E_{gb}$ is the band gap of bulk semiconductor.

$r$ is the radius of the particle.

$m_e^*$ is the electron effective mass.

$m_h^*$ is the hole effective mass.

$C_0$ permittivity of free space

$C_r$ permittivity of ZnS which is equal to 8.76 nm.

$e$ is Charge of electron

$$1/m^* = 1/m_e^* + 1/m_h^* \quad \text{..........(3)}$$
The second term of the above equation represents the kinetic energy of both electron and hole. The third term represents their Coulomb energy. The last term is a result of the correlation between the two particles. Generally the kinetic energy is dominant and the last two terms are much smaller. Therefore these two can be neglected [12] in many cases but for strong confinement the third term is small and can be neglected. The EMA is basically applicable to relatively large quantum dots. But for the smallest crystalline sizes this method is not suitable since the crystal potential is described as a spherical well with an infinitely high potential at the interface. Again though the effective masses were assumed to be constant it is true only when the electronic states near the band edges are considered. To overcome these shortcomings, hyperbolic band model (HBM) has been taken.

5.3.1(b) The Tight Binding Model

For the calculation of electronic band structure, Tight Binding Model is an approach applied to a wide variety of solids. In many cases this model [12] gives good qualitative results. Generally this model is a one-electron model, but it is applicable to the calculation of many-body problem and quasi particle. For better results, this model can be combined with other models also. In this model, the electrons should be tightly bound to its own atom. Actually in this method an approximate set of wave functions for isolated atoms of each atomic site are used. In this model, the electrons should have limited interactions with states and potentials on surrounding atoms. As a result the energy of the electron will close to the ionisation energy, i.e. the crystal potential is same to ionic potential. Primarily this model is [13] suited for low-lying narrow bands
for which the shell radius is much smaller than the lattice constant. This model is a quantum mechanical model.

By this method the band gap of the nanoparticles can be calculated by the following relation [14]-

\[ E^* - E_{\text{g bulk}} = \frac{1}{aD^2} + bD + c \ldots \ldots \ldots (4) \]

Where \( E^* \) is the band gap of nanoparticles.

\( E_{\text{g bulk}} \) band gap for a bulk.

D is the particle diameter, a, b and c are material dependent constants.

The electronic structure for very small crystallites can be obtained by using Tight Binding Model. But it is not suitable to calculate band structure of big clusters since here large numbers of atoms have to be taken into account. However, this method can easily be used to study complex systems such as complex alloys, doped compounds etc.

5.3.2 Optical Properties from Quantum confinement

Semiconductor nanoparticles exhibit unique size dependent optical properties. When the crystallite dimension is less than a exciton Bohr radius (i.e. the critical size), then quantum confinement effect takes place. By varying the nanocrystallites sizes, the electric and optical properties of the materials can be changed from molecular to bulk. Also by doping these semiconductors new composite photonic materials can be prepared. Quantum Confinement affects the semiconductor nanoparticles optical properties. The optical band gap energy
\[ E_g = h \nu = \frac{hc}{\lambda} \ldots \ldots (5) \]

Where \( E_g \) is the band gap energy difference.

\( h \) = Plank’s Constant

\( c \) is the velocity of light

\( \lambda \) is the Wavelength of incident light

Band gap energy is inversely proportional to the wavelength of light.

The narrow band gap materials absorb high wavelength visible range. They require low energy to jump to the conduction band. On the other hand the large band gap materials absorb short wavelength UV region. They require high energy to jump from Valence band to Conduction band. Generally semiconductors have a very narrow band gap of \( 1-3 \) eV and they absorb in the near UV region.

When an excited electron relaxes to the ground state and combines with a hole then there occurs Fluorescence.

From theory and experiments it is clear that the electronic and optical properties are influenced by lattice strain that causes shifts in the energy levels and Coulomb effects [15]. Thus we come to know that in semiconductor quantum dots (QDs) the confinement of electron-hole pairs leads to tunable optical properties which are sensitive to the size, shape and material composition. In semiconductor nanostructures the Quantum Confinement of excitons can cause widening of the band gap which makes them applicable to optoelectronic devices. Again surface disorder of the nanoparticles due to Quantum Confinement can cause huge value of electrical conductivity [16].
5.3.3 Some Theoretical considerations on optical and optoelectronic measurements

5.3.4. Band Gap Determination from optical Absorption

In a crystal lattice, the interactions among the atomic energy levels cause a series of energy bands. Every solid has own characteristic energy-band structure. The highest occupied energy band is called the Valence band(VB) and lowest unoccupied band is called conduction band(CB). The energy difference between the top of the valence band and the bottom of the conduction band is called the band energy \( E_g \). When the electrons in the valence band get sufficient energy, they can jump to the conduction band. Electrons can get the energy by absorbing either a phonon (heat) or a photon (light). For insulators the band gap energy value is larger than 3eV whereas for semiconductor it is in between 10^{-2} \text{eV} (for HgTe) and \( E_g > 3 \text{eV} \) (for ZnO and ZnS). In case of metals, the highest energy band is partially filled. When incident radiation energy i.e. \( h\nu > E_g \), then electrons can be excited from VB to CB i.e. from low-energy state(ground state) to a high energy state( excited state).

The absorption of light occurs when \( E_g = h\nu =hc/\lambda \)

\[
= 1240/ \lambda_g \text{ eV} \quad (6)
\]

Where \( \lambda_g \) is the threshold wavelength which is determined at the point of the absorbance (A) versus wavelength (\( \lambda \)) curve or transmittance (T %) versus wavelength (\( \lambda \)) curve where there is an abrupt change.

There is a relation between the absorbance with the path length that the radiation travels within the system and concentration of the species. This relation called the Beer-Lambert law which is given by-
\[ A = \alpha L c \] \hspace{1cm} (7)

Where \( A \) is absorbance

\( A \) is the molar absorbility with units of \( \text{Lmol}^{-1}\text{cm}^{-1} \) which depends on wavelength.

\( L \) is the path length of the sample (unit in cm)

\( c \) is the concentration of the solution (unit is \( \text{molL}^{-1} \)).

In this equation the absorbance is directly proportional to the other parameters. Concentration plays a very important role. Higher the concentration of solution more molecules will interact with light that’s why greater will be the absorbance. Near the optical absorption band edges, the absorption coefficient (\( \alpha \)) satisfies the following relation called Tauc’s formulae-

\[ \alpha \nu = A (\nu - E_g)^n \] \hspace{1cm} (8)

Where \( E_g \) is the energy gap.

\[ n = \frac{1}{2} \text{ for direct transition and } n = 2 \text{ for indirect transition.} \]

\( \nu \) is the photon energy.

\( A \) is a constant related to the extent of the band tailing. An indirect transition involves the meeting of three particles i.e. an electron, a photon and a phonon where as a direct transition involves two particles meeting an electron and a photon. That is why the indirect transition is a less probable process compared to the direct transition. As a result the light absorption coefficient (\( \alpha \)) is greater in direct transition compared to the indirect transition.

Plots of \( (\alpha \nu)^2 \) against photon energy (\( \nu \)) are drawn with the help of origin software. By extrapolating the straight –line portion of the spectrum to the energy axis where \( (\alpha \nu)^2 = 0 \), the energy band gap of the material can be estimated.
For the nano particle in thin film form, the relation between the incident light intensity, the transmitted light intensity and the penetration distance of light i.e. thickness is-

\[ I = I_0 \exp(-\alpha t) \] ....(9)

where \( \alpha \) is the absorption coefficient.

Again \( \alpha = \sigma N \) ....(10) where \( N \) is the concentration of absorption centres.

\( \sigma \) is the effective absorption cross section for one photon per unit time. In an absorbing medium \( \sigma^{-1} \) or \( (\sigma N)^{-1} \) may be termed as mean free path \( t_{ph} \) of a photon.

\[ t_{ph} = (N^{-1}) = (\alpha)^{-1} \] ....(11)

The absorption coefficient \( \alpha \) is the probability of a photon absorption over a unit path.

The absorption coefficient \( \alpha \) (cm\(^{-1}\)) can be calculated from the absorbance (A) or transmittance (T) and the film thickness (t) as-

\[ \alpha = 2.3026(A/t) \] .... (12)

Transmittance T is expressed as-

\[ T = 100(I/I_0) \] .... (13)

Transmittance is defined as \( T = I/I_0 \), where I is the light intensity after it passes through the sample and \( I_0 \) is the initial light intensity. The relation between A and T is

\[ A = -\log T = -\log \left( \frac{I}{I_0} \right) \]

Absorption of light by a sample
Actually when $I$ is less than $I_0$, then there will be absorption of light. In our work, UV-VIS spectroscopy has been used to study the optical properties of ZnS nanoparticles and their changes with doping with Al and Ni. We use double beam automated Spectrophotometer (HITACHI-U3210) available at chemistry department of Gauhati University.

5.5 Principle of Photoluminescence

Photoluminescence (PL) spectroscopy is an excellent technique for probing atomic and molecular electronic energy levels of materials. When light of sufficient energy is incident on a material, Photons are absorbed and imparts excess energy into the material by the process called photo-excitation. The excitations relax and the electrons return to the ground state. The radiative relaxation is called photoluminescence. This light is collected and various important material properties such as band gap determination, impurity levels and defect detection can be obtained. Emission spectrum can be used for identification of surface, interface and interface roughness. By varying the temperature and applied voltage the PL intensity can be varied. The PL intensity can be used to characterize the electronic states and bands. In a typical PL set-up, there is an optical source and optical power meter or spectrophotometer. Since the measurement does not rely on electrical excitation, sample preparation is minimal. PL depends on the nature of optical excitation on the density of photo excited electrons. PL originates near the surface of a material. It can be used to study virtually any surface in any environment [17]. Generally PL is not sensitive to the
pressure in the sample chamber. Hence it is possible to study surface properties in relatively high-pressure semiconductor growth reactors.

There are two types of photoluminescence. They are- intrinsic and extrinsic luminescence. Intrinsic photoluminescence is classified into three types-

i) band-to-band

ii) exciton and

iii) cross-luminescence

In band-to-band transition an electron in the valence band recombines with the holes in the conduction band. This process is observed in very pure crystals at relatively high temperatures. In exciton luminescence there is interaction between an excited electron and a hole. At low temperature exciton luminescence is seen. On the other hand cross luminescence is produced by recombination of an electron with a hole in the outer most core band. This occurs when the energy difference between the top valence band and that of outermost band is smaller than the band gap energy.

Extrinsic luminescence is produced by doped impurities. It is classified into two types-

1. Un-localised and

2. Localized.

In the first type, the electrons and holes are involved in the luminescence process. But in the second type, the luminescence excitation and emission processes are restricted in a luminescence centre.

Though PL has many advantages it has a drawback also. In PL, the sample under investigation must emit light. In indirect band gap semiconductors have low PL efficiency because of the separation of conduction band minimum and the valence band
maximum. Another drawback of PL is the difficulty of density of interface and impurity states estimation.

5.6 Band gap and particle size estimation of ZnS nanoparticles

To determine the optical band gap is done simply by determining the photon energy at which there is sudden increase in absorption. Band gap of the bulk samples is determined by plotting $(\alpha h\nu)^2$ vs. $h\nu$ plot, where $\alpha$ is the absorption coefficient and $h\nu$ is the photon energy. Band gap for nanocrystallite samples are determined from the absorption maxima of the absorption peak using the formulae,

$$E_g = \frac{hc}{\lambda}$$

Where $h$ is the Plank’s constant.

$C$ is the velocity of light and

$\lambda$ is the wavelength at which the absorption peak is observed.

From the absorption band the position of the band and intensity of interaction between the radiation and electronic system can be obtained. To determine the value of the optical band gap the absorption corresponding to electron excitation from valence band to conduction band is used. The absorption coefficient $\alpha$ is determined from Beer Lambert’s law-

$$A = \alpha lc$$

$$\alpha = A/lc$$

$\alpha$ will be different since value of $A$ i.e. Absorption is different. By extrapolating the straight line portion of $(\alpha h\nu)^2$ vs $h\nu$ graph to $\alpha^2=0$, the band gap values of different
samples are calculated. To calculate an approximate size of the nanoparticles the absorption spectrum can be used.

Brus in 1983 proposed the effective mass approximation approach which is given by-

\[ E_g - E_b = h^2 / 8R^2 (1/m_e^* + 1/m_h^*) - 1.8 \epsilon^2 / 4\pi \epsilon_0 \epsilon_r \gamma_e - 0.124 e^4 / \hbar^2 (4\pi \epsilon \epsilon_0)^2 ((1/m_e^* + 1/m_h^*)^{-1} \ldots (14) \]

Where,

- \( E_g \) is the energy of ZnS nano particles.
- \( E_b \) is the energy of bulk ZnS.
- \( h \) is the Planck’s constant.
- \( m_e^* \) is the effective mass of electron
- \( m_h^* \) is the effective mass of hole.
- \( \epsilon_0 \) is the permittivity in free space.
- \( \epsilon_r \) is the permittivity of material (for ZnS = 8.76)
- \( \gamma_e \) is the Bohr exciton radius.
- \( e \) is the electronic charge.

The first term is the Kinetic energy term, the second term is the Coulomb interaction between the electron and hole and the third term is the salvation energy loss and is usually small and ignored. For strong confinement the second term can be neglected [18].

Another method of estimating nanoparticles sizes is Hyperbolic Band Model (HBM) which is given by-

\[ E_g^2 = E_b^2 + 2h^2 E_b/m^*(\pi/R)^2 \ldots \ldots \] (15)

Where

- \( E_g \) is the energy of nano particles.
Eb is the energy of bulk ZnS.

$m^*$ is the effective mass of exciton.

R is the radius of the particles.

Figure: 5.1(a) UV-Vis Spectroscopy of Undoped ZnS (ZnS₁, ZnS₂ & ZnS₃)

(4 Wt % ZnCl₂, 2 wt % Na₂S and 5 wt% PVA at pH= 1.1)
Figure: 5.1(b) UV-Vis Spectroscopy of ZnS:Al & ZnS:Ni nanoparticles (4 Wt % ZnCl₂, 2 wt % Na₂S and 5 wt% PVA at pH= 1.1, 0.1 wt % AlCl₃ for ZnS₂ and 0.1wt% for ZnS₃)

Figure: 5.2(a): UV-Vis Spectroscopy of ZnS, ZnS:Al & ZnS:Ni (2 wt % ZnCl₂ & volume ratio 5:2, pH=1)
Figure: 5.2(b) UV-Vis Spectroscopy of ZnS, ZnS:Al & ZnS:Ni

(2 wt % ZnCl₂ & volume ratio 5:3, pH=1)

Figure: 5.2(c) UV-Vis Spectroscopy of ZnS, ZnS:Al & ZnS:Ni

(2 wt % ZnCl₂ & volume ratio 5:4, pH=1)
Figure: 5.3(a) UV-Vis Spectroscopy of ZnS, ZnS:Al & ZnS:Ni

(3 wt % Zncl₂ & volume ratio 5:2, pH=1)

Figure: 5.3(b) UV-Vis Spectroscopy of ZnS, ZnS:Al & ZnS:Ni

(3 wt % Zncl₂ & volume ratio 5:3, pH=1)
Figure: 5.3(c): UV-Vis Spectroscopy of ZnS, ZnS:Al & ZnS:Ni

(3 wt % ZnCl₂ & volume ratio 5:4)

Figure: 5.4(a). UV-Vis Spectroscopy of ZnS, ZnS:Al & ZnS:Ni

(3 wt % ZnCl₂ & volume ratio 5:2, & pH = 1)
Figure 5.4(b): UV of ZnS, ZnS:Al & ZnS:Ni

(3 wt % ZnCl$_2$ & volume ratio 5:2, & pH = 1.5)

Figure 5.4(c): UV of ZnS, ZnS:Al & ZnS:Ni

(3 wt % ZnCl$_2$ & volume ratio 5:2, & pH = 2)
Figure: 5.4(d): UV of ZnS, ZnS:Al & ZnS:Ni

(3 wt % ZnCl$_2$ & volume ratio 5: 2, & pH =2.5)

Fig 5.4(e): Plots of $(\alpha h\nu)^2$ vs $h\nu$ obtained from absorption spectra (for ZnS)
Fig 5.4(f): Plots of $(\alpha h\nu)^2$ vs $h\nu$ obtained from absorption spectra (for ZnS-Al)

Fig 5.4(g): Plots of $(\alpha h\nu)^2$ vs $h\nu$ obtained from absorption spectra (for ZnS:Ni)
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<tr>
<th>Sl.No</th>
<th>Sample</th>
<th>Concentration</th>
<th>Volume ratio, PVA:ZnCl₂</th>
<th>Absorption peak (nm)</th>
<th>Intensity (a.u.)</th>
<th>Band gap value of nanoparticles (eV)</th>
<th>Blue shift energy (eV)</th>
<th>Particle size by EMA (nm)</th>
<th>Av. P. size (nm)</th>
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<td>ZnS₃(b)</td>
<td>2 wt% ZnCl₂, 2 wt% Na₂S, 5 wt% PVA, 0.1 wt% NiCl₂</td>
<td>05:04</td>
<td>327</td>
<td>0.328</td>
<td>4</td>
<td>0.4</td>
<td>4.65</td>
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</table>

Table 5.2
The UV-VIS absorption spectroscopy of the different prepared samples was recorded by double beam automated Spectrophotometer (HITACHI-U3210) over the wavelength range of 200-1000 nm. The UV-Vis absorption spectra of all the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Concentration</th>
<th>Volume ratio ZnCl₂: Na₂S</th>
<th>Absorption peak(nm)</th>
<th>Intensity of absorption(a.u.)</th>
<th>Band gap value of nano particles(eV)</th>
<th>Blue shift energy(eV)</th>
<th>Particle size(nm) measured by EmA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>3 wt % ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA</td>
<td>05:02</td>
<td>311</td>
<td>1.474</td>
<td>3.98</td>
<td>0.38</td>
<td>4.75</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>3 wt % ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA</td>
<td>05:02</td>
<td>310</td>
<td>0.22</td>
<td>4</td>
<td>0.4</td>
<td>4.64</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3 wt % ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA</td>
<td>05:02</td>
<td>304</td>
<td>1.36</td>
<td>4.1</td>
<td>0.5</td>
<td>4.144</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>3 wt % ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA</td>
<td>05:02</td>
<td>301</td>
<td>1.3</td>
<td>4.2</td>
<td>0.6</td>
<td>3.8</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>3 wt% ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA, 0.1 wt% AlCl₃</td>
<td>05:02</td>
<td>309</td>
<td>0.4</td>
<td>4.01</td>
<td>0.41</td>
<td>4.6</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>3 wt% ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA, 0.1 wt% AlCl₃</td>
<td>05:02</td>
<td>306</td>
<td>0.55</td>
<td>4.1</td>
<td>0.5</td>
<td>4.15</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>3 wt% ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA, 0.1 wt% AlCl₃</td>
<td>05:02</td>
<td>302</td>
<td>1.18</td>
<td>4.11</td>
<td>0.51</td>
<td>4.104</td>
</tr>
<tr>
<td>8</td>
<td>2.5</td>
<td>3 wt% ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA, 0.1 wt% AlCl₃</td>
<td>05:02</td>
<td>284</td>
<td>0.11</td>
<td>4.37</td>
<td>0.77</td>
<td>3.34</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>3 wt% ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA, 0.1 wt% NiCl₂</td>
<td>05:02</td>
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<td>4.1</td>
<td>0.5</td>
<td>4.15</td>
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<td>10</td>
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<td>3 wt% ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA, 0.1 wt% NiCl₂</td>
<td>05:02</td>
<td>300</td>
<td>0.04</td>
<td>4.13</td>
<td>0.53</td>
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</tr>
<tr>
<td>11</td>
<td>2</td>
<td>3 wt% ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA, 0.1 wt% NiCl₂</td>
<td>05:02</td>
<td>299</td>
<td>0.7</td>
<td>4.15</td>
<td>0.55</td>
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<tr>
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<td>3 wt% ZnCl₂, 2 wt% Na₂S &amp; 5 wt% PVA, 0.1 wt% NiCl₂</td>
<td>05:02</td>
<td>295</td>
<td>0.51</td>
<td>4.2</td>
<td>0.6</td>
<td>4.1</td>
</tr>
</tbody>
</table>
were recorded and numerical data were plotted in the “origin 6.5” software. Absorption edge energies of the crystalline samples is the minimum photon energy required for exciting an electron from the top of the valence band to the bottom of the conduction band. This energy can be obtained from UV-VIS absorption spectra.

Fig 5.1(a) shows the UV-Visible absorption spectrum of undoped ZnS samples prepared at 4 wt% ZnCl$_2$, 2 wt % Na$_2$S and 5 wt% PVA at pH=1.1. Fig 5.1(b) shows the absorption spectra of doped ZnS (with 0.1 wt% AlCl$_3$ and 0.1 wt % NiCl$_2$). We have observed (fig 5.1(a &b), 5.2(a, b &c) & 5.3(a, b & c)) that the peaks are shifted with the change of ZnCl$_2$: PVA and with doping which may be due to Quantum size effect. From the absorption peak of figures (5.1(a & b)) we get the optical parameters such as band gap and blue shift of the nanoparticles. Particle sizes are calculated using the theoretical EMA model. Intensity of absorption (a.u.), blue shift energy etc are shown in Table 5.1. UV-Visible absorption spectrum of undoped ZnS samples prepared at (2 wt% ZnCl$_2$, 2 wt% Na$_2$S, 5 wt% PVA and 3 wt% ZnCl$_2$, 2 wt% Na$_2$S & 5 wt% PVA) and doped ZnS (with 0.1wt% Al and 0.1wt% Ni) at pH =1 and volume ratios of 5:2, 5:3 & 5:4 are shown in figure 5.2(a, b & c) and in figure 5.3(a, b & c). From figure 5.3(a,b & c) it is observed that the peak intensities increase with Zn concentration which may be an indication of quantum confinement effect. Optical parameters such as intensity of absorption, particle sizes, blue shift energy etc calculated from figure 5.2 and 5.3 are shown in table 5.2. Same parameters for undoped and doped ZnS samples prepared at pH value of 1, 1.5, 2 & 2.5 are calculated from figure 5.4(a, b, c & d) and are shown in table 5.3.

ZnS has a good absorption for light in the wavelength range of 200 -1000 nm. The absorption peak of UV-Vis spectra reflects band gap of the particles. Absorption
corresponds to electron excitation from the valence band to conduction band and is used for the determination of the nature and value of the optical band gap of the nanoparticles. Due to small size of the nanoparticles, the absorption edge is blue shifted. Blue shift confirms formation of nanoparticles [19]. Doping with Al and Ni [20] causes quantum confinement of the particles. The shifts of absorption edge towards higher wavelength indicate the decrease in the optical band gap for the doped particles. This shift is due to changes in the electron -hole in the conduction and valence bands [21].

The calculated band gap energies of the synthesized ZnS nano –structures are larger than the bulk value of ZnS band energy due to quantum confinement effect. From Table 5.1, 5.2 and 5.3 it is observed that with decrease in particle size, the band structure of the semiconductor increases and the edges of band split into discrete energy levels called quantum confinement effect. Increase in band gap energies of ZnS nanostructure may be an indication of the quantum confinement effect due to the decreasing size of the nanostructure. We have seen from Table 5.1 and 5.2 that there is variation of optical properties with the change of volume ratio of capping agent and ZnCl₂ and also the volume ratio of reactants. With the increase of pH the band gap values of the nanoparticles increase and the particle sizes decrease. With the increase in Zn source concentration the particle sizes decrease [22]. Particle sizes observed by EMA approximation is close to the sizes observed by TEM[23].

The band gap energy of ZnS, ZnS:Al and ZnS:Ni are 4nm, 4.1nm and 4.05 nm respectively as calculated from Tauc’s plot shown in Fig 5.4(e, f & g).

UV-VIS absorption is a very fast characterization method for the nanoparticles because the absorption features give information about the nanoparticles formation, the
band gap and the size distribution of the nanoparticles. However it is an indirect method for determining the nanoparticles.

5.7 PL Characterization

Figure: 5.5 (a): PL spectra of ZnS₁, ZnS₂ & ZnS₃ (4 Wt % ZnCl₂, 2 wt % Na₂S and 5 wt% PVA at pH = 1.1 & ZnCl₂:PVA at 5:2, 5:3 & 5:4)

Figure: 5.5 (b): PL spectra of ZnS: Al (ZnS₄) and ZnS: Ni(ZnS₅) (4 Wt % ZnCl₂, 2 wt % Na₂S and 5 wt% PVA at pH = 1.1, 0.1 wt % AlCl₃ for ZnS₄ and 0.1 wt% for ZnS₅)
Figure: 5.5(c): PL Spectra of ZnS$_1$(1(a)), ZnS$_2$(1(b)) & ZnS$_3$(1(c)) (Prepared at Volume ratios of 5:2, 5:3 & 5:4 of ZnCl$_2$: PVA, 2 Wt % ZnCl$_2$, 5 wt % PVA & 2 wt % Na$_2$S)

Figure: 5.5(d): PL Spectra of ZnS$_4$(2(a)), ZnS$_5$(2(b)) & ZnS$_6$(2(c)) (Prepared at Volume ratios of 5:2, 5:3 & 5:4 of ZnCl$_2$: PVA, 3 Wt % ZnCl$_2$, 5 wt % PVA & 2 wt % Na$_2$S)
Figure 5.5(e): PL Spectra of ZnS$_2$(3(a)), ZnS$_3$(3(b)) & ZnS$_4$(3(c)) (Prepared at Volume ratios of 5:2, 5:3 & 5:4 of ZnCl$_2$: PVA, 2 Wt % ZnCl$_2$, 5 wt % PVA & 2 wt % Na$_2$S, 0.1 wt% of AlCl$_3$)

Figure 5.5(f): PL Spectra of 4(a), 4(b) & 4(c) (Prepared at Volume ratios of 5:2, 5:3 & 5:4 of ZnCl$_2$: PVA, 2 Wt % ZnCl$_2$, 5 wt % PVA & 2 wt % Na$_2$S, 0.1 wt% of NiCl$_2$)
Figure: 5.5 (g): PL Spectra of 5(a), 5(b) & 5(c) (Prepared at Volume ratios of 5:2, 5:3 & 5:4 of ZnCl₂: PVA, 3 Wt % ZnCl₂, 5 wt % PVA & 2 wt % Na₂S, 0.1 wt% of AlCl₃)

Figure: 5.5(h): PL Spectra of 6(a), 6(b) & 6(c) (Prepared at Volume ratios of 5:2, 5:3 & 5:4 of ZnCl₂: PVA, 3 Wt % ZnCl₂, 5 wt % PVA & 2 wt % Na₂S, 0.1 wt% of NiCl₂)
Figure: 5.6(a) : PL Spectra of ZnS (pH=1, 1.5, 2 & 2.5)
Figure 5.6(b): PL Spectra of ZnS: Al (pH=1, 1.5, 2 & 2.5)

Figure 5.6(c): PL Spectra of ZnS: Ni (pH=1, 1.5, 2 & 2.5)
### Table 6.1

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Samples</th>
<th>Volume ratios of PVA:ZnCl₂ (Conc)</th>
<th>Emission peaks</th>
<th>Band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnS₁</td>
<td>5:2 (4 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA)</td>
<td>472</td>
<td>2.63</td>
</tr>
<tr>
<td>2</td>
<td>ZnS₂</td>
<td>5:3 (4 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA)</td>
<td>503 &amp; 763</td>
<td>2.47 &amp; 1.63</td>
</tr>
<tr>
<td>3</td>
<td>ZnS₃</td>
<td>5:4 (4 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA)</td>
<td>502</td>
<td>2.5</td>
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<tr>
<td>4</td>
<td>ZnS-Al(ZnS₃)</td>
<td>5:4 (4 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % AlCl₃)</td>
<td>500 &amp; 759</td>
<td>2.5 &amp; 1.634</td>
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<tr>
<td>5</td>
<td>ZnS-Ni(ZnS₃)</td>
<td>5:4 (4 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % NiCl₂)</td>
<td>446 &amp; 497</td>
<td>2.8 &amp; 2.5</td>
</tr>
</tbody>
</table>

### Table 6.2

<table>
<thead>
<tr>
<th>Sl no</th>
<th>Sample</th>
<th>Volume ratio of PVA: ZnCl₂ (conc)</th>
<th>Emission peaks</th>
<th>Band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1(a)</td>
<td>5:2 (2 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA)</td>
<td>367</td>
<td>3.38</td>
</tr>
<tr>
<td>2</td>
<td>1(b)</td>
<td>5:2 (2 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA)</td>
<td>544</td>
<td>2.28</td>
</tr>
<tr>
<td>3</td>
<td>2(a)</td>
<td>5:3 (2 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA)</td>
<td>543.5</td>
<td>2.282</td>
</tr>
<tr>
<td>4</td>
<td>2(b)</td>
<td>5:3 (2 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA)</td>
<td>450.5 &amp; 547</td>
<td>2.752 &amp; 2.27</td>
</tr>
<tr>
<td>5</td>
<td>3(a)</td>
<td>5:3 (2 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % AlCl₃)</td>
<td>547.5</td>
<td>2.265</td>
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<tr>
<td>6</td>
<td>3(b)</td>
<td>5:3 (2 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % AlCl₃)</td>
<td>410.5 &amp; 538</td>
<td>3.021 &amp; 2.305</td>
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<td>4(a)</td>
<td>5:4 (2 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % NiCl₂)</td>
<td>525 &amp; 793.5</td>
<td>2.362 &amp; 1.563</td>
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<tr>
<td>8</td>
<td>4(b)</td>
<td>5:4 (2 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % NiCl₂)</td>
<td>547 &amp; 792</td>
<td>2.27 &amp; 1.566</td>
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<tr>
<td>9</td>
<td>5(a)</td>
<td>5:4 (3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % NiCl₂)</td>
<td>544 &amp; 793.5</td>
<td>2.28 &amp; 1.563</td>
</tr>
<tr>
<td>10</td>
<td>5(b)</td>
<td>5:4 (3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % NiCl₂)</td>
<td>446 &amp; 497</td>
<td>2.8 &amp; 1.566</td>
</tr>
<tr>
<td>11</td>
<td>6(a)</td>
<td>5:4 (3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % NiCl₂)</td>
<td>547 &amp; 792</td>
<td>2.27 &amp; 1.566</td>
</tr>
<tr>
<td>12</td>
<td>6(b)</td>
<td>5:4 (3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % NiCl₂)</td>
<td>547 &amp; 792</td>
<td>2.27 &amp; 1.566</td>
</tr>
</tbody>
</table>

### Table 6.3

<table>
<thead>
<tr>
<th>Sl no</th>
<th>Sample</th>
<th>Concentration</th>
<th>Volume Ratio(ZnCl₂:Na₂S)</th>
<th>pH</th>
<th>Emission peak</th>
<th>Band gap</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>ZnS₁</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA</td>
<td>05:02</td>
<td>493</td>
<td>2.825</td>
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<tr>
<td>2</td>
<td>ZnS₂</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA</td>
<td>05:02</td>
<td>421</td>
<td>2.35</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>ZnS₃</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA</td>
<td>05:02</td>
<td>449</td>
<td>2.762</td>
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</tr>
<tr>
<td>4</td>
<td>ZnS₄</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA</td>
<td>05:02</td>
<td>443</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>ZnS-Al₁</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % AlCl₃</td>
<td>05:02</td>
<td>437 &amp; 568</td>
<td>2.84 &amp; 2.18</td>
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<tr>
<td>6</td>
<td>ZnS-Al₂</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % AlCl₃</td>
<td>05:02</td>
<td>437 &amp; 567</td>
<td>2.84 &amp; 2.19</td>
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</tr>
<tr>
<td>7</td>
<td>ZnS-Al₃</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % AlCl₃</td>
<td>05:02</td>
<td>421 &amp; 558</td>
<td>2.95 &amp; 2.22</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>ZnS-Al₄</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % AlCl₃</td>
<td>05:02</td>
<td>438 &amp; 562</td>
<td>2.831 &amp; 2.206</td>
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<tr>
<td>9</td>
<td>ZnS-Ni₁</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % NiCl₂</td>
<td>05:02</td>
<td>421 &amp; 562</td>
<td>2.95 &amp; 2.21</td>
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<tr>
<td>10</td>
<td>ZnS-Ni₂</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % NiCl₂</td>
<td>05:02</td>
<td>441 &amp; 562</td>
<td>2.812 &amp; 2.206</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>ZnS-Ni₃</td>
<td>3 wt % ZnCl₂, 2 wt % Na₂S, 5 wt % PVA, 0.1 wt % NiCl₂</td>
<td>05:02</td>
<td>437 &amp; 560</td>
<td>2.84 &amp; 2.214</td>
<td></td>
</tr>
</tbody>
</table>
Information about band gap energies can be obtained from PL measurements. Photoluminescence emission (PL) spectra of undoped and doped ZnS (with Al & Ni) nanoparticles were studied for its luminescent applications by using F-2500FL Spectrophotometer. Fig 5.5(a) & 5.5(b) show PL Spectra of samples prepared at 4 wt % ZnCl₂, 2 wt % Na₂S and 5 wt % PVA at pH = 1.1, with excitation wavelength 280 nm and scan speed 1500nm/min. The emission spectra of ZnS nanoparticles show peaks at 472, 394 & 502 nm respectively for ZnS₁, ZnS₂ and ZnS₃ (undoped ZnS) respectively. It is observed that peak positions change with the change of ZnCl₂: PVA which indicates that there is change of energy level to the conduction band. For the same excitation wavelength ZnS:Al (ZnS₄) shows emission peaks at wavelength 500 and 759 nm and ZnS:Ni (ZnS₅) show emission wavelength at 446 and 497 nm. The emission spectra of ZnS:Al and ZnS:Ni at 759 nm and 497 nm indicate the doping effect of Al & Ni in the ZnS nanostructures. PL in this region is due to the presence of S vacancies in the lattice. Al and Ni ions occupy Zn²⁺ lattice sites in the ZnS host lattice as a result the peak intensity decrease. In the PL process, an electron from the ZnS valence band is excited across the band gap and decays by a normal recombination process to some defects states. From fig 5.5(c) and 5.5(d) we have seen a strong emission band at 545, 367 and 544nm for samples 1(a), 1(b) and 1(c)( i.e. 2 wt% ZnCl₂, 2 wt% Na₂S, 5 wt% PVA) and at 544, 543 and 545nm for 2(a),2(b) and 2(c)( i.e. 3 wt% ZnCl₂, 2 wt% Na₂S, 5 wt% PVA). Other weaker peak is observed between 700-800 nm. Strong emission band implies high crystalline nature of the nanoparticles [24]. Figure 5.5(e) and figure 5.5(f) show emission peaks of the samples 3(a),3(b) & 3(c)( i.e. samples Prepared at Volume ratios of 5:2, 5:3 & 5:4 of ZnCl₂: PVA, 2 Wt % ZnCl₂, 5 wt % PVA & 2 wt % Na₂S, 0.1 wt% of AlCl₃ and 4(a),4(b) & 4(c)( i.e. samples Prepared at Volume ratios of 5:2, 5:3 & 5:4 of ZnCl₂: PVA,
2 Wt % ZnCl₂, 5 wt % PVA & 2 wt % Na₂S, 0.1 wt% of NiCl₂). The emission peaks for Al doped samples i.e. for 3(a), 3(b) & 3(c) are at 543.5, 545.5 and 547.5 nm. But for Ni doped ZnS i.e. for 4(a), 4(b) & 4(c) emission peaks are at (450.5 & 547)nm, (410.5 & 538)nm and at (525 & 793.5) nm respectively. Figure 5.5(g) and figure 5.5(h) show emission peaks of the samples 5(a), 5(b) & 5(c) (Prepared at Volume ratios of 5:2, 5:3 & 5:4 of ZnCl₂: PVA, 3 Wt % ZnCl₂, 5 wt % PVA & 2 wt % Na₂S, 0.1 wt% of AlCl₃) and 6(a), 6(b) & 6(c) (Prepared at Volume ratios of 5:2, 5:3 & 5:4 of ZnCl₂: PVA, 3 Wt % ZnCl₂, 5 wt % PVA & 2 wt % Na₂S, 0.1 wt% of NiCl₂) at (544 & 793.5), (543 & 791.5) and (543 & 791)nm and (544.5 & 797.5), (544 & 793.5) and (547 & 792) nm respectively. From fig 5.6(a) we get peaks for undoped ZnS at different pH values from pH=1, 1.5, 2 & 2.5. The peaks are at 439, 421, 449 and 443 nm respectively. For Al doped ZnS (from figure 5.6(b)) at the same pH values we get two peaks for each at (437 & 568) nm, (347 & 567), (433 & 568) nm and (421 & 558) nm respectively. For Ni doped ZnS (from figure 5.6(c)) with the variation of pH from 1 to 2.5 we get peaks at (438 & 562), (421 & 562), (441 & 562) and at (437 & 560) nm respectively. The broadened emission band with multiple of peaks maxima in figure 5.6(b) & 5.6(c) are because of the involvement of different luminescence centres in the irradiative process. From figure 5.6(a, b & c) it is observed that the PL intensities increase with the increase of pH from 1 to 2.5. This may be due to radiative transition. The band gap energies calculated from the PL peaks are shown in Table 6.1, 6.2 & 6.3.

All the samples in the spectra irrespective of doping show a broad luminescence peak between 350 to 550 nm, which may be attributed to $\text{S}^{2-}$ ion vacancies [25]. We have seen that the intensities of PL peaks increase with doping and with the variation of energy gap peak shifts towards blue shift.
PL efficiency of semiconductor nanoparticles depends on the surface properties. It is related to growing conditions and synthesis system. Due to high surface to volume ratio, the smaller particles contain more carriers for photoluminescence.

**Conclusion:**

From UV-VIS observations it is found that the band gap value for doped nanoparticles are higher than the bulk ZnS and have a tendency towards blue shift. New peaks are observed in doped particles which indicate successful doping. The broadening of PL peaks for ZnS:Al than ZnS:Ni indicates more incorporation of ZnS in ZnS:Al than ZnS:Ni.

**References:**


17) Timothy H. Gfroerer, “Photoluminescence in Analysis of surfaces and Interfaces”, Encyclopaedia of Analytical Chemistry, John Wiley & Sons Ltd, Chichester, 2000, P.No-1 to 2.


