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THE INFLUENCE OF THE ZN/S SOURCE CONCENTRATION RATIO ON ITS STRUCTURAL, OPTICAL AND MAGNETIC PROPERTIES OF ZnS QUANTUM DOTS

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In the present work, a systematic study has been carried out to understand the influence of concentration ratio of sulfur to zinc sources on the structural and optical properties of the ZnS Quantum dots. ZnS quantum dots have been prepared at room temperature using chemical precipitation method without using catalysts, capping agent or surfactants. X-ray diffraction analysis reveals that ZnS quantum dots exhibit cubic zinc blende structure. The lattice constants of ZnS quantum dots is observed to decrease slightly with increasing sulfur source concentration and the grain size is found to be in the range of 4.7 to 5.1 nm. TEM image shows that the all the particles are spherical in nature and the particle size of ZnS quantum dots is in the range of 4 to 5 nm. The optical absorption spectrum of ZnS quantum dots shows the effect of strong quantum confinement effect. The photoluminescence spectra ZnS quantum dots shows decrease in intensity and also exhibit blue shift with respect to the change in molar concentrations. The magnetic behavior of prepared ZnS quantum dots shows diamagnetic in nature.

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1. Introduction

Nanomaterials exhibit structural and optical properties which depend sensitively on the size of the nanocrystals and the properties are of both fundamental and technological interest. Binary chalcogenide nanocrystalline semiconductors such as PbS, ZnS, ZnSe, CdS and CdSe have attracted considerable attention in recent years due to their unique properties, which arise due to size quantization [1-5]. Among them, ZnS is one of the most important group II-VI semiconductors, having a typical band gap of 3.68 eV at room temperature and has attracted much research interest due to its potential applications in optoelectronic devices such as photocatalysis,solar cells, and display panels [6-9]. It is particularly interesting to see what happens when the size of the nanoparticle becomes smaller than or comparable to the radius of the orbit of the electron-hole pair (Bohr exciton radius). There are two situations, called the weak confinement and the strong confinement regimes. In the weak regime the particle radius is larger than the radius of the electron-hole pair, but the range of motion of the exciton is limited, which causes a blue shift in the absorption spectrum. When the radius of the particle is smaller than the orbital radius of electron-hole pair, the motion of electron and hole become independent and the exciton does not exist. The hole and the electron have their own set of energy levels. Here also there is a blue shift [10]. The Bohr radius of the exciton is 2.5 nm for ZnS and the quantum confinement occurs when the size of the crystallite is around 2 -6 nm and below [11]. This confinement induces discrete electronic states in the valence and conduction band of the quantum dots compared to the continuous state of energy in the bulk material. If the crystallite size is below

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the exciton Bohr radius of the semiconductor, strong quantum confinement occurs. The confinement effect appears as a shift in the absorption spectra (blue shift) and the absorption edge is shifted to lower wavelengths, which is due to the change in the band gap. The absorption shift and spectral features can be used to measure the particle size. For ZnS, the quantum confinement effect can be observed when the particle size is less than 6 nm.

Several methods have been adopted for the synthesis of nanoparticles, such as wet chemical method [12], micro emulsion [13], chemical vapor deposition [14], etc.ZnS can be synthesized by different routes, such as chemical route, microwave irradiation,etc.

In the present work, ZnS Quantum dots were synthesized by chemical precipitation method using different source concentration without the usage of capping agent or surfactants and the systematic study of structural, optical and magnetic properties of ZnS Quantum dots were carried out.

2. Experimental

In the present study, ZnS quantum dots have been synthesized through chemical precipitation method. Materials used in the present synthesis are Zn $(NO_3)_2.6H_2O$ (as Zinc source), Na_2S (as sulphur source) and deionized water. Aqueous solution 0.2 mol zinc nitrate was added to 100 ml of double distilled water, and was stirred for 1 hour at room temperature to which aqueous solution of 0.2 mol sodium sulphide solution was added drop wise and was stirred for 2 hours. A white precipitate was formed soon after the addition of the Na_2S solution. Using the same method, we have repeated the procedure for various S/Zn ratios. This was attained by keeping the zinc nitrate concentration constant at 0.2 mol and by varying the Na_2S concentration for four different values of 2.0, 2.5, 3.0 and 3.5 mol, respectively. The white precipitates of ZnS were obtained by centrifuging at 2000 rpm for 5 minutes with excess double distilled water. The sample was obtained as precipitate and after that the all sample was dried at 150 °C for four hours.

X-ray diffraction studies have been carried out using PANalytical x-ray diffractometer [XRD-6000, SHIMADZU]. Elemental composition of the prepared samples has been studied using Energy dispersive analysis of X-ray (EDAX) spectroscopy attached with Transmission electron microscope (TEM) using a JEOL JEM 2010 microscope. FTIR spectroscopy was recorded using THERMO SCIENTIFIC NICOLET (iS10) by mixing the samples with KBr. The optical properties were studied using absorbance spectra recorded by spectrophotometer (JASCO V-570). Photoluminescence emission spectra have been studied using Cary Eclipse spectrophotometer. To know the magnetic state of the prepared samples, room temperature magnetization was studied as a function of applied magnetic field in the range of -15,000 to +15,000 G using a Lakeshore Vibrating sample magnetometer, VSM-7410.

3. Results and discussion

The structural characterization of the quantum dots has been carried out by x-ray diffraction technique using CuKα radiation. X-ray diffraction patterns of ZnS Quantum dots are shown in Fig. 1. The diffraction pattern exhibits broad peaks revealing that the prepared particles are of nano size. All the peaks in the diffraction pattern are found to be characteristic of ZnS. The diffraction peaks at 2θ (degree) values of 28.8°, 48.15° and 56.85° of ZnS correspond to the (111), (220) and (311) planes of cubic zinc blende structure. The lattice constants have been found to be a=5.4020 A° which is in agreement with the standard JCPDS data (JCPDS card No.03-0570,). Table1 shows the variation in structural parameters of the ZnS quantum dots. It is observed from the table1 that the lattice constant 'a' decreases with increase in sulfur to zinc ratio. It is also found that the Bragg angle (2θ) of the intense (111) reflection exhibits a slight shift towards higher values. Particle size of ZnS quantum dots has been calculated using Scherrer's equation [15]

$$D = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

where, D is the grain size, K is a constant taken to be 0.94, λ is the wavelength of the x-ray radiation, β is the full width at half maximum and θ is the angle of diffraction. The particle size has been calculated and is found to be 4.74, 4.83, 4.92 and 5.08 (±0.1) nm for sodium sulphide concentration of 2.0, 2.5, 3.0 and 3.5 mol.

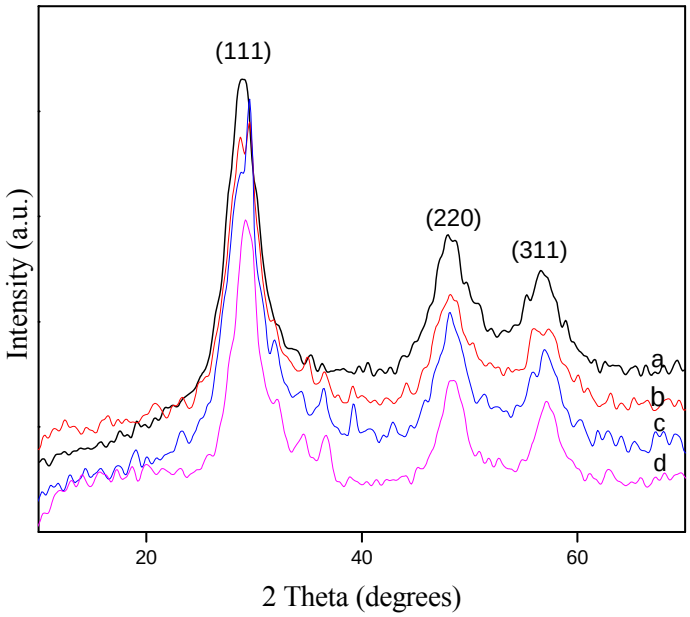

Fig. 1. X-ray diffraction pattern ZnS QDs of different source concentration. a)0.2:0.20 b)0.2:0.25 c)0.2:0.30 and 0.2:0.35 mol/mol.

Fig. 2 shows the typical TEM micrograph of ZnS nanoparticles with different sodium sulphide concentration. For TEM analysis, the specimen was prepared by depositing a drop of the dilute solution of the sample in methanol on a carbon coated copper grid and dryied at room temperature. From the TEM image shows all samples seems to be nearly spherical in nature and the particle size was found to be 4.12,4.36,4.7 and 5.02 nm for sodium sulphide concentration of 2.0,2.5,3.0 and 3.5mol ,respectively. Fig. 2e, shows selected-area diffraction (SAED) patterns for ZnS of 0.2 mol sodium sulphide concentration. The selected-area diffraction patterns exhibit concentric circles, revealing that the ZnS are nanocrystalline, being made up of small particles. The rings correspond to the (111), (220), and (311) planes of the cubic zinc blende phase.

Energy dispersive x-ray analysis carried out to study the composition of the ZnS nanoparticles revealed that the S/Zn ratio in the prepared samples increased with increasing S/Zn concentration ratio. The EDAX spectrum of ZnS nanoparticles of source concentration 0.2 : 0.2 mol/mol is shown in figure3.FTIR spectra of ZnS nanoparticles recorded at room temperature in the wavelength range of 4000-400 cm^{-1} are shown in Fig 4a-d.From the spectra the broad band between 3000 and 3700 cm^{-1} is assigned to O-H stretching vibration of water as characterized by its bending vibration at 1612 cm^{-1} [16], because all FTIR spectra were recorded by mixing samples with KBr. Hence there may be some adsorbed water vapour ,as KBr is hygroscopic. The peak at 1375cm^{-1} and 1100cm^{-1} is assigned to the symmetric bending vibration of methyl group(-CH_3) and C-O group, while the alkenes will have a characteristic C=C stretch at 1600-1680 cm^{-1} .The peak at 616 $cm^{-1}$is assigned to the ZnS band corresponding to sulphides [17].

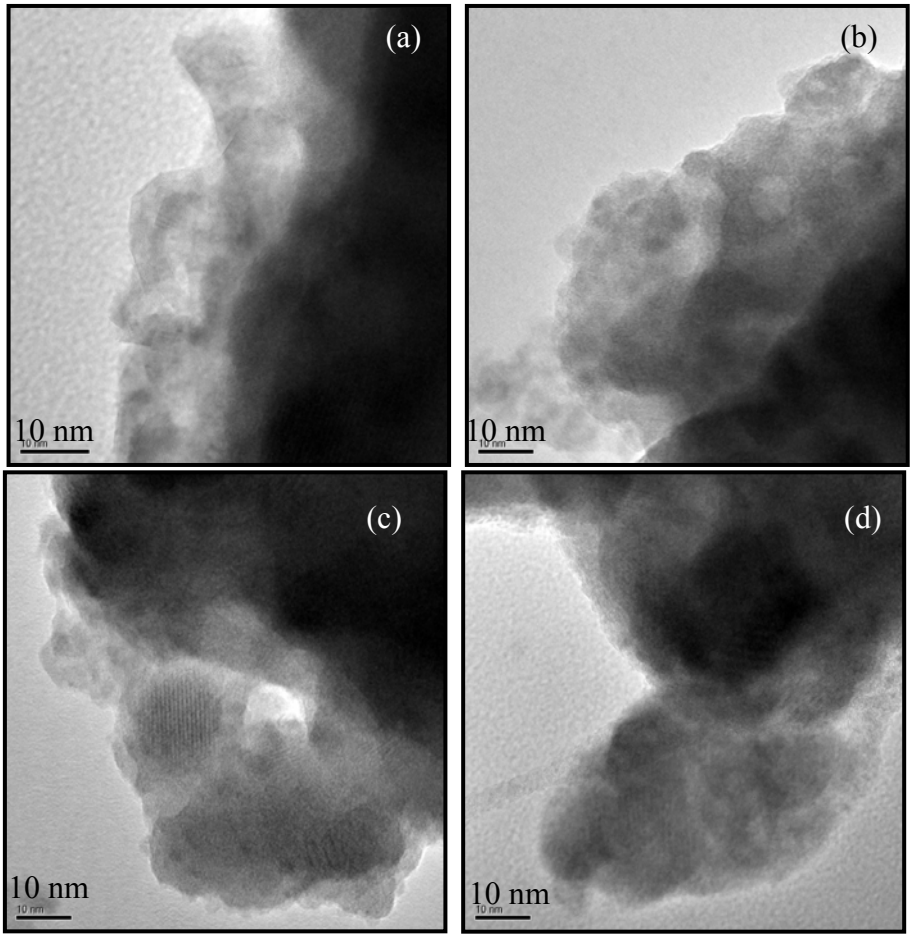

Fig. 2. TEM images of ZnS QDs at different source concentration a)0.2:0.20 b)0.2:0.25 c)0.2:0.30 and d) 0.2:0.35 mol/mol

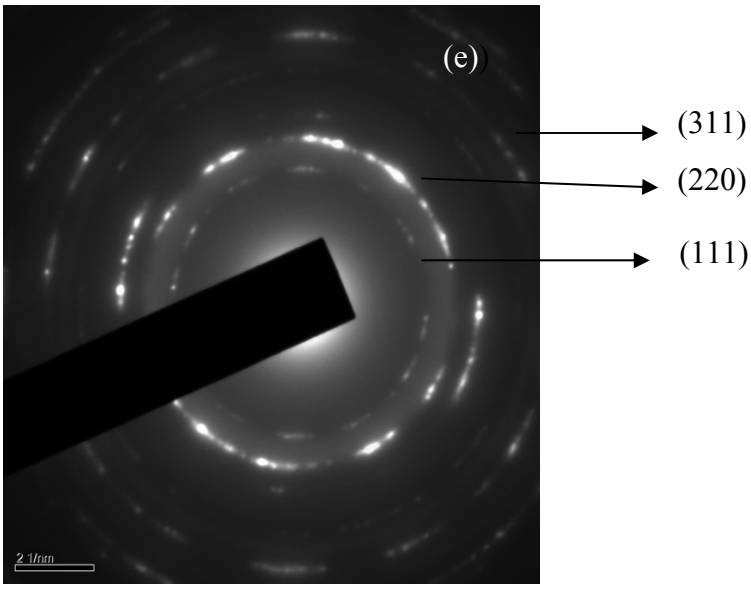

Fig. 2. TEM images of ZnS QDs at different source concentration.
e) SAED pattern of source concentration 0.2/0.2 mol/mol

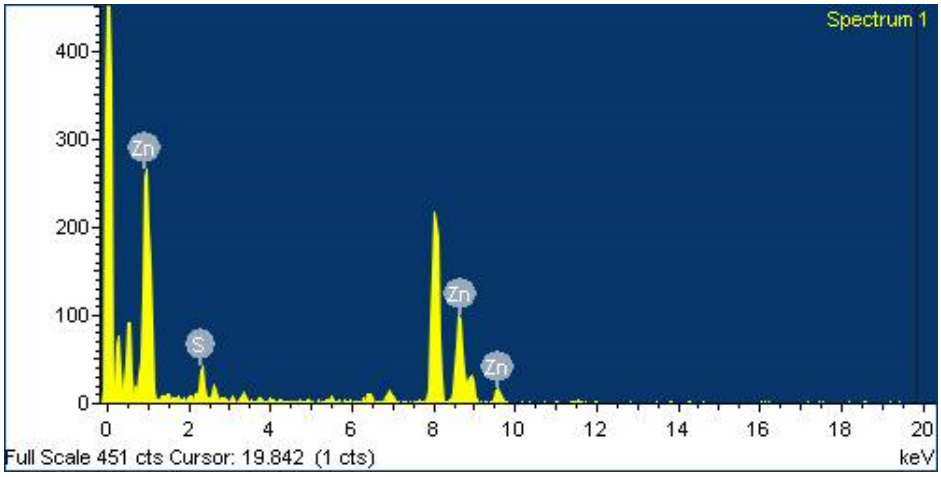

Fig. 3.EDAX pattern of ZnS QDs of 0.2:0.2 mol/mol source concentration.

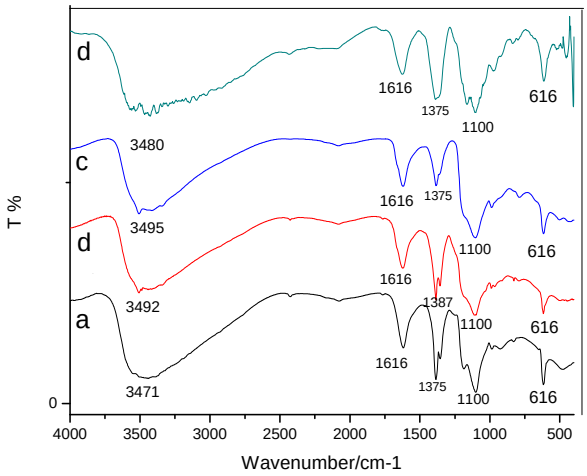

Fig. 4.FTIR spectrum of ZnS QDs with different source concentration.
a)0.2:0.20 b) 0.2M:0.25 c) 0.2:0.30 D) 0.2:0.35 mol/mol.

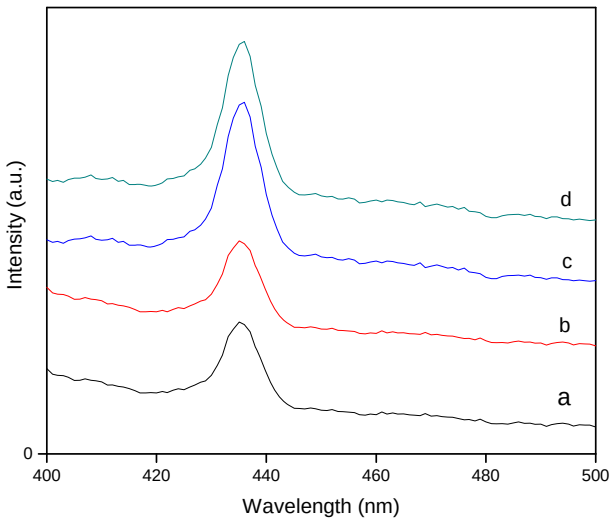

Fig. 5. Photoluminescence spectra of ZnS QDs with different source concentration.
a)0.2:0.20 b) 0.2M:0.25 c) 0.2:0.30 D) 0.2:0.35 mol/mol.

Room – temperature PL spectra of ZnS nanoparticles recorded using an excitation wavelength of 340nm is shown if Fig5.From the PL spectra it was observed that ZnS nanoparticles with different source sulphide concentration showed broad emission peak centered at 435nm originated from the host ZnS. This blue emission can be ascribed to a self-activated centre presumably formed between a Zn vacancy and a shallow donor associated with a sulfur vacancy [18].Sulfur vacancies at the surface are expected to give rise to Zn dangling bonds that form shallow donor levels. Several research groups [19-20] have studied the blue emission from ZnS nanoparticles under UV excitation.

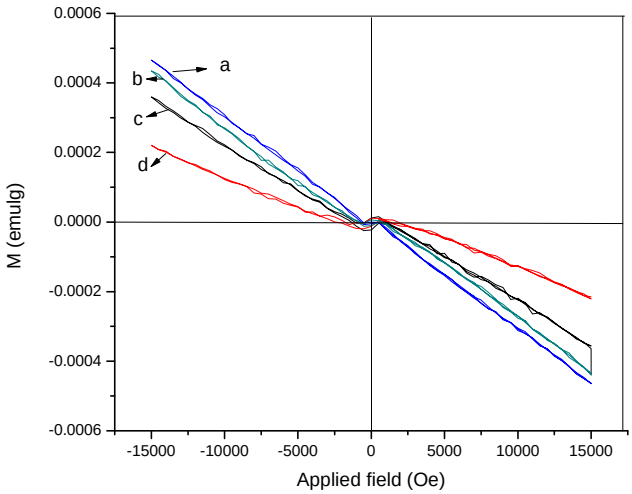

Fig. 6. Plot of magnetization versus Applied magnetic field of ZnS QDs with different source concentration. a)0.2:0.20 b) 0.2M:0.25 c) 0.2:0.30 D) 0.2:0.35 mol/mol.

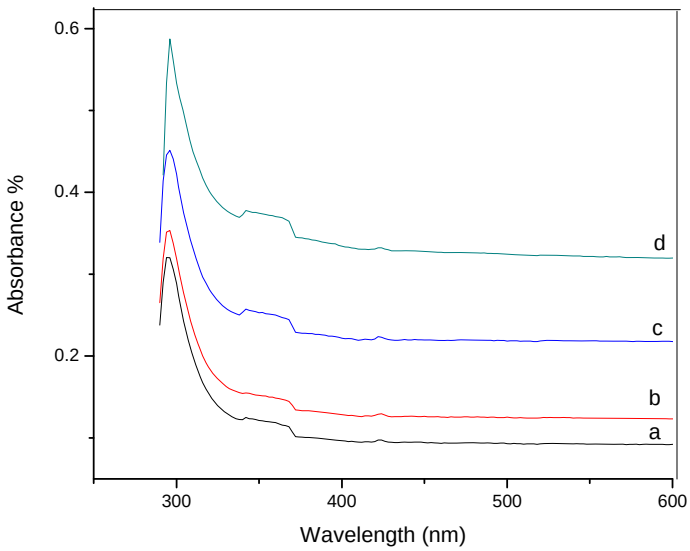

Fig. 7.UV absorbance spectrum of ZnS QDs with different source concentration. a) 0.2:0.20 b) 0.2M:0.25 c) 0.2:0.30 D) 0.2:0.35 mol/mol.

Table 1. Structural parameters of ZnS QDs

Zn/S Concentration Mole/mole	2 $\theta_{(111)}$	d (Å)	Calculated values	Grain size (nm)
			a (Å)	
0.2:0.20	28.91	3.126	5.414	4.74
0.2:0.25	28.94	3.106	5.397	4.83
0.2:0.30	29.02	3.074	5.324	4.92
0.2:0.35	29.28	3.049	5.281	5.08

Fig. 6 illustrates the magnetization versus applied magnetic field (M-H) curves recorded at room temperature using VSM for ZnS quantum dots for different source concentration. From the figure a typical diamagnetic behavior has been observed in the host ZnS and it is attributed to the absence of unpaired electrons in its'd' orbital. D.A.Reddy and co-authers [21] have observed the diamagnetism in ZnS nanoparticles.

Optical absorption spectra of ZnS quantum dots are shown in figure7. From the absorption spectra, it is seen that the absorption edge of ZnS nanoparticles is blue shifted and is located at 300 nm compared to that of bulk ZnS which has an absorption edge at 337 nm. This blue shift is mainly attributed to the strong quantum confinement effect caused by the reduction in the particle size [22]. It is well known that in case of semiconductors the band gap between the valence and conduction band increases as the size of the particle decreases in the nanosize range. Absorption spectrum of ZnS nanoparticles of increasing sodium sulphide concentration shows that the absorption edge is slightly shifted towards the longer wavelength. This shift towards longer wavelength indicates the decrease of optical band gap.

The fundamental absorption, which corresponds to the electron excitation from the valance band to the conduction band, can be used to determine the nature and value of the optical band gap. The absorption maxima of ZnS nanoparticles for 0.2, 0.25, 0.30 and 0.35 mol of sodium sulphide concentration lie at 294, 295, 296 and 297nm, respectively. The band gaps of all the samples were calculated using a simple wave energy equation

$$E = h\gamma = \frac{hc}{\lambda} \tag{2}$$

The bandgap values corresponding to these maxima are 4.23, 4.21, 4.20 and 4.18eV,respectively. Band gap of ZnS nanoparticles are higher than that of bulk ZnS (3.8eV) and this blue shift of the band gap takes place because of the quantum confinement effect. Semiconductor nanocrystals with the particle size smaller than the Bohr radius of exciton, exhibit the dominant quantum confinement effect, in which the size dependent standing wave diffraction of electrons occurs as an electron moves through the interior and senses the periodical lattice potential and the crystallite boundaries. The increase in the band gap of nanoparticles due to quantum confinement is of the quantitative form [23]

$$E_g^{nano} = E_g^{bulk} + \frac{\hbar^2\pi^2}{2\mu R^2} - \frac{1.8e^2}{\varepsilon R} \quad (3)$$

where E_g^{nano} and E_g^{bulk} are the band gap value of the nanoparticles and the bulk material respectively, $\mu = m_e m_h / (m_e+m_h)$ is the reduced mass and m_e and m_h are effective masses of electron (0.19 m for ZnS) in conduction band and holes (0.80 m for ZnS) in valance band respectively, e is the electron charge, ε is the relative permittivity of the semiconductor, R is the radius of the particle and the second term is the columbic term and is generally neglected. The particle size has been calculated using equation 3. The particle size of ZnS is found to lie in the range of 4 to 5 nm. which is good agreement with XRD and TEM results.

4. Conclusion

The ZnS QDs of different sulfur sourcevconcentration have been successfully synthesized by a simple precipitation method without capping agent. It is found that the change in the concentration change significantly the particle size. Structural analysis indicated that the ZnS QDs were cubic zinc blende structure and the particle size found to be lie in the range 4-5 nm. The lattice constant found to be decreases with increasing sulfur source concentration. The TEM image shows the formation of all samples seems to be nearly spherical in nature and the particle size was found to be 4.9 to 5.1nm. UV-visible absorption and photoluminescence spectra with blue-shifts from the bulks, indicating the quantum confinement effect of the semiconductor. The magnetic behavior of prepared ZnS quantum dots shows diamagnetic in nature. Prominent IR peaks are analyzed and assigned from FTIR spectra.

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