Optical charcterization of Mn doped CdS nanoparticles synthesized by simple chemical route

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Nanoparticles of undoped and Mn doped CdS ($Cd_{1-x}Mn_XS$; x=0.01) were synthesized by co-precipitation method.X-Ray diffraction (XRD) studies reveal that CdS crystallized in Cubic (Zinc blende) phase.Field Emission Scanning Electron Microscopy (FESEM) study reveals that the undoped nanopowders are formed into aggregates while doped particles are in spherical shape. The nanoparticles were characterized using UV-Visible (UV-Vis) and Fourier Transform Infra Red (FTIR) studies. The band gap of the doped CdS is more than the undoped and this is due to quantum size effect of the nanoparticles. The average crystallite size of the doped and the undoped CdS nanoparticles is 1.58nm and 1.95 nm respectively. The photoluminescence spectrum of the Mn doped CdS show the blue band emission and green emission.

1. Introduction

Nanosized materials such as ZnO, ZnS, CdO and CdS are being used for a number of applications such as transistor, light emitting diodes (LED) and nanolaser [1, 3, 4-6]. Semiconductor nanoparticles doped with transition metalions have attracted wide attention due to their excellent luminescent properties and the unique optical properties. Semiconducting optoelectronic materials play functional role in variety of applications due to their extraordinary optical, electrical and magnetic properties. The physical behavior of semiconductor nanoparticles strictly depends on their size, structure and morphology [2]. Also, it is well known that Quantum size effects (QSE) associated with the low dimensionality leads to several remarkable modifications in the properties of materials [7, 8].

Cadmium sulfide is an $A^{II}B^{II}$ compound semiconductor with a direct band gap of 2.42 eV (515 nm) and a small exciton Bohr radius of 2.5 nm. Mn doped CdS nanoparticles received much attention due to the modified structural, electrical and luminescence properties [9-15]. Cadmium sulphide crystallites are formed in the hexagonal or cubic crystal structure. CdS is an important n-type semiconductor and its photoconductive and electro luminescent properties nanoparticles have been reported for different shapes and morphologies [16-20]. Nanoparticles can be prepared by different methods such as sonochemical method, sol-gel method, chemical precipitation method, microwave method, solid state method, hydrothermal method and reverse micelles method. Among these, the chemical precipitation method is the simplest chemical method in which the nanoparticles can be prepared quickly with very good crystallinty. Preparation of doped CdS by this simple method is rarely reported. In the present work, we report on the synthesis of undoped and 1% Mn doped CdS nanoparticles by this simple chemical precipitation technique. The obtained optical properties are analyzed in detail for the doped and $Cd_{1-x}Mn_xS$ (x=0.01) nanoparticles.

2. Experimental

2.1 Sample preparation

Undoped and 1% Mn doped CdS nanoparticles were prepared by chemical precipitation method. All the chemicals used were of analytical Reagent grades (Merck) which do not require further purification. The deionized water was used as solvents for all the solutions prepared. The source of Cd, S and Mn are $CdCl_2$, $MnCl_2$ and Na_2S respectively. First, desired molar proportions of $CdCl_2$ and $MnCl_2$ were dissolved in the deionised water and continuously stirred for 1 hour using a magnetic stirrer at 90ºC and then powder of CdS: Mn nanoparticles was obtained by precipitation. The precipitate was washed several times with acetone to remove impurities. Finally, the powder was dried ina vacuum oven at 115ºC for 3 hours and a yellowish orange powder was obtained finally.

2.2 Characterization techniques

The CdS nanoparticles were characterized by X-ray diffractometer (XRD), Field Emission Scanning Electron Microscope (FESEM), UV-Vis spectrometer and Fourier Transform Infra Red (FTIR) spectrometer. The crystal structure of this samplewas determined by using Siemens D-500 X-ray diffractometer with Cu-K_α radiation of

wavelength 1.5405Å at the scanning rate of 0.02min⁻¹ in the range of 2θ being 20º to 70º. The morphology of CdS nanoparticles was observed by a Field Emission Scanning Electron Microscope (FESEM-Hitachi SU-6600). UV-Visible spectrum of the nanoparticles was recorded (using Cary UV-2400PC series UV-Vis spectrophotometer) in the wavelength range 200 to 900 nm. The Photoluminescence (PL)spectrum were obtained with 360nm line of Xe laser excitation using Shimadzu Rf-5000 spectrometer. The presence of functional groups were identified by Fourier Transform Infra Red spectrometer (FTIR, Shimadzu) in the range of 400-4000 cm⁻¹.

3. Results and discussion

3.1. Structural Characterization

Fig. 1 shows the XRD patterns of undoped CdS and Mn doped CdS nanoparticles. The diffraction peaks are indexed as (111), (220) and (311) reflections of cubic Zinc blend phase in conformation with the JCPDS card no 43-0985. The broad diffraction peaks indicates that the size of the crystallites are in the nanometer scale. XRD spectrum shows that there are no extra peaks due to manganeous metal, other sulfides or any cadmium manganese phase. This suggests that pure cubic zinc blend phase of CdS was formed in the synthesis. The intensities of the peaks were observed to vary from the undoped to Mn doped CdS samples and this may be due to the replacement of Cd^{2+} by Mn^{2+}. The ionic radius of Mn (0.66Å) is smaller than Cd (0.98Å) which indicates that lattice constant is decreased when CdS is doped with Mn. So, a shift of the diffraction peaks towards the higher angle side was observed in the Mn doped CdS (see Table 1 and 2). The shift of the XRD peaks for Mn doped CdS indicates that Mn has been doped into the CdS structure.

The mean crystallite size was calculated from the Full Width Half Maximum (FWHM) of XRD peaks by using Debye-Scherrer formula given below.

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl}\cos\theta}$$

where D is the average crystallite diameter, λ is the wavelength, β is the Full Width at Half Maximum (FWHM) and θ is the Bragg angle of diffraction. The micro strains of the samples were calculated using the formula given by

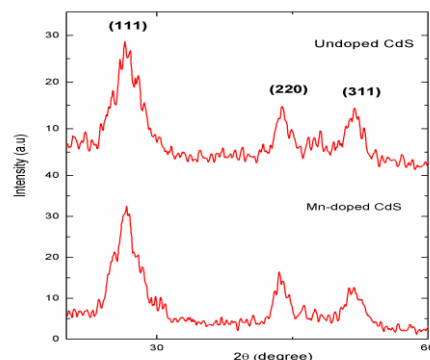$$\varepsilon = \frac{\beta_{hkl}\cos\theta}{4}$$

Fig.1. XRD pattern of undoped and Mn doped CdS nanoparticles.

Table 1 and 2 show the crystallite size, lattice constant and micro strain size of the undoped and Mn doped CdS respectively. The average crystalline size was found to be 1.95 nm and 1.58 nm respectively for undoped and doped CdS samples. It is clearly evident from these tables that the lattice constant and the crystallite size decreases when CdS is doped with Mn. The microstrain is found to increase from the undoped to doped sample and this is due to the doping of Mn in the host CdS lattice to replace Cd by Mn.

*Table 1. XRD data for undoped CdS nanoparticles.*

2θ (degree)	Crystallite size (nm)	hkl value	Lattice constant a in (Å)	Micro strain 10⁻³
26.37	2.13	111	5.8491	0.019
43.51	1.78	220	5.879	0.0185

Table 2. XRD data for 1%Mn doped CdS nanoparticles.

2θ (degree)	Crystallite size (nm)	hkl value	Lattice Constant a in (Å)	Micro strain10⁻³
27.04	2.00	111	5.7076	0.0291
43.90	1.15	220	5.8293	0.027

3.2. Morphology study

Fig. 2 shows the FESEM images of undoped and Mn doped CdS nanoparticles. The morphology of Mn doped samples are different from undoped samples. For the undoped sample, only aggregates are formed whereas for the Mn doped CdS nanoparticles, the SEM image shows the spherically shaped nanopaticles which are well separated [26].
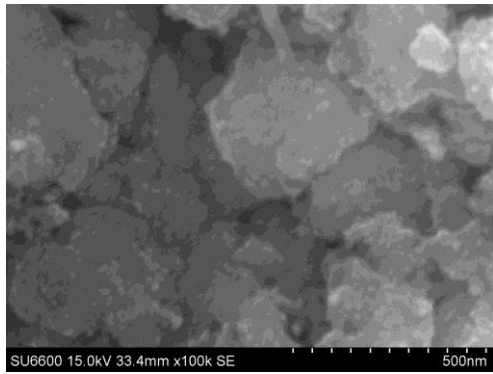
(a)
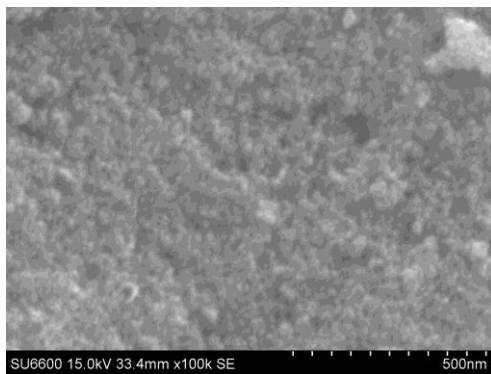
(b)

*Fig.2. FESEM image of (a) undoped CdS and
(b) Mn doped CdS nanoparticles.*

3.3. Functional group analysis

FTIR spectrum of undoped CdS and Mn doped CdS NPs are shown in Fig. 3. These spectrum is used to obtain the details about the chemical bonding in a material. It is used to identify the elemental constituents of a sample. The peaks at 748.33 cm^{-1}, 655.75 cm^{-1} indicate the presence of Cd-S stretching [21, 22] and the peak at 1120.56 cm^{-1} indicates the sulfide compound [23]. The peaks at 1336.56 cm^{-1} indicate oxygen stretching and the peaks at 3441.63 cm^{-1}, 3197.76 cm^{-1} indicate the OH stretching. The peak at 464.81 cm^{-1} indicates the Mn-O bond [27].
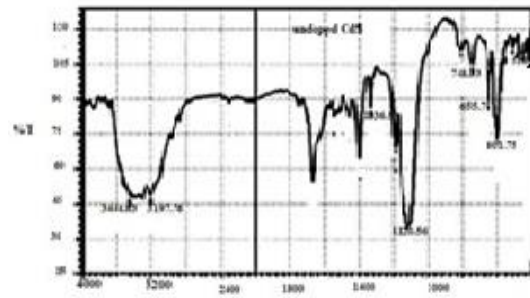
(a)
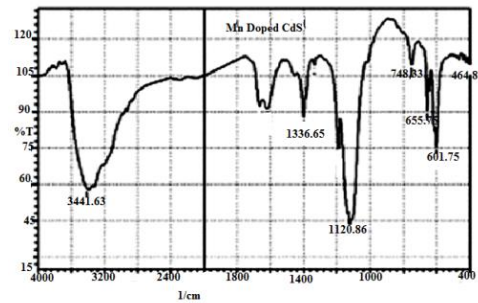
(b)

*Fig. 3. FTIR spectra of (a) undoped CdS and (b) Mn
Doped CdS nanoparticles.*

3.4. Optical study

The diffused reflectance spectrum (DRS) of Mn doped CdS and undoped CdS are shown in Fig. 4. The reflectance is about 90% for the doped and 83% for the undoped CdS nanoparticle in the IR region whereas it is less in the visible region. The DRS of the samples was used to calculate the band gap of the undoped and the doped CdS nanoparticles. The band gap energy of bulk CdS is 2.42eV [24]. The energy band gap was determined by Kubleka-Munkrelation [25].

$$[F (R_\alpha) h\nu]^{1/n} = C(h\nu - E_g)$$

Where hν is the incident photon energy, R_α is the Reflectance coefficient, E_g is the band gap energy, C is a constant and F (R_α) is the Kubleka –Munk function which is given by the equation

$$F(R_\alpha) = \frac{(1 - R)^2}{2R}$$

R is the reflectance. Exponent n depends on the type of transition and it may have values ½, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. Here, n=1/2 for allowed direct band gap. The plot of [F (R_α) hν]^2 versus hν is given in Fig. 5 and the energy gap is found by extrapolating the linear part of the plot to meet the energy axis at [F (R_α) hν]^2 =0. The band gap is 2.72 eV for the undoped and 3 eV for the 1% Mn

doped CdS. We observe an increase in the band gap for the prepared doped and undoped nanoparticles as compared to the bulk CdS (E_g = 2.42 eV). In the present study, the band gap is found to increase from undoped to 1% Mn doped samples and this suggests a blue shift in the absorption band edge due to doping [28, 29]. This is due to quantum size effect of nanoparticles. The obtained band gap values are in agreement with the fact that the band gap increases with decrease in the crystallite size.
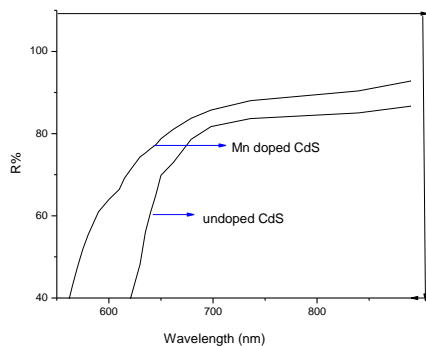

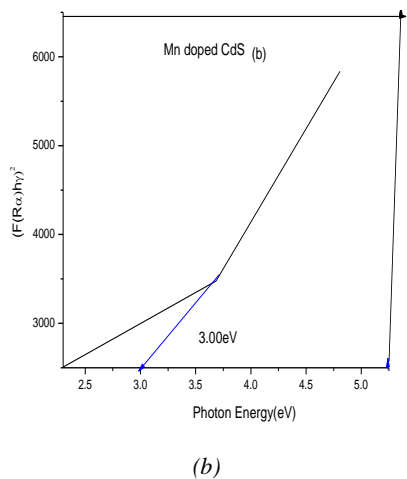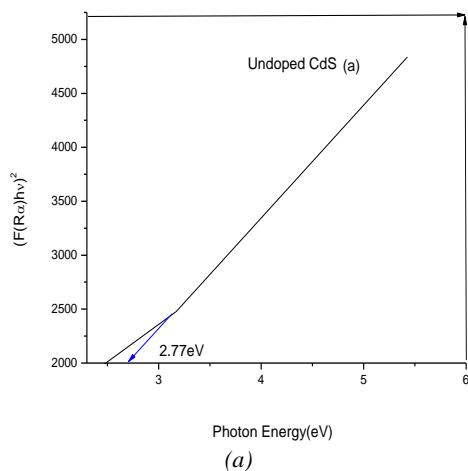*Fig. 4. Diffuse Reflectance Spectrum of undoped and Mn doped CdS nanoparticles.*

(a)

(b)

Fig. 5. F $(R_a hv)^2$ versus hv for (a) undoped CdS and (b) Mn doped CdS nanoparticles.

3.5. Photoluminescence study

The Photoluminescence [PL] spectra of $Cd_{1-x}Mn_xS$ nanoparticles with x=0.01 is shown in Fig. 5. The photoluminescence excitation wavelength was 360nm. The peaks for the undoped (412 nm and 486 nm) are very weak and this is due to the nonradiative recombination of electrons and holes.

The PL of doped sample consists of three prominent strong peaks at 433 nm (2.86 eV), 465 nm (2.67eV) and 496 nm (4eV) and it shows a relatively weak peak at 486 nm. The strong peaks of Mn doped indicates the effective radiative electron − hole recombination. The first three strong peaks correspond to blue emission and the last one corresponds to the green emission. The green emission originates from the electron transition between the Mn states which are present in the band gap of CdS. The blue emission is the result of the electron transition from the conduction to the valence band of CdS.
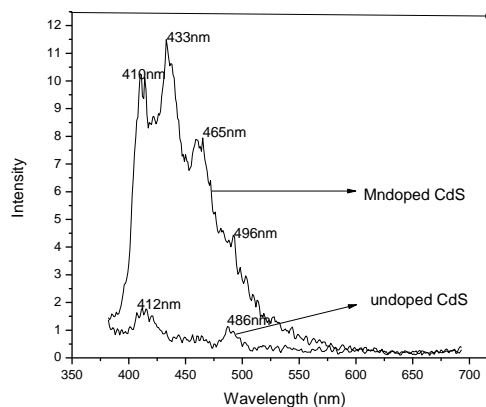

Fig.6. Photoluminesence spectra of undoped CdS And Mn doped CdS nanoparticles.

The intensity of the PL peaks are strong for doped CdS compared to the undoped nanoparticles which indicates that Mn^{2+} is well incorporated into the CdS host lattice. Thus the emission peaks of Mn doped CdS nanoparticles conforms the presence of Mn in the CdS host lattice.

4. Conclusion

Nanoparticles of undoped and Mn doped CdS were synthesized by using a chemical co-precipitation method. The crystalline structures are determined by XRD. XRD analysis confirms that the samples are in cubic zinc blend phase. The average crystallite size of the Mn doped CdS and undoped CdS nanoparticles are 1.58 nm and 1.95 nm respectively. UV-Visible studies indicate a blue shift in the band edge of the spectrum. The band gap values of the prepared undoped and Mn doped CdS nanoparticles are found to be and 2.77eV, 3.00 eV respectively. The obtained band gap values are in agreement with the fact

that the band gap increases with decrease in the crystallite size. FESEM studies reveals that the morphologies are different for the doped and undoped CdS nanoparticless. FTIR studies confirm the presence of Cd-S and Mn-O bond in the nanoparticle lattice structure. The photoluminescence spectrum of the doped sample shows the blue band emission from 410 to 465 nm and green emission at 496 nm. This green emission and also the difference in the PL emission intensity of the doped and undoped samples confirm the substitution of Mn in CdS and indicates that Mn^{2+} is well incorporated into the CdS host lattice.The green emission suggests that the Mn doped CdS nanoparticles are suitable for the optoelectronic applications.

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