Optical Properties of Ce Doped Cdse Nanoparticles Synthesized By Microwave Technique

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Abstract- *Ce- doped CdSe nanoparticles were prepared by a novel microwave technique and their optical absorbance spectra and PL emission spectra were studied. The effect of different molar concentrations of Cerium doping on the optical properties was investigated. The prepared nanoparticles were further characterized by XRD, FESEM and EDX studies. Blue shift in optical absorbance spectra in comparison to bulk CdSe suggests quantum confinement. The optical band-gaps determined from absorption spectral studies were found to be in the range of 1.87eV to 2.48 eV. XRD studies show diffraction peaks corresponding to hexagonal wurtzite CdSe. Morphological properties studied using FESEM show elongated rod shaped structures with non uniform particle distribution. The elemental composition was confirmed using EDS studies. PL spectra show band edge emission as well as emission due to defect levels in CdSe. A low power, aqueous solution-phase strategy has been used in this work to grow nanostructured metal chalcogenides which is low cost and less hazardous.*

Keywords- Nanoparticle; CdSe; Ce-doped CdSe; Chalcogenides.

I. INTRODUCTION

Semiconductor nanoparticles have been a subject of great interest mainly due to the quantum confinement effect exhibited by them, where the semiconductor crystallites have a surface electron which possesses a size-dependent wave function. The area to volume ratio of the particles is amplified and surface atoms contribute dominantly to the physical and chemical properties [1]. CdSe is a narrow band-gap II-VI semiconductor (chalcogenides) with band-gap of 1.75 eV at 300 k and have found wide applications in field electronic transistor (FET), optoelectronics, spintronics, sensing and photovoltaic cells [2-6]. The nanopowder of CdSe provides excellent and unique properties and their properties depend upon the shape and size of nanostructure [1, 7, 8]. Doping of these chalcogenide nanoparticles with rare earth elements improves the fluorescence life time and also produces a large separation between excitation and emission there by making it more suitable for opto-electronic application [9]. There are several reports on various techniques used by researchers for the synthesis of CdSe nanoparticles like chemical injection method [10-12], radiation method [13], microwave irradiation [14-15] and photochemical method [16-18].

In the present work, nanoparticles of CdSe and Ce doped CdSe were synthesized by a microwave assisted solution growth technique and their absorption and PL spectra were studied.

Different concentrations of Ce are doped at the lattice of CdSe and its effect on the optical band-gap and particle size was investigated from optical absorption spectra. XRD, FESEM and EDS studies were carried out to study the structural, morphological properties and the elemental composition respectively.

II. MATERIAL AND METHOD

CdSe and Ce doped CdSe nanoparticles were synthesized by microwave assisted solution growth method in the presence of hydrazine hydrate. $CdCl_2$ was used as source of Cd, Selenium powder as selenium source; Cerium oxide was used as source of Ce. Hydrazine hydrate acts as a reducing agent. $CdCl_2$ with the required amount of Se powder was mixed with deionized water, ethylene glycol and hydrazine hydrate in the volume ratio 7:3:1 respectively. For the doped samples, different molar concentrations of Cerium Oxide by weight were mixed in the above mixture. This solution was magnetically stirred for 30 minutes and placed in microwave oven for 45 minutes (4min on/ 4min off). The black precipitate obtained was filtered, washed and centrifuged with distilled water several times, then dried in vacuum at 70^0 C for 4 hours.

Optical Absorption spectra was studied using ELICO SL 210 UV-Visible spectrophotometer. PL studies were carried out using shimadzu RF5301 Fluorospectrophotometer at Pt. Ravishankar Shukla University, Raipur. XRD studies were done using PAN analytical 3KW Powder X Ray Diffractometer at NIT Raipur and FESEM, EDS studies were done at VNIT Nagpur using JSM 7610F Scanning Electron Microscope.

III. RESULT AND DISCUSSIONS

3.1 X-Ray Diffraction:

Figures 1. (a) And (b) show the X-ray diffractograms of pure and Ce doped CdSe nanoparticles respectively. The hexagonal wurtzite structure of CdSe is confirmed from both the patterns.

The XRD spectrum was observed from 20 to 70 ^{0}C using Cu-Kα1 line of characteristic wavelength = 1.54 A^0. All the peaks match with the crystalline phase of hexagonal wurtzite structure of CdSe (JCPD card NO. 08-0459) and the corresponding data along with values of lattice constants are presented in tables 1 and 2. The peaks corresponding to (100), (102), (103), (110), (202), (002), (101), (112), (203) planes are observed. [19].

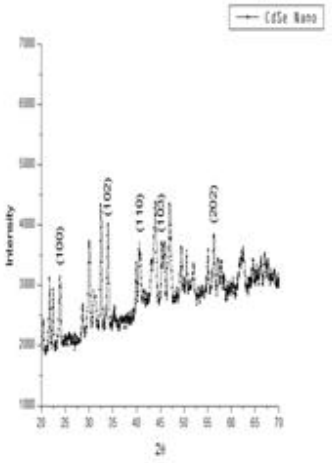

Fig: .1(a): Undoped CdSe nanoparticles.

Table: .1(a): XRD data of pure CdSe, prepared by microwave assisted solution growth method.

D value (A°)		Relative Intensity		hkl	Lattice Constant (A□)	
(Obs)	(Rep)	(Obs)	(Rep)		(Obs)	(Rep)
3.716	3.722	71	12	(100)	a=4.2908	a=4.2990 c=7.0100
2.634	2.552	91	56	(102)	a=4.2908 c=7.4483	a=4.2990 c=7.0100
2.219	2.1495	84.2	4	(110)	a=4.2908 c=7.4691	a=4.2990 c=7.0100
2.000	1.9791	84	8	(103)	a=4.2908 c=7.1106	a=4.2990 c=7.0100
1.633	1.644	87	17	(202)	a=4.2908 c=7.2787	a=4.2990 c=7.0100
1.484	1.455	82	5	(203)	a=4.2908 c=9.7154	a=4.2990 c=7.0100

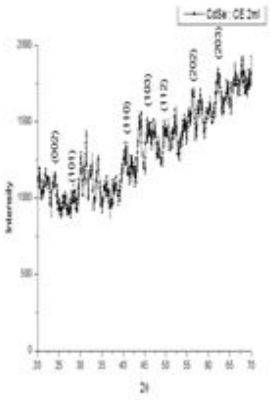

Fig: .1(b): Ce-doped CdSe nanoparticles.

Table: .1(b): XRD data of Ce doped CdSe, prepared by microwave assisted solution growth method.

D value (A°)		Relative Intensity		hkl	Lattice Constant (A□)	
(Obs)	(Rep)	(Obs)	(Rep)		(Obs)	(Rep)
3.7006	3.5050	63	14	(002)	a=4.448	a=4.2990 c=7.010
3.1863	3.288	64	24	(101)	a=4.448 c=5.670	a=4.2990 c=7.010
2.2245	2.1495	73	4	(110)	a=4.448	a=4.2990 c=7.010
1.9785	1.9791	82	8	(103	a=4.448 c=6.915	a=4.2990 c=7.010
1.8344	1.832	81	9	(112	a=4.448 c=7.223	a=4.2990 c=7.010
1.626	1.644	93	17	(202	a=4.448 c=7.176	a=4.2990 c=7.010
1.487	1.455	100	5	(203	a=4.448 c=9.676	a=4.2990 c=7.010

3.2 FESEM and EDS studies.

Figures 2(a) and 2(b) show the FESEM images of undoped CdSe and Ce doped CdSe nanoparticles at a magnification of 50K. It can be observed from the micrographs that the particle growth is not uniform and the average particle size is approximately 100 nm.

Elongated rod shaped structures with some spherical particles spread over the surface non homogenously is seen in the case of undoped CdSe while in Ce doped CdSe, only elongated rod like structure is visible. The particle growth is not observed.

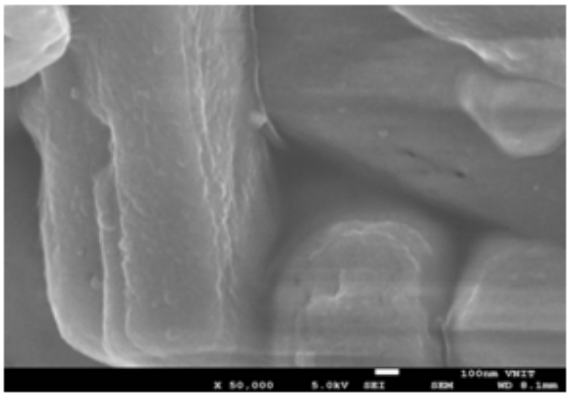

Fig: 2(a): FESEM micrograph of undoped CdSe nanoparticles.

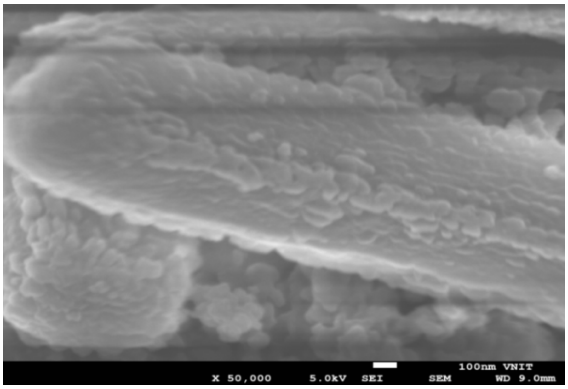

Fig: 2 (b): FESEM micrograph of Ce doped CdSe nanoparticle.

EDS Studies:

EDX spectroscopy was employed to examine the elemental composition of the prepared nanoparticles. Figure 3(a) and 3(b) represent the EDX spectra of undoped and doped CdSe nanoparticles. The peaks observed correspond majorly to elemental Se and elemental Cd along with a small percentage of impurities.

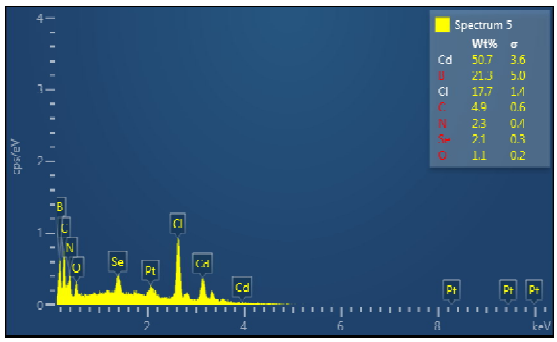

Fig: 3 (a): undoped CdSe nanoparticles.

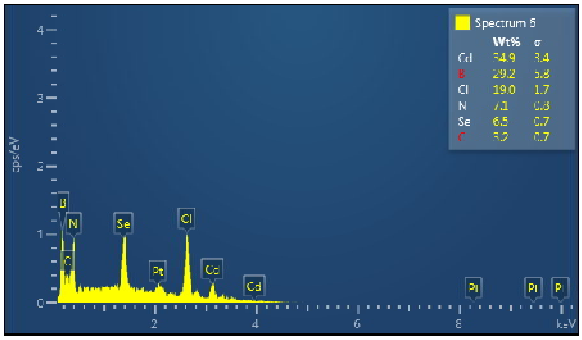

Fig: 3(b): Ce doped CdSe nanoparticles.

3.3 Absorption Spectral Studies:

Figure 4(a) and (b) presents the optical absorption spectra of undoped and Ce doped CdSe nanoparticles respectively. Absorption spectral studies are helpful in understanding the electronic structure of the optical bandgap of the material. Absorption in the near ultra violet region arises due to the excitonic transitions within the sample.

The study of absorption edge predicts the band gap structure is mostly affected near the band extreme [1]. It can be observed from the figure 4(a) that a shift in the absorption edge towards shorter wavelength side (~ 650 nm) occurs in the nano materials in comparison to that of the bulk (715 nm). This can be attributed to the well known quantum confiment effect [20]. Sharp absorption peaks are observed at around 380 nm for the undoped and doped CdSe nanoparticles and also for bulk CdSe which may be due to excitonic absorption . However the absorbance is higher in the case of nanoparticles. In the case of Ce doped CdSe nanoparticles prepared with different concentrations of Ce (figure 4b), absorbance in the near ultra violet region has been found to be maximum for 0.01M concentration of Ce. To test the nature of bandgap and also to determine its values, plots between $(\alpha hv)^2$ and hv were drawn (Tauc's plot) where α is the absorption coefficient. The absorption coefficient α and bandgap Eg for direct bandgap materials are represented by the equation.

$$\alpha = c\,(h\nu - Eg)^{1/2}/h\nu \ldots\ldots \quad (1)$$

The values of bandgap are summarized in table 3. It can be seen that higher bandgap values are obtained for the undoped and doped nanoparticles in comparison to that of bulk which further confirms size quantization effects.

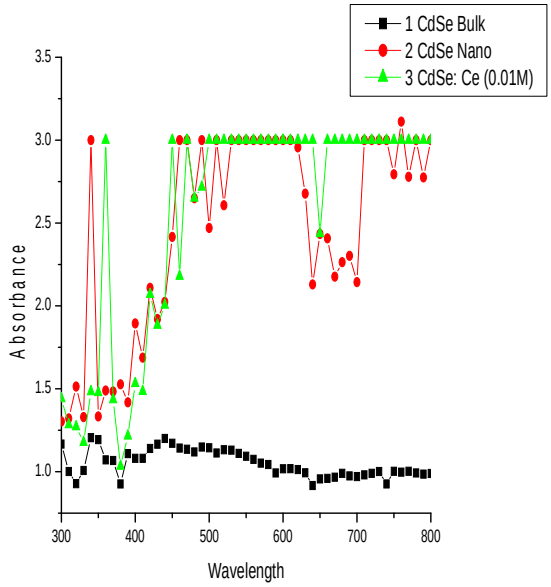

Fig: 4(a): Optical absorption spectra of CdSe nanoparticles – 1. CdSe Bulk, 2. CdSe Nano, 3. CdSe: Ce (0.01M)

Table: .3: Bandgap values of CdSe bulk, undoped and doped CdSe nanoparticles.

Sample	Bandgap (e V)
CdSe Bulk	1.87
CdSe Nano	2.3
Ce: CdSe (0.005M)	2.2
Ce: CdSe (0.05)	2.08
Ce: CdSe (0.01)	2.1
Ce: CdSe (0.1)	2.48

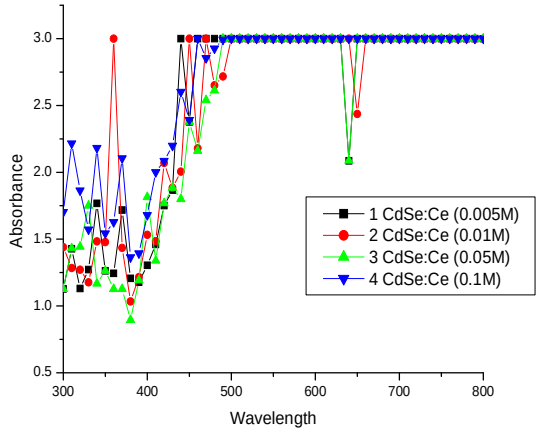

Fig: 4(b): Optical absorption spectra of Ce doped CdSe nanoparticles at different molar concentration of Ce- 1. CdSe: Ce(0.005M), 2. CdSe :Ce(0.01M), 3. CdSe :Ce(0.05M), 4. CdSe: Ce(0.1M)

3.4 Photoluminescence Studies:

The PL emission spectra of the doped and un-doped CdSe nanorods were recorded at excitation wavelength of ~ 350 nm. The spectra obtained are shown in the fig 5. In the case of CdSe bulk a broad emission peak at 468 nm and sharp peak at 724 nm is observed. The peak at 468 nm may be due to the formation of defects level or excitonic emission in CdSe nanoparticles while the peak at 724 nm may be due to the band edge emission. In the case of undoped and Ce doped CdSe, a blue shift in the emission peaks are observed. A much enhanced PL intensity is seen for the CdSe nanoparticles (doped and undoped) in comparison to that of the bulk for the blue shifted peak at around 700 nm.[21]

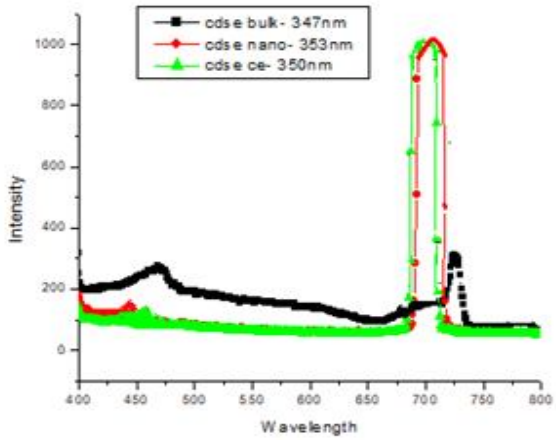

Fig:5. PL emission spectra of the undoped and doped CdSe nanorods.

IV. CONCLUSION

Hexagonal CdSe nanorods have been successfully synthesized by microwave assisted solution growth method. Wurtzite and elongated rod shaped structure was observed from XRD and FESEM studies. Synthesis of CdSe nanoparticles was further extended to dope these particles with different molar concentrations of Ce. The optical properties were studied by the UV-Visible absorption spectra and PL spectra. Blue shift in absorption edge has been observed in the case of the nanorods in comparison to the bulk. Absorbance in the near ultra violet region has been found to be maximum for 0.01M concentration of Ce .The bandgap values were found to be in the range of 1.87eV to 2.48 eV for bulk, undoped and doped CdSe nanorods respectively. The Pl studies show band edge emission as well as emission due to defect levels with enhanced intensity for both undoped and doped CdSe at around 700nm. These CdSe nanorods are therefore quite promising materials for applications in opto-electronics and photovoltaic cells and moreover the synthesis technique employed in this work is low cost and less hazardous.

V. ACKNOWLEDGEMENT

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