# Examination of the growth of rare earth doped CdSe thin films through optical and electrical characterization

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***Abstract***

*Some rare-earth elements doped nanocrystalline cadmium selenide thin films were grown on glass substrate at room temperature by chemical deposition method and characterized by optical and electrical investigations.Different deposition parameters have been improved to get high quality films.UV–VIS–NIR double beam spectrophotometer was used to observe optical absorption spectra in the range 400 nm to 700 nm at room temperature and to determine various important optical parameters viz. absorption coefficient, optical energy band gap, refractive index, dielectric constant etc. of thin films. Blue shift and quantum confinement were confirmed by increase in energy band gap from 1.74 eV (bulk-CdSe). Size of the nano particles was calculated by Effective Mass Approximation method. Photoluminescence emission spectra were also observed for the prepared films. Electrical characterization has been done with the help of DC two probe method. Electrical results confirm the semiconducting nature of the films. Activation energy was also calculated.*

***Keywords****: Thin film, nanocrystalline, band gap, activation energy.*

## 1 Introduction

Recently, nano dimension quantum dots of II-VI semiconducting materials have attracted many researchers due to wide and tunable band gap, high absorption coefficients, high stability and variety of applications [1]. In nano dimensions due to confinement of electron–hole pairs and due to the small size of the particles below the Bohr excition radius, gives various size dependent optical and electronic properties, like increase in energy band gap and blue shift of absorption edge with decrease of particle size. CdSe is an important semiconductor belongs to II-VI group with band gap of 1.74 eV and Bohr excitation radius of 5.6 eV which leads to variety of applications in photodetectors, display devices, light emitting diodes and other optoelectronic applications [2-5]. Nano dimension CdSe thin films can be prepared with various methods such as thermal evaporation, electrodeposition, melt quenching technique, vacuum evaporation, electron beam evaporation technique, SILAR, chemical bath deposition etc [6-12]. Among them chemical deposition method is a simple, green and cost-effective method which requires very less sophisticated equipments. Doping of CdSe is one effective way to improve the optical properties of CdSe for various applications. In recent years doping of rare earth elements in CdSe thin films has gained of interest in tailoring its optical properties. Rare earth elements are basically used as impurities in optical amplifiers. These elements are well known for lasing properties and photoluminescence properties and are used in display devices. In our present study optical and electrical properties of rare earth doped CdSe thin films were investigated and presented.

## 2 Experimental Details

Nanocrystalline CdSe thin films were successfully deposited on cleaned glass substrates by chemical bath deposition technique at room temperature. The glass slides of dimensions 24 mm x 75 mm were previously dipped in nitric acid for 48 h, and then cleaned with detergent and ultrasonic cleaner with triple distilled water. The cleaned glass substrates were vertically dipped into a glass beaker, containing solution of cadmium acetate, sodium selenosulphate, ammonia, triethanolamine. Nitrates of Neodymium and Ceriumwere used for doping. All chemicals were from AR grade. Sodium selenosulphate was prepared just prior to deposition by mixing selenium powder in hot sodium sulfite solution and refluxed for five hours using hot plate with magnetic stirrer. All parameters were optimized and already reported in our previous work [4]. pH of the solution was 11±0.2 and films were deposited at room temperature for a period of 24 hours. Low temperature deposition was chosen here to obtain crack free and uniform deposition. After deposition slides were washed with triple distilled water and dried at room deposition. CdSe with different rare earth doping percentages were deposited and due to better deposition and photoluminescence properties 1% doping percentage was preferred and further considered. Optical measurements were carried out using double beam UV–VIS spectrophotometer (CHEMITO SPECTRASCAN UV-2600). For photoluminescence study UV source with filters ranging from 235 to 320 nm was used as excitation source. PL emission was measured in visible range from 400 to 700 nm using constant deviation spectrometer. For detection of light a photomultiplier tube RCA 931A was used which operates with high regulated power supply EHT-11 (SES Roorkee). DC two probe method was used to investigate electrical properties.

## 3 Results and discussion

The deposited films were homogeneous, well adherent to the substrate with dark orange in color. Thickness was measured using commonly used weigh difference method and found to be 198 nm and 382 nm for Nd and Ce doped CdSe thin films respectively.

### 3.1 Optical absorption studies

The optical absorption spectra of 1% Nd and 1% Ce doped CdSe thin films are shown in Fig. 1. These spectra were recorded using double beam spectrophotometer in the wavelength range 400–700 nm at room temperature. Absorption is higher for shorter wavelengths side whereas it decreases for longer wavelengths. The shapes of both the spectra are relatively similar but a difference in absorbance and extinction coefficient was observed. By using obtained absorption spectra, the absorption coefficient ($\alpha$), and optical band gap ($E_g$)were calculated.

The absorption data was analyzed using well known Tauc relation. Here the transition is of direct nature because the variation of$(\alpha h\nu)^2$ versus $h\nu$ is linear as shown in Fig. 2. The observed band-gap energy as shown in Fig. 2 is listed in table 1. Calculated band gap values ($E_g$) are higher than the optical band gap of bulk CdSe which is around 1.74 eV due to formation of nano particles. Particle size was calculated using effective mass approximation formula,

$$E_g = E_{g(bulk)} + \frac{2\hbar^2\pi^2}{\mu D^2} \quad (1)$$

where $\mu$ is the effective mass of electron–hole pair and D is the diameter of crystallites. The crystallite size calculated is listed in table 1.

It is clear that the obtained values are less than the bohr exciton diameter (11.2 nm), which confirms strong quantum confinement effect.

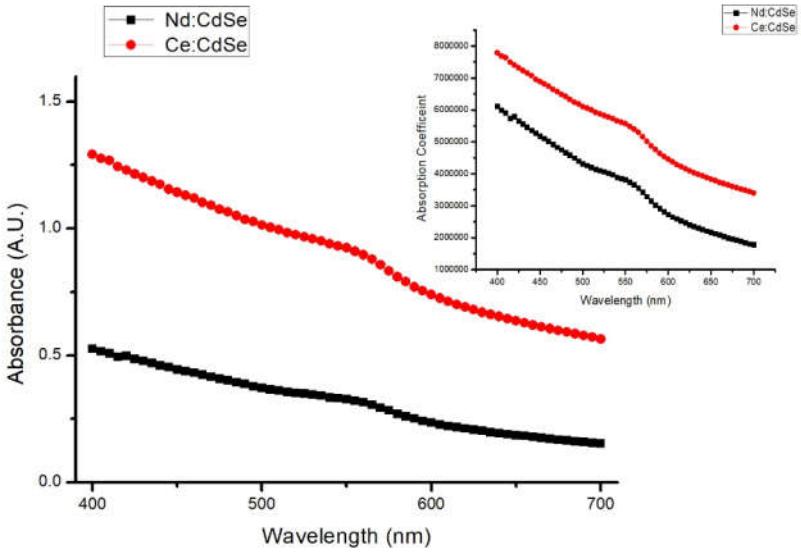


**Fig. 1 Absorbance and absorption coefficient of Nd and Ce doped CdSe thin films.**

Optical and electrical properties of thin films also depend on refractive index $(n)$ and dielectric constant $(\varepsilon)$ which can be used to construct various optoelectronic devices.

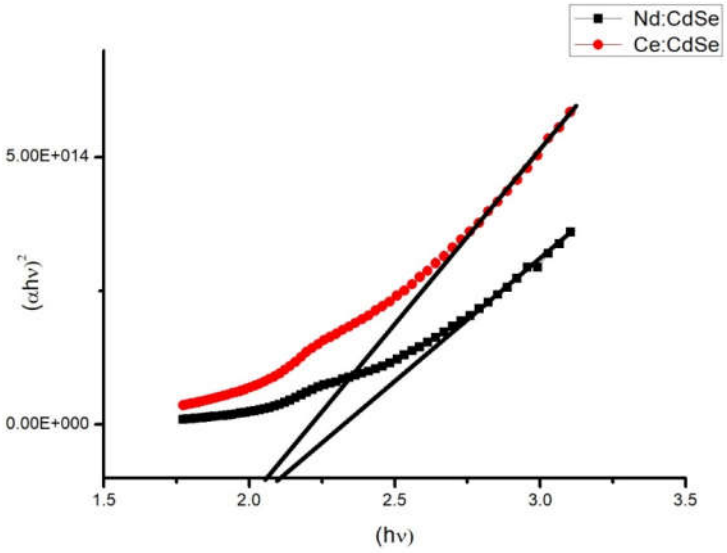


**Fig. 2 Estimation of band gap in Nd and Ce doped CdSe thin films.**

The refractive index of the films was calculated using Moss relation [15]

$$E_g n^4 = k \qquad (2)$$

Here refractive index is directly related to the energy band gap ($E_g$ ), where $k$ is a constant having a value of 108 eV. The high frequency dielectric constant ($\varepsilon_\infty$) and static dielectric constant ($\varepsilon_0$) were calculated using the given formulae [17]

$$\varepsilon_\infty = n^2 \tag{3}$$

$$\varepsilon_0 = -33.26876 + 78.61805E_g - 45.70795E_g^2 + 8.32449E_g^3 \tag{4}$$

The calculated values of bang gap, refractive index and dielectric constants are listed in table 1.

**Table 1.Values of Band gap ($E_g$), crystallite size ($D$), refractive index($n$), high frequency dielectric constant ($\varepsilon_\infty$) and static dielectric constant ($\varepsilon_0$) for nanocrystalline rare earth doped CdSe thin films calculated from spectrophotometer data**

| Films | Band gap $E_g$ (eV) | $D$ (nm) | $n$ | $\varepsilon_\infty$ | $\varepsilon_0$ |
|---|---|---|---|---|---|
| Nd:CdSe | 2.11 | 5.10 | 2.69 | 7.24 | 7.49 |
| Ce:CdSe | 2.06 | 5.92 | 2.67 | 7.15 | 7.32 |

### 3.2 Photoluminescence studies

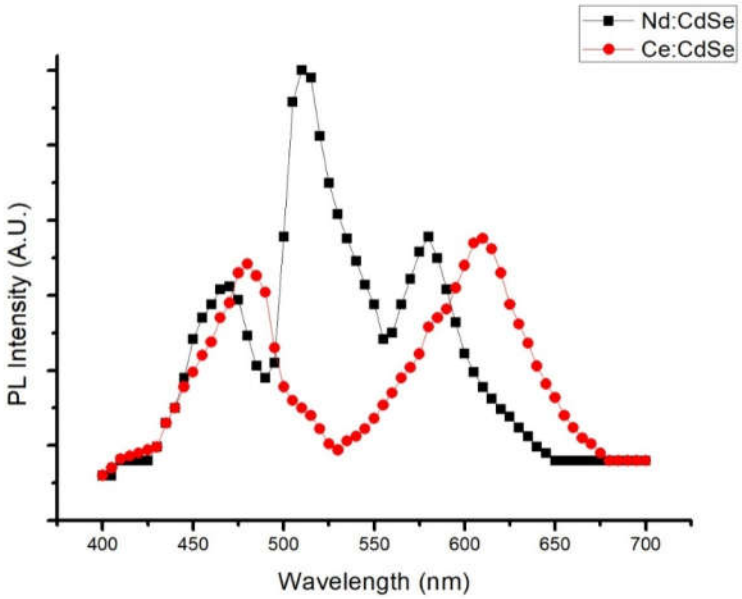


**Fig. 3 PL emission spectra of Nd and Ce doped CdSe thin films under excitation of 235 nm.**

Fig. 3 shows PL emission spectra of Nd and Ce doped CdSe thin films under excitation wavelength of 235 nm. PL emission peaks of Nd doped CdSe thin films are located approximately around 470 nm, 510 nm and 580 nm. Out of these peaks 580 nm was due to the band edge transition. Other two peaks at 470 nm and 510 nm are due to the interlevel transitions of the electronic energy states of $Nd^{3+}$. 470 nm emission can be attributed to transition from $^2G_{9/2}$ to ground state $^4I_{15/2}$ and similarly 510 nm emission is due to de-excitation from $^4G_{9/2}$, $^2D_{3/2}$ to ground state $^4I_{15/2}$. Bhushan et al. also got the similar peaks for Nd doped CdSSe thin filmsat 472 nm, 510 nm and 582 nm [13].

PL emission spectra of Ce doped CdSe thin film shows two peaks at 480nm and 610 nm. 610 nm emission peak can be associated to band to band transition whereas blue emission of 480 nm can be due to interlevel transition of $Ce^{3+}$ from $^2D_{3/2}$ excited state to ground states $^2F_{7/2}$ and $^2F_{5/2}$[14].

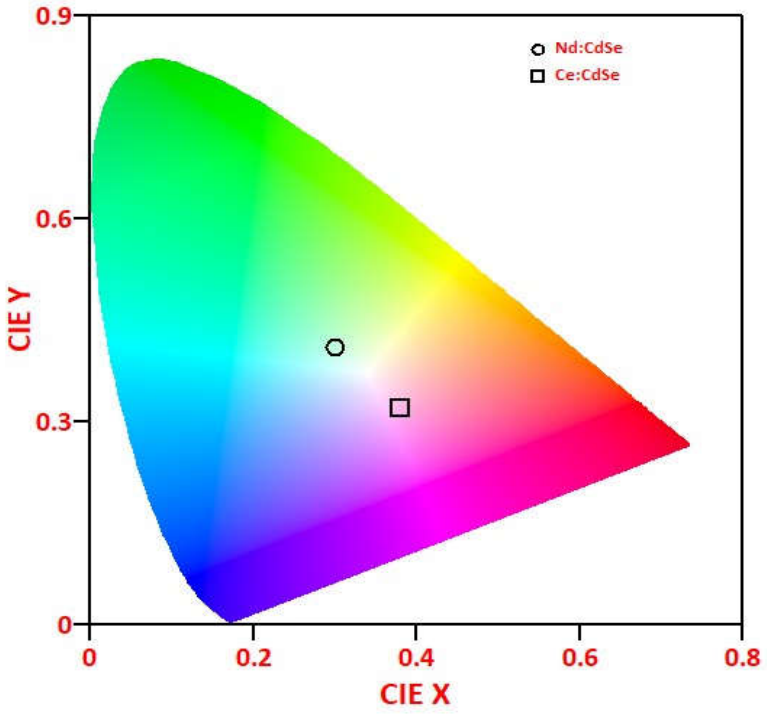


**Fig. 4 CIE chromatic coordination (x, y) of the deposited Nd and Ce doped CdSe thin films**

The CIE chromaticity coordinates (x, y) of the prepared films was calculated and shown in fig. 4. For Nd doped CdSe thin film the coordinates were calculated as (0.3008, 0.4120) corresponds to light blue region. Whereas on Ce doping, we got this value as (0.3763, 0.3151) corresponds to light pink region. From figure it can be concluded that the prepared films may be used as blue-pink phosphors.

### 3.3 Electrical studies

The temperature dependent dark dc-electrical resistivity measurements were carried out in the temperature range 308 K to 473 K. The dark dc-electrical resistivity ($\rho$) was calculated from the following equation:

$$\rho = RA/L \quad (5)$$

where R is the resistance of thin films, L is the distance between two electrodes prepared with carbon, and A is the cross-sectional area of thin.

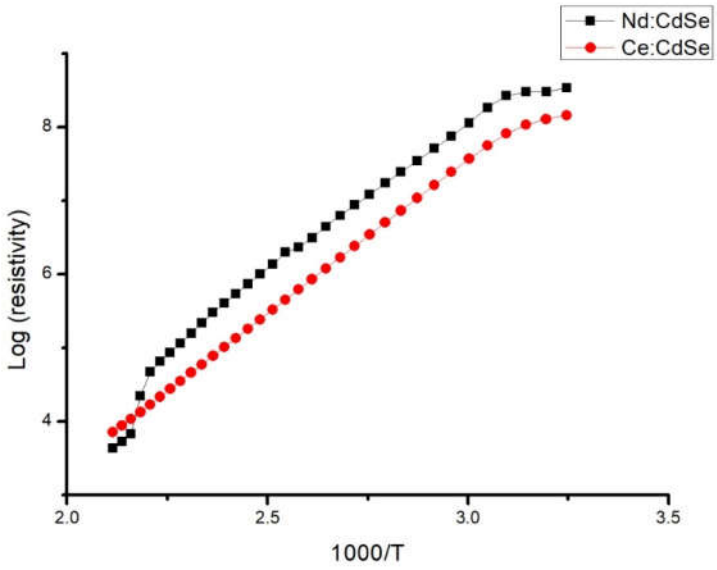


**Fig. 5 Plot of log (resistivity) versus inverse of absolute temperature.**

Fig. 5 shows a plot of log ($\rho$) versus $1000/T$. It is clear from graph that the resistivity decreases with increase in temperature which confirms the semiconducting nature of the films. The resistivities of the thin films are in the range of $10^8$ –$10^5$ Ω.cm. The high resistivity of the thin films may be due to the nano dimension of the films and presence of disorders inside the film. Resistivity decreased slightly for Ce doped CdSe as compared to Nd doped CdSe. It may be due to small decrease in band gap for Ce doped CdSe thin film. Nd and Ce doped CdSe thin films show two types of conduction mechanisms as the graph is not linear throughout. Graph can be divided into two regions viz. low temperature region and high temperature region. Low temperature conductivity is due to the presence of impurity atoms called as extrinsic conductivity. Similarly, high temperature conductivity is due to the intrinsic conduction. The plot shows that for low temperature the resistivity of doped films is almost constant, and it increases sharply in the high temperature range due to thermal stimulation.

The activation energy $E_a$ was calculated by the relation

$$\rho = \rho_0 \exp(E_a/KT) \quad (6)$$

Where $\rho$ is the electrical resistivity, $\rho_0$ is the pre-exponential factor, $K$ is the Boltzmann constant, $T$ is the absolute temperature.

The activation energy of prepared films was found to be 0.106 eV and 0.121 eV for lower temperature region and 0.345 eV and 0.356 eV for higher temperature region for Nd and Ce doped thin films respectively.

### 3.4 Contact angle measurements

Fig.6 shows the contact angle of the prepared films with water. It shows the surface energies of the system and it is related to the interaction between a solid surface and a liquid which are in contact which can be used in many applications. Water contact angle of the prepared films was measured with the help of travelling microscope having least count of 0.001 cm. It is clear from figure that both films are hydrophilic in nature because their water contact angle is less than $90^0$. Calculated values of contact angle are $36^0$and $41^0$ for Nd and Ce doped CdSe thin films. These types of hydrophilic films are useful in many applications including photoelectrochemical cell.

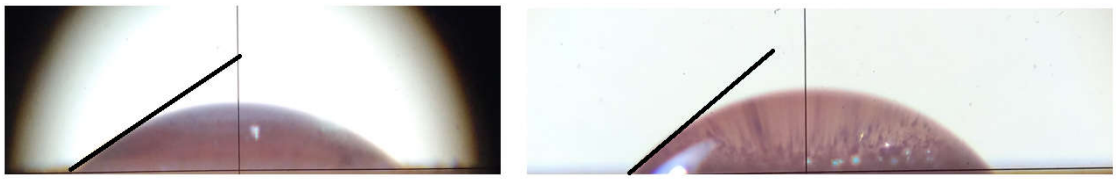


**Fig.6 Water contact angle for (a) Nd:CdSe thin films and (b) Ce:CdSe thin films.**

## 4 Conclusions

Semiconducting and luminescent nanocrystalline thin films of Nd and Ce doped CdSe thin films were successfully deposited on glass substrate at room temperature. Thickness of all the prepared thin films is in the range of 198 – 382 nm. Prepared films show blue shift due to quantum confinement effect. Band gap was found to be 2.11 eV and 2.06 eV for Nd and Ce doped films. The electrical resistivity of these thin films is of the order of $10^8$ to $10^5\Omega$.cm.Under ultraviolet excitation of 235 nm, Nd and Ce doped thin films show emissions in the blue/pink region, hence these films are suitable candidates for blue-green phosphors. Hydrophilic nature of these films can be used in photoelectrochemical applications. Overall optical and electrical properties shown by the films with different rare earth dopants offered the opportunity in applications in semiconducting, phosphor and dielectric industry. Still, more examination and optimization need to be done for rare earth doped CdSe thin films.

## Acknowledgements

The authors are grateful to Bhilai Institute of Technology, Durg management for providing all financial support.

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