

## PHYSICAL AND SPECTRAL INVESTIGATIONS OF Co(II) IONS DOPED PVA CAPPED CdSe NANOPARTICLES

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Co (II) ions doped CdSe nanoparticles were prepared using Poly vinyl alcohol as assisting agent. The physical parameters like density, refractive index, molar refractivity, ionic concentration, electronic polarizability, polaron radius, inter ionic distances and Urbach energy are measured for the prepared sample and spectroscopic techniques such as XRD, Optical and FT-IR studies have been carried out. The particle size is observed to be around 7 nm. Optical absorption studies revealed that the site symmetry of Co (II) ion is predominantly octahedral. FT-IR spectrum of Co (II) ion doped PVA capped CdSe nanoparticles recorded at room temperature in the region 500-4000 cm<sup>-1</sup>. The spectrum exhibited bands which are the characteristic of stretching and bending vibrations of O-H, C-H, C=C and C=O groups.

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### 1. Introduction

Nanoscience is concerned with the study of the unique properties of matter at its nano level and exploits them to create novel structures, devices and systems for a variety of different uses [1, 2]. Particles having sizes less than 100 nm are generally called nanoparticles. Nanosized semiconductor crystallites could change optical properties which are different from bulk materials. This is so-called quantum confinement that is observed as a blue-shift in absorption spectra with a decrease of particle size [3, 4]. There is active Physics research going on in nanomechanics, quantum computation, quantum teleportation, artificial atoms etc. Properties not seen on a macroscopic scale now become important- such as quantum mechanical and thermodynamic properties. Rather than working with bulk materials, one works with individual atoms and molecules. By learning about an individual molecules property, we can put them together in very well-defined ways to produce new materials with new and amazing characteristics.

Semiconductor nanoparticles have currently been attracting widespread scientific and technological interest due to their unique size-tunable optical and electronic properties as well as their potential applications in solar cells, light-emitting diodes (LEDs) and bio-labels [5-7]. The synthesis and characterization of these particles are quite important for betterment of optical devices. Polymers are macromolecules built-up by the linking together by a large number of small molecules; the individual small molecules are called “monomers”. The polymers are used as stabilizers during the preparation of semiconductor nanoparticles [8, 9]. The incorporation of nanoparticles into polymer matrices is a useful method to allow nanoparticles to be used in electroluminescent devices [10, 11].

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Polyvinyl alcohol (PVA) was first prepared by Hermann and Haehnel in 1924 by hydrolyzing polyvinyl acetate in ethanol with Potassium hydroxide [12]. PVA is produced commercially from polyvinyl acetate, usually by a continuous process. PVA is an odorless and tasteless, translucent white or cream colored granular powder, it has excellent film forming, emulsifying and adhesive properties. It is nontoxic. It is used as a polymer to stabilize CdSe nanoparticles [13]. Cadmium selenide (CdSe) is an important II-VI, n-type direct band gap semiconductor has engrossed substantial consideration due to its applications in light-emitting diodes, photo detectors and full color display [14, 15]. The wide band gap (bulk band gap of 2.6 eV) makes CdSe as inorganic passivation, in order to improve stability, and also an attractive host for the development of doped nanoparticles [16, 17]. CdSe is a semiconducting material, but has yet to find many applications in manufacturing. CdSe nanoparticles have received a lot of attention because of their unique optical and electronic properties [18, 19].

CdSe film has been prepared by various growth techniques, such as molecular beam epitaxy (MBE) [20], atomic layer epitaxy (ALE) [21], chemical bath deposition [22] etc. In the present investigation, we have prepared the CdSe nanoparticles using PVA as assisting agent from the technique used in the literature [23]. The presence of manganese ions induces the formation of nanostructured materials. To the best of our knowledge, there is no previous literature report on the Co(II) ions doped PVA capped CdSe nanoparticles. Thus in the present work, we have performed some systematic analysis of the samples using X-ray diffraction (XRD), Optical absorption spectrum and Fourier transform infrared (FT-IR) techniques. Different Physical parameters have been evaluated for the prepared samples and the results are discussed.

## 2. Experimental

Cadmium chloride ( $\text{CdCl}_2$ , 99mM, 4mL), PVA (2.2g), NaHSe (50mM),  $\text{CoCl}_2$  (1mM) are used as starting materials. Cadmium chloride ( $\text{CdCl}_2$ ) 99 mM of 4 mL volume was added to 2.2g PVA (13,000 g/mol) and the volume of solution was made up to 50 mL by double distilled water. Solution was left for 24 h at room temperature to swell. The solution was warmed up to 60°C and stirred for 4 h until viscous transparent solution was obtained. One milliliter of Sodium Hydrogen Selenide (NaHSe) (50 mM) was dropped into the solution with gentle stirring and 1mM of 4mL volume of  $\text{CoCl}_2$  was added to get transparent solution. Solution was casted on flat glass plate dishes. After the solvent evaporation, a thin film containing Co(II) ions doped PVA-capped CdSe nanoparticles was obtained. The film was washed with de-ionized water to remove other soluble salts before measurements.

The refractive index of the prepared sample is measured using an Abbe's refractometer. Density of the prepared sample is measured by using density meter. The XRD pattern of the prepared sample is recorded on PANalytical X Pert Pro X-ray powder diffractometer with copper  $K_\alpha$  radiation. The Optical absorption spectrum is recorded at room temperature by using JASCO V670 spectrophotometer in the wavelength region 200-1400 nm. Bruker FT-IR Spectrophotometer is used for recording the FT-IR spectrum of the prepared sample in the wavelength region 500-4000  $\text{cm}^{-1}$ .

## 3. Results and discussion

Co (II) ions doped CdSe nanoparticles were prepared using Poly vinyl alcohol as assisting agent. The physical parameters are measured for the prepared sample and spectroscopic techniques such as XRD, Optical and FT-IR studies have been carried out.

### 3.1 Physical parameters

Refractive Index and density of the prepared sample was measured by using Abbe's refractometer and density meter. By using refractive index, density and other physical parameters are calculated and are given in Table-1.

Table-I Physical Parameters of Co (II) ions doped CdSe nanoparticles

S. No.	Physical Parameter (units)	Evaluated Value
1	Average molecular weight (g/mol)	2.2833
2	Mass of the Co(II) ions doped CdSe (g)	0.0028
3	Volume of the film (cm <sup>3</sup> )	0.0032
4	Density ( $\rho$ ) (g/cm <sup>3</sup> )	3.5875
5	Refractive index ( $\mu$ )	1.6505
6	Optical dielectric Constant ( $\epsilon$ ) ( $\pm 0.005$ )	2.7241
7	Reflection loss (R)	0.0602
8	Molar Refractivity ( $R_m$ ) (cm <sup>3</sup> ) ( $\pm 0.005$ )	0.2946
9	Ion concentration (N) (10 <sup>22</sup> ions/cm <sup>3</sup> )	0.0266
10	Electronic polarizability ( $\alpha_e$ ) (10 <sup>-23</sup> ions/cm <sup>3</sup> )	4.1002
11	Inter-ionic distance ( $r_i$ ) (Å) ( $\pm 0.005$ )	7.1841
12	Polaron Radius ( $r_p$ ) (Å) ( $\pm 0.005$ )	2.8946
13	Urbach Energy ( $\Delta E$ ) (eV)	0.0480

The Dielectric constant ( $\epsilon$ ) was calculated from the refractive index by using the relation [24]

$$\epsilon = n_d^2$$

The reflection loss from the refractive index can be calculated by using the formula [25]

$$R = [(n_d-1)/(n_d+1)]^2$$

The molar refractivity ( $R_M$ ) for the prepared sample was evaluated using the relation [26]

$$R_M = [(n_d^2-1)/(n_d^2+2)]M/D$$

Where M is the average molecular weight and D is the density in g/cc.

Electronic polarizability  $\alpha_e$  is calculated using the formula [27]

$$\alpha_e = 3(n_d^2 - 1)/4\pi N(n_d^2 + 2)$$

Where N is the number of ions per unit volume

The Polaron radius and Inter-ionic separation are calculated using the Formulae [28]

$$r_p = (1/2) [\Pi / 6N]^{1/3} \text{ and } r_i = (1/N)^{1/3}$$

### 3.2 XRD Studies

Fig.1 represents the XRD pattern of PVA capped Co(II) ions doped CdSe. The reaction between Cd and Se ions in the PVA medium doped with Co ions has a great effect on crystallization as well as the size of the formed CdSe nanoparticles. The PVA sample has diffraction peak angle at  $2\theta = 19.46^\circ$ . The crystalline nature of PVA results from the strong intermolecular interaction between PVA through intermolecular hydrogen bonding. The crystallite size (D) was calculated according to the Scherrer's formula [29].  $D = (K \lambda / \beta \cos\theta)$ , where K is a constant (shape factor, about 0.9),  $\lambda$  is the wavelength of X-ray radiation ( $\lambda = 1.5405 \text{ \AA}$ ),  $\beta$  is the full width at half maximum (FWHM) of the diffraction line and  $\theta$  is the diffraction angle. Based on the FWHM, the average crystallite size was estimated to be 7 nm.

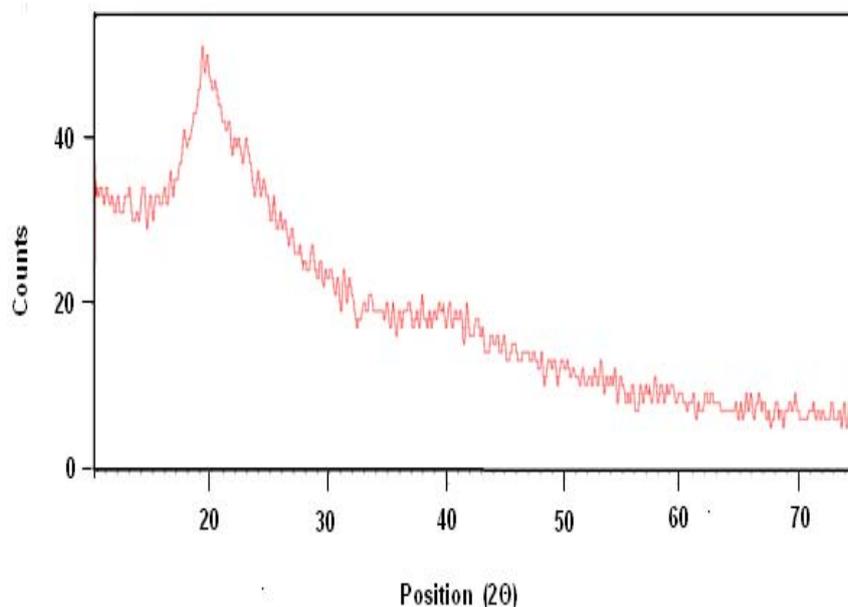


Fig. 1 XRD pattern of Co (II) ions doped CdSe nanoparticles

### 3.3 Optical absorption studies

UV-Vis absorption spectrum of Co(II) ions doped CdSe nanoparticles recorded at room temperature. The spectrum of Co(II) ion doped PVA capped CdSe nanoparticles exhibit five bands at 1185, 620, 602, 548 and 465 nm ( $8437, 16125, 16607, 18243$  and  $21499 \text{ cm}^{-1}$ ) [30]. The bands positioned at 1185, 548 and 465 nm are corresponds to the three spin allowed transitions  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  respectively. From the band positions the ratio of  $\nu_2/\nu_1$  is 2.144. The other bands positioned at 602 nm and 620 nm are assigned to spin forbidden transition  ${}^4T_{1g}(F) \rightarrow {}^2T_{2g}(G)$ ,  ${}^4T_{1g}(F) \rightarrow {}^2T_{1g}(G)$  using Tanabe-Sugano diagram for  $d^7$  configuration [30, 31]. Based on these assignments, energy matrices are solved for different values of inter-electronic repulsion parameters B, C and crystal field parameter, Dq. The values  $Dq = 960$ ,  $B = 930$  and  $C = 3800 \text{ cm}^{-1}$  gives a good fit between the observed and calculated positions of the bands [30, 32]. In the present investigations Co(II) ion exhibited octahedral sites in the host. The evaluated value of the Urbach energy is 0.048 eV [30].

### 3.4 FT-IR Studies

Fig.2 Shows the FT-IR spectrum of Co(II) ion doped PVA capped CdSe nanoparticles recorded at room temperature in the region 500-4000  $\text{cm}^{-1}$ . The spectrum exhibited bands which are the characteristic of stretching and bending vibrations of O-H, C-H, C=C and C=O groups. The bands observed at 3868, 1067  $\text{cm}^{-1}$  corresponds to the overtone band vibrations of CO group [33]. The band observed at 3334  $\text{cm}^{-1}$  corresponds to the stretching mode of -OH group which indicates the presence of hydroxyl group [34]. The band observed at 2930  $\text{cm}^{-1}$  corresponds to the overtone band vibration of C-H group of  $\text{CH}_2$  group [35]. The band at 1731  $\text{cm}^{-1}$  is assigned to C=O group of residual acetate [36]. The band at 1517  $\text{cm}^{-1}$  has been assigned to the stretching mode of C=O group [37, 38]. The band at 1427  $\text{cm}^{-1}$  has been assigned to normal  $\text{CH}_2$  group and OH group bending [33]. The band at 1373  $\text{cm}^{-1}$  has been assigned to normal  $\text{CH}_2$  group wagging and OH group bending [39]. The band at 1067  $\text{cm}^{-1}$  and the band at 841  $\text{cm}^{-1}$  have been assigned to the stretching mode of C-O and C-C groups [35]. The FT-IR band positions and their assignments are presented in Table-2.

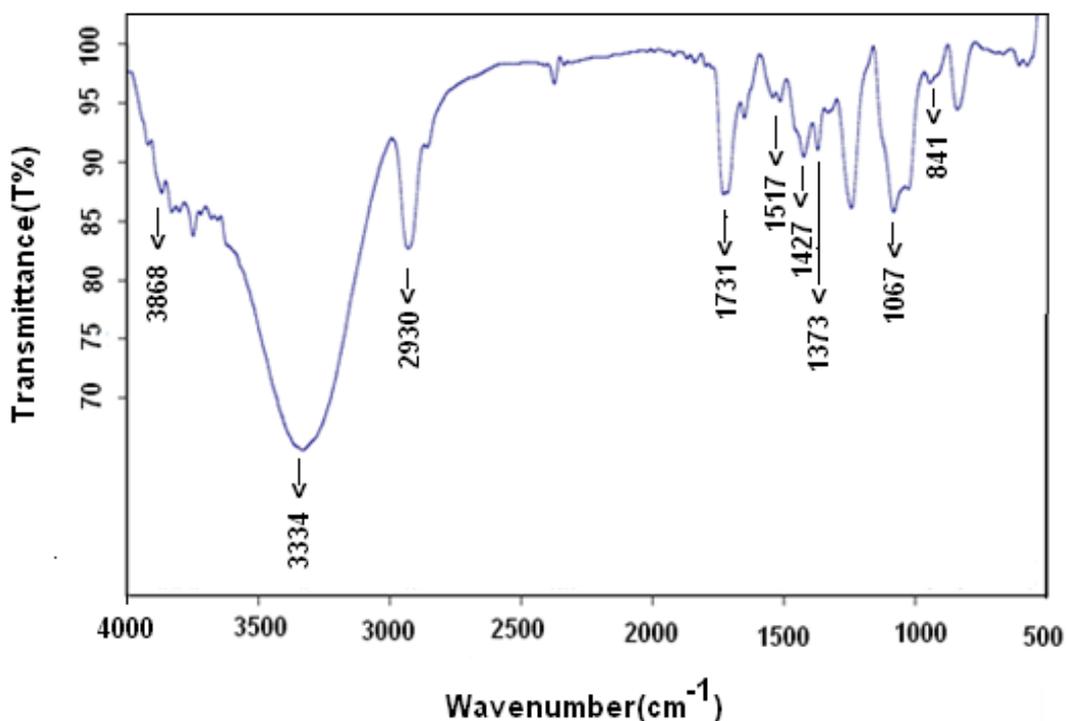


Fig. 2 FT-IR spectrum of Co (II) ions doped CdSe nanoparticles

Table- 2. Assignment of peak positions and their corresponding frequencies in IR spectrum of Co (II) ions doped CdSe nanoparticles

S. No.	Vibrational frequency (cm <sup>-1</sup> )	Band assignment
1	841	CC (st)
2	1067	CO (st)
3	1373	CH <sub>2</sub> (w), OH (b)
4	1427	CH <sub>2</sub> (b), OH (b)
5	1571	C=O (st)
6	1731	C=O (residual acetate)
7	2930	CH (st) of CH <sub>2</sub>
8	3334	-OH (st)
9	3868	CO (st)

st: stretching    b: bending    w: wagging

#### 4. Conclusions

From the physical and spectral investigations of Co(II) ions doped PVA Capped CdSe nanoparticles, the following conclusions were drawn: The physical parameters like density, refractive index, molar refractivity, ionic concentration, electronic polarizability, polaron radius, inter ionic distances and Urbach energy are evaluated. Powder XRD pattern confirms the prepared sample is nanosized. The optical absorption spectrum of Co(II) ions doped PVA capped CdSe exhibited three characteristic bands which are indicating octahedral site symmetry. The optical absorption studies revealed that the site symmetry of the Co(II) ions is predominantly octahedral. The observed bands in the FT-IR spectrum indicated the presence of stretching and bending vibrational modes of O–H, C–H, C=C and C=O groups.

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