# SYNTHESIS AND CHARACTERIZATION OF Fe DOPED CdSe NANOPARTICLES FOR SPINTRONIC DEVICES

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In the present study pure and Fe (5% and 10%) doped CdSe nanoparticles were prepared by chemical co-precipitation method. XRD diffraction patterns show that the diffracted peaks are well matched with the standard powder diffraction data and had a hexagonal structure. The average crystallite size of Fe doped CdSe nanoparticles estimated from Scherrer formula decreases from 18 to 12 nm with the increase of Fe concentration from 5 to 10%. The optical band gap of Fe doped CdSe nanoparticles increases from 1.88 to 2.20 eV with the increase of Fe doping concentration which can be attributed to decrease in particle size and due to quantum confinement. The prepared samples were also characterized with DSC and FTIR analysis.

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# 1. Introduction

II–VI based semiconductors doped with transition metals (DMS: dilute magnetic semiconductors) is emerged as a potential candidate for applications in spintronic devices such as spin-valve transistor, spin light emitting diodes, optical isolator, non-volatile memory etc.,[1-3]. Among the various II-VI based DMS, CdSe is a versatile nanomaterial suitable for spintronics and magneto-optical device applications [4, 5]. It has useful properties for optoelectronic devices, laser diodes, nanosensing, biomedical imaging and high efficiency solar cells [6, 7]. CdSe can have two different crystal structures cubic zinc blende and hexagonal wurtzite structure. It is a direct band gap n-type semiconducting material with a band gap of 1.74 eV at 300 K. It has been evidenced that transition metal doped semiconductor behaves as improved DMS. By doping with the external impurity element fine band gap tuning can be achieved to enhance the magnetic and optical properties. Various methods such as hydrothermal, sol-gel approach, surfactant-assisted approach etc had been utilized for the synthesis of CdSe nanoparticles [8-12]. In the present work we report the synthesis of pure and Fe-doped CdSe nanoparticles by chemical co-precipitation method. Structural, optical and thermal properties were studied to understand the role of Fe dopant in CdSe nanoparticles.

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### 2. Experimental details

In the present work, DMS (diluted magnetic semiconductors) nanoparticles of CdSe:Fe<sup>2+</sup> were prepared by colloidal chemical co-precipitation method using cadmium acetate, sodium selenide and ferrous acetate as starting compounds. Appropriate quantities of these were weighed in a microbalance (M/s SICO, India) according to the stoichiometry to obtain 5 and 10 at % target dopant concentrations and were dissolved in 100 ml of methanol to make 0.1M solutions. The stoichiometric solution was taken in a burette and was added in drops with continuous stirring to a mixture of  $Na_2Se(0.1M) + 50ml$  of  $H_2O + 1.1$  ml of thiophenol + 100 ml of methanol until fine precipitate of CdS:Fe was formed. After complete precipitation, the solution in conical flask was constantly stirred for about 20 hours. A single step chemical reaction is given below for the precipitation of the Fe doped CdSe nanoparticles. Then the precipitates were filtered out separately and washed thoroughly with de-ionized water. Finally these samples are subjected to sintering process. The samples were calcined at 300 °C/2hrs vacuum. X-ray diffraction (XRD) patterns have been recorded over the range of  $20^{\circ}$ - $70^{\circ}$  at the scan rate of  $2^{\circ}$ /min using Powder X-ray diffractometer (Model: SIEFERT 3003 TT) with CuKa ( $\lambda$ =1.5420 Å) as target material. Surface morphology and compositional analysis of the samples has been studied using Field emission scanning electron microscope (FESEM) (Model: HITACHI S-3400) attached with Energy dispersive spectroscopy (EDS). The absorption spectra of the samples were recorded on Cary-5E UV-VIS-NIR spectrophotometer at room temperature in the range of 200-800 nm. Differential scanning calorimetry (DSC) curves were recorded for the sample using Perkin Elmer SDT 600 with a heating rate of 10°/min in the temperature range RT (30°C)-350°C. FTIR spectrum was recorded on FTIR Spectrometer (Model: Perkin Elmer Spectrum1) in the range 400-4000 cm<sup>-1</sup>. The powders were mixed well with KBr and then palletized. The output spectrum was obtained by subtracting the background due to the solvent.

## 3. Results and discussion

#### **3.1 Structural analysis**

XRD patterns of pure and Fe doped CdSe nanoparticles are shown in Fig. 1. X-ray diffraction studies revealed that pure CdSe is found to be polycrystalline in nature with hexagonal structure. With the increase of Fe concentration from 5 to 10 % in CdSe, the XRD patterns show a poor crystalline structure. The different peaks in the diffractograms were indexed and compared with standard values of JCPDS data [13]. Some additional peaks are also observed in the XRD pattern due to the presence of secondary phase FeSe<sub>2</sub> (indicated by \*) in the sample.

The decrease in crystallinity and the peak broadening was observed with the increase of Fe concentration in CdSe, it may be due to substitution of Fe in host CdSe lattice. The lower ionic radius of Fe<sup>2+</sup> (0.76 Å) ions as compared to Cd<sup>2+</sup> (0.97Å) ions generates compressive strain in the nanoparticles leading to peak broadening in XRD pattern and also leads to lattice distortion. The average crystallite size (D) of CdSe nanoparticles was calculated using Debye-Scherrer's formula [14]

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$
(1)

where K is a constant with a value 0.94,  $\lambda$  (=1.5420 Å) is the wavelength of X-ray radiation,  $\beta$  is the full-width at half maxima (FWHM) and  $\theta$  is the diffraction angle. The average crystallite size was determined from the half-width of the diffraction peaks using the Debye-Scherrer equation.

The crystallite size for pure CdSe, 5% Fe doped CdSe and 10% Fe doped CdSe is found to be 18 nm, 16 nm and 12 nm respectively. The crystallite size decreases with the increase of Fe concentration in CdSe nanoparticles. A similar trend has also been noticed in other reports [15,16].



Fig. 1 XRD patterns of a) Pure CdSe, (b) 5% Fe doped CdSe and (c) 10% Fe doped CdSe nanoparticles

# 3.2 Surface morphological studies

FESEM images of pure and Fe doped CdSe nanoparticles are shown in Fig. 2. It can be observed that the surface morphology of pure and Fe doped CdSe nanoparticles is not uniform and contains many small irregular nanoparticles with an average grain size ranging from 14 to 22 nm. It has been clearly observed that the small nanosized grains are engaged with a compact and rough surface.



Fig. 2 FESEM images of (a) Pure CdSe, (b) 5% Fe doped CdSe and (c) 10% Fe doped CdSe nanoparticles

## 3.3 Energy dispersive spectroscopy studies

The compositional analysis of the prepared samples has been done using EDS in order to confirm the elements and quantify their weight percentage composition as shown in Fig. 3(a) - 3(c). The peaks of Cadmium (Cd), Selenium (Se) and Iron (Fe) have been observed, which confirm the presence of Fe in the CdSe nanoparticles. It is clear from the figure that Cd and Se are present in their stoichiometric ratio. The increase in Fe peak intensity with increasing doping concentration confirms that Fe is replacing Cd site in the host system which is in well agreement with the XRD data.



Fig. 3 EDS of (a) pure CdSe (b) 5% Fe doped CdSe and (c) 10 % Fe doped CdSe nanoparticles

#### 3.4 Optical studies

The most dramatic property of semiconductor nanoparticles is the size evolution of the optical absorption spectra. Hence UV-visible absorption spectroscopy is an efficient technique to monitor the optical properties of quantum-sized particles. Fig. 4(a) shows the absorption spectra of pure and Fe doped CdSe nanoparticles. The observed spectra show a clear blue shift in the pure as well as Fe doped CdSe nanoparticles as compared to their bulk counterpart. Quantum confinement of an electron-hole pair (exciton) may be responsible for the observed blue shift in the absorption spectra.

The absorption spectra is used to calculate the band gap of the synthesized nanoparticles using Tauc's relation [17, 18]

$$(\alpha hv)^{\frac{1}{n}} = A (hv - E_g)$$
<sup>(2)</sup>

where A is a constant and  $E_g$  is the band gap of the materials and exponent n depends on the type of transition. For direct allowed transition n=1/2, indirect allowed transition n=2, direct forbidden transition n=3/2 and forbidden indirect transition n=3 [19]. To determine the possible transitions,  $(\alpha hv)^2$  vs hv is plotted and corresponding band gap were obtained from extrapolating the straight portion of the graph on hv axis. The direct band gap values of the samples have been obtained

from  $(\alpha hv)^2$  vs plot as shown in the Fig. 4(b). The optical band gap values for pure, 5% Fe and 10% Fe doped CdSe nanoparticles are found to be 1.88, 1.94 and 2.20 eV respectively. The increase of optical band gap from 1.88 to 2.20 eV with the increase of Fe concentration in CdSe can be attributed due to decrease in particle size and quantum confinement effect. The quantum confinement effect is due to localization of electrons and holes in the semiconductor nanocrystallites causing change in the electronic band structure and thereby leading to higher value of optical band gap as compared to the bulk.



Fig. 4 (a) UV-Vis absorption spectra and (b) Tauc's plot of pure CdSe and Fe doped CdSe nanoparticles

### 3.5 Thermal studies

The thermal stability studies were conducted to check the thermal behavior of pure and Fe doped CdSe nanoparticles. DSC curves of Fe doped CdSe powdered samples were recorded at the heating rate of 10°C/min are shown in Fig. 5(a) - 5(c). The spectrum shows a sharp decrease at 150 °C which may be attributed to adsorbed water traces. The endothermic peak appears at about 220 °C corresponds to the melting point of Se [20, 21] and this again reflects the presence of Se peak ( $2\theta = 34.35^{\circ}$ ) in the XRD of Fig. 1. The melting point of pure and Fe doped CdSe nanoparticles are shifted towards a lower value as a result of the reduction in the particle size of the synthesized sample. The glass transition temperature ( $T_g$ ) decreases from 223.4 to 187.2 °C with the increase of Fe concentration in CdSe nanoparticles. The heat capacity ( $C_p$ ) values for pure



CdSe, 5% Fe and 10% Fe doped CdSe nanoparticles are found to be 0.526, 0.223 and 0.082 J/g.K respectively.

Fig. 5 DSC spectra of (a) Pure CdSe, (b) 5% Fe doped CdSe and (c) 10% Fe doped CdSe nanoparticle

#### 3.6 IR spectral studies

Fig. 6(a) - 6(c) shows the FTIR spectra of pure and Fe doped CdSe nanoparticles. From pure CdSe spectra, it has been observed that the broad peak at 3443 cm<sup>-1</sup> is assigned to -OH stretching intra molecular hydrogen bonds due to the small quantity of H<sub>2</sub>O on the sample. The peak observed at 1625 cm<sup>-1</sup> is assigned to OH of water absorbed from the molecular precursors. The peak positions at 2925 cm<sup>-1</sup> and 2342 cm<sup>-1</sup> are mainly due to O–H stretching modes and C-H stretching vibrations respectively. The C-O stretching vibration of absorbed methanol gives its intense peak at 1109 cm<sup>-1</sup>. In addition to surface coverage of the samples by methanol, presence of thiophenol is also evident from this spectrum. Its ring C-H vibration occurs at about 3000 cm<sup>-1</sup>, it is very weak peak. Similar such weak peaks due to C-H bending vibrations are also observed at 618 cm<sup>-1</sup>. There is a band at 660 cm<sup>-1</sup> is due to the stretching frequency of Cd-Se bond. Hence, it can be inferred that the capping agent passivates the surface of the nanoparticles. From the FTIR profiles, we can observed that the broadness of the peak observed at 1109 cm<sup>-1</sup> in pure CdSe decreases with the increase of Fe dopant. From the FTIR spectra (shown in Fig.6(c)), we also noticed that increasing the amount of the dopant ion ( $Fe^{2+}$ ) in CdSe resulted in the absence of IR peaks at 748 cm<sup>-1</sup>, 618 cm<sup>-1</sup>, 579 cm<sup>-1</sup> and 579 cm<sup>-1</sup>. This is probably due to a substitution of  $Fe^{2+}$ ions by  $Cd^{2+}$  ions in the crystal lattice structure.





Fig. 6 FTIR spectra of (a) Pure CdSe, (b) 5% Fe doped CdSe and (c) 10% Fe doped CdSe nanoparticles

## 4. Conclusions

Pure CdSe and Fe doped CdSe nanoparticles have been successfully synthesized by using chemical co-precipitation method. XRD studies reveal that pure CdSe nanoparticles possess wurtzite structure having hexagonal phase. The formations of the nanoparticles were confirmed by the broadening of XRD peaks. The crystallite size decreases with the increase of Fe concentration in CdSe nanoparticles. The elemental analysis confirms the presence of Fe in CdSe. It was also found that observed percentage of Fe in the samples is less than the actual amount by 5% in the doped samples. The band gap analysis from UV–Vis spectroscopy shows enhanced band gap with Fe doping in CdSe due to quantum confinement effects. The above results suggest that these synthesized nanoparticles are very promising for the applications in spintronic devices.

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