Study of the Structural, Morphological, Vibrational & Optical Properties of Synthesized Eu³⁺-Doped CdS nanocrystals

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--**ABSTRACT**--

Here, we have reported that the structural, morphological, vibrational & Optical properties of the synthesized CdS: Eu³⁺ nanocrystals. X-ray diffraction (XRD), Scanning electron microscope (SEM), Photoluminescence (PL) and Fourier transform infrared spectroscope (FTIR) studies have been done on all these samples. XRD patterns have clearly shown the cubic phase structure is present. The crystallite sizes of these nanoparticles were calculated using the Scherrer's equation and our estimated average crystallite size is 6.5 nm. The size of particle determined from the TEM image is close to the calculated value from XRD. In FESEM, Average particle size is found 7.5 nm. The role of dopant concentration of CdS: Eu³⁺ nanocrystals and their photoluminescence properties are well investigated. It is found that photoluminescence properties are sensitive to the crystal structure which is controlled by dopant concentration. The emission intensity of the peak at 617 nm ($^5D_0$-$^7F_2$) of the Eu³⁺-ions is found to be sensitive to the doping of CdS nanocrystals. Our analysis suggests that site symmetry of ions plays a very important role in the modifications of radiative and nonradiative relaxation mechanisms. In this present article, X-ray diffraction (XRD), Scanning electron microscope (SEM), High Resolution Transmission Electron Microscope (HRTEM), Photoluminescence (PL) and Fourier transform infrared spectroscopy (FTIR) properties have been investigated in detail.

Keywords: *CdS: Eu³⁺ nanocrystals, Cubic, Hexagonal, X-ray diffraction (XRD), Scanning electron microscope (SEM), Photoluminescence (PL) and Fourier transform infrared spectroscope (FTIR).*

I. Introduction

The study of the photo physics of the lanthanides has given rise to intriguing science, since the beginning of the twentieth century. A wide variety of the lanthanide complexes have been synthesized and studied as probes in biochemistry [1]. Recently, significant attention has been paid to rare earth ions doped semiconductor nanoparticles to find out the potential applications in photonic and bio photonic field [2]. As these potential applications are still very much in the design phase, further fundamental research in the field remains a challenge. A number of papers were published on the luminescence of nanocrystalline II–VI semiconductors doped with rare earth [RE] ions [3-5]. An important issue needs to be addressed whether rare-earth ions are really being incorporated in nanocrystalline or are they adsorbed at the nanoparticles surface, and their effect on optical properties. Recently, Erwin et al. [6] have reported the important roles of crystal structure and shape of the nanocrystals in optimizing the efficiency of rare earth doped nanocrystals. Many literatures have shown the successful incorporation of rare-earth ions into the core of CdS nanocrystals. From the fundamental point of view, the physical understanding of of RE ions in nanocrystals is very important and recently, it is recognized that the photoluminescence properties depend on the particles size, crystal phase and concentration of dopant ions [7]. A member of the most significant II–VI compound semiconductors is CdS, which has a room-temperature direct bulk band gap of 2.4 eV. Because of its ability to tune emission in the spectrum of visible light with shapes and sizes that vary, it is widely utilized in optoelectronic devices [10]. Of particular interest for our research program is how the photophysical properties vary with changing the concentration of impurity and changing the location of ions with a view of constructing efficient nanomaterials for photonic and bio photonic applications. Here, we present the influences of dopant concentration on the crystal structure and the structural, morphological, optical and vibrational properties of prepared CdS: Eu³⁺ nanocrystals have been investigated in detail.

Experimental Section
Synthesis

The various sizes of CdS nanocrystals were synthesized using cadmium acetate dehydrate (A.R, Glaxo, India) and thioacetamide (G.R. Loba Chemie, India) in glacial acetic acid and 2-methoxy ethanol (S.D. Fine Chem. India). A typical synthesis involves dissolving of cadmium acetate in 25 mL of glacial acetic acid with constant stirring. To this, the solution of thioacetamide in 20 mL of 2-methoxy ethanol was added while stirring.

Then the reaction mixture was kept in an oil bath at 85 ^{0}C under stirring condition for 2 h. The precipitate was centrifuged and then washed twice with acetone and twice with methanol. All the samples were dried at 62 ^{0}C for 13 h in a vacuum oven. The required amount (2 mol%) of Eu $(NO_3)_3.6H_2O$ (Aldrich) was added to the aqueous solution of cadmium acetate solution for Eu^{3+}-ions doped CdS nanoparticles, and then the same procedure was followed. The sonication was carried out for 1 h employing a direct immersion titanium horn in an open beaker kept in an ice bath. Five milliliters of 20% triethylamine were added dropwise during the sonication. The resulting product after sonication was washed extensively with water, centrifuged and dried under vacuum.

Characterization Study

The crystalline phases and size determination of the particles were identified by X-ray diffraction (XRD) using a D8 Advanced powder X-ray diffractometer using a Cu-Kα source (1.5418 Å radiation). Crystallite sizes (D, in Å) were estimated from the Scherrer equation: $\mathbf{D = K\lambda/\beta \cos\theta}$, where λ is the wavelength of Cu-Kα radiation, β is the corrected half-width of the diffraction peak, θ is the diffraction angle and K is equal to 0.94. The size of the particles was also determined from SEM & TEM images obtained using a JEOL-SEM/TEM-2010 Scanning electron microscopy/transmission electron microscope with operating voltage of 200 kV. The excitation and emission spectra of all the nanocrystals were recorded at room temperature in a Shimadzu RF-5301 fluorescence spectrometer with both the excitation and the emission spectrum. All measurements were done at room temperature, using a solid sample holder. All samples were excited at 347 nm (bandwidth (Ex) = 10 nm, bandwidth (Em) = 10 nm), under same conditions. FT-IR spectra over the range 500–4000 cm^{-1} were performed on a Bruker Alpha FT-IR Spectroscopy. The CdS: Eu nanocrystals mixed with solid KBr power was ground to a fine powder.

II.   Results & Discussion

Structural Analysis

Fig. 1 shows the XRD patterns of 2 mol % concentrations of Eu doped CdS nanocrystals. The XRD patterns of the nanocrystals are considerably broadened due to the very small size of the crystallites. The 2θ values are 26.57 (111), 44.16 (220) and 52.27 (311), which are identified for cubic (c) CdS phase (JCPDS card 10-454) [9]. The symmetry of the lattice is *m*3*m*. However, this shift cannot be measured in our nanocrystalline samples, because the europium concentration is very low and the width of the diffraction lines is strongly broadened due to the small size of the crystallites. The crystallite sizes of these nanoparticles were calculated using the Scherrer's equation and our estimated average crystallite size is 7.5 nm. However, in our case of 2 mol% Eu^{3+} doped CdS nanocrystals, the mixture of single phase is obtained. In this case, the percentage of cubic phase is 48.76%. It reveals that the impurity states in doped semiconducting nanocrystals play a special role in affecting the crystal-field distortion, symmetry breaking. It is expected that Eu^{3+} ions are incorporated in CdS because the ionic radius of the Cd ion (0.98 Å) is very close to Eu^{3+} ion (0.95 Å). Eu ion occupies a tetrahedral lattice site based on analysis of the XPS and XAS data.
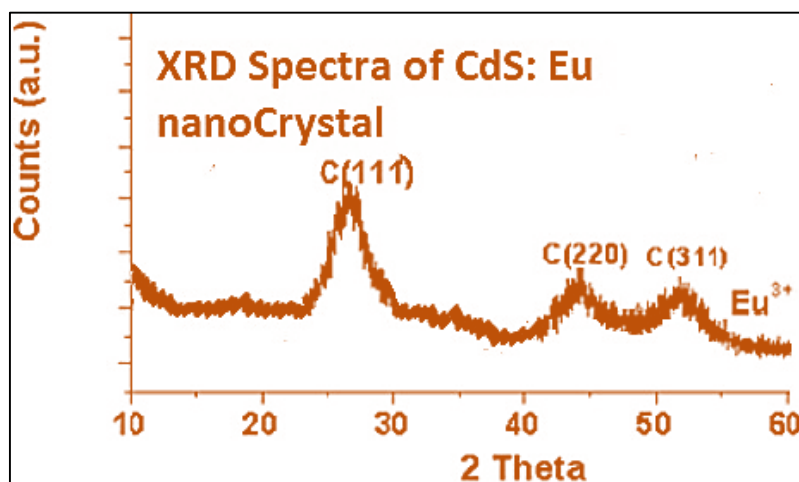

Fig. 1 XRD patterns of 2 mol % concentrations of Eu-doped CdS nanocrystals.

Scanning Electron Micrographs

Fig. 2 shows the FESEM images of Eu^{3+} doped CdS samples taken at the same magnification. These micrographs clearly indicate that the samples have nano crystalline nature and grain size varies from 5.5 to 11.5 nm. Average particle size is found 7.5 nm.
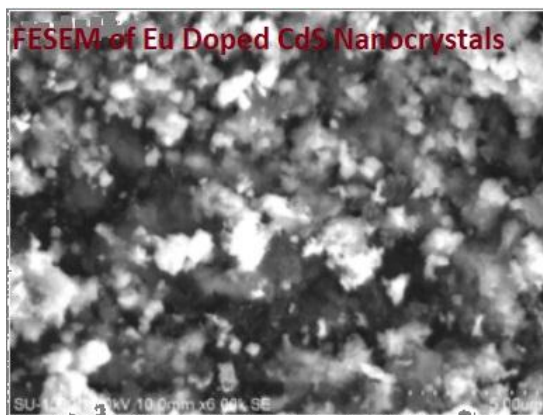
Fig. 2 FESEM Image of 2 mol % concentration of Eu-doped CdS nanocrystals

HRTEM Analysis

Samples for HRTEM were prepared by making a clear dispersion of the nanocrystals in acetone and placing a drop of the solution on a carbon coated copper grid. The solution was allowed to evaporate leaving behind the nanocrystals on the carbon grid. The size of particle determined from the TEM image is close to the calculated value from XRD. Fig. 3 shows the high-resolution TEM image of 2 mol% Eu-doped CdS nanocrystals with the corresponding fast Fourier transformation (FFT) pattern and the measured lattice spacing in the HRTEM image is 4.94 Å, which corresponds to (311) plane of the monoclinic phase of Eu^{3+} ions. The small concentration (2 mol%) of Eu^{3+} ions would correspond to less than a monolayer on the surface of the ~ 6.5 nm CdS nanoparticles. Therefore, the observed Europium lattice spacing and XRD peaks may be due to the appearance of isolated Europium nano crystallites.
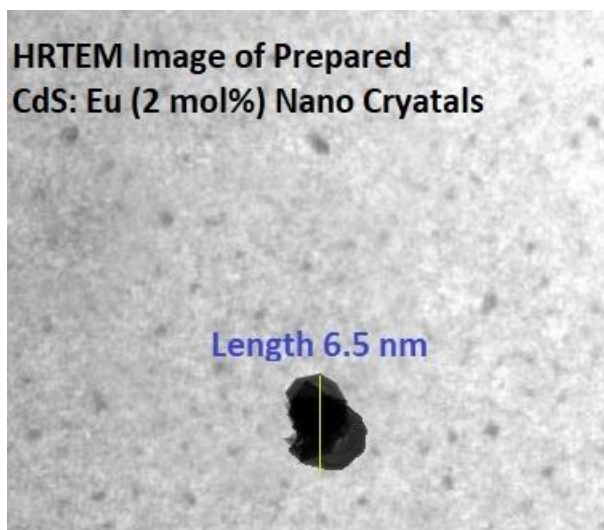

Fig. 3 HRTEM image of 2 mol% Eu-doped CdS nanocrystals

Photoluminescence Analysis
Excitation & Emission Spectra

Fig. 4 shows the excitation and emission spectra of 2 mol% Eu-doped into CdS nanocrystals. The sharp peak at 347 nm is assigned to the excitonic transition of CdS nanocrystals. After excitation at 347 nm, the strong emission band have peaked at 617 nm ($^5D_0$-$^7F_2$) and 590 nm ($^5D_0$-$^7F_1$) are observed for Eu^{3+} doped CdS nanocrystals. The emission spectra are attributed to the $^5D_0$-^7F_J (J = 0–2) transition of the Eu^{3+} ions, i.e. the bands of 570–603 and 603–640 nm is related to the transitions of $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_2$, respectively. It is to be mentioned here that the Eu^{3+} ion has very negligible absorption excited at 347 nm because the excitation cross section at 347 nm of Eu^{3+} is very small relative to the CdS excitation. It is reported that upon excitation of the CdS host, the energy from non-radiative recombination of electron-hole pairs can be transferred to the high lying energy levels of the Eu ions [8]. Fig. 4 depicts the emission spectra of undoped and Eu activated CdS nanocrystals. At the same experimental conditions, namely, same wavelength excitation with same bandwidth, we have investigated the luminescent intensity of Eu^{3+} doped nanocrystals. In the case of Eu activated CdS nanocrystals (doped), the peaks

at 617 nm ($^5D_0$-$^7F_2$) and 590 nm ($^5D_0$-$^7F_1$) are observed for doped samples after excitation at 347 nm. The most dramatic effect is that the intensities are significantly higher in doped nanoparticles.
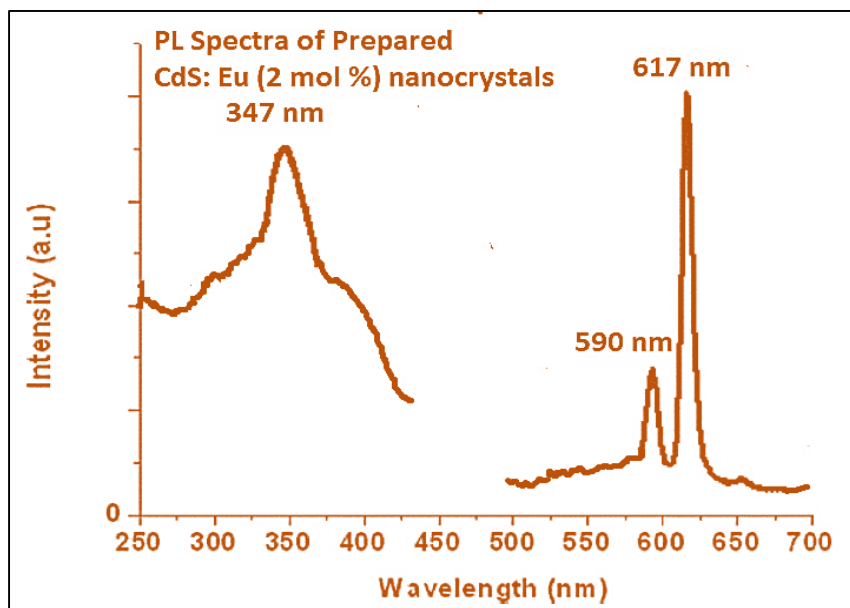

Fig. 4 Excitation and emission spectra of 2 mol% Eu doped CdS nanocrystals.

Effect of Dopant Concentration Ions

From these results, it is clear that Eu^{3+} ions occupy low symmetry sites in doped samples. Usually, the dopant ions are randomly distributed in the host lattice in doped samples, and as a whole, the local environments of the europium ions become anisotropic between europium ion and its surrounding crystal lattice. The europium ions distributed on the surface in the coated sample then the local environments of the europium ions become an isotropic coordination with higher symmetry and therefore the interaction between europium ion and its surrounding crystal lattice becomes weaker. As the electronic f–f transitions of the rare earth ions are localized in the atomic orbital of the ions. The electronic structure of the RE ions is dominated by electron–electron and spin–orbit interaction within the 4f shell. The changes of atomic coordination number around Eu^{3+} and/or the Eu–O bond lengths reduce the Eu^{3+} local structure symmetries whose degradation enhances the effects of crystal field in the host matrix. As a result of the reduced symmetries, the interaction between the europium ion and its surrounding crystal lattice decreases the population of hypersensitive $^5D_0$ energy level through a nonradiative relaxation process.

FTIR Spectral Analysis

The FT-IR spectrum of CdS: Eu nanocrystals is shown in Fig. 5. The peak at 2938 cm^{-1} is attributed to the bending vibrating mode of C-H, the presence of characteristic peak at 1648 cm^{-1} assign to O-H stretching vibrations, the peak at 1429 cm^{-1} is mainly due to C-O stretching vibrations, the presence of characteristic peak at 1093 cm^{-1} corresponds to C-C stretching. The weak peak around 695 cm^{-1} in the spectrum indicates the presence of Cd-S bond. There are two O-H bonds in ethylene glycol molecules. The peak at 3178 cm^{-1} is due to the inter H-bonding and the peak at 3287 cm^{-1} is due to O-H stretching vibrations, which is bonding with CdS: Eu nanocrystals.
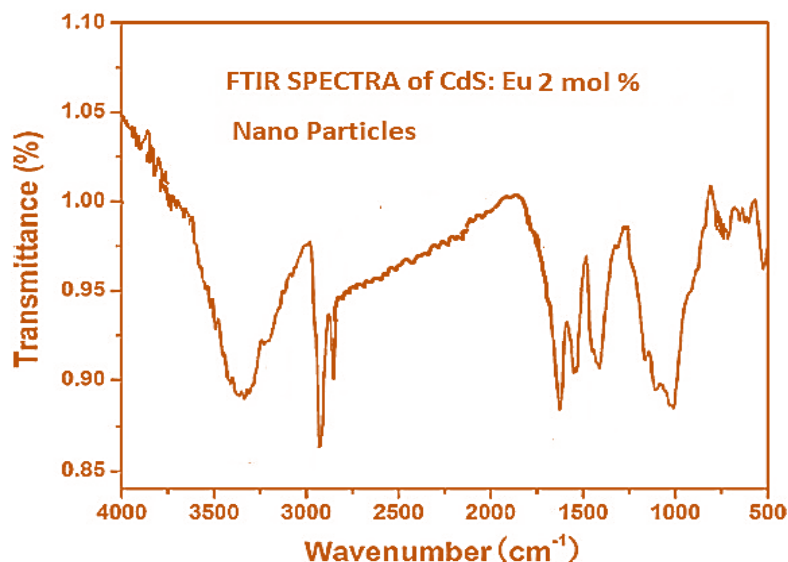
Fig. 5. FTIR spectra of traces on CdS: Eu nanocrystals.

III.   Conclusion

In conclusion, we have reported that the structural, morphological, vibrational & Optical properties of the synthesized CdS: Eu^{3+} nanocrystals. In XRD patterns have revealed the cubic phase structure. our results highlight the role of doping of CdS: Eu^{3+} nanocrystals and their effect on the photophysical properties. It is expected that Eu^{3+} ions are incorporated in CdS because the ionic radius of the Cd ion (0.98 Å) is very close to Eu^{3+} ion (0.95 Å). Eu^{3+} ion occupies a tetrahedral lattice site. In FESEM analysis, the average particle size is found 7.5 nm. In HRTEM study, the small concentration (2 mol%) of Eu^{3+} ions would correspond to less than a monolayer on the surface about ~ 6.5 nm CdS nanoparticles. In FTIR spectra, all vibrational bond and various functional groups have obtained. In PL Spectra, after excitation at 347 nm, the strong emission band have peaked at 617 nm ($^5D_0$-$^7F_2$) and 590 nm ($^5D_0$-$^7F_1$) are observed for Eu^{3+} doped CdS nanocrystals. The dopant ions play a special role in changing their crystal phase by changing the crystal-field distortion, and symmetry breaking. The luminescence intensity increases with increasing the concentration of dopant ions. Maximum intensity has found at 2 mol % of dopant ions. Again, it can be seen that the emission intensity of the Eu^{3+}-ions is sensitive to the doping of CdS: Eu^{3+} nanocrystals. Our analysis suggests that site symmetry of ions plays a most important role in the modifications of radiative relaxation mechanisms.

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