

Structural and luminescent properties of Fe³⁺ doped PVA capped CdTe nanoparticles

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During recent decades, magnetic and semiconductor nanoparticles have attracted significant attention of scientists in various fields of engineering, physics, chemistry, biology and medicine. Fe³⁺ doped PVA capped CdTe nanoparticles were prepared by co-precipitation method and characterized by powder X-ray diffraction, SEM, TEM, FT-IR, optical, EPR and PL techniques to collect the information about the crystal structure, coordination/local site symmetry of doped Fe³⁺ ions in the host lattice and the luminescent properties of prepared sample. Powder XRD data revealed that the crystal structure belongs to a cubic system and its lattice cell parameters were evaluated. The average crystallite size was estimated to be 8 nm. The morphology of prepared samples was analyzed by using SEM and TEM investigations. Functional groups of the prepared sample were observed in FT-IR spectra. Optical absorption and EPR studies have shown that on doping, Fe³⁺ ions enter the host lattice in octahedral site symmetry. PL studies of Fe³⁺ doped PVA capped CdTe nanoparticles revealed UV and blue emission bands. CIE chromaticity coordinates were also calculated from the emission spectrum of Fe³⁺ doped PVA capped CdTe nanoparticles.

Keywords: CdTe; PVA; co-precipitation; iron ions; optical absorption; EPR; FT-IR; photoluminescence

1. Introduction

Nanoparticle materials are finding many applications ranging from information technology, through biosensors to therapeutics. Many of these uses rely on the fact that the particles have different optical properties from those of bulk material, because of quantum confinement effect [1]. This causes remarkable size-dependent photoluminescence behavior in the case of chalcogenide semiconductors or shape-dependent wavelength tunable absorption spectra in noble metal particles. In recent years, there has been a growing interest in the synthesis of nanometer-sized II-VI binary semiconductor materials [2]. Nanocrystalline semiconductor films are emerging as a new class of future photonic materials due to their unique nonlinear optical effects and quantum confinement [3].

Incorporation of semiconductor nanocrystals into functional polymers is a highly desirable approach to generate novel materials for use in op-

toelectronic devices, such as light emitting diodes and photovoltaic cells [4]. There has been a great interest to control the size of nanoparticles using surface capping agents. Polymers are able to ensure surface passivation, preventing particles from agglomeration which enables controlling the particle size and size distribution effectively. The use of polymers is a prominent method for the synthesis of semiconductor nanoparticles. The reason is that the polymer matrices provide good processability and solubility. Polyvinyl alcohol (PVA) is a hydrophilic biodegradable, biocompatible, non-toxic, non-carcinogenic polymer. It is used in various pharmaceutical, medical, cosmetic, food and agricultural products [5]. PVA is an optically transparent polymer which is characterized by good chemical resistance and film forming ability [6].

CdTe is a semiconductor material with a bandgap energy of 1.56 eV that finds applications in different research areas ranging from microelectronics to fluorescent materials. This is due to the great tunability of its electro-optical properties, which is achieved by size, surface

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and morphology control of the particles in the quantum confinement regime [7]. CdTe nanoparticles have been a subject of numerous investigations. Because of high quantum efficiency and multicolor availability, CdTe nanoparticles can find applications in solid-state lighting, displays, optical communications, sensors, as well as in biological imaging and detection [8]. Doping is a widely used method to improve electrical, optical and luminescent properties of semiconductor compounds, facilitating the construction of many electronic and optoelectronic devices. In 3d transition metal ions, ferric ions (d⁵ configuration) can show an efficient luminescence and their luminescence properties involve intra-configurational d-d transitions which are both spin and parity forbidden [9].

Many fabrication techniques have been attempted for depositing CdTe nanoparticles. Some are controlled atmosphere based techniques like sputtering [10], thermal evaporation [11], e-beam evaporation [12], molecular beam epitaxy (MBE) [13], co-precipitation [14], metal-organic chemical vapor deposition (MOCVD) [15]. All these techniques are extremely expensive and require specialized equipment. Among these, co-precipitation is the most convenient method because of its simplicity, low cost, easy to add doping materials and the possibility of varying the film properties by changing composition of starting solution. In the present work, Fe³⁺ doped CdTe nanoparticles were prepared by co-precipitation method. The prepared samples were characterized by XRD, SEM with EDS, TEM, FT-IR, optical and photoluminescence studies to collect the information about the structural and luminescent properties of prepared samples.

2. Experimental

2.1. Materials and synthesis

Analytical reagent (AR) grade cadmium chloride (CdCl₂), sodium hydrogen telluride (NaHTe), polyvinyl alcohol (PVA), iron oxide (Fe₂O₃) were used as starting materials without further purification. Double distilled water was used as a solvent in the experiment. 0.045 g of cadmium

chloride was added to 2.3 g PVA and volume of the solution was completed to 50 mL by double distilled water. The resultant solution was left for 24 h at room temperature to swell. After that, the solution was warmed up to 80 °C and stirred for 6 h until viscous transparent solution was obtained. One millilitre (mL) of sodium hydrogen telluride (NaHTe) was dropped into the solution with gentle stirring and then 0.01 mol% iron oxide was added to it to get a transparent solution. The prepared solution was casted on flat glass plate dishes. After the solvent evaporation, a thin film containing iron doped PVA capped CdTe nanoparticles was obtained. The excess of insoluble salts was removed from the surface of the films before characterization by washing the films using deionized water.

2.2. Characterization

Powder X-ray diffraction patterns of prepared samples were recorded on PANalytical X'Pert PRO diffractometer with CuK α radiation. Scanning electron microscope (SEM) and energy dispersive spectrum (EDS) images were taken on ZEISS EVO 18. Transmission electron microscope (TEM) images were recorded on HITACHI H-7600 and CCD CAMERA system AMTV-600 by dispersing samples in ethanol. Bruker FT-IR spectrophotometer was used for recording FT-IR spectra of prepared samples in the region of 400 cm⁻¹ to 4000 cm⁻¹. Optical absorption spectra were obtained at room temperature using JASCO V-670 spectrophotometer in the wavelength range of 200 nm to 1400 nm. Electron paramagnetic resonance (EPR) spectrum was obtained at room temperature on JEOL JES-FA series X-band EPR spectrometer having 100 kHz field modulation. Photoluminescence (PL) spectra were taken at room temperature on Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer with Xe continuous (450 W) and pulsed (35 W) lamps as excitation sources.

3. Results and discussion

Fe³⁺ doped PVA capped CdTe nanoparticles were prepared by using co-precipitation method. The prepared samples were characterized

by powder X-ray diffraction, SEM with EDS, TEM, FT-IR, optical, EPR and PL studies to collect the information about the luminescent properties of prepared sample. The analysis of X-ray diffraction pattern revealed that the prepared samples are pure crystalline in nature.

3.1. Powder X-ray diffraction studies

A powder XRD pattern of Fe^{3+} doped PVA capped CdTe nanoparticles is shown in Fig. 1. The XRD pattern shows the highest intensity diffraction peak at $2\theta = 23.87^\circ$ along with a small intensity peak at 40.27° . The XRD pattern of this optimized sample is in a good agreement with the reference pattern of CdTe with standard diffraction data of JCPDS Card No. 15-0770 [16].

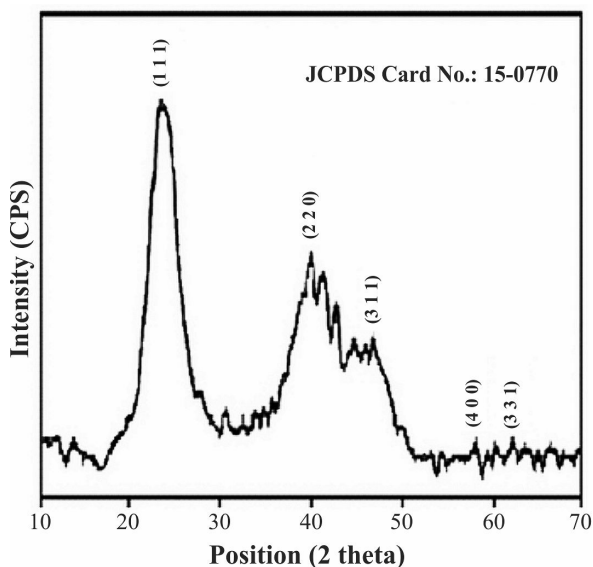


Fig. 1. Powder XRD pattern of Fe^{3+} doped PVA capped CdTe nanoparticles.

The diffraction data was indexed to a cubic phase and the corresponding lattice cell parameter $a = 0.639 \text{ nm}$ with volume $V = 26.742 \text{ nm}^3$ was evaluated. The average crystallite size was calculated from the full width at half maximum intensity of the XRD peaks using Debye-Scherrer formula:

$$D = (K\lambda / \beta \cos \theta) \quad (1)$$

where D is the mean crystallite size, $K = 0.9$ is Scherrer constant, λ is the wavelength of the incident beam, θ is the diffraction angle and β is

the full width at half maximum intensity of the diffraction peak. The value of average crystallite size calculated from the XRD pattern is 8 nm. The broadening of diffraction peaks indicates the formation of nanosized particles.

3.2. Morphological studies

The morphology and chemical composition of as synthesized samples was investigated by SEM and EDS analysis. Fig. 2 shows the SEM micrographs of Fe^{3+} doped PVA capped CdTe nanoparticles. It can be clearly observed from the low resolution SEM images that the prepared sample shows agglomeration with an irregular morphology. The agglomeration could be caused by densification resulting from the narrow space between the particles. The SEM images reveals that the sample consists of irregular shaped sphere like structures.

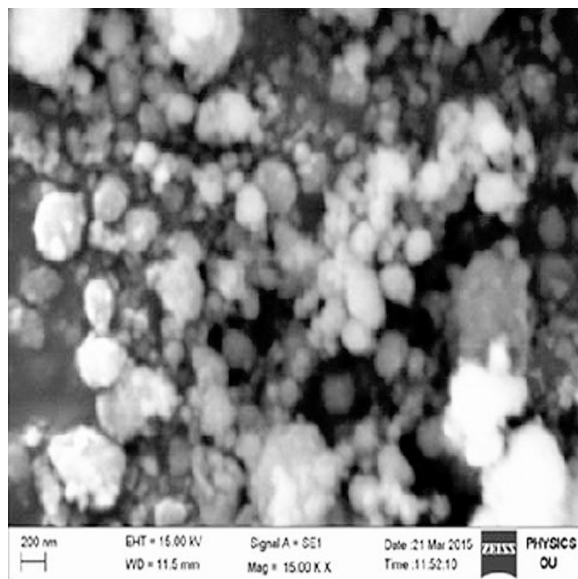


Fig. 2. SEM image of Fe^{3+} doped PVA capped CdTe nanoparticles.

The incorporation of iron into the host material was confirmed by EDS measurements. The observed EDS pattern is shown in Fig. 3. The pattern shows the elemental compositions of Cd, Te and Fe. From this it was confirmed that the prepared samples contain Fe doped species. TEM measurements were performed to confirm the nanocrystalline nature of the samples and to study

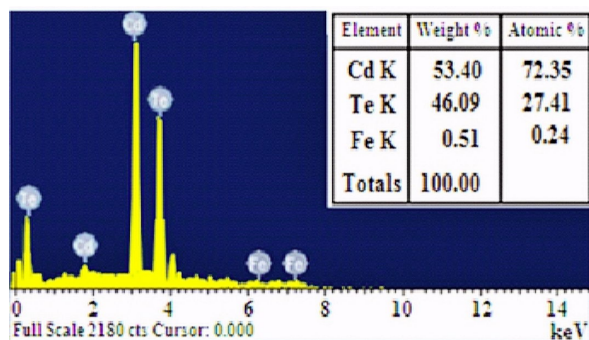


Fig. 3. EDS spectrum of Fe³⁺ doped PVA capped CdTe nanoparticles.

the morphology of the particles. The TEM image of Fe³⁺ doped PVA capped CdTe nanoparticles is depicted in Fig. 4. The particles are more or less uniform in size and of irregular shape.

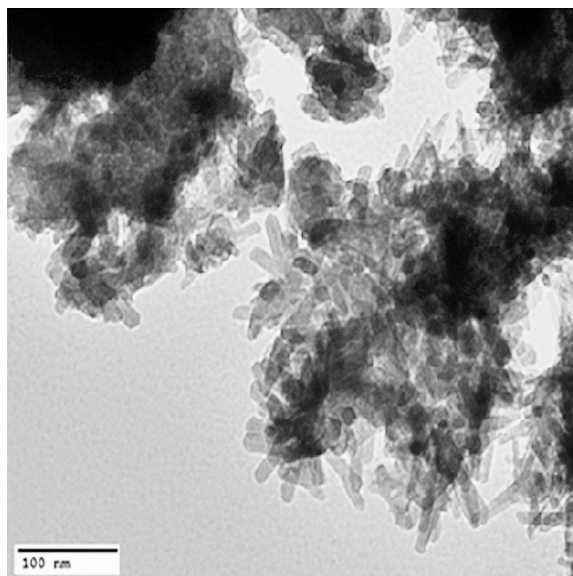


Fig. 4. TEM image of Fe³⁺ doped PVA capped CdTe nanoparticles.

3.3. FT-IR studies

Fig. 5 presents the FT-IR spectrum of Fe³⁺ doped PVA capped CdTe nanoparticles in the wavenumber ranging from 500 cm⁻¹ to 4000 cm⁻¹. The absorption peaks at 1379 cm⁻¹ and 1647 cm⁻¹ are due to C=C stretching vibrations [17]. The absorption peak at 2952 cm⁻¹ can

be assigned to C-H stretching vibrations [18]. Additionally, it can be found that the peak characteristic of O-H group at 3375 cm⁻¹ appears in the spectrum, which is regarded as associated with hydrogen bonds among the molecules [19].

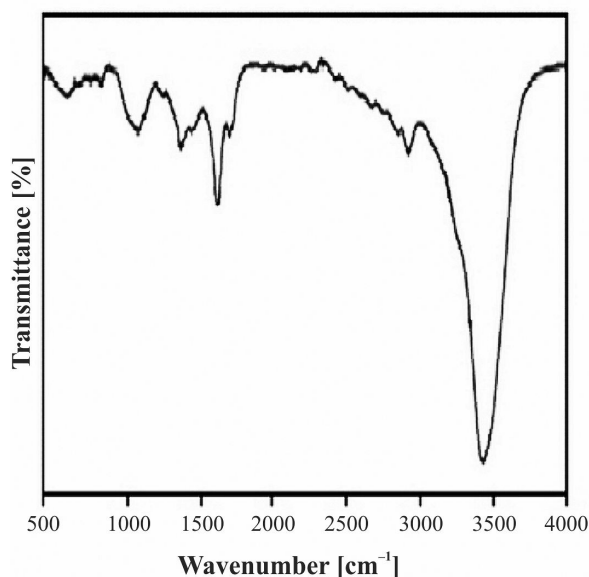


Fig. 5. FT-IR spectrum of Fe³⁺ doped PVA capped CdTe nanoparticles.

3.4. Optical absorption studies

Fe³⁺ has an electronic configuration of [Ar] 3d⁵ corresponding to a half filled d-shell and it is the most stable state of iron. The ground state of d⁵ ions is ⁶S which transforms into ⁶A_{1g} state in the field of any symmetry, and it is the only sextet term. This ground state is the same for both octahedral and tetrahedral fields. It does not split by the effect of crystal field, hence, all the transitions are spin forbidden and appear with less intensity. In the excited state it gives rise to the quartet (⁴P, ⁴D, ⁴F, ⁴G) and doublet (²S, ²P, ²D, ²F, ²H) terms. Among the mentioned terms ⁶A_{1g} lies lowest according to Hund's rule. It corresponds to the strong field configuration t_{2g}³ e_g². In a weak crystal field, the lower quartet terms transform as follows: ⁶S → ⁶A_{1g}, ⁴G → ⁴T_{1g} + ⁴T_{2g} + ⁴E_g + ⁴A_{1g}, ⁴D → ⁴T_{2g} + ⁴E_g, ⁴P → ⁴T_{1g}. The transitions from ⁶A₁ to ⁴T₁ and ⁴T₂ depend on the crystal field strength Dq, whereas the other bands are independent of Dq.

However, the crystal field parameters in the two cases are essentially different. The Dq values in the two cases are correlated as $Dq_{tet} = 4/9 Dq_{oct}$ [20]. An optical absorption spectrum of Fe^{3+} doped PVA capped CdTe nanoparticles in the region between 200 nm to 1400 nm at room temperature is shown in Fig. 6.

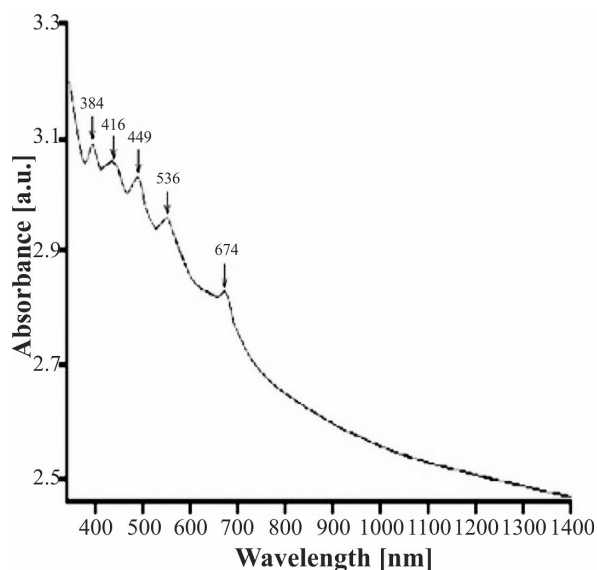


Fig. 6. Optical absorption spectrum of Fe^{3+} doped PVA capped CdTe nanoparticles.

These bands are assigned to various transitions of Fe^{3+} in octahedral site symmetry. The bands at around 384 nm, 416 nm, 449 nm, 536 nm and 674 nm are attributed to the transitions ${}^6A_{1g}(S) \rightarrow {}^4E_g(D)$, ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$, ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G) + {}^4E_g(G)$, ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ respectively. The energy matrices for d^5 configuration are solved with Tree's correction factor ($\alpha = 90 \text{ cm}^{-1}$) [21, 22] for various values of crystal field (Dq) and interelectronic repulsion terms (B and C). The band head data along with the calculated values are given in Table 1. The ratio of Dq/B in the present case is around 1.31 which is in tune with other Fe^{3+} bearing minerals [23].

3.5. EPR studies

Fig. 7 shows EPR spectrum of PVA capped CdTe nanoparticles at room temperature. Since Fe^{3+} belongs to d^5 configuration with 6S ground

state in free ion and there is no spin-orbit interaction [24], g value is expected to lie very near to free ion value of 2.0023. In perfect T_d or O_h , i.e. cubic ligand fields, only one signal appears at $g = 2.0$ in X-band EPR spectrum. Orbital angular momentum is zero for Fe^{3+} and therefore the EPR spectrum can be observed even at room temperature. The EPR spectrum exhibits a signal at around $g = 2.04$, which can be attributed to iron in the host lattice at distorted octahedral site symmetry [25]. The features of the EPR spectrum can be qualitatively explained as follows: resonance peak for Fe^{3+} at around $g = 2.04$ can only occur if Fe^{3+} is located in a site where crystal field interaction energy is less than the magnetic Zeeman energy and arises due to isolated Fe^{3+} . From these results, the site symmetry of Fe^{3+} in the host lattice is identified as octahedral site symmetry which also confirms the results of optical absorption studies [26].

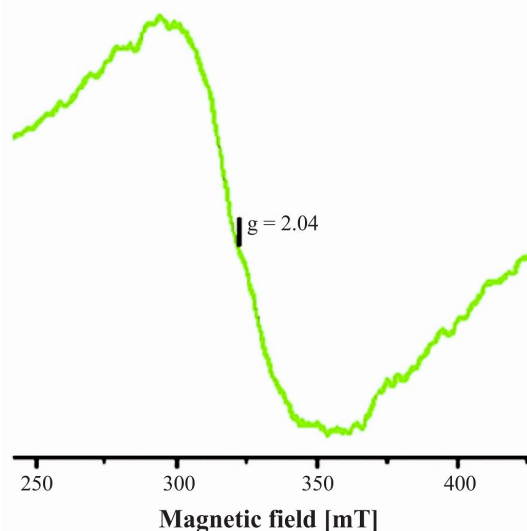


Fig. 7. EPR spectrum of Fe^{3+} doped PVA capped CdTe nanoparticles.

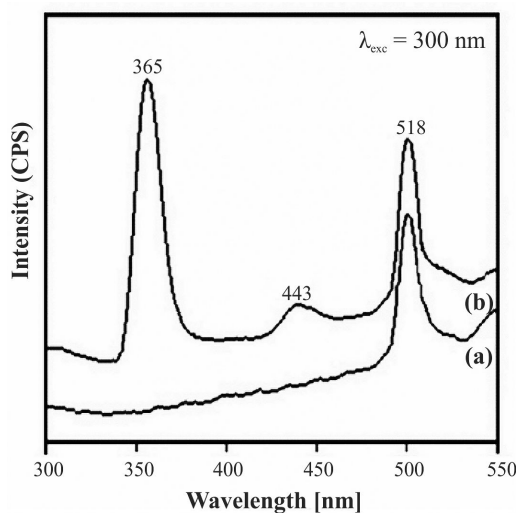
3.6. Photoluminescence studies

PL spectroscopy is an important tool to characterize optical properties of a semiconductor. PL intensity may be directly correlated with the defect density in a nanomaterial. The luminescent properties of nanopowders are strongly dependent on the crystal structure of host materials.

Table 1. Optical band positions, crystal field and inter-electronic repulsion parameters of Fe³⁺ doped PVA capped CdTe nanoparticles.

Transitions from ⁶ A _{1g} [S] ↓	Wavelength [nm]	Wave number [cm ⁻¹]		Dq [cm ⁻¹]	B [cm ⁻¹]	C [cm ⁻¹]
		Observed	Calculated			
⁴ E _g (D)	384	26042	26079			
⁴ T _{2g} (D)	416	24038	23987			
⁴ A _{1g} (G) + ⁴ E _g (G)	449	22271	22259	920	700	2700
⁴ T _{2g} (G)	536	18657	18674			
⁴ T _{1g} (G)	674	14837	14852			

In general, PL spectrum of CdTe nanoparticles exhibits emission peak at 518 nm, which corresponds to green region. The room temperature photoluminescence spectrum of Fe³⁺ doped PVA capped CdTe nanoparticles excited at 300 nm is shown in Fig. 8.

Fig. 8. PL spectrum of (a) Undoped and (b) Fe³⁺ doped PVA capped CdTe nanoparticles.

The spectrum exhibits two emission bands: a strong UV emission band at 365 nm and a weak blue emission band at 443 nm. The emission bands of PVA capped CdTe nanoparticles at 365 nm and 443 nm are assigned to the transitions ⁴T_{2g}(D)→⁶A_{1g}(S) and ⁴A_{1g}(G)→⁶A_{1g}(S). The emission spectrum of Fe³⁺ doped PVA capped CdTe nanoparticles exhibits near band edge (NBE) emission in UV region and the deep level emission in visible regions [27]. In this study, a sharp and dominated UV emission at

365 nm and a suppressed blue emission at 443 nm in Fe³⁺ doped PVA capped CdTe nanoparticles indicates that the prepared samples have better crystal quality and good optical properties with less defect states [28]. These characteristic features may represent the possible applications in the fields of UV back lights, UV LEDs and display devices.

3.7. Chromaticity properties

The chromatic coordinates(x, y) were calculated using the CIE coordinate calculator [29]. The CIE chromaticity coordinates of Fe³⁺ doped PVA capped CdTe nanoparticle were calculated from the emission spectrum. The location of the color coordinates for Fe³⁺ doped PVA capped CdTe nanoparticles in the CIE chromaticity diagram is shown in Fig. 9 by a solid sign ■. From this figure, one can see that the color of undoped PVA capped CdTe nanoparticles is located in the green region and that of Fe³⁺ doped PVA capped CdTe nanoparticles is located in the blue-green region; the corresponding CIE coordinates are (x = 0.132, y = 0.527), (x = 0.162, y = 0.309), respectively. These materials may be useful for LEDs, electroluminescence panels and plasma display panels.

4. Conclusion

Fe³⁺ doped PVA capped CdTe nanoparticles were prepared successfully by co-precipitation method. From the powder X-ray diffraction studies, the crystal system has been indexed to cubic phase and the lattice cell parameters were evaluated. The evaluated average crystallite size of Fe³⁺

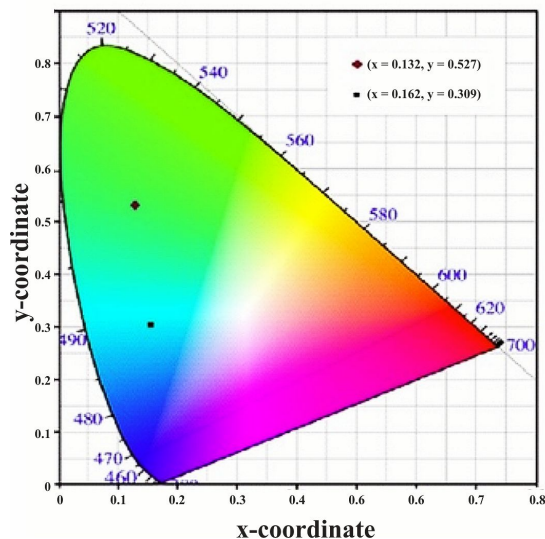


Fig. 9. CIE diagram of undoped and Fe^{3+} doped PVA capped CdTe nanoparticles.

doped PVA capped CdTe nanoparticles is around 8 nm. SEM micrographs showed irregular shaped sphere-like structures and EDS analysis confirmed the presence of constituent elements in the prepared material. TEM images clearly confirmed the formation of nanorods. FT-IR spectrum showed the characteristic vibrational modes of the host lattice. Optical absorption spectrum displayed five characteristic bands, which are characteristic of Fe^{3+} in distorted octahedral symmetry. This was also confirmed by EPR studies, which showed a strong resonance signal at around 2.04 which is the evidence of Fe^{3+} in octahedral symmetry. PL spectrum of Fe^{3+} doped PVA capped CdTe nanoparticles showed UV and blue emission. From CIE diagram, it was stated that Fe^{3+} doped PVA capped CdTe nanoparticles are located in blue-green region and the CIE coordinates are ($x = 0.162$, $y = 0.309$). These materials may be useful for LEDs, electroluminescence panels and plasma display panels.

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Received 2016-10-08

Accepted 2017-05-03