

Investigation on the Structural, Optical and Thermal Behaviour of Terbium (Tb^{3+}) Doped CdSe Nanorods by Hydrothermal Method

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Abstract: Semiconductor nanocrystals have attained considerable attention due to their size dependent properties, photonic applications and cellular imaging. The structural and optical properties of the rare earth Terbium (Tb^{3+}) doped CdSe nanorods have been explored. The terbium (Tb^{3+}) doped CdSe nanorods were synthesized by hydrothermal method. The crystal structure and grain size were determined by XRD. The optical properties were studied by UV-Visible spectroscopy. Surface morphology of the terbium (Tb^{3+}) doped CdSe were studied by SEM analysis. The functional groups of the synthesized compound have been identified by FTIR spectral analysis. The thermal stability of Tb^{3+} doped CdSe nanorods has been analyzed by TGA / DTA studies.

Keywords : Nanoparticles, nanorods, CdSe, Tb^{3+} doped CdSe, SEM, FTIR, TG/DTA.

1. Introduction

The 1-D semiconductor nanomaterials (CdSe, CdS, ZnS, etc.) have been extensively investigated because of its novel optical and electrical properties, which are of interest for photovoltaic devices, electroluminescence and bio attachment applications¹⁻³ due to high aspect ratio. Nanostructure semiconductors (II –IV) have been intensively studied in recent days due to their industrial implementation in electronic devices. It is also due to the size dependant properties and several applications such as non linear optics, photoelectron chemicals, heterogeneous photo catalysis, optical switching and single electron transistors⁴⁻⁵.

Among various nanoparticles a great interest has been shown towards CdS nanoparticles because of availability of discrete energy levels, size dependant optical properties, tunable band gap and well synthetic protocol, easy preparation technique with good stability⁶. CdS nanoparticles can be synthesized at different phases like in solid phase, liquid phase and in gaseous phase which mainly relies on the property of the material⁷. Hydrothermal or solvothermal is an useful method for preparation of low dimensional sulphide nanomaterials, synthesis of flower like CdS and spherical ZnS microcrystalline in aqueous solution was reported by these techniques⁸. A large emission – excitation separation and long fluorescence life time was found in chalcogenides nanoparticles doped with rare earth elements. Tb doped CdS nanoparticles as probe for mercury ions based on quenching of Tb and Tb/CdS doped nano particles enhanced fluorescence in silica xerogels⁹ are available in the literature. Evidence of co-doping of nanorods ZnO nanorods co-doped with transition elements are available in literature¹⁰⁻¹¹. The prepared terbium (Tb^{3+}) doped CdSe nanorods were characterized structurally and optically and electrically using powder X – ray diffraction (XRD), Scanning electron microscope (SEM), UV–Vis spectroscopy, FTIR spectroscopy, DG/DTA studies.

2. Experimental Procedure

2.1. Synthesis of CdSe Nanoparticles

The analytical grade of highly pure Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Merck 99%) and Sodium selenite (Na_2SeO_3 , Merck 90%) were used for synthesis. During the synthesis, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and Na_2SeO_3 was taken in the molar ratio of 2:1. Cadmium nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.01 mol) was dissolved in 10 ml of Milli Q – water and then $\text{NH}_3\text{H}_2\text{O}$ was slowly added into the solution, which initially led to the formation of white precipitate, however, with further addition of ammonia, a clear solution was formed. This indicates the conversion of Cd^{2+} into $\text{Cd}(\text{NH}_3)_4^{2+}$. The selenium source, Na_2SeO_3 (0.005 mol) was stirred for 5 min with 15 ml of hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) and it was mixed with the previously prepared solution (Cd source), this resulted in colorless and transparent solution. The final solution was transferred into Teflon – coated autoclave and then filled with Milli Q – water up to 70% of filling. The autoclave was sealed and heated at 180°C for a reaction time of 4 hr. After the completion of the reaction, the autoclave was allowed to return to room temperature. Finally, the deep dark red product was collected, washed repeatedly with Milli Q – water, ethanol and then dried at 80°C . The Tb^{3+} doped CdSe also prepared in the same procedure.

3. Results and Discussion

3.1. XRD Analysis

A typical XRD pattern from the as-prepared Tb^{3+} doped CdSe nanoparticles and the positions of the X-ray peaks for hexagonal Tb^{3+} doped CdSe are shown in Fig. 1. All the diffraction peaks from the Tb^{3+} doped CdSe nanoparticles are consistent with the wurtzite structure of Tb^{3+} doped CdSe with measured lattice constants of $a = 4.214 \text{ \AA}$ and $c = 6.904 \text{ \AA}$ (these can be compared to the lattice constants of $a = 4.299 \text{ \AA}$ and $c = 7.010 \text{ \AA}$ from JCPDS file No. 08-0459). The sharp diffraction peaks also indicate that the products are highly crystalline. The average grain size (D) of Tb^{3+} doped CdSe is calculated by the Debye – Scherrer formula, $D = 0.89\lambda/\beta\cos\theta$, where λ is the wavelength of CuK α line, D is the crystalline size, β is the full width half maximum (FWHM) and θ is the diffraction angle. From the XRD analysis the average crystalline size of Tb^{3+} doped CdSe surface were found to be 25 nm.

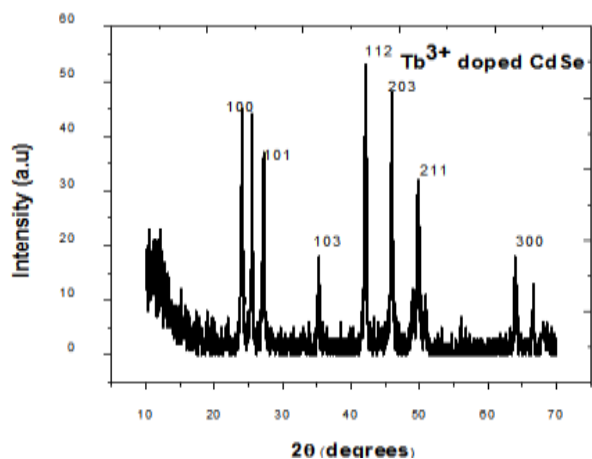


Figure 1. XRD Pattern of Tb^{3+} doped CdSe Nanorods

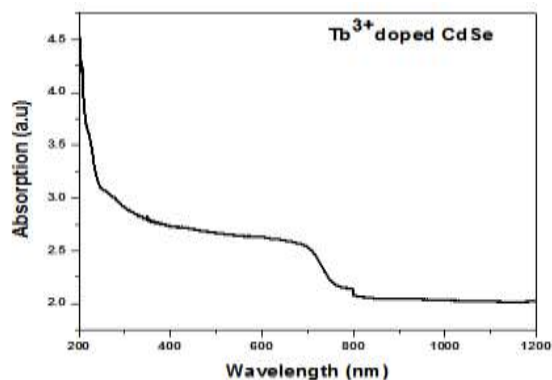


Figure 2. UV-vis Absorption Spectra of Tb³⁺ doped CdSe Nanorods

3.2. UV – Vis Spectroscopy

The reason of excellent optical properties of the nanostructure materials is the interactions between electrons and holes. The nanorods absorb energy when the excitation energy surpasses the band gap. The band gap and absorbance studies of the Tb³⁺ doped CdSe nanorods samples were performed via UV–Visible spectrophotometer. The curve obtained is shown in Fig.2 in the wavelength range of 200-1200 nm. The absorption spectra clearly show the broad peak at 690 nm for Tb³⁺ doped CdSe nanorods. These peaks are blue shifted due to quantum confinement. The blue shift of the absorption curve results in the reduction of the band gap energy. The band gap for Tb³⁺ doped CdSe nano rods was calculated using the formula,

$$\alpha h\nu = C(h\nu - E_g)^{1/2}$$

where ‘ α ’ is absorption coefficient, ‘C’ is a constant, ‘ $h\nu$ ’ is energy of photons and ‘ E_g ’ is the energy band gap. By plotting $(\alpha h\nu)^2$ versus ‘ $h\nu$ ’ the value of the band gap was found to be 1.93 eV for Tb³⁺ doped CdSe nanorods respectively. The observed values are greater than the bulk counterpart due to quantum confinement effects.

3.3. SEM Analysis

For the morphological analysis, Scanning Electron Microscope (SEM) was used. The SEM micrographs of CdSe samples were obtained at room temperature. In the doped CdSe, nanorods were observed at magnification level of 500 nm. Fig. 3 shows the SEM image of the as prepared Tb³⁺ doped CdSe samples. The solvent hydrazine hydrates (HH) and ammonia (NH₃.H₂O) is playing an important role in the growth of as formed terbium doped Cadmium selenide nano rods. When the loss of hydrazine is faster, selenide molecules will agglomerate together and condense as rod shaped crystals. Therefore in the synthesis of metal selenide 1D nano structure, several factors such as the reaction temperature and time of heating should be considered.

3.4. FTIR Spectral Analysis

FTIR spectroscopy is used to identify and characterize the organic species present in the CdSe nanostructural material. The FTIR spectra of the as prepared Tb³⁺ doped CdSe nanorods are shown in (Fig. 4). From this spectrum, it can be observed apparently that strong band in the range of 580 to 660 cm⁻¹ is associated with the characteristic modes of Tb³⁺. The band positioned at 1009 cm⁻¹ for CdSe due to the C-O stretching. The peak observed at 1602 cm⁻¹ is assigned to OH of water absorbed from the molecular precursors. C-N stretching vibration peak is positioned at 1142 cm⁻¹ is due to the interaction of ethylene glycol with the hydrazine hydrate and regular periodic structure of molecular precursors. The band at 1619 cm⁻¹ and 1395 cm⁻¹ may be due to asymmetric and symmetric stretching vibration of –COOH groups. N-H stretching vibration peak is observed at 3282 cm⁻¹ due to the presence of hydrazine hydrate in our sample. The strong absorption peak at 3424 cm⁻¹ for CdSe is due to the hydroxyl bond (O-H) stretching which confirms that the OH groups remain instant on the surface etc. Thus the FTIR spectra confirm the presence of functional group and their mode of vibrations. The peaks were observed at similar positions indicating the similarity in the adsorbed groups in both cases.

3.5. Thermal Studies

The thermal analysis is a very useful technique in the characterization and thermal stability of the nanocrystal. The recorded thermograms of TGA and DTA for Tb³⁺ doped CdSe nanoparticles are shown in Fig 5. The sample with weight of 4.283 mg was taken for the measurement. From the thermogravimetric analysis (TGA) it is observed that weight loss starts at 223 °C no loss in weight is recorded. Hence, the compound is stable up to 223 °C. The total weight loss is almost 100% at 261 °C. The differential thermogram (DTA) curve of the Tb³⁺ doped CdSenanorods reveals that no endothermic/exothermic peak is observed below 210 °C, suggesting its stable structure in this particular temperature range. Also, there is no phase transition in this respective region. The DTA curve records the endothermic peak at 261 °C. The endothermic peak at 261 °C corresponds to the melting of the sample. It coincides with weight loss in the TGA trace. The sharpness of these endothermic peaks shows the good degree of crystallinity of the Tb³⁺ doped CdSenanorods.

4. Conclusion

The rare earth Tb³⁺ doped CdSe nanoparticles were synthesized via low temperature hydrothermal method. The crystal structure, XRD analysis depicted the wurtzite (hexagonal) structure of the Tb³⁺ doped CdSe nanorods and grain size of the particles were determined. The morphology of the Tb³⁺ doped CdSe nanoparticles were characterized using scanning electron microscopy (SEM). The various functional groups present in the material have been determined by FTIR analysis. The UV-Vis studies show broad peaks near to 690 nm due to band edge emission. The band gaps were found to be 1.93 eV for Tb³⁺ doped CdSe nanorod. TG - DTA studies on the Tb³⁺ doped CdSe reveals that the title compound is thermally stable up to 223 °C and it decomposes completely at 261 °C. The thermodynamic parameters were evaluated from TGA curve to explain the thermal properties of the prepared sample.

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