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INFLUENCE ON OPTICAL PROPERTIES OF NICKEL DOPED CADMIUM SULFIDE

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In the present investigation, conventional chemical co-precipitation method was used for the preparation of Nickel (2, 4, 6, 8 & 10 at% of Ni) doped CdS nanoparticles. The UV/Vis absorption spectrum and Photoluminescence spectra (PL) were recorded for studying the optical properties of Ni doped CdS nanoparticles. The band gap energy of the Nickel doped CdS samples corresponding to absorption edge are found in the range of 3.14eV- 3.54eV. The increase in band gap with the decrease of size of the particles is due to quantum confinement which modulates the band structure of nanoparticles in semiconductors.

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1. Introduction

II-VI semiconducting chalcogenides nanoparticles, especially sulfides and selenides have been investigated extensively, owing to their interesting opto-electronic properties [1]. Cadmium sulfide (CdS) with a direct band gap of 2.42eV at room temperature (RT) is a useful candidate for solar cells, green lasers, photoconductors, light emitting diodes, and thin film transistors [2]. Transition metal(TM) doped semiconductors, known as diluted magnetic semiconductors (DMS), have attracted widespread scientific attention due to their prospective applications. However, the usefulness of CdS for the futuristic devices resides in the ability to dope it with impurities so as to achieve the desired properties and to make them multifunctional. Transition metal (TM) (Mn,Fe,Co,etc.,) doped CdS has drawn considerable attention as it offers a great opportunity to integrate electrical, optical and magnetic properties into a single material, which makes it an ideal candidate for nonvolatile memory, magneto-optical and future spintronic devices[3,4]. Different techniques such as electrodeposition, coevaporation [5], chemical vapor deposition [6], spray pyrolysis [7] and other chemical routes [3] have been used to synthesize TM doped CdS.

It has been reported that TM doping, Fe and Ni in particular, diminishes the quantum size yields in the visible and near-band-gap region by acting as a quenching or killer centers for fluorescence and photoconduction, and results in short carrier lifetimes useful in fast optoelectronic devices[8-10]. In this study, we investigate optical properties of Ni-doped CdS nanoparticles prepared by chemical co-precipitation method. The prepared samples were characterized using UV/VIS absorption spectra and Photoluminescence spectra (PL) for studying optical properties.

2. Experimental

In the present work, DMS nanoparticles of CdS: Ni^{2+} was prepared by colloidal chemical co-precipitation method using cadmium acetate, sodium sulfide and Nickel acetate as starting compounds. Appropriate quantities of these were weighed in microbalance (M/s SICO, India) according to the stoichiometry to obtain 2,4,6,8 & 10 at% target dopant concentrations and were dissolved in 100ml 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_2S(0.1M) + 50ml of H_2O + 1.1ml of thiophenol +100ml of methanol until fine precipitate of CdS:Ni was formed. After complete, precipitation, the solution in conical flask was constantly stirred for about 20h. A single step chemical reaction is given below for the precipitation of the Ni doped CdS nanoparticles. Then the precipitates were filtered out separately and washed thoroughly with de-ionized water. Finally these samples are subjected to sintering process. The green colored nanocrystalline CdS or CdS: Ni^{2+} powders were obtained. The samples were calcined at 300^0C/2hrs vacuum. UV-visible spectrum of the nanoparticles is recorded using Varian Cary Model 5000 spectrophotometer in the wavelength range 190-900 nm. Photoluminescence (PL) Spectra were recorded at room temperature with the help of a monochromator in combination with a photomultiplier tube, where a Xe lamp (λ=365nm) was used as an excitation source.

3. Results and discussion

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. Figure 1 shows optical absorption spectra of CdS. The materials of the present study are of direct band gap nature and with the increase in Ni doping, the band gap is also found to increase. The broadening of band gap due to Nickel doping may be due to filling up of conduction band edge by the excessive carriers donated by the impurity atoms. This leads to blue shift in optical band to band transitions by blocking the low energy transitions [11]. These values are compared in Table 1. The comparison of the absorption spectra of CdS and Ni^{2+} doped CdS nanoparticles suggests that there is direct energy transfer between the semiconductor excited states and the 3d levels of the Ni^{2+} ions. The bulk band gap of CdS is 2.42eV, as reported by earlier workers [12]. In the present work optical band gap is calculated using the Tauc relation [13, 14]. Tauc's relation is described as

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

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 [15]. To determine the possible transitions, $(\alpha h\nu)^2$ vs hν is plotted and corresponding band gap were obtained from extrapolating the straight portion of the graph on hν axis. The direct band gap values of the samples have been obtained from $(\alpha h\nu)^2$ vs plot as shown in the figure 2. The direct band gap value for CdS is found to be 3.56eV, where as for Ni doped CdS the band gap values are reported in Table 1. On increasing the doping concentration of Ni^{2+}, optical band gap reduces from 3.54 to 3.14eV. For 10% Ni doped CdS the reduction is 0.40eV. These results are well agreed with Fe^{2+} doped CdS reported by Balram Tripathi et al [16]. The reduction in particle size gives a shift in the optical band gap of the sample. Since the band gap increases as compared with bulk CdS the particle size is reduced, emission wavelength shifts towards higher energies (lower wavelengths). The observed shift in band gap values with varying Ni% may be attributed to the change in energy eigen values as a result of perturbation potential due to exchange interaction.

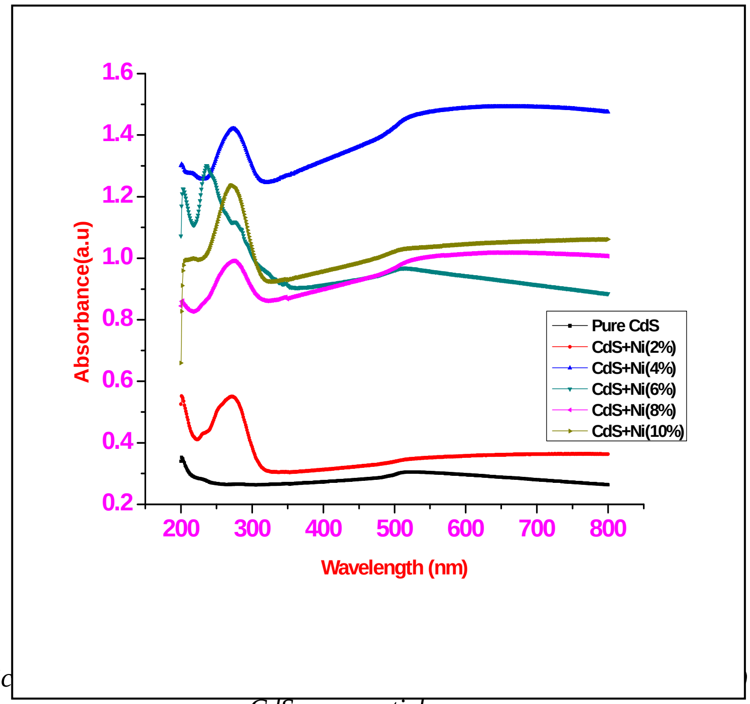

Fig. 1. Optic *doped*
CdS nanoparticles

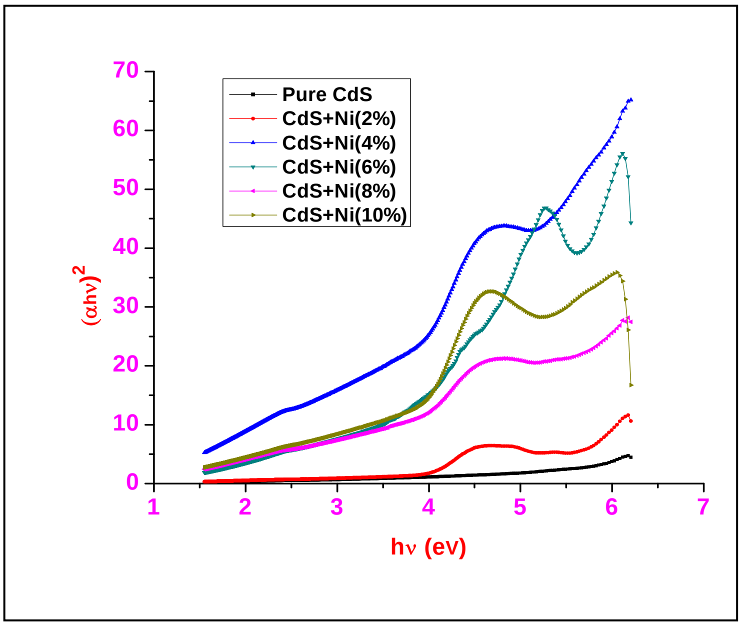

Fig.2. Tauc's plot for Ni(2%,4%,6%8% and 10% concentration) doped CdS nanoparticles for determination of direct band gap energy

Table 1. Optical band gap values from Tauc's plot

S.No	**Compound Name**	**Band gap, E_g eV**
1	Pure CdS	3.54
2	CdS+Ni(2%)	3.47
3	CdS+Ni(4%)	3.12
4	CdS+Ni(6%)	3.32
5	CdS+Ni(8%)	3.17
6	CdS+Ni(10%)	3.14

In literature various models related to the size confinement effect (SCE) were reported. A simple model was initially adapted by Efros [17] in 1982 to spherical clusters with infinite potential walls as boundary conditions. These authors assumed an energy dispersion close to the valence band maximum (VBM) and the conduction band minimum (CBM) with effective masses of CBM electron and VBM hole. This model is called the "effective mass approximation" (EMA). A further development of the EMA model has been made by Brus [18]. The latter has introduced the Coulomb interaction, leading to the following equation:

$$E_g^{nano}-E_g^{bulk} = h^2/8r^2\,(1/m_e^* + 1/m_h^*) -1.8e^2/4\Pi\varepsilon_0\varepsilon_r- 0.248\;E^*_{Ry} \qquad (1)$$

Where E_g^{nano} and E_g^{bulk} are the respective nanoparticles and bulk energy gaps, r is the radius of the particle, m_e* & m_h* are the reduced masses of the conduction band electron and valence band hole in units of electron mass, h is Planck's constant, ε_0 is the vacuum permittivity, ε is the high-frequency dielectric constant, E^*_{Ry} is effect Rydberg energy given by

$$E^*_{Ry} = e^4/2\varepsilon^2h^2\,(1/m_e* + 1/m_h*)^{-1} \qquad (2)$$

The average nanoparticle diameter calculated from the absorption spectra by means of quantum confinement theory and Hengleins empirical formula [19] are reported in Table 2.

Table 2. Estimated Nanoparticle Diameter for Ni doped CdS

S.No	**Compound Name**	**Nanoparticle Diameter (nm)**
1	Pure CdS	1.73
2	CdS+Ni(2%)	1.78
3	CdS+Ni(4%)	2.02
4	CdS+Ni(6%)	2.03
5	CdS+Ni(8%)	1.89
6	CdS+Ni(10%)	1.93

PL is a process in which an electron, excited by monochromatic photon beam of certain energy undergoes radiative recombination either at valence band (band edge luminescence) or at traps/surface states within the forbidden gap. The photoluminescence originates from the recombination of surface states [20]. The PL spectrum consists of two emission bands - sharp (band-edge) and broad (trap -state) emission. The band edge emission is due to recombination of the exciton in the mostly delocalized states in nanoparticles. It means that this emission proves high-crystalline nanoparticles. The strong PL implies that the surface states remain very shallow, as it is reported that quantum yields of band edge will decrease exponentially with increasing depth of surface state energy levels [21]. Figure 3 shows the photoluminescence spectra of Ni (2%, 4%, and 6%) doped CdS nanoparticles. The excitation wavelengths for Ni (2%, 4%, 6%, 8%, and 10%) doped CdS is found at 332nm, 346 nm, 335 nm,327nm, 322nm corresponding energy gaps of 3.73eV,3.58eV, 3.70eV, 3.78eV respectively. It is suggested that the emission peak at 425nm is attributed to transition from conduction band to valance band. And the emission peak blue shifts due to the quantum confined effect [22].

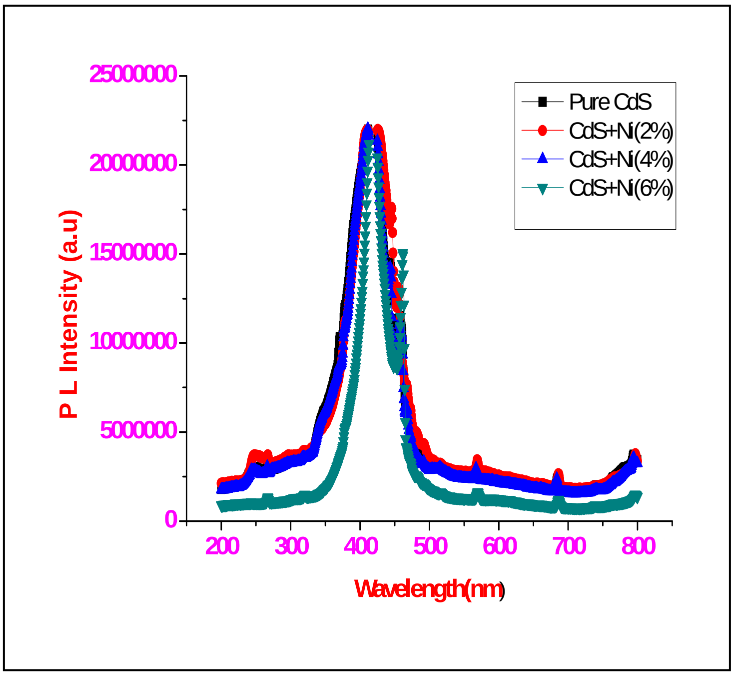

Fig.3. Photoluminescence spectra for Ni(2%,4%, and 6% concentration) doped CdS nanoparticles

4. Conclusions

From optical absorption measurements it is found that the band gap increases while the wavelength of absorbance onset shifts to shorter wavelengths. Therefore, the onset wavelength is directly related to nanoparticle size. The observed shift in band gap values with varying Ni% may be attributed to the change in energy eigen values as a result of perturbation potential due to exchange interaction. From PL spectra, the position of emission peaks shifts towards higher energy with the decrease of nanoparticles size.

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