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RESEARCH ARTICLE

Optical and electronic characterization of CdS: Nd^{3+} nanoparticles using diffuse reflectance spectroscopy techniques

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Abstract

Cadmium sulphide semiconductor nanomaterial doped with neodymium ions (CdS: Nd^{3+}) were synthesized by simple chemical precipitation method. It has been characterized by UV-visible diffusion reflectance spectra. The, UV-visible absorption and transmittance spectra of CdS: Nd^{3+} nanomaterial have also been recorded at room temperature. Energy band gap were computed using Kubelka-Munk theory. Optical properties as like the blue shift in the band gap energy in the reflectance UV spectra is observed. The resulting nanoparticles show enhanced visible light sensitivity and hence it can be used effectively in LED and sensor devices.

Keywords CdS: Nd^{3+} nanomaterial · DRS · UV-visible transmittance

Introduction

Diffuse reflectance phenomenon is commonly used in UV-visible, near infrared and mid infrared region to obtain molecular spectroscopic information of a sample. This diffuse reflectance spectroscopy (DRS) was started by exploring the use of reflected light to investigate the characteristics of porous and powdered samples [1–3]. It is usually used to obtain spectra of powders with minimum sample preparation. A reflectance spectrum is obtained by the collection and analysis of surface reflected spectrum i.e., electromagnetic radiation as a function of frequency or wavelength. Specular reflection usually associated with reflection from smooth or polished surfaces like mirrors whereas diffuse reflection is associated with reflection from so called mat or dull surfaces, textured like powder. Techniques such as external reflectance and total internal reflectance spectroscopy use the phenomenon of specular reflections to obtain the spectroscopic information of a sample.

UV-visible DRS is mostly used in the applied science for the analysis of ceramics, dyestuffs, paints and pigments paper, printing inks etc. For color matching analysis visible DRS is used for cosmetics, denture materials, medicinal tablets and tiles to name a few applications. Most of this application does not variety UV-visible DRS for chromophore researches. Most of these researches investigated the chemistry of light induced reduction and yellowing processes [4–7]. To discuss diffuse reflectance, the assumption inherent in the widely applied Kubelka-Munk (K-M) theory [8] is necessary and practical experimental considerations are necessary to acquire reliable spectra. The K-M theory is simple solution for the semi-infinite samples. All geometric peculiarities of the inhomogeneous sample are assembled into a single parameter s, known as the scattering coefficient. The diffuse reflectance is obtained as [2]:

$$R_\infty = 1 + \frac{k}{s} - \sqrt{\frac{k}{s}\left(2 + \frac{k}{s}\right)} \tag{1}$$

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here $k = \frac{4\pi}{\lambda}$ represents the absorption coefficient of the sample and λ is the wavelength. Equation (1) can be solved to obtain the familiar K-M transform of the sample as:

$$\frac{k}{s} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \qquad (2)$$

From Eq. (2), it is obvious that the K-M transform is approximately proportional to the absorption coefficient as well as the concentration.

In this paper, spectroscopic studies of trivalent neodymium (Nd^{3+}) ions is being considered as it has received much interest because of good optical efficiency in the visible and infrared region [9]. The understanding of the optical properties of Nd^{3+} ions is very much important to realize its necessary technological applications. Many factors, will be considered to investigate the optical and electronic characterization of Nd^{3+} ion doped cadmium sulphide (CdS) nanoparticles using DRS techniques. Initially, definitions and analogies to transmission spectroscopy will be provided. This will be followed by the form of the K-M function and finally the advantage of using DRS over UV-visible absorption spectroscopy in the sample is studied comparatively.

Experimental details

CdS semiconductor nanomaterial doped with Nd ions was synthesized by simple chemical precipitation method. At first, 50 ml 0.1 M cadmium nitrate tetrahydrate solution ($Cd(NO_3)_2.4H_2O$) were collected in conical flask. 20 ml of diethylene glycol (DEG) was then added to this $Cd(NO_3)_2$ solution under constant stirring. After that, different concentration (0.1, 0.2 and 0.3 mol%) of neodymium chloride was added drop wise in 50 ml sodium sulfide solution under constant stirring. Reactant was kept for 4 h at constant temperature of 60°C and finally a yellow precipitate of CdS is formed. The nanomaterial was washed with ethanol and distilled water and then dried at room temperature [10].

Results

Morphology

Typical scanning electron microscopy (SEM) image of Nd^{3+} doped CdS (CdS: Nd^{3+}) nanoparticles prepared by simple chemical synthesis precipitation method at room temperature is shown in Fig. 1. This clearly suggests that synthesized nanoparticles are nearly spherical and it is also observed that the grain size is decreased with the increase in the concentration of the Nd^{3+} ions [10]. It indicates clearly the change of the morphology of the nanoparticles with the addition of the Nd^{3+} ions doping concentration [11].

Transmittance spectra

Optical transmittance with incident wavelength for CdS nanomaterial doped with different Nd^{3+} ion concentration are studied by using the transmission spectra as shown in Fig. 2. These spectra are obtained for a wavelength range 300–1000 nm. It is clear that all samples are highly transparent in the visible wavelength. The presence of multiple interference fringes in transmittance spectrum denotes that the surface is smooth with a value of transmittance around 40%.

Absorption spectra

Typical UV-visible absorption spectrum for 0.2 mol% Nd^{3+} ion doped CdS nanomaterial at room temperature is shown in Fig. 3. This absorption spectrum corresponds to transitions from ground level to different excited levels. One can find the absorption spectra for 0.1 mol% and 0.3 mol% Nd^{3+} doped CdS nanomaterial from J. P. Singh et al. [10]. The various energy interaction parameters, peak values of the absorption bands in terms of λ (nm) and E_{exp} (cm^{-1}) together with their respective oscillator strength (P_{exp}) for the various absorption levels in the absorption spectra is shown in Table 1.

Diffuse reflectance spectra

To investigate the diffuse reflectance properties, the DRS of Nd^{3+} ion doped CdS nanomaterial in the 250–800 nm wavelength range was examined and the results are shown in Fig. 4 (a), (b) and (c) respectively for 0.1 mol%,

Table 1 Experimental values of wavelength (λ), energy (E_{exp}) and oscillator strength (P_{exp}) for various absorption levels of 0.2 mol% Nd^{3+} ions doped CdS nanomaterial

Absorption levels	Wave-length λ (nm)	Wave number 1/ λ (E_{exp}) (cm)	Oscillator strength ($P_{exp} \times 10^{-6}$)
$^4F_{5/2}, ^2H_{9/2}$	826	12,106	17.57
$^4F_{7/2}, ^4S_{3/2}$	776	12,886	19.53
$^4F_{9/2} {}^2H_{11/2}$	607	16,474	0.433
$^4G_{5/2}, ^2G_{7/2}$	553	18,083	27.55
$^2K_{13/2}, ^4G_{7/2}$	542	18,450	17.04
$^4G_{9/2}$	508	19,801	4.51
$^2K_{15/2}, ^2G_{9/2}, ^2D_{3/2} {}^2D_{3/2}, ^4D_{11/2},$	458	21,834	6.19

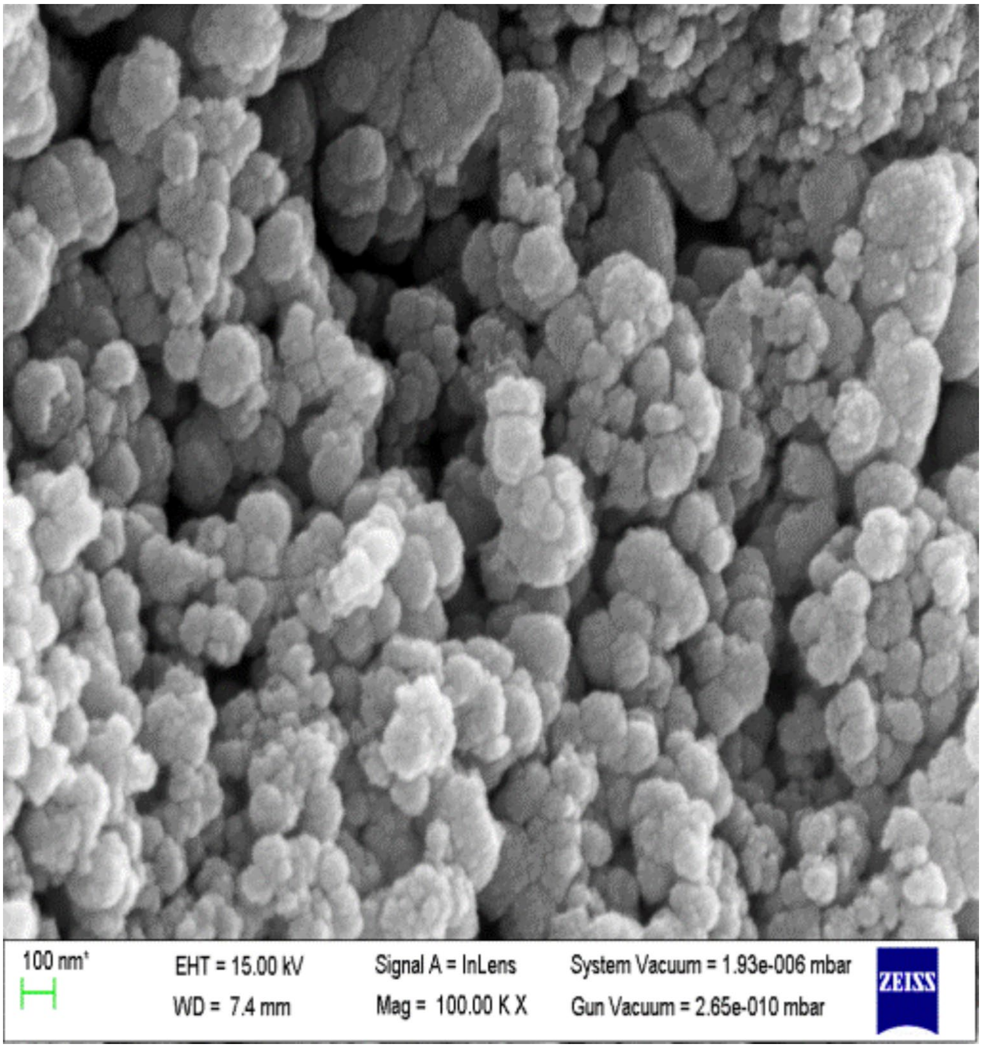

Fig. 1 Typical scanning electron microscopy (SEM) image of CdS: Nd^{3+} nanomaterial

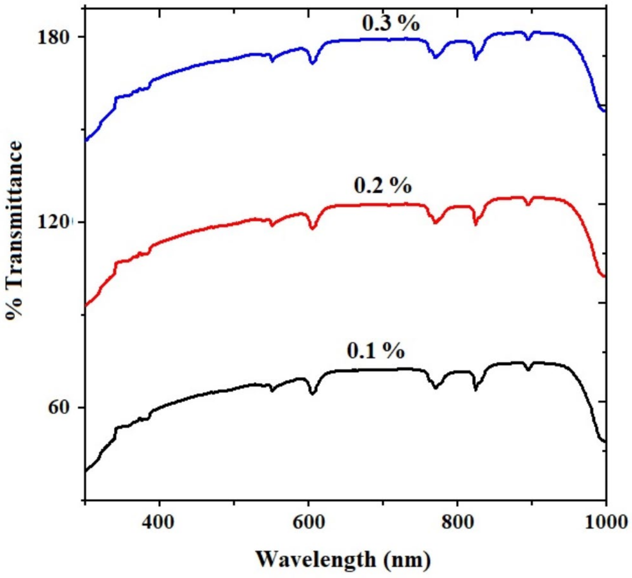

Fig. 2 Transmittance spectra for different concentration (0.1 mol%, 0.2 mol% and 0.3 mol%) of Nd^{3+} ion doped CdS nanomaterial

0.2 mol% and 0.3 mol% doping of Nd^{3+} ions by using the K-M theory. From these graphs it is noticed that, due to the quantization effect, absorption is dominant mainly in the blue region. This results in the increase of the band gap value with the decrease in the size of the crystallites, suggesting the development of CdS nanoparticles.

Figure 4 indicates band gap absorption peaks around 250 nm and a broad absorption corresponding to band gap. While broad absorption peaks corresponding to 0.1 mol% (290 nm, 376 nm, 570 nm, 630 nm, 722 nm) 0.2 mol% (295 nm, 379 nm, 555 nm, 717 nm, 728 nm) and 0.3 mol% (300 nm, 381 nm, 555 nm, 722 nm, 728 nm) doping may be ascribed to absorption in the defected states. We used K-M function to convert reflectance into absorbance which is to be used further in the determination of band gap. Comparative study of Nd^{3+} ion doped CdS nanomaterial for UV-visible spectra and diffused reflectance spectra is given in Table 2.

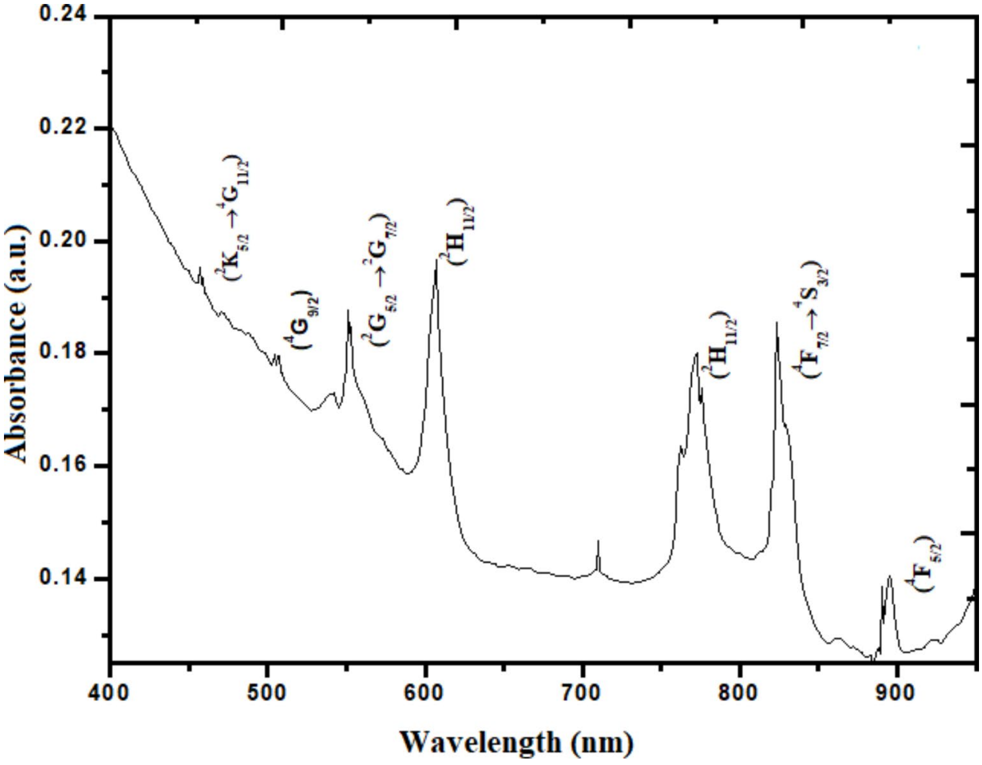

Fig. 3 UV-visible absorption spectra for 0.2 mol% Nd^{3+} ion doped CdS nanomaterial

Energy band gap

Energy band gap has been determined from diffuse reflectance spectra of CdS nanomaterial with different doping concentration (0.1 mol%, 0.2 mol% and 0.3 mol%) of Nd^{3+} ions. This idea was originated from K-M theory which describes the behavior of light travelling inside a light scattering nanomaterial. From the graph of the square product of the absorption coefficient and energy $[(F(R)h\upsilon)^2]$ versus energy, band gap energy is determined. This is shown in Fig. 5 in which the band gap is obtained by extending the straight line portion in the graph.

Table 2 Comparative study of Nd^{3+} ion doped CdS nanomaterial for UV-visible spectra and diffused reflectance spectra

Nd^{3+} ion concentration	Wavelength (nm)	
	Absorption spectra peaks	Diffuse reflectance spectra peaks
0.1 mol%	576	588
	523	490
	465	437
0.2 mol%	575	585
	523	490
	419	423
0.3 mol%	574	586
	469	495
	427	427

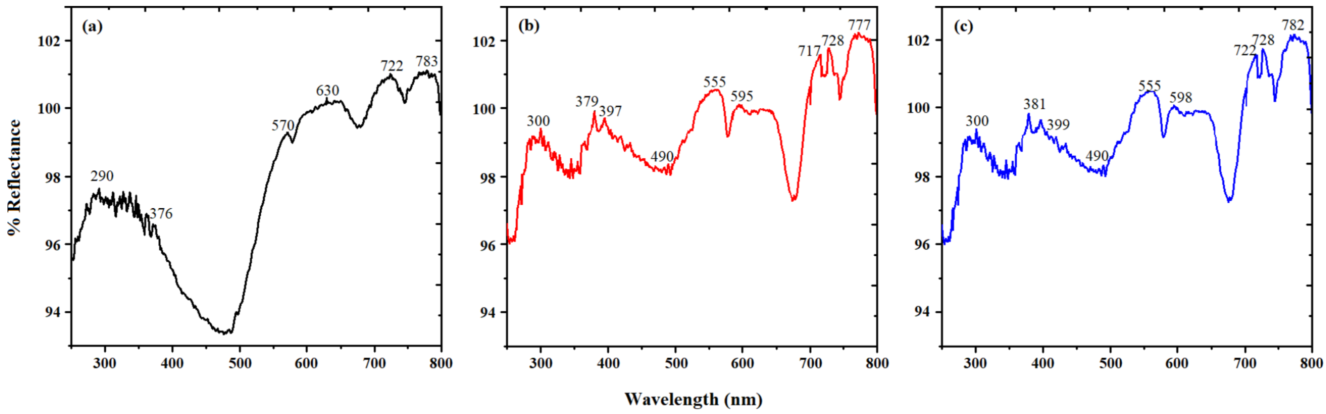

Fig. 4 UV-visible DSR spectra of CdS nanomaterial doped with (**a**) 0.1 mol%, (**b**) 0.2 mol% and (**c**) 0.3 mol% Nd^{+3} ion

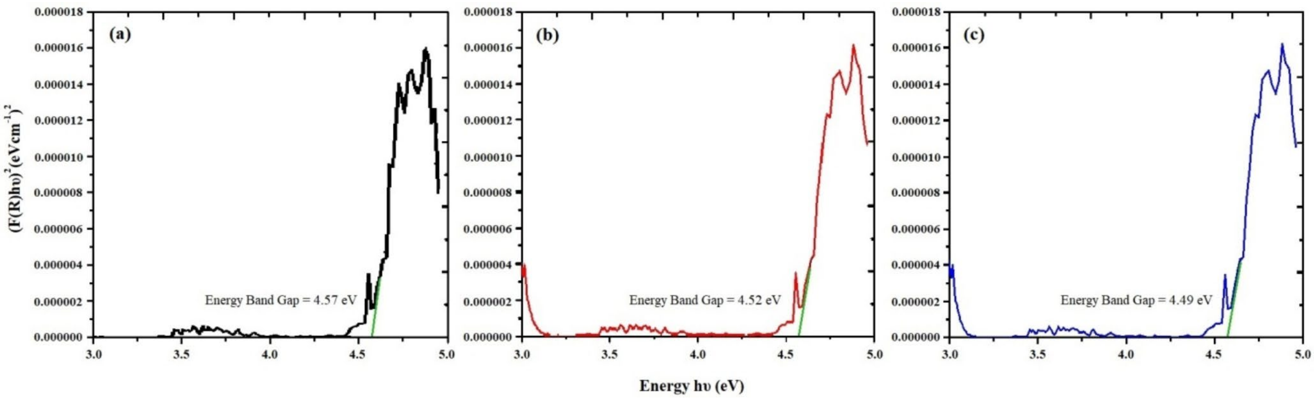

Fig. 5 Kubelka-Munk plot of DSR energy band gap of CdS nanomaterial doped with (**a**) 0.1%, (**b**) 0.2% and (**c**) 0.3 mol% Nd^{+3} ion

Table 3 DSR energy band gap of CdS nanomaterial doped with Nd^{+3} ion

Nd^{3+} ion concentration	Energy band gap (eV)
0.1 mol%	4.57
0.2 mol%	4.52
0.3 mol%	4.49

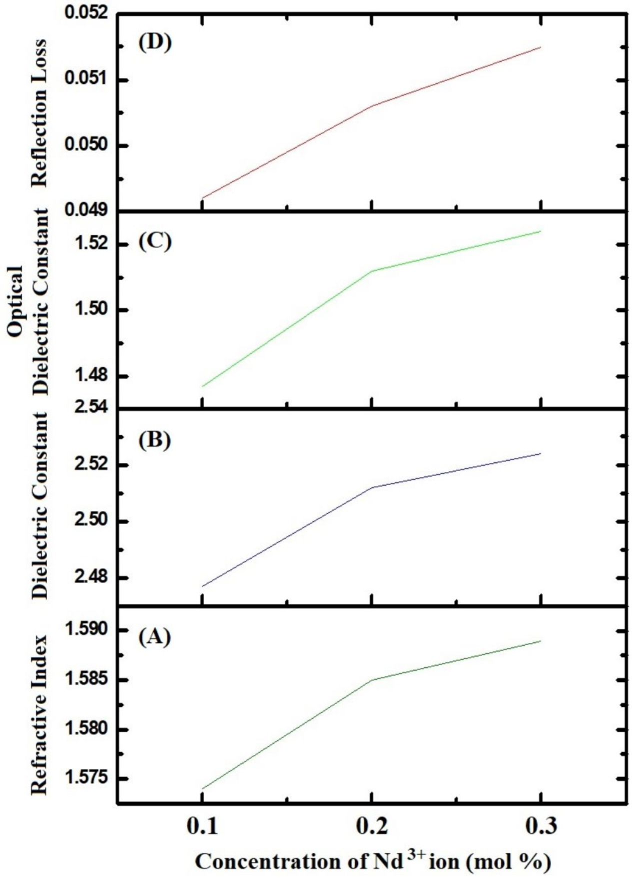

Fig. 6 Variation of (**A**) refractive index, (**B**) dielectric constant, (**C**) optical dielectric constant and (**D**) reflection loss of CdS nanomaterial for different doping concentration of Nd^{3+} ions

The energy band gap of the sample was found to decrease from 4.57 eV to 4.49 eV as the doping concentration of Nd^{3+} ion with the CdS nanomaterial increases from 0.1 mol% to 0.3 mol% (Table 3). This narrowing of the band gap is due to the substitution of CdS with Nd^{3+} ions. As a result of this, electron states are introduced into the band gap of CdS to form the new lowest unoccupied molecular orbital [12].

Optical parameters

The optical properties of the synthesized nanomaterial are characterized in terms of the refractive index, dielectric constant, optical dielectric constant and reflection loss.

Refractive index

Refractive index of a nonmaterial is an important parameter related to the optical feature of the nanomaterial. Due to this researchers had tried to find out a relation between refractive index and nanomaterial composition. Refractive index of the present CdS: Nd^{3+} nanomaterial samples were measured by using the relation

$$n_d = 1.57376 + \frac{153.137}{\lambda - 686.2} \tag{3}$$

where λ represents the peak wavelength in $\AA\ Equationdelete$. Variation of the refractive index of the CdS nanomaterial for different doping concentration of Nd^{3+} ions is shown in Fig. 6 (A).

Dielectric constant

Dielectric constant of the nanomaterial is calculated by using refractive index as [13, 14]:

$$\epsilon = n_d^2 \tag{4}$$

Table 4 Various optical physical parameters for CdS nanomaterial doped with Nd^{3+} ions

Nd^{3+} ion concentration	Refractive index	Dielectric constant	Optical dielectric constant	Reflection loss
0.1 mol%	1.582	2.502	1.502	0.0508
0.2 mol%	1.585	2.510	1.505	0.0510
0.3 mol%	1.591	2.515	1.507	0.0515

where n_d is the refractive index of powder. Variation of the dielectric constant of the CdS nanomaterial for different doping concentration of Nd^{3+} ions is shown in Fig. 6 (B).

Optical dielectric constant

The optical dielectric constant of the nanomaterial is obtained by using the relation:

$$\epsilon_{op} = \epsilon - 1 = n_d^2 - 1 \tag{5}$$

where ε is the dielectric constant. Variation of the optical refractive index of the CdS nanomaterial for different doping concentration of Nd^{3+} ions is shown in Fig. 6 (C).

Reflection loss

The reflection loss (R) is calculated by using Fresnel's formula [15] as:

$$R = \left(\frac{n_d - 1}{n_d + 1}\right)^2 \tag{6}$$

Variation of the refraction loss of the CdS nanomaterial for different doping concentration of Nd^{3+} ions is shown in Fig. 6 (D).

All these optical parameters i.e., refractive index (n_d), dielectric constant (ε), optical dielectric constant and reflection loss (R) of the Nd^{3+}doped CdS nanomaterial were computed by their relevant formulas given in Eq. (3) to (6) and is shown in Table 4.

These values show that the refractive index, dielectric constant, optical dielectric constant and reflection loss increases with increasing concentration of the doping of Nd^{3+} ions with CdS nanomaterial. This is also reflected in Fig. 6.

Conclusion

We have successfully synthesized Nd^{3+} ion doped CdS nanomaterial by using simple chemical precipitation method at the room temperature. Experimentally, direct band gap of the synthesized CdS: Nd^{3+} nanomaterial were obtained from the DRS. The DRS also utilized to investigate absorption properties of CdS: Nd^{3+} nanomaterials. The variation in the band gap corresponding to the doping concentration of Nd^{3+} ions with CdS nanomaterials was measured from the UV-visible reflectance spectra. It was also revealed that increasing Nd^{3+} ion doping concentration decreases the band gap value of the synthesized CdS: Nd^{3+} nanomaterials. We observed the emission from band edge state for all the concentrations of Nd^{3+} ions. From the comparative study of the peak positions in the UV-visible absorption spectra and diffused reflectance spectra of the Nd^{3+} ion doped CdS nanomaterials, it can be concluded that the precise determination of their band gap energies is confirmed by the diffused reflectance spectra [16]. Optical properties as like the blue shift in the band gap energy in the reflectance UV-visible spectra is observed. As the synthesized CdS: Nd^{3+} nanoparticles show enhanced visible light sensitivity, it can be used effectively in LED and sensor devices.

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Declarations

Conflict of interest The authors declare that they have NO Conflict of Interest.

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