Optical and structural properties of Ni-doped Cd$_{0.9}$Zn$_{0.1}$S nanostructures

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Abstract---The present work describes the synthesis of Cd$_{0.9}$Zn$_{0.1}$S and Cd$_{0.87}$Zn$_{0.1}$Ni$_{0.03}$S by chemical co-precipitation method. The XRD profile proved the cubic crystal structure of the samples without any impurity related phases. The reduced size from 63 to 51 Å has been discussed by Ni addition in Cd$_{0.87}$Zn$_{0.1}$Ni$_{0.03}$S structure. The noticed anomalous optical studies and the elevated transmittance at Ni doped sample suggested them for the fabrication of efficient opto-electronic devices. The energy gap reduction during the substitution of Ni = 3% is explained by the generation of extra energy levels associated with defects within the two bands.

Keywords---Ni-doped Cd$_{0.9}$Zn$_{0.1}$S, XRD, Crystallite size, Energy gap.

Introduction

In the different semiconducting materials, CdS is an outstanding material for different applications [1, 2] and employed as an excellent antibacterial agent [3]. Moreover, the physical and chemical related properties of CdS can be easily tuned using doping of metal ions, the antibacterial and photo-catalytic performance can also be improved by doping suitable metal ions. TM ions added CdS get huge attraction by its better physical and chemical nature [4, 5] and potential applications [6]. In the different TM ions Zn$^{2+}$ is an initial dopant because it has smaller ionic radius than Cd$^{2+}$ and so Zn$^{2+}$ can go into CdS lattice easily and restore Cd$^{2+}$ ions by elevating its properties [7].

The doping of 2nd metal ion from TM group is useful to improve the optical, structural and photo-catalytic properties Cd$_{0.9}$Zn$_{0.1}$S nanostructures. Within the different TM ions, the ions with 3d electrons create the various deep energy levels in Cd-S lattice. The stimulation of deep energy levels is technologically important
in luminescent devices. The increased optical absorption in the visible region by the addition Ni$^{2+}$ makes the Ni doped Cd$_{0.9}$Zn$_{0.1}$S nanostructures as a good catalyst for photo-degradation under solar irradiation [8]. $E_g$ of CdS is reduced by Ni addition [9]. Ni$^{2+}$ ions enclose 8’d’ electrons which makes the strong p-d hybridization [10] in Ni/Zn-Cds lattice. Since the ionic radius of Ni$^{2+}$ (0.069 nm) is smaller than Cd$^{2+}$ (0.097 nm) and also the electro-negativity (1.91 Pauling) is greater than Cd$^{2+}$ (1.61 Pauling) [11], the inclusion of Ni produces more number of charge carriers and hence increased the conductivity.

It is found from the literature that no detailed investigation on the photo-catalytic and antibacterial studies of Zn/Ni-doped CdS was made. Therefore, in the current work, Cd$_{0.9}$Zn$_{0.1}$S and Ni = 3 wt% doped Cd$_{0.9}$Zn$_{0.1}$S have been synthesized by co-precipitation route. Further, the role of Ni on the optical, structural, photo-catalytic and antibacterial properties has been investigated and results were interpreted.

**Experimental details**

Zn and Ni two element doped CdS nanostructures were prepared using co-precipitation route. Cadmium acetate dihydrate (Cd(CH$_3$COOH)$_2$·2H$_2$O), zinc acetate dihydrate [Zn(CH$_3$COO)$_2$·2H$_2$O], Nickel acetate tetrahydrate (Ni(OCOCH$_3$)$_2$·4H$_2$O) and sodium sulfide (Na$_2$S) were used as the precursors without further purification. The pH value is maintained as 9.2 by the addition of aqueous ammonia solution. A yellow color output was filtered and rinsed a number of times by high purity distilled water and ethanol to remove the pollution. The collected precipitates were dried using an oven at 100˚C for 18h. The diffracted patterns of the synthesized samples have been carried out using RigaKuC/max-2500 diffractometer with Cu Kα radiation from 2θ = 20˚ to 60˚. The optical absorption and transmittance spectra have been obtained using UV-Visible spectrometer (Model: lambda 35, Make: Perkin Elmer) from 300 to 550 nm at ambient temperature with necessary software.

**Result and Discussions**

Fig. 1 represents the XRD profile of Cd$_{0.9}$Zn$_{0.1}$S and Cd$_{0.87}$Zn$_{0.1}$Ni$_{0.03}$S nanostructures between 20 and 60˚. The existing broadened XRD peaks instead of sharp one indicates the synthesized nanostructures exhibits the particles or grains in the nano-scale dimension. Both samples contain three broaden orientations such as (111), (220) and (311) directions where (111) orientation possesses highest peak intensity than others. After careful background correction and Rietveld refinement of XRD peaks, the observed XRD patterns showed the cubic CdS structure (JCPDS card no.: 10-454) [12]. From the previous literature it is noted that the addition Ni into Cd$_{0.9}$Zn$_{0.1}$S lattice induces the mixed phase (both cubic and hexagonal). Particularly, Dutkova et al. [13] described the changeover of hexagonal structure of CdS into cubic structure by the addition of Zn = 10% into CdS. In the present work, the XRD spectra confirmed the cubic structure of CdS and also it was altered by the addition of Ni. No additional peaks found in the XRD profile proved the phase purity of the samples without any metal or oxide phases of Zn/Ni in the Cd-Zn-S lattice.
During the addition of Ni = 3% into Cd-Zn-S host lattice, the XRD peak intensity decreased and also the peak position of (111) orientation shifted along the smaller angle side. The noted intensity reduction and the peak position shift by Ni addition reveals the proper replacement of Ni$^{2+}$ instead of Cd$^{2+}$ in Cd-Zn-S lattice. The addition of Ni not only restore Cd$^{2+}$ and also exists as an interstitials which induces structural disorder and defect associated states and are responsible for the modification in peak intensity and position, 2θ [14]. The defect states are related to the chemically prepared nanomaterials as they develop spontaneously at the same of chemical reaction. It may also take place owing to the lack of enough energy required by an atom to shift to an appropriate site in the crystal.

Table 1 illustrates the changes in peak position and FWHM through (111) orientation, cell parameter 'a', 'd' value, mean crystallite size (D) and micro-strain (ε) of Cd$_{0.9}$Zn$_{0.1}$S and Cd$_{0.87}$Zn$_{0.1}$Ni$_{0.03}$S. Here, the crystallite size is derived from Scherrer relation [15], 0.9 $\lambda$ / $\beta$ cosθ. Micro-strain is obtained from the relation [16], $\beta$ cosθ / 4. Both in the calculation of crystallite size and micro-strain, the used parameters $\beta$ and θ were obtained from (111) orientation. Addition of Ni through Cd-Zn-S lattice, the crystallite size is decreased to 51 Å from 63 Å (Cd$_{0.9}$Zn$_{0.1}$S). The similar change was noted in Ni - CdS films as reported by Ref. [17]. The shrinkage of size as noticed from Table 1 supports the increase of FWHM and the enhancing micro-strain from 5.471 x 10$^{-3}$ (Cd$_{0.9}$Zn$_{0.1}$S) to 6.706 x 10$^{-3}$ by Ni$^{2+}$ addition. The raise of FWHM could also take place from the micro-straining of the crystals originated from defects like dislocation and twinning. The lattice parameters 'a' and 'c' are increased by the doping of Ni through Cd$_{0.9}$Zn$_{0.1}$S. The enhanced lattice parameters and the reducing crystallite size were evidenced by Woltersdorf et al. [18].
Table 1

The variation of peak position (2θ), FWHM (β) value, d-value, cell parameter ‘a’, average crystallite size (D) and micro-strain (ε) (along 111 orientation) of Cd$_{0.9-x}$Zn$_x$Ni$_x$S (x = 0 and 0.03) nanoparticles

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak position (2θ) (˚)</th>
<th>FWHM (β) (˚)</th>
<th>d-value (Å)</th>
<th>Cell parameter a=b=c (Å)</th>
<th>Average crystallite size (D) (Å)</th>
<th>Micro-strain(ε) (10$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$<em>{0.9}$Zn$</em>{0.1}$S</td>
<td>27.15</td>
<td>1.29</td>
<td>3.28</td>
<td>5.69</td>
<td>63</td>
<td>5.471</td>
</tr>
<tr>
<td>Cd$<em>{0.87}$Zn$</em>{0.1}$Ni$_{0.03}$S</td>
<td>26.81</td>
<td>1.58</td>
<td>3.32</td>
<td>5.76</td>
<td>51</td>
<td>6.706</td>
</tr>
</tbody>
</table>

The optical properties and the energy gap of the nanomaterials decide the function and the usage of opto-electronic devices. Fig. 2a displays the optical absorption of both Cd$_{0.9}$Zn$_{0.1}$S and Cd$_{0.87}$Zn$_{0.1}$Ni$_{0.03}$S from 300 to 550 nm. Fig. 2a reflected that Zn = 10% doped CdS (Cd$_{0.9}$Zn$_{0.1}$S) exhibits single absorption peak centered at 306 nm. Cd$_{0.9}$Zn$_{0.1}$S possesses strong absorption below 340 nm without any anomalous absorption in the higher wavelength visible region. The sudden fall down of absorption below 340 nm is responsible for the energy of Cd$_{0.9}$Zn$_{0.1}$S nanostructures [19]. The addition of Ni = 3% induces three anomalous absorption peaks; first one centered at 323 nm (corresponding to ~3.85 eV), second at 355 nm (~3.50 eV) and the third centered around 436 nm (~2.85 eV).

In the absorption profile, the first peaks related to UV light and the third peak is accountable for bluish-violet light. In addition to the anomalous absorption generation, absorption edge moved towards larger wavelength side (known as red shift) by the Ni inclusion in Cd$_{0.9}$Zn$_{0.1}$S nanostructures. The current red shift i.e., decrease of energy gap by Ni addition was explored by Chandramohan [20]. The present shift along higher wavelength side for Ni doped samples evidently signified that Ni$^{2+}$ ions were substituted into Cd-Zn-S lattice [21].

Generally, the absorption in the UV region i.e., below 380 nm (peaks at 326 and 355 nm) is begins from the electron transitions from valence to conduction bands corresponding to $E_g$ of the nanomaterials. The appearance of anomalous absorption peaks i.e., more peaks by Ni doping is owing to the establishment of different defects like vacancies, interstitials, etc. which act as trapping centers in the lattice. The visible peak at 436 nm (~bluish violet radiation) is due to the presence of Zn/Cu interstitials in the host lattice. The defects and disorder in the lattice induced by Ni generates the new inter-energy levels in the conduction band [22] and the inter-band transition creates the absorption peak near 436 nm.
Fig. 2b represents the transmittance spectra of Cd$_{0.9}$Zn$_{0.1}$S and Cd$_{0.87}$Zn$_{0.1}$Ni$_{0.03}$S between 300 - 550 nm. Zn = 10% doped CdS exhibits dominant transmittance in the visible wavelengths and possesses highest transmittance at 78%. At the same time, Ni = 3% doped Cd$_{0.9}$Zn$_{0.1}$S sample exhibits relatively higher transmittance of around 83% after 450 nm. The same trend of transmittance was observed by Ouachtari et al. on CdS thin films prepared by CBD method [23]. The noted relative higher transmittance at Ni doped sample in the visible region suggested them for an efficient transparent window in the solar cells.

The energy gap of Zn = 10% added CdS and Ni = 3% added Cd$_{0.9}$Zn$_{0.1}$S samples is derived [24] from the graph, $(a\hbar^2)^2$ versus the energy (Fig. 3) show the $(a\hbar^2)^2$ versus $E$ curves of Cd$_{0.9}$Zn$_{0.1}$S and Ni = 3% doped Cd$_{0.9}$Zn$_{0.1}$S for energy gap ($E_g$) calculation. $E_g$ of the above materials is decreased from 3.8 eV (Cd$_{0.9}$Zn$_{0.1}$S without Ni concentrations) to 3.38 eV for Ni = 3% added Cd$_{0.9}$Zn$_{0.1}$S. Here, the derived $E_g$ (~ 3.38-3.8 eV) is higher than normal CdS which exhibits $E_g$ ~ 2.42 eV [25]. The similar enhanced $E_g$ was noted in TM ions added CdS materials due to its reduced spatial nano dimension [26, 27]. We noted from Fig. 6 that $E_g$ possesses considerable decline ($\Delta E_g$ = 0.42 eV) during the substitution of Ni = 3%. The same declining trend of $E_g$ was described by Senthil [28] in Ni substituted CdS.

Ni$^{2+}$ inclusion produces the extra free charge carriers which are accountable for the $E_g$ reduction. The creation of additional charges is confirmed by the increase of electrical conductivity and decrease of resistance in Ni-Cd-S lattice. The creation of free electrons is named as “free carrier absorption” which is accountable for the present decrease in $E_g$. Moreover, the noted reducing $E_g$ by Ni addition is induced from the 'p-d' hybridization of Ni/Cd and sulfide in the existence of intermediary energy levels in $E_g$. The present shrinkage of $E_g$ recognized the existence of Ni$^{2+}$ within Cd-Zn-S lattice. This noticeable reduction in $E_g$ by Ni doping is by the generation of extra energy levels inside the $E_g$ of Cd-
Zn-S which broaden the light absorption towards the longer wavelengths [29]. The same defect associated reduction in $E_g$ was described by Premararani et al. [30] by the introduction of new energy levels around the two bands in Ni doped system.

![Energy gap calculation](image)

**Fig. 3. Energy gap calculation**

**Conclusions**

Cd$_{0.9}$Zn$_{0.1}$S and Cd$_{0.87}$Zn$_{0.1}$Ni$_{0.03}$S were prepared by chemical co-precipitation method. The XRD profile proved the cubic crystal structure of the samples without any impurity related phases and no changes in the cubic phase were noted by Zn/Ni doping in CdS. The reduced size from 63 to 51 Å and the dissimilarities in lattice parameters and micro-strain has been discussed by Ni addition and the defects connected with Ni$^{2+}$. The noticed anomalous absorption bands in the visible wavelength and the elevated transmittance at Ni doped sample suggested that the synthesized materials are useful for the fabrication of efficient opto-electronic devices. The band gap reduction during the substitution of Ni = 3% is explained by the generation of extra energy levels associated with defects within the two bands.

**References**