Chapter-V

Structural and nonlinear optical studies of Mg doped CdS-PVP nanocomposite films

Abstract

Mg doped CdS-PVP nanocomposite films with different Mg dopant concentration were prepared by in situ method using cadmium nitrate and sodium sulphide as cadmium and sulfur sources, respectively. X-ray diffraction studies reveal that all the films are found to be well crystallized with cubic structure of CdS. The average nanocrystallite size of CdS was estimated using Debye-Scherrer formula and is found in the range of 2.42-2.15 nm for 0-7 mol% Mg doped CdS-PVP nanocomposite films. The morphology of the films was investigated using scanning electron microscopy. Fourier transform infrared studies are carried out on all the films to confirm the formation of CdS-PVP nanocomposite films. The large blue shift of the band gap energy of the Mg doped CdS-PVP nanocomposite films compared to the bulk CdS is observed via UV-Vis absorption spectra. Photoluminescence spectra of all the films show the yellow emission band. The intensity of the yellow emission band is increased with increasing Mg concentration which indicates the presence of smaller CdS nanoparticles distributed in PVP matrix. The third-order nonlinear optical properties of the composite films were studied at 532 nm in the nanosecond regime by using the Z-scan technique. The results showed that the Mg doped CdS-PVP nanocomposite films have a promising optical property exhibited by a negative nonlinear optical refractive index and absorption coefficient of $10^{-10}$ m$^2$MW$^{-1}$ and $10^{-3}$ mMW$^{-1}$, respectively. The third order nonlinear optical susceptibility and figure of merit were calculated and found to be high with the comparison of some representative nonlinear optical materials.
5.1 Introduction

As an important historical member of the photoelectric material family, cadmium sulfide (CdS) has been widely and deeply explored worldwide [1-4]. Due to the quantum-size effect, the decrease in the CdS nanoparticle size will lead to significant changes in its optical and electrical properties [5]. Bulk CdS has a direct band gap of 2.4 eV at 300 K, and the typical Bohr exciton diameter of CdS is around 5.8 nm. Consequently, CdS nanocrystals in the size range of 1-6 nm would show the size related quantum confinement effects and apparently different optical properties [6, 7]. Many experimental and theoretical techniques have already been used to study the size dependent, unusual optical and electronic properties of CdS nanocrystals [8-11]. Moreover, it has been found that the quantum-sized CdS has an exceptional third-order nonlinear optical property useful for optical switches or limiting devices [12].

CdS nanostructures embedded in polymer matrix have been reported to exhibit excellent optical as well as electrical characteristics, which are attractive not only for fundamental physics but also for their possible applications in the next generation nonlinear optical devices. The use of polymers is a prominent method for the synthesis of nanoparticles [13, 14]. The reason is that the polymer matrices provide for processability, solubility, and control of the growth and morphology of the nanoparticles. For instance, the third-order nonlinearities of quantum-confined CdS have been extensively studied, such as CdS/PVA and CdS/PMMA. The nonlinearities were reported to have originated from the efficient bleaching of the exciton absorption due to the generation of surface-trapped electron-hole pairs [15,16].

Polyvinylpyrrolidone (PVP) has outstanding colloidal and complexing properties and belongs to a neutral charged polymeric dispersant [17, 18]. PVP has been widely used as matrix for manufacturing the optical devices [19] and the protecting agent or stabilizer for synthesizing nanoparticles [20]. For example, PVP has been used to prepare UV written plane waveguides owing to its photo-curability, excellent film formation ability and high transparency within the ultraviolet, visible and near infrared regions [21]. It was reported very recently that Au nanocolloids have been synthesized and subsequently dispersed into the PVP matrix and that the Au/PVP nanocomposites exhibited high third-order nonlinear optical properties [22]. In this work, Mg doped
CdS-PVP nanocomposite films with a different concentration of Mg dopant were synthesized using in situ method and the resulting composite films were characterized using various techniques.

5.2 Materials and methods

5.2.1 Experimental

For the preparation of nanocomposite films, aqueous solution of PVP (10 wt%) was prepared by dissolving PVP powder in distilled water under magnetic stirring for 1 h. A mixture of cadmium nitrate (Cd(NO$_3$)$_3$.4H$_2$O) and magnesium chloride (MgCl$_2$) dissolved in distilled water was added to the PVP solution. Aqueous solution of sodium sulphide (Na$_2$S) was added to above solution drop wise until the solution turns into yellow color. The solution was vigorously stirred at room temperature for 2 h. After 2 h, the mixture was cast on the glass slide and dried at room temperature for 2 days in order to remove solvent traces. Similarly, three samples of Mg doped CdS-PVP nanocomposite films were prepared by varying the concentration of MgCl$_2$ as 0, 3 and 7 mol%. The film thickness was in the range of 56-125 µm for 0-7 mol% Mg doped CdS-PVP nanocomposite films.

5.2.2. Characterization techniques

X-ray diffraction studies of undoped and Mg doped CdS-PVP nanocomposite films were carried out using a Rigaku X-ray diffractometer with CuK$_\alpha$ radiation ($\lambda = 1.54$ Å) in the range of 20-60°. The surface morphologies of three samples were characterized by using JEOL Model JSM-6390LV scanning electron microscope. The spectra of undoped and Mg doped nanocomposite films were carried out using a PerkinElmer Spectrum GX Fourier transform infrared (FTIR) spectrophotometer in the wavenumber range of 4000-400 cm$^{-1}$. The optical absorption spectra were recorded for undoped and Mg-doped CdS-PVP nanocomposite films in the range of wavelength from 300 to 800 nm at room temperature using a PerkinElmer Lambda 35 spectrometer. Photoluminescence (PL) spectra of undoped and Mg doped CdS-PVP nanocomposite films were recorded using PerkinElmer LS 45 fluorescence spectrophotometer in wavelength range of 400-800 nm. The nonlinear optical properties of the CdS-PVP and Mg doped CdS-PVP nanocomposite films were investigated using the Z-scan technique.
with the advantage of separating the contributions of refractive and absorptive nonlinearities in the samples. In the experiments, a mod-locked Nd-YAG with a frequency doubled at 532 nm and characterized by a pulse duration of 5 ns at a repetition rate of 10 Hz was used as the light source. The laser beam was focused on the sample by a 120 mm focal length lens, leading to a measured beam waist \( \omega_0 \) of 25\,\mu m.

5.3 Results and discussions

5.3.1 X-ray diffraction studies

Figure 5.1 shows the X-ray diffraction patterns of (a) CdS-PVP, (b) 3 mol% and (c) 7 mol% Mg doped CdS-PVP nanocomposite films. The broadening of peaks indicates the presence of nanometer-sized particles in the samples. The diffraction patterns of undoped CdS-PVP (Figure 5.1(a)) nanocomposite exhibit three peaks at 20 value of 26.5°, 44.1° and 52.1° corresponding to the (111), (220) and (311) planes of cubic CdS structure, which is well consistent with the standard data (JCPDS card no.80-0019). These three peaks get shifted towards to higher angle in the XRD patterns (Figures 5.1(b) and (c)) of Mg doped nanocomposites which indicating an expansion of CdS lattice for all doped samples. It is also worthful to notify that no diffraction peaks pertaining to the Mg related impurity phase or secondary phase were found in the Mg doped samples. The lattice constant ‘\( a \)’ has been calculated and is found to be 5.810 Å for CdS-PVP whereas for 3 and 7 mol% Mg doped CdS-PVP nanocomposite films, these values are found to be 5.803 Å and 5.797 Å. It can be observed that the decrease in lattice constant with increasing Mg concentration which confirms that the occupation of Mg\(^{2+}\) into Cd\(^{2+}\) lattice sites. Such a change is indeed to be expected if Mg ions replace Cd\(^{2+}\) ions in the lattice, as the Mg\(^{2+}\) ions have smaller ionic radii (0.66 nm) [23]. The average crystallite size of the samples was calculated using Debye Scherrer formula [24]:

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

where \( D \) is the average crystallite size, \( \lambda \) is the X-ray wavelength (1.54 Å), \( \theta \) is Bragg diffraction angle, and \( \beta \) is full width at half maximum, respectively. The calculated crystallite size was found to be 2.42 nm for undoped CdS-PVP, 2.37 nm and 2.15 nm for 3 mol% and 7 mol% Mg doped CdS-PVP nanocomposite films.
Figure 5.1 X-ray diffraction patterns of all the films

Figure 5.2 SEM images of (a) CdS-PVP, (b) 3 mol% Mg doped CdS-PVP and (c) 7 mol% Mg doped CdS-PVP nanocomposite films
5.3.2 Morphology studies

Figure 5.2 shows the SEM images of (a) undoped, (b) 3 mol% and (c) 7 mol% Mg doped CdS/PVP nanocomposite films. As shown in Figure 5.2(a), the CdS nanoparticles are well monodispersed throughout PVP matrix which indicates the PVP matrix is a suitable matrix to disperse the CdS nanoparticles without aggregation. It can be seen from the Figures 5.2((a) and (b)) that the size of the CdS nanoparticles decreased with increasing Mg dopant concentration. The morphology of CdS nanoparticles within the PVP matrix of all the films is roughly sphere.

5.3.3 FTIR analysis

FTIR spectra are used to investigate the type of chemical bonding between CdS nanoparticles and PVP host polymer. FTIR spectra of (a) undoped, (b) 3 and (c) 7 mol%
Mg doped CdS-PVP nanocomposite films are shown in Figure 5.3. The spectrum of undoped CdS-PVP exhibits a several bands of stretching and vibrations i.e. 3405, 2910, 2360, 1653, 1428, 1281, 1166, 1006, 842 and 732 cm\(^{-1}\) which are assigned to the O-H stretching, asymmetrical stretching of C-H, C-O stretching, -C=O stretching, CH\(_2\) wagging, -C-N stretching, cyclic –C-C- stretching, CH\(_2\) rocking, CH\(_2\) stretching and CH\(_2\) rocking of PVP. The peak observed at 639 cm\(^{-1}\) could be assigned to the vibration of Cd-S. It can be observed that the shift in the peaks towards to lower wavenumber with the comparision of reported bands of pure PVP [25], confirming the strong interaction between the CdS nanoparticles and PVP polymer matrix. The FTIR spectra of Mg doped samples are found to be identical that of CdS-PVP nanocomposite. However, the decrease in the absorbance with increasing of Mg dopant concentration, suggesting the decrease in the particle size within polymer matrix [26].

5.3.4 UV-Vis optical absorption studies

Figure 5.4 shows the optical absorption of undoped, 3 mol% and 7 mol% Mg doped CdS-PVP nanocomposite films. The absorption spectrum of CdS-PVP nanocomposite film shows an absorption band at 458 nm. The blue shift of 458 nm can be found compared with the band gap of characteristic absorption of bulk CdS (517 nm), indicating the formation of nanostructured CdS particles in the PVP matrix. With the Mg doping concentration increased from 3 to 7 mol% the absorption band showed a blue shift from 454 to 451 nm. The optical band gap values have been estimated using the following relation:

\[
\alpha(h\nu) = A(h\nu - E_g)^n
\]

(5.2)

Where \(h\) is Planck's constant, \(\alpha\) is the linear absorption coefficient and \(\nu\) is the transition frequency of incident photon. The exponent \(n\) tells about the nature of band transition, \(n = 1/2\) and \(n = 3/2\) and corresponds to direct allowed and direct forbidden transitions and \(n = 2\) and 3 corresponds to indirect allowed and indirect forbidden transitions respectively [24]. The optical band gap of the films is estimated by plotting graph of \(h\nu\) vs. \((\alpha h\nu)^2\) for the linear absorption coefficient \(\alpha\) as shown in Figure 5.5.
**Figure 5.4** UV-Vis optical absorption spectra of all the films

**Figure 5.5** \((a\nu)^2\) versus \(h\nu\) plot of all the films
By extrapolating the straight portion of the graph on $h\nu$ axis at $\alpha = 0$, we found the band gaps of the CdS-PVP, 3 mol% Mg doped CdS-PVP and 7 mol% Mg doped CdS-PVP nanocomposite films to be 2.70 eV, 2.73 eV and 2.75 eV, respectively. The decrease in band gap value reveals that the size of the CdS nanocrystals has been increased on Mg doping. The size of the CdS nanoparticles in PVP matrix can be calculated using the Brus equation as follows [27]:

$$E_{np} = E_g + \frac{\hbar^2}{8r^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.786e^2}{\varepsilon r}$$

(5.3)

where $E_{np}$ is the band gap of the CdS nanoparticles, $E_g$ is the band gap of bulk CdS (2.42 eV), $m_e^*$ is the effective mass of electron ($=0.19m_e$), $m_h^*$ is the effective mass of hole ($0.8m_e$), $\varepsilon$ is the dielectric constant (5.7) and $r$ is the radius of CdS particles [28]. Employing the calculated size of CdS from XRD studies in the Brus equation, we can calculate the optical band gap of samples. The estimated size of CdS nanoparticles is found to be 2.5 nm for CdS-PVP, 2.35 nm for 3 mol% Mg doped CdS-PVP, and 2.25 nm for 7 mol% Mg doped CdS-PVP nanocomposite films, respectively. The size estimated in UV-Visible optical absorption studies is almost agreed well with the size estimated in the XRD studies as discussed above.

5.3.5 Photoluminescence studies

Photoluminescence (PL) studies provide information of different energy states available between valence and conduction bands responsible for radiative recombination. The excitation wavelength for all samples was fixed at 390 nm. Figure 5.6 displays the PL spectra of (a) undoped, (b) 2 mol% and (c) 5 mol% Mg doped CdS/PVP nanocomposites. The spectra for all samples show emission peak at 587 nm which is attributed to the yellow emission of CdS. The yellow emission is described in the literature as a result of recombination via surface localized states, radiative transition from donor levels i.e. Cd atoms located in interstitial sites ($I_{Cd}$) to the valence band [29], or the transition from interstitial cadmium vacancy complexes ($I_{Cd-V_{Cd}}$) which is a donor to acceptor level transition [30]. In the photoluminescence spectra the peak is found to broaden out with increase in Mg concentration, which is attributed to high concentration of defects. As the size of nanoparticles decreases, the increased band gap makes certain
defect states energetically accessible, i.e. the number of surface states increases, thus increasing luminescence intensity with smaller particles [31]. It is also noted that the intensity of emission peak increases as the concentration of Mg increases which is might be attributed to decrease in CdS particle size with the Mg content.

![Photoluminescence spectra of all the nanocomposite films](image)

**Figure 5.6 Photoluminescence spectra of all the nanocomposite films**

### 5.3.6 Nonlinear optical studies

The nonlinear optical properties of the CdS-PVP and Mg doped CdS-PVP nanocomposite films were investigated using the Z-scan technique with the advantage of separating the contributions of refractive and absorptive nonlinearities in the samples [32]. As the glass substrate has a very weak nonlinear optical response, the observed large optical nonlinearities resulted from the composite film. The Z-scan curves obtained for all the samples are shown in Figure 5.7. The closed-aperture Z-scan curves (Figure 5.7(a)) for all the nanocomposite films show a pre-focal peak followed by a post-focal valley signature, indicating negative nonlinear refraction and exhibiting strong self-defocusing behavior. It is observed that the peak to valley measurements of closed aperture Z-scan satisfy the condition of third-order optical nonlinearity, i.e. \( \Delta z_{p-v} \approx 1.7z_0 \),
thus confirming the presence of pure electronic third-order nonlinearity. The open aperture Z-scan traces (Figure 5.7(b)) for all the films show a normalized transmittance peak which indicates the presence of negative nonlinear absorption. This result suggests that the nonlinearity is mainly due to the saturable absorption behavior. The circles in Figure 5.7(b) represent the measured data while the solid lines indicate a theoretical fit.

The data were analyzed using the procedures described by Sheik-Bahae et al [32]. The nonlinear refractive index \( n_2 \) and real part of the third order nonlinear susceptibility (\( \text{Re} \chi^{(3)} \)) are given by the following relations:

\[
\begin{align*}
n_2 &= \frac{\Delta T_{p-v} \lambda}{0.406(1-S)^{0.25}2\pi I_0 L_{eff}} \quad (5.4) \\
\text{Re} \chi^{(3)} (\text{esu}) &= \frac{cn_0^2 n_2}{120\pi^2} \left( \frac{m^2}{W} \right) \quad (5.5)
\end{align*}
\]

where \( c \) is the velocity of light, \( n_0 \) is the linear refractive index of the sample, \( \lambda \) is the wavelength of light, \( \Delta T_{p-v} \) is the difference between the normalized peak and valley transmittance, \( S \) is the aperture transmittance at linear regime, \( L_{eff} = 1-\exp(-\alpha L)/\alpha \) is the effective thickness of the sample (\( L \) is the sample thickness, \( \alpha \) is the linear optical absorption coefficient) and \( I_0 \) is the laser intensity at the focal point. The nonlinear absorption coefficient \( (\beta, \text{MW}^{-1}) \) of the sample can be calculated from the normalized transmittance for the open aperture by the following relation:

\[
T(z,s=1) = \sum_{m=0}^{\infty} \left[ -q_0(z) \right]^m \left[ \frac{1}{m+1} \right]^{3/2} \quad \text{for} \quad \frac{q_0(0)}{1}, \quad \text{where} \quad q_0(z) = \frac{\beta I_0 L_{eff}}{1 + z^2 / z_\rho^2} \quad (5.6)
\]

The imaginary part of third order nonlinear susceptibility \( \text{Im} \chi^{(3)} \) is given as follows [28]:

\[
\text{Im} \chi^{(3)} (\text{esu}) = \frac{c^2 n_0^2 \beta}{240\pi^2 \omega} \left( \frac{m}{W} \right) \quad (5.7)
\]

where \( \omega \) is the angular frequency of light field. The absolute values, \( \chi^{(3)} \), of these films were calculated from the following equation

\[
|\chi^{(3)}| = \left[ (\text{Re} \chi^{(3)})^2 + (\text{Im} \chi^{(3)})^2 \right]^{1/2} \quad (5.8)
\]
Figure 5.7 (a) Closed aperture and (b) open aperture Z scan results
The nonlinear optical parameter values such as $n_2$, $\beta$, $\text{Re}\chi^{(3)}$, $\text{Im}\chi^{(3)}$ and $\chi^{(3)}$ could be estimated and the results are summarized in Table 5.1. Since the glass substrate and pure PVP possess a very weak nonlinear optical response at 532 nm, the optical nonlinear properties observed in our Z-scan measurements can be attributed to CdS nanocrystals distributed in the PVP matrix. Table 5.1 shows that the nonlinear optical parameter values increase with increasing mass concentration of Mg dopant. The calculated nonlinear optical parameter values of Mg doped CdS-PVP nanocomposite films are one order of magnitude greater than that of CdS-PVP nanocomposite film. This enhancement in optical nonlinearity is attributed to the presence of more defects in the Mg doped CdS-PVP nanocomposite films and also quantum confinement effect plays major role in the enhancement of the nonlinearity as the estimated particle size of all the nanocomposite films lie much below the Bohr exciton diameter (5.8 nm) of bulk CdS. Accordingly, the nonlinear refractive index and absorption coefficient could reach the magnitudes of $10^{-10}$ cm$^2$/MW and $10^{-3}$ cm/MW, respectively. It is known that the wavelength and the pulse width of the light used in the Z-scan measurements have influences on the nonlinear refractive index and the absorption coefficient [33, 34]. It can be seen that the $n_2$ and $\beta$ values of the as-synthesized CdS-PVP film are higher than that of the bulk CdS and reported values of CdS/PDA nanocomposite film in the literature [35, 36]. It is worth pointing out that the nonlinear refractive index of the composite film (CdS/PDA, CdS/PVP) was measured under almost identical conditions (530 nm, 5 ns; 532 nm, 5 ns). In comparison with the CdS/PDA film, the CdS-PVP film shows an increase of about four orders of magnitude in NLO refractive efficiency. As compared with the estimated value of nonlinear refractive index and absorption coefficient of CdS-PVP nanocomposite film with varying concentration of CdS reported in the literature, one order of magnitude of nonlinear refractive index and four orders of magnitude of nonlinear absorption coefficient are high in the 7 mol% Mg doped CdS-PVP nanocomposite film. Many considerations have been taken to investigate the effectiveness of nonlinear materials for practical use in nonlinear optical devices in the recent years. In order to evaluate the Mg doped CdS-PVP nanocomposite films for applications in such devices; Figure of merit (FOM) has to be calculated for all the films. The estimated FOM using the relation, $\chi^{(3)}/\alpha$, are given in Table 5.1. Compared with
some representative nonlinear optical materials [37-39], the FOM is greatly enhanced for the Mg doped CdS-PVP nanocomposite films. Furthermore, this material can be obtained at room temperature and has excellent film formation ability, and hence the results indicate that the Mg doped CdS-PVP nanocomposite films have a great potential for nonlinear optical devices.

Table 5.1 Nonlinear optical parameters of different concentrations of Mg (x mol%) doped CdS-PVP freestanding nanocomposite films.

<table>
<thead>
<tr>
<th>x</th>
<th>$n_2 \times 10^{-10}$ (cm$^2$/MW)</th>
<th>$\beta \times 10^{-3}$ (cm/MW)</th>
<th>Re$\chi^{(3)}$ ($\times 10^{-4}$, esu)</th>
<th>Im$\chi^{(3)}$ ($\times 10^{-6}$, esu)</th>
<th>$\chi^{(3)} \times 10^{-4}$ (esu)</th>
<th>$\chi^{(3)}/\alpha$ ($\times 10^{-9}$, esu m)</th>
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<td>-0.747</td>
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<td>-6.515</td>
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<td>-1.233</td>
<td>-7.288</td>
<td>1.432</td>
<td>8.558</td>
</tr>
</tbody>
</table>

5.4 Conclusions

Mg doped CdS-PVP nanocomposite films with a Mg concentration of 0-7 mol% were prepared through an in situ chemical method. XRD studies of all the films confirmed the cubic phase formation of CdS nanocrystals in PVP matrix. The morphology of CdS-PVP and Mg doped CdS-PVP nanocomposite films were investigated using SEM micrograph. FTIR spectra revealed the interaction of CdS nanoparticles within the PVP polymer matrix. UV-Visible optical absorption studies showed that the large blue shift with the comparison of bulk CdS. The photoluminescence spectra of all the nanocomposite films exhibited the yellow band emission. The third order nonlinear optical properties were investigated by the Z-scan technique at a wavelength 532 nm with laser pulse duration of 5 ns. The nonlinear refractive indices ($n_2$) were in the order of $10^{-10}$ cm$^2$/MW, having a negative sign that the self-defocusing phenomenon has taken place and the nonlinear absorption coefficients ($\beta$) were in the order of $10^{-3}$ (cm/MW), having a negative sign that represents that the saturable absorption effect. The large third-order nonlinear optical susceptibility ($\chi^{(3)}$) and
FOM ($\chi^{(3)}/\alpha$) reached $10^{-4}$ esu and $10^{-9}$ esu m, respectively, which are both about one or two orders of magnitude larger than some representative metal/dielectric composite materials. The large optical nonlinearity and FOM indicate that the material has great potential application in future optical devices.

5.5 References

