Chapter 4

Linear and nonlinear optical properties of luminescent ZnO nanoparticles embedded in PMMA matrix
4.1. Introduction

Zinc oxide is a wide direct band gap (~ 3.37 eV) semiconductor that has tremendous potentials for blue-ultraviolet light emitters and detectors, transparent high-power electronics and piezoelectric transducers. The low threshold for optical pumping and large exciton binding energy (~ 60 MeV) allow lasing action in ZnO to be reached at extremely low pumping power at room temperature. Recently, ultrafast carrier dynamics in nanostructured ZnO [1, 2] and huge nonlinear refraction and absorption in ZnO thin films have been observed [3]. Ultrafast all-optical switching devices are the key component for next generation broadband optical networks. The implementation of such devices requires materials with low linear and nonlinear losses, high Kerr-type refractive nonlinearities and response times of a few picoseconds or less [4]. To search for materials which meet the above requirements, it has been suggested to target at semiconductors with their band gap at least twice the photon energy used \( E_g > 2E_{\text{photon}} \) avoiding optical absorption due to one or two-photon transitions [5-6]. In this regard, wide-gap semiconductors are a suitable candidate; and ZnO has been recently reported to be one of the promising candidates [7].

Nonlinear absorbers can be used as optical limiters, which have a linear transmission up to a threshold input fluence \( I_{th} \) and the value of \( I_{th} \) may vary in different materials. If the input fluence is increased above the \( I_{th} \), the transmittance remains a constant. The nonlinear absorption in ZnO originates from the so called multi photon absorption processes of which
two photon absorption is the significant mechanism at laser wavelength 532nm. Two-photon absorption is an instantaneous nonlinearity in which, an electron absorbs two photons at approximately the same time (or within less than a nanosecond) and achieves an excited state that corresponds to the sum of the energy of the incident photons. The present study deals with absorptive as well as refractive nonlinearity of ZnO nanoparticles embedded in poly methyl methacrylate (PMMA) matrix.

4.2. Experimental

ZnO nanoparticles were prepared at room temperature by wet chemical route without any capping agents [9], using 0.1 mol of zinc acetate and varying concentration of NaOH (0.025M to 0.2M) in methanol and stirred for 2 hours. The chemical reaction involved is as follows:

\[ \text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{ZnO} + 2(\text{CH}_3\text{COO})\cdot\text{Na} + 3\text{H}_2\text{O} \]

The size of the nanoparticles was verified by transmission electron microscopy (TEM). It was not possible to filter out the nanoparticles prepared at the lower concentration of NaOH in the reaction mixture because of their smaller size. The concentrations of the ZnO nanoparticles in the resulting colloidal solution were found by atomic absorption spectroscopy (AAS). A part of the colloidal solution was filtered out to get fine ZnO powder for the X-ray diffraction (XRD) studies. The XRD patterns of the ZnO powder obtained at higher concentrations of NaOH in the reaction mixture were taken using Rigaku DMAX-C X-ray diffractometer. 2 grams of PMMA was mixed with 10 ml of chloroform and
beam was focused using a lens of focal length 25cm on to the sample. The sample was translated in the spatially varying intensity region on either side (-z to +z) of the focal point (z=0) using the translation stage of an automated stepper motor. The reference laser fluence, transmitted fluence and ratio between them were measured using the probes D1 and D2 of an automated energy ratio meter (RI-7620 energy ratio meter) simultaneously for different positions of z. The dependence of incident laser fluence on the nonlinear absorption and nonlinear refraction were analyzed using open (without aperture) and closed aperture (with aperture) Z-scan techniques respectively.

4.3. Results and discussions

The XRD pattern (Figure 4.2) of ZnO synthesized by wet chemical method has large full width at half maximum (FWHM) compared to the bulk commercial ZnO which confirms the formation of ZnO nanoparticles. The FWHM shows a gradual increase with decrease in concentration of the NaOH in the reaction mixture indicating decrease in particle size. The ZnO nanoparticles produced by the wet chemical route has a thin passivation layer of Zn(OH)$_2$. The oxygen is being supplied by the NaOH. The increase in the concentration of NaOH increases the dissolved oxygen, which promotes the growth of ZnO. Thus increasing the concentration of NaOH will increase the growth of ZnO and agglomeration enhances the size of ZnO.
the visible region which is attributed to the defects in ZnO. The PL spectra of ZnO nanoparticles shown in figure 4.9 have emission bands in the UV and visible regions for excitation at 325 nm. Efficient UV emission near band edge is attributed to free exciton emission with high electronic density of states, which shift to higher energies due to the reduction in nanoparticle size as the NaOH concentration in the reaction mixture is decreased. As the particle size decreases, due to the quantum confinement, the energy levels of the conduction and valence bands shift apart, giving rise to a blue shift in the PL exciton emission [14]. The emission in the visible region is related to the defects in the ZnO [15]. The green emission at 532nm is commonly attributed to oxygen interstitial [16]. The energy levels involved in the PL emission are shown in the inset of figure 4.9. Blue emissions at 468nm correspond to the electron transition from the shallow donor level of zinc interstitials to the valence band [17]. Therefore the blue emission would be originating from the electron transition from the bottom of the conduction band to an acceptor level (caused by Zn vacancy) [18].
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\[ T(z, S = 1) = \frac{1}{\sqrt{\pi} q_0(z, 0)} \int \ln \left[ 1 + q_o(z, 0)e^{-z^2} \right] d\tau \quad (4.2) \]

where \( q_o(z, 0) = \beta I_0 \) and \( \beta \) is the two photon absorption coefficient, \( I_{\text{adj}} \) is given by \( \frac{1 - e^{-\alpha L}}{\alpha} \) where \( L \) is the sample length, \( \alpha \) is the linear absorption coefficient, \( I_o \) is the incident irradiance at \( z=0 \) [8].

From the open aperture Z-scan curves, it is found that as the band gap decreases (increase in particle size), the rate of two photon absorption increases which is attributed to an inverse proportionality between \( \beta \) and third power of band gap \( E_g^3 \) [19] and enhancement in the nonlinear susceptibility due to enhanced oscillator strength with particle size [20]. Hence the dip in the open aperture curve increases with increase in particle size such that, the observed increase in the limiting efficiency with increase in the particle size (decrease in band gap) resulted. The value of the nonlinear absorption coefficient \( \beta \) taken using Shake Bahae eqn.(4.2) ranges from 21cm/GW to 682cm/GW as the band gap decreases from 3.72eV to 3.41eV. It is also found that the experimental curves deviate from the theoretical equations using Shake Bahae formalism for thin films containing larger sized nanoparticles (\( E_g = 3.43eV \) and \( E_g = 3.41eV \)) prepared at larger NaOH concentration. The nanoparticles with \( E_g = 3.43eV \) show a shift from reverse saturable absorption (RSA) to saturable absorption (SA) and again back to RSA behaviour which is a fifth order nonlinear process [21]. In larger nanoparticles, there is chance for two photon absorption induced free carrier absorption [22]. This leads to broadening of the open aperture curve.
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Since in materials having both refractive and absorptive nonlinearity closed aperture measurements have contribution from both. So the closed aperture Z-scan data of these samples are divided with the open aperture data in order to eliminate the effect of nonlinear absorption and the resulting curves are fitted with the theoretical equation for pure nonlinear refraction eqn.(4.3) and the value of the nonlinear refractive index $\gamma$ corresponding to best theoretical fit is found. The aperture linear transmittance $S = 1 - e^{-\left(\frac{2x^2}{\epsilon^2}\right)}$ is taken as $S=0.35$ in this case.

The on axis phase shift at the focus $\Delta \phi_0$ can be obtained through the best theoretical fit from the normalized closed aperture transmittance [8, 23]. The theoretical equation for the normalized Z-scan transmittance $T(z, \Delta \phi_0)$ is given by eqn.(4.3),

$$T(z, \Delta \phi_0) = \left[1 - \frac{4\Delta \phi_0 x}{(x^2 + 9)(x^2 + 1)}\right]$$

(4.3)

where $x = \frac{z}{z_0}$ and $\Delta \phi_0 = +ve$ and $\Delta \phi_0 = -ve$ respectively for self focussing and self defocusing type refractive nonlinearity.

The nonlinear refractive index can be calculated from the following eqns. (4.4) and (4.5),

$$\gamma = \frac{\lambda \Delta \phi_0}{2L_{ef} I_0}$$

(4.4)

$$n_2(\text{esu}) = \frac{c n_0 \gamma}{40\pi} m^2 / W$$

(4.5)
The peak to valley shape of the curves indicates a negative value of refractive index. The deviation of the experimental closed aperture curve from the theoretical plot is attributed to the small variation in the Gaussian shape of the laser pulse. Obviously from figure 4.11, the thin films containing larger sized nanoparticles \( (E_g=3.43\, \text{eV} \text{ and } E_g=3.41\, \text{eV}) \) shows very large nonlinear phase change \( \Delta \phi_0 \) causing the experimental curves to deviate from the Shake Bahae eqn. (4.3). This larger phase change may be due to two photon generated free carrier refraction in higher sized nanoparticles which is a fifth order nonlinear process [24]. However detailed analysis may be required in order to exactly determine which mechanism is responsible for the discrepancy in the shape of the closed aperture curve. The energy loss of the incident laser pulses due to Fresnel reflection by the surfaces of ZnO:PMMA film in the Z-scan analysis is not considered [25].

The value of the nonlinear absorption cross section \( (\sigma_{TPA}) \) is related to nonlinear absorption coefficient \( (\beta) \) [26] as given by eqn. (4.6),

\[
\sigma_{TPA} = \frac{\omega \beta \hbar}{2\pi N}
\]

where \( N \) is the concentration of the ZnO molecules per cm\(^3\) and \( \frac{\hbar \omega}{2\pi} \) is the exciting photon energy. The cross section \( \sigma_{TPA} \) is expressed in Geopert Mayer units where 1 GM = 10\(^{-5}\) cm\(^4\) s phot\(^-1\) mol\(^-1\). The variation of the nonlinear absorption cross section with particle size is plotted in figure 4.12. Obviously the nonlinear absorption cross section is found to increase with increase in the particle size (decrease in band gap).
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Figure 4.12. The two photon absorption cross section versus the band gap of the ZnO nanoparticles.

It is observed that the efficiency of nonlinear refraction increases with decrease in band gap or increase in the particle size. The enhancement in the nonlinear refractive index with increase in particle size is attributed to the size dependent enhancement of the oscillator strength of the coherently generated excitons [26, 27]. Confinement of the excitons in the ZnO nanoparticle leads to the enhancement of oscillator strength per nanoparticle by a factor $\frac{R^3}{a_b^3}$ where R is the radius of the nanoparticle and $a_b$ is the exciton Bohr radius. The value of $n_2$ is found to be varying from -0.47.
×10^7 esu to -4.159×10^7 esu when the band gap varies from 3.72eV to 3.41eV.
The variation of the particle size, band gap, concentration, TPA coefficient and TPA cross section of ZnO with NaOH concentration in the reaction mixture is shown in the table 4.1.

<table>
<thead>
<tr>
<th>Concentration of NaOH (M)</th>
<th>Particle size (nm)</th>
<th>Band gap (eV)</th>
<th>Concentration of ZnO (M)</th>
<th>β (cm/GW)</th>
<th>σ_{TPA} (GM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>2.79</td>
<td>3.72</td>
<td>0.141</td>
<td>21.1</td>
<td>9.28</td>
</tr>
<tr>
<td>0.05</td>
<td>2.89</td>
<td>3.7</td>
<td>0.133</td>
<td>109.3</td>
<td>51.1</td>
</tr>
<tr>
<td>0.075</td>
<td>3.17</td>
<td>3.65</td>
<td>0.131</td>
<td>210.7</td>
<td>99.6</td>
</tr>
<tr>
<td>0.1</td>
<td>3.37</td>
<td>3.62</td>
<td>0.119</td>
<td>448.5</td>
<td>236</td>
</tr>
<tr>
<td>0.125</td>
<td>3.61</td>
<td>3.59</td>
<td>0.116</td>
<td>475.8</td>
<td>254</td>
</tr>
<tr>
<td>0.15</td>
<td>3.81</td>
<td>3.56</td>
<td>0.081</td>
<td>567</td>
<td>436</td>
</tr>
<tr>
<td>0.175</td>
<td>6.83</td>
<td>3.43</td>
<td>0.051</td>
<td>622</td>
<td>755</td>
</tr>
<tr>
<td>0.2</td>
<td>10.25</td>
<td>3.41</td>
<td>0.038</td>
<td>682</td>
<td>1110</td>
</tr>
</tbody>
</table>

Table 4.1. Variation of the particle size, band gap, concentration, TPA coefficient and TPA cross section of ZnO nanoparticles with NaOH concentration in the reaction mixture.

Therefore the high value of nonlinear coefficients enables the use of ZnO:PMMA as a potential nanocomposite material for the development of nonlinear optical devices with a relatively small limiting threshold. The mechanical properties of the polymer films enable its use for device fabrication as compared to ZnO nanoparticles dispersed in a solution. The nanoparticles in solution are unstable and settle down with ageing, the
quantum dots embedded in PMMA matrix are extra stable and hence stable optical devices can be fabricated.

4.4. Conclusions

ZnO nanoparticles embedded in PMMA matrix are prepared by wet chemical synthesis. The band gap of the samples shows a decrease with increase in concentration of NaOH in the reaction mixture indicating an increase in particle size. The photoluminescence spectra of the ZnO colloids show strong UV emission attributed to exciton emission and the strong green and blue emissions attributed to the defect emission in the ZnO. The optical absorptive nonlinearity of the ZnO:PMMA thin films are analyzed using open aperture Z-scan technique which shows optical limiting type nonlinearity which is due to the two photon absorption in ZnO. Broadening of the open aperture curve is observed in particles prepared with larger concentration of NaOH. This deviation from the theoretical curve of two photon process in ZnO:PMMA films containing larger sized nanoparticles is attributed to two photon absorption induced free carrier absorption. The efficiency of nonlinear absorption is found to increase with increase in the band gap. The nonlinear refraction in the ZnO:PMMA shows a self-defocusing type; i.e., a negative value of nonlinear refractive index ($n_2$). The value of nonlinear absorption coefficient as well as refractive index are found to be increasing with increase in particle size. The enhancement in the $n_2$ and $\beta$ is attributed to the enhanced oscillator strength in bigger nanoparticles. The mechanical properties of the polymer films enable its use for device
fabrication as compared to ZnO quantum dots dispersed in a solution. Stability of the nanoparticles embedded in the PMMA matrix is more as compared to the ZnO nanoparticles dispersed in solution.

4.5. References

