Chapter 3

Size dependent enhancement of nonlinear optical properties in nano colloids of ZnO

Abstract

Results of the investigations carried out on the third-order nonlinearity in ZnO nano colloids with particle size in the range 6– 18 nm by z-scan technique are included in this chapter. ZnO nano colloids show negative nonlinearity and good nonlinear absorption behaviour at 532 nm. The observed optical nonlinearity is explained on the basis of two photon absorption followed by free carrier absoption. The third-order optical susceptibility ($\chi^{(3)}$) increases with increasing particle size (R) due to the size dependent enhancement of exciton oscillator strength. In the weak confinement regime, R^2 dependence of $\chi^{(3)}$ is obtained for ZnO nano colloids. Nonlinear susceptibility is highly fluence dependent and it becomes quadratic in nature for large particle size. The optical limiting response is also studied as a function of particle size.

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3.1 Introduction

The linear and nonlinear optical properties of semiconductors are the subject of much current theoretical and experimental interest[1]. Amongst the various nonlinear optical (NLO) materials investigated, wide bandgap semiconductors, especially zinc oxide (ZnO) have attractive nonlinear properties that make them ideal candidates for NLO based devices. Nanosized ZnO in the form of quantum dots, nano wires, nano belts, etc are referred to as the material of 21st century[2].

Most of the nonlinear optical devices rely mainly on higher order susceptibility of materials, viz., $\chi^{(3)}$. There are a number of nano-sized organic nonlinear optical materials and semiconductor structures of low dimension are a new entry into the field of nonlinear optics. The second and third harmonic generation in ZnO microcrystalline thin films has already been reported[3]. Bulk ZnO crystals have been investigated for NLO properties by z-scan technique itself[4]. However, very little work has been done in NLO properties of ZnO quantum dots and its nano colloids because semiconductor nanoparticles in solution with well-controlled size, shape, and surface properties are difficult to obtain[5]. Moreover, the volume fraction of crystallites in a stable solution is usually very small. As a consequence, the resultant nonlinear response is relatively weak. Due to the speciality of the synthesis route adopted in our present investigation, the volume fraction of nano particles increases with particle size. Hence high nonlinear absorption at larger particle size can be expected and this in turn excites our interest in investigating the nonlinear optical properties of ZnO nano colloids. Z-scan is a simple and accurate method to study the NLO properties of materials. Hence, in the present investigation our focus is on the third order NLO susceptibility of this wide bandgap semiconductor, employing the technique of z-scan.

In ZnO, the exciton Bohr radius is 2 nm, which is roughly 4 times that of CuCl, and one can investigate confinement effects and size dependence of $\chi^{(3)}$ over a wide range of crystallite sizes[6]. This chapter deals with a detailed study of the size dependent optical nonlinearity in ZnO nanocolloids over a range of 6-18 nm.

3.2 Theory

The electronic structure as a function of size is discussed both theoretically and experimentally in chapter 2. When the crystallite size is reduced to the order of an exciton Bohr radius a_B, quantum size effects appear and drastic changes in optical properties are expected. Nonlinear optical properties in nanocrystals have been investigated for the different confinement regimes.

In the strong-confinement regime, the photo-excited electron and hole are individually confined. Theoretical and experimental works have revealed that the state-filling effect accounts for the optical nonlinearity in this regime[7]. The size dependence of third-order susceptibility $\chi^{(3)}$ has also been studied, but the results are inconsistent; a larger nonlinear susceptibility for a larger size has been found for CdS_xSe_{1-x} nanocrystals by the saturation spectroscopy and degenerate four-wave mixing (DFWM) measurements, while Roussignol *et al.* have shown that larger $\chi^{(3)}$ values are obtained with decreasing sizes for the same material[7-8].

In the weak-confinement regime, the coulomb interaction between the electron and hole yields an exciton and it is confined as a quasiparticle. The optical nonlinearity arises from the exciton-exciton interaction, which results in a deviation from the harmonicity of the boson-like exciton within the nanocrystal. The size dependent enhancement of nonlinear susceptibility has been investigated theoretically[9-10] as well as experimentally[11-12]. The effect of very large oscillator strength is brought out only in the weak confinement regime.

In the weak confinement regime, the size quantization of the exciton is brought out and consider a quantum sphere of radius R. The electronic excited state, ψ_n is described by the Frenkel exciton as,

$$\psi_n = \sum_j F_n(j) W_j^e(r_j) \prod_{(i \neq j)} W_i^h(r_i) \tag{3.1}$$

where W_j^h and W_j^e are Wannier functions of the valence and conduction bands respectively and $F_n(j)$ is the envelope function in the quantum sphere and is given by

$$F_n(j) = \left[\frac{2}{N}\right]^3 \sin\left[\frac{\pi n_x j_x}{N}\right] \sin\left[\frac{\pi n_y j_y}{N}\right] \sin\left[\frac{\pi n_z j_z}{N}\right] \tag{3.2}$$

where N is the number density, the quantum numbers n=(n_x, n_y, n_z) and the site index j=(j_x, j_y, j_z) are chosen from positive integers between 1 and N and. The ground state of the quantum sphere is given by,

$$\psi_g = \prod_{(i)} W_i^h(r_i) \tag{3.3}$$

The transition dipole moment to the excited states, ψ_n from the ground state, ψ_g is evaluated for the Frenkel exciton in the weak confinement regime[9].

$$\begin{aligned} \langle \psi_n | P | \psi_g \rangle &= \sum_j F_n(j) \langle W_j^e(r_j) | p_j | W_j^h(r_j) \rangle \\ &= p_{eh} \left[\frac{2}{N}\right]^{2/3} \cot\left[\frac{\pi n_x}{2N}\right] \cot\left[\frac{\pi n_y}{2N}\right] \cot\left[\frac{\pi n_z}{2N}\right] \end{aligned} \tag{3.4}$$

where P is a component of the dipole moment operator and $P = \sum_i p_i$ and $\langle W_j^e(r_j) | p_j | W_j^h(r_j) \rangle = p_{eh} \delta_{jj^1}$. δ_{jj^1} denotes the well localized electron hole relative motion at the same unit cell, u and p_{eh} is the effective dipole

moment of the exciton . The transition dipole moment to the lowest excited state (n_x, n_y, n_z)=(1,1,1) is

$$\left\langle \psi_{111} \left| P \right| \psi_g \right\rangle = \left[\frac{2\sqrt{2}}{\pi} \right]^3 p_{eh} N^{3/2} \tag{3.5}$$

For the transition to such a low excited state (n_x, n_y, n_z) as $n_{x,\,y,\,z} \ll N$,

$$\left\langle \psi_n \left| P \right| \psi_g \right\rangle = \left[\frac{2\sqrt{2}}{\pi} \right]^3 \frac{p_{eh} N^{3/2}}{(n_x, n_y, n_z)} \tag{3.6}$$

Then the oscillator strength, f_n per quantum spheres is given by

$$f_n = \frac{2m}{\hbar} \omega_n \left| p_{eh} \right|^2 \left[\frac{2\sqrt{2}}{\pi} \right]^6 \frac{N^3}{(n_x, n_y, n_z)^2} \tag{3.7}$$

where m and ω_n are the mass and angular frequency of the exciton respectively. The oscillator strength is given by

$$F_n = f_n \frac{u^3}{\pi a_B^3} \tag{3.8}$$

where the length of unit cell, u is R/N and R is the size of the quantum sphere[9].

$$F_n = \frac{2m}{\hbar} \omega_n \left| p_{eh} \right|^2 \left[\frac{2\sqrt{2}}{\pi} \right]^6 \frac{R^3}{\pi a_B^3 (n_x, n_y, n_z)^2} \tag{3.9}$$

Thus theoretical studies have shown that the confinement of excitonic envelope wave function due to the infinite barrier potential gives rise to the enhancement in oscillator strength for an exciton within the nanocrystal by a factor of $R^3/{a_B}^3$ and hence $\chi^{(3)}$ depends on the crystallite size[9]. Such a giant oscillator strength effect has been confirmed for CuCl nanocrystals. The radiative decay rate of confined excitons is proportional to $R^{2.1}$ for the glass matrix[13] and R^3 for the NaCl crystal matrix[14]. The validity of the size dependent enhancement effect is limited by the long wavelength

approximation and a nonlocal theory applicable to the mesoscopic system larger than the wavelength has been developed[10]. The important role of the giant oscillator strength effect in the size dependent enhancement of optical nonlinearity has been experimentally shown for CuCl nanocrystals[12].

As the quantum-confined exciton system can be modeled as a two level atomic system, the imaginary part of $\chi^{(3)}$ is given by[15]

$$\mathrm{Im}\left(\chi^{(3)}\right) = \left[\frac{e^2}{2m\omega_n}\right]^2 \hbar N F_n^2 \frac{T_1}{\Gamma_h^2} \tag{3.10}$$

where T_1 and Γ_h are the longitudinal relaxation time and homogeneous width, respectively, and F_n and N are the oscillator strength and the number density of nanocrystals, respectively. The detailed study measuring the susceptibility on resonance and the relaxation parameters T_1 and Γ_h revealed that the oscillator strength exhibits a $R^{2.2}$ dependence on particle size for CuCl nanocrystals[15].

The oscillator strength increases with the size of the particle as long as the excited state is coherent. However, an exciton in a bulk crystal behaves almost as a harmonic oscillator which does not show enhanced nonlinear optical response. Deviation of the electronic excitation from an ideal harmonic oscillator increases as the size of the microcrystallite decreases. Thus the enhancement originates from two conflicting concepts. One is due to the size dependent exciton oscillator strength and the other enhancement comes from the deviation of the electronic excitation from the ideal harmonic oscillator. In the weak confinement regime, as the particle size increases, the optical nonlinearity increases till the excited state is coherent due to the size dependent exciton oscillator strength. After that, the optical nonlinearity decreases with increase in particle size since the deviation from ideal harmonic oscillator decreases with increase in particle

size. As a result, there is an optimum size for obtaining the most effective optical nonlinearity in the weak confinement regime.

3.3 Nonlinear optical properties of nano colloids of ZnO

Colloids of nano ZnO are synthesized by a modified polyol precipitation method[16-18] as described in chapter 2. We have employed the single beam z-scan technique with nanosecond laser pulses to measure the nonlinear optical absorption and refraction properties of ZnO nano colloids and observed that the colloids exhibit large nonlinear effects. A detailed theory of z-scan technique[18-20] is described in chapter 1.

A Q-switched Nd:YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) is used as the light source. The sample is moved in the direction of light incidence near the focal spot of the lens with a focal length of 200 mm. The radius of the beam waist ω_o is calculated to be 35.4 μm. The Rayleigh length, $z_o = \pi\omega_o^2/\lambda$ is estimated to be 7.4 mm which is much greater than the thickness of the sample cuvette (1mm) and an essential prerequisite for z-scan experiments. The transmitted beam energy, reference beam energy and their ratio are measured simultaneously by an energy ratiometer (Rj7620, Laser Probe Corp.) having two identical pyroelectric detector heads (Rjp735). The linear transmittance of the far field aperture S, defined as the ratio of the pulse energy passing the aperture to the total energy is measured to be approximately 0.21. The whole experimental set up is automated using LabView program. The z-scan system is calibrated using CS_2 as a standard. The effect of fluctuations of laser power is eliminated by dividing the transmitted power by the power obtained at the reference detector[18].

3.4 Size dependent enhancement of third order nonlinear susceptibility

3.4.1 Open aperture z-scan

Figure 3.1 gives the open aperture z-scan traces of ZnO colloids of different particle sizes at a typical fluence of 866 MW/cm^2. The open aperture curve exhibits a normalized transmittance valley, indicating the presence of induced absorption in the colloids[18].

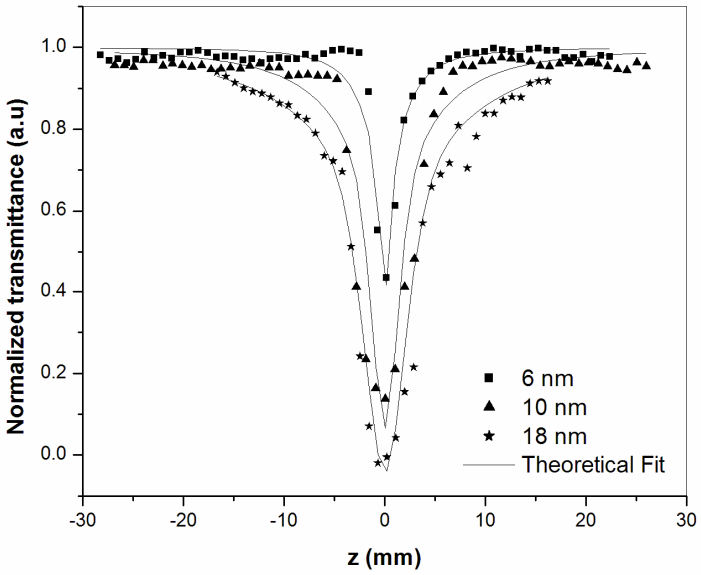

Figure 3.1:The open aperture z-scan traces of ZnO colloids of different particle sizes at a typical fluence of 866 MW/cm^2

The data are analyzed by using the procedure described by Sheik Bahae *et. al*[19] for two photon absorption process and the nonlinear absorption coefficient β is obtained by theoretical fitting as described in chapter 1 using matlab program. From the value of β, the imaginary part of third order susceptibility, $\mathrm{Im}\left(\chi^{(3)}\right)$ is calculated.

3.4.2 Closed aperture z-scan

Figure 3.2 gives the closed aperture z-scan traces of ZnO colloids of different particle sizes at a fluence of 866 MW/cm^2. The closed-aperture curve exhibited a peak-to-valley shape, indicating a negative value of the nonlinear refractive index[18]. It is observed that the peak-valley of closed-aperture z-scan satisfied the condition $\Delta z \sim 1.7\ z_0$, thus confirming the presence of cubic nonlinearity[19]. The value of nonlinear refractive index and real part of nonlinear susceptibility are obtained by the theoretical fit from the results of divided z-scan curve as described in chapter 1.

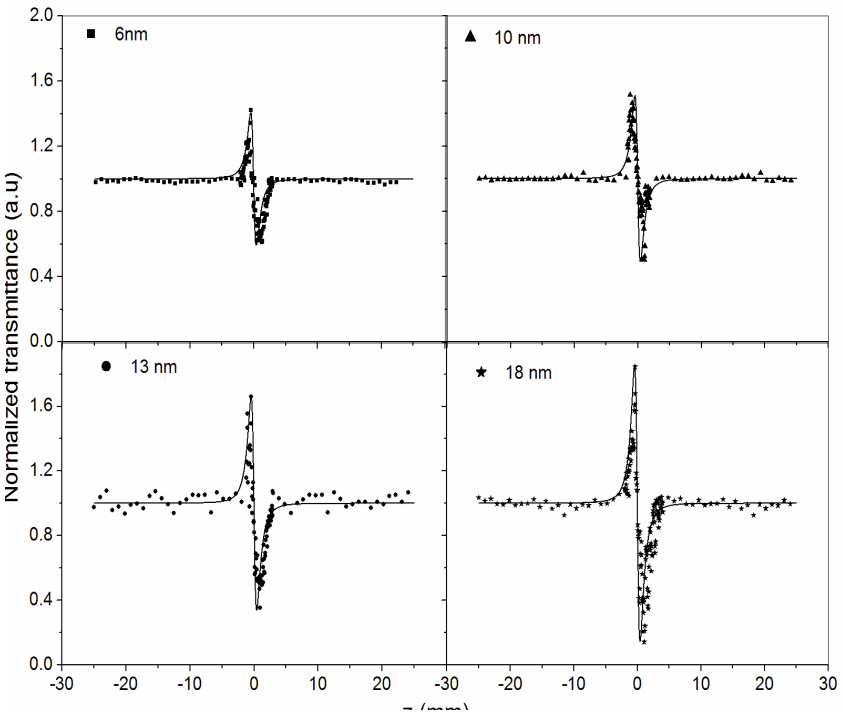

Figure 3.2: The closed aperture z-scan traces of ZnO colloids of different particle sizes at a fluence of 866 MW/cm^2

The obtained values of nonlinear optical properties of ZnO colloids of different particle sizes at a fluence of 866 MW/cm^2 are shown in table 3.1.

The enhancement of nonlinear optical properties with increasing dimension in the weak confinement regime essentially originates from the size dependent enhancement of oscillator strength of coherently generated excitons[9]. Since the exciton is confined in a quantum dot, the confinement of excitonic wave function is expected to give rise to enhancement of the oscillator strength per quantum dot by a factor of R^3/a_B^3. This size dependent oscillator strength was experimentally confirmed in CuCl quantum dots[13-14]. Such oscillator strength effect will result in an enhancement of the nonlinear susceptibility[12]. Hence the observed enhancement of nonlinear optical properties with increase in particle size in our present investigation can be attributed to the size dependent enhancement of exciton oscillator strength.

R (nm)	β (cm/GW)	n_2 x10^{-10} esu	Im ($\chi^{(3)}$) x10^{-10} esu	Re ($\chi^{(3)}$) x10^{-10} esu	$\lvert\chi^{(3)}\rvert$ x10^{-10} esu
6	42.4	-6.3	0.2	-1.3	1.3
10	231	-7.8	1.0	-1. 7	2.0
13	487.2	-11.7	2.1	-2.5	3.3
18	2085.2	-13.1	9.0	-2.8	9.4

Table 3.1 : Measured values of nonlinear absorption, nonlinear refraction and nonlinear susceptibility of ZnO colloids at an intensity of 866MW/cm^2

In order to obtain the crystallite size dependence of the third-order susceptibility, the R dependence of $\chi^{(3)}$ is shown in figure 3.3. This dependence helps us to write $\log\left(\chi^{(3)}\right) = 2\log R - 0.024$ and $\chi^{(3)} \approx R^2$.

The data show a general trend of increasing $\chi^{(3)}$ values with increasing radius from R=6-18 nm. When we apply a least-squares fit, a size dependence of R^2 is obtained indicating an enhancement of more than two orders of magnitude. This dependence is in good agreement with that observed for CdS, CuCl and CuBr nanocrystals[12, 15, 18, 21].

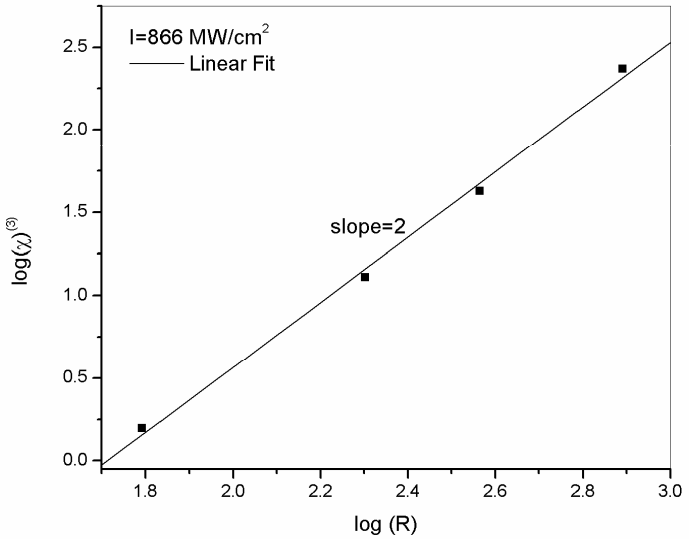

Figure 3.3: The third order susceptibility as a function of particle size for ZnO nano colloids. The straight line with a slope of 2 indicates the R^2 dependence

3.5 Fluence dependence of third order nonlinear susceptibility

The open and closed aperture z-scan curve of ZnO colloid of size 6nm at different input fluences is shown in figure 3.4. We can see that nonlinear optical properties are highly fluence-dependent[18]. The results show three orders of enhancement for the nonlinear absorption coefficient from the reported value of 5cm/GW for bulk ZnO[22].

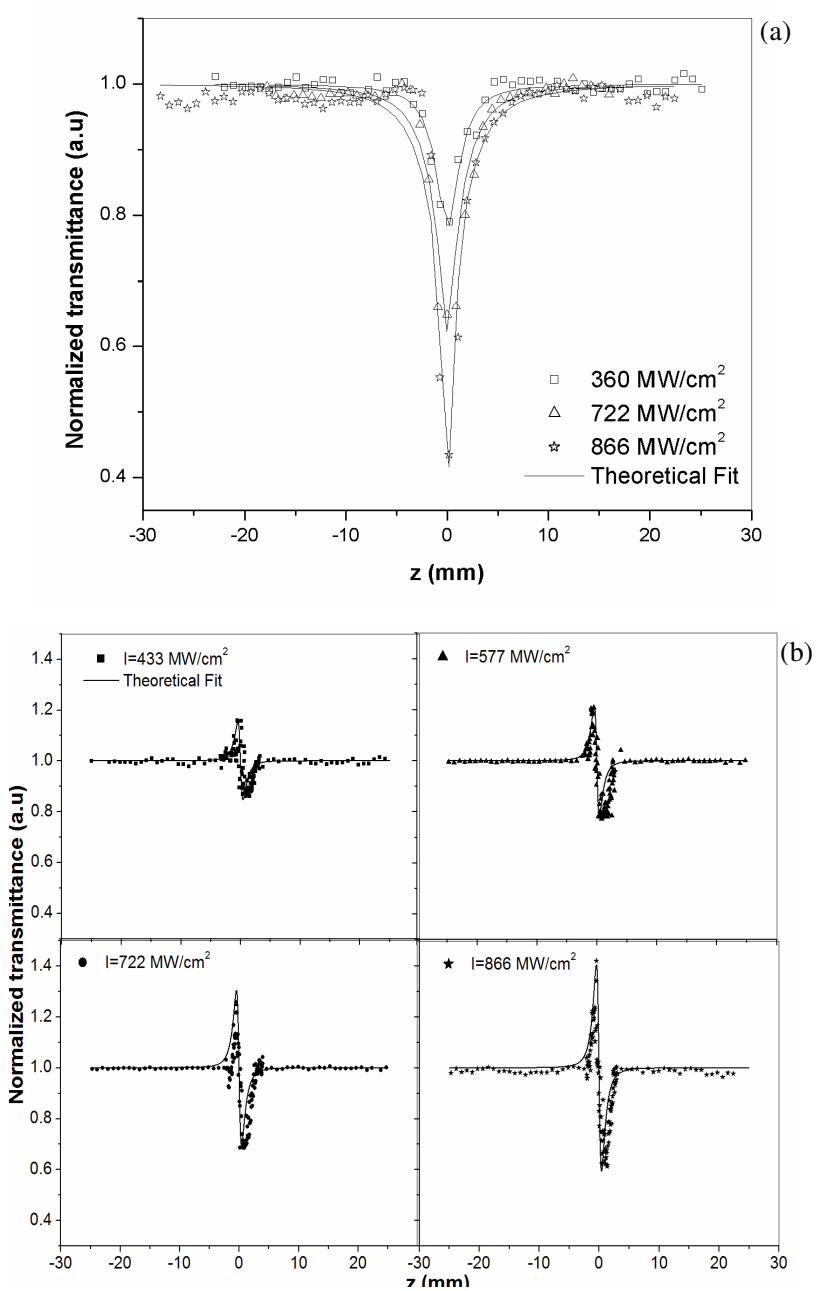

Figure 3.4 (a): Open aperture (b): Closed aperture z-scan curves of ZnO colloid of size 6 nm at different input fluences

It has been reported that the reduced dimensionality of the particles resulted in considerable enhancement of the second-order susceptibility $\chi^{(2)}$ in thin films of ZnO[3]. Similar results in the third order nonlinear parameters were evident in our measurements also.

The theory of two photon absorption process fitted well with the experimental curve infers that TPA is the basic mechanism. The dependence of nonlinear absorption with input intensity is due to TPA as clearly seen from log q versus log I plot shown in figure 3.5. The parameter q is the depth of the open aperture z-scan curve obtained from the theoretical fit and is a measure of the intensity dependent absorption and I is the irradiance at the focus.

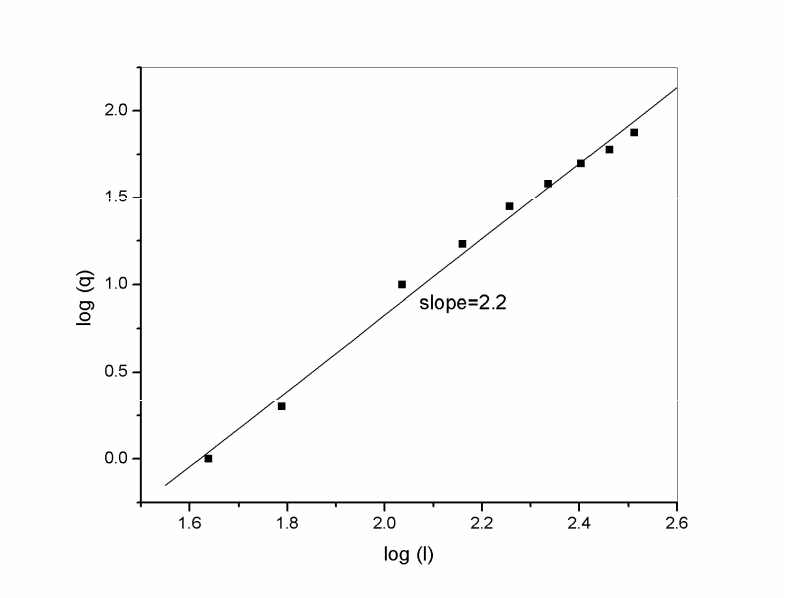

Figure 3.5: Variation of log q as a function of log I for ZnO colloid of size 18 nm.

Slope of the plot in figure 3.5 gives 2.2 which infers that TPA is the basic mechanism and there is the possibility of higher order nonlinear

processes such as free carrier absorption (FCA) contributing to induced absorption[18]. The free carrier life time of ZnO is reported to be 2.8 ns[4]. Hence there is a strong possibility that the 7 ns pulses used in the present study is exciting the accumulated free carriers generated by TPA by the rising edge of the pulse.

Figure 3.6 shows the variation of nonlinear susceptibility with irradiance for ZnO colloids of different particle sizes. Results show that $\chi^{(3)}$ is a function of intensity of laser radiation which can be written as

$$\chi^{(3)} = \chi_0^{(3)} + \chi_1^{(3)} I + \chi_2^{(3)} I^2 \qquad (3.11)$$

For lower fluence and colloids with small size, $\chi^{(3)}$ is independent of intensity indicating that it is a third order effect resulting from two photon absorption (TPA). For colloids of larger particle size and at higher fluences, $\chi^{(3)}$ becomes a nonlinear function of intensity[18].

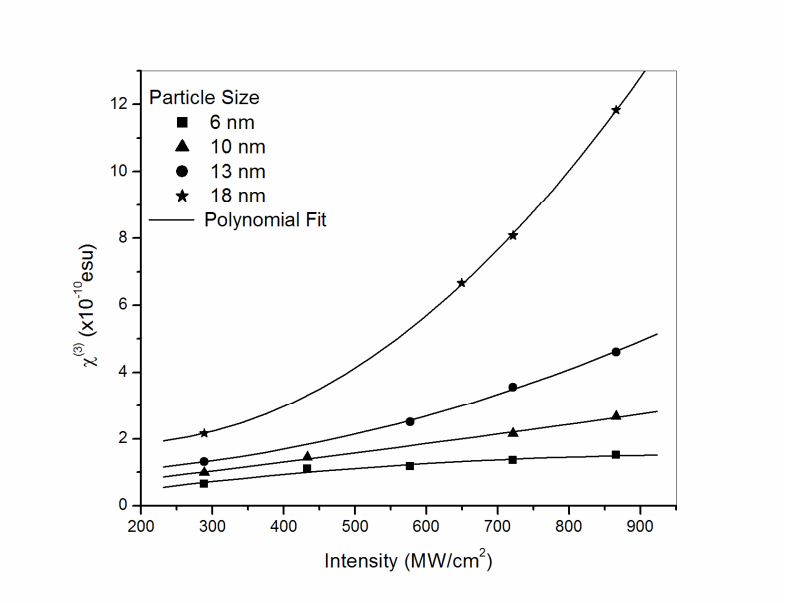

Figure 3.6: Variation of nonlinear susceptibility with irradiance for ZnO colloids of different particle sizes

This nonlinear dependence of $\chi^{(3)}$ with intensity is clearly shown in figure 3.6 indicating the occurrence of higher order nonlinear processes such as free-carrier absorption. Considering all these factors and also that we used nanosecond excitation pulses, it is reasonable to assume that TPA and weak FCA are the important mechanisms contributing to induced absorption in our samples[18].

The values of $\chi^{(3)}$ measured at room temperature by degenerate four wave mixing technique on CuBr nanocrystals range from $8x10^{-11}$ to $1.1x10^{-9}$ esu for R=2.7-42 nm and are comparable to the results presented here[15,18]. In this chapter, we report the experimental evidence for the enhancement of third order nonlinear susceptibility due to the size dependent oscillator strength of confined excitons, which was theoretically predicted by Hanamura[9]. The enhancement of $\chi^{(3)}$ for thin nanocrystalline films compared to microcrystalline films of ZnO was attributed to the nanosized structure of the film[23]. Recently significant (~500 times) enhancement of nonlinear refractive index with respect to the bulk value has been observed for polymer capped ZnO nanocrystals with an estimated average size of 4 nm[24]. The third-order nonlinear optical response of these PVP capped ZnO nanoparticles in a dilute solution is reported to be of the order of $6.3x10^{-11}$ esu. This value is at least two orders of magnitude greater than that of the bulk ZnO. This remarkable enhancement in the third-order nonlinear optical response may be related to the exciton confinement and optical Stark effects[5].

It is worth noting that certain representative third-order nonlinear optical materials, such as CuO chain compounds[25], Ag_2S/CdS nanocomposites[26], Metallophthalocyanines[27], porphrins[28], organic dyes[29], organic polymers[30], organic coated quantum dots[31], metal clusters[32] etc., yielded values of order of 10^{-10} to 10^{-14} esu for $\chi^{(3)}$ at a wavelength of 532 nm. These values are lower by one order of magnitude in comparison to the

value of $\chi^{(3)}$ obtained in the present investigation. Thus, the real and imaginary parts of third-order nonlinear optical susceptibility measured by the z-scan technique revealed that the ZnO colloids investigated in the present study have good nonlinear optical response and could be chosen as ideal candidates with potential applications for nonlinear optics.

3.6 Optical limiting

Optical power limiting is operated through the nonlinear optical processes of nanomaterials[33]. However, the great potentials of nanomaterials as optical power limiters have just begun to be recognized. An important term in the optical limiting measurement is the limiting threshold. It is obvious that the lower the optical limiting threshold, the better the optical limiting material.

3.6.1 Optical limiting and open aperture z-scan

The optical limiting property occurs mostly due to absorptive nonlinearity[34]. Thus it is possible to generate optical limiting curves from open aperture z-scan data. It is because while the sample is translated through the foucs of the Gaussian beam, the sample experiences variation in the incident fluence levels. From the value of fluence at focus, the fluence values at other positions could be calculated, $I(z) = \frac{E}{\pi\omega^2(z)t}$, using the standard equations for Gaussian beam waist, $\omega^2(z) = \omega_0^2\left(1 + \frac{z^2}{z_0^2}\right)$ where the beam waist radius at focus, $\omega_0 = \frac{f\lambda}{D}$, f being the focal length of the lens, D and λ the radius and wavelength of the beam respectively, E is the energy per pulse and t is the pulse width. The plot of fluence versus transmittance represents the optical limiting curve and figure 3.7 illustrates the influence of nanoparticle size on the optical limiting response.

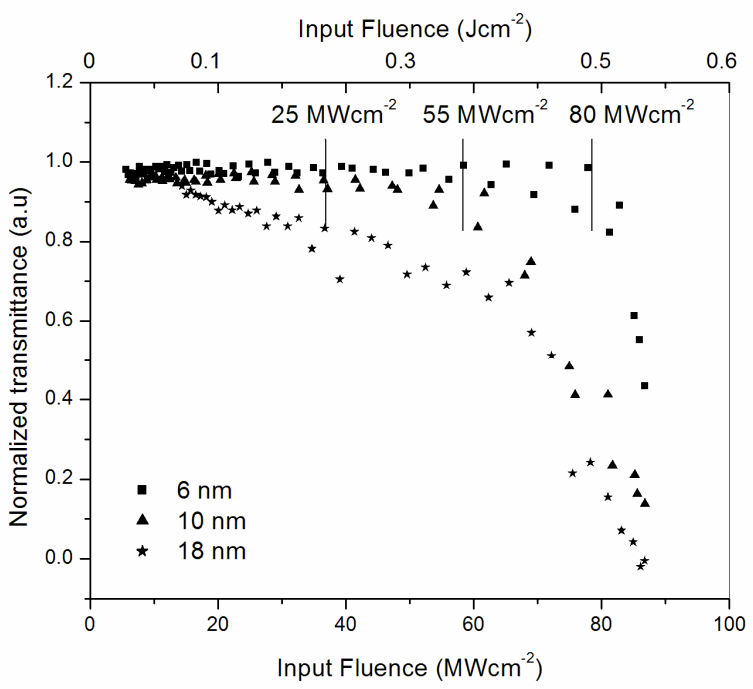

Figure 3.7: Optical limiting curves of ZnO colloids of different particle sizes generated from open aperture z-scan data.

The arrow in the figure 3.7 indicates optical limiting threshold which is the approximate fluence at which the normalized transmission begins to deviate from linearity. The optical limiting threshold is found to be high in the case of ZnO colloids of size 6 nm (80 MW/cm^2) in comparison to the ZnO colloids of size 10 nm (55 MW /cm^2) and ZnO colloids of size 18 nm (25 MW/cm^2). These values are comparable to the reported optical limiting threshold for CdS nano colloids[18, 21]. Particle size has a significant effect on the limiting performance of ZnO nano colloids. Increasing particle size reduces the limiting threshold and enhances the optical limiting performance. From the measured values of β for the colloids, it can be seen

that the colloids with larger particle size is a better nonlinear absorber and hence a good optical limiter.

3.7 Conclusions

Nonlinear optical properties of ZnO semiconductor nano colloids are investigated for optical power self-limiting application. ZnO nano colloids show negative nonlinearity and good nonlinear absorption behaviour at off resonance wavelength. The observed optical nonlinearity is explained on the basis of two photon absorption followed by free carrier absoption. We have investigated the variation of optical nonlinearity as a function of size and an R^2 dependence of nonlinear susceptibility is obtained for ZnO nano colloids. Nonlinear susceptibility is highly fluence dependent and it becomes quadratic in nature for large particle size. The observed optical nonlinearities are very high compared to the value of bulk ZnO. The optical limiting response of ZnO nano colloids, in the diameter range of 6–18 nm, increases with the increase of particle size.

3.8 References

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