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# Nonlinear Absorption Measurements in Undoped and Manganese doped CdS Quantum Dots

Physics

**KEYWORDS:** - Quantum dots, Nonlinear absorption coefficient, Z-scan technique.

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## ABSTRACT

Quantum dots of CdS and Mn doped CdS were synthesized through chemical co-precipitation method. The synthesized QDs have been characterized by X-Ray Diffraction (XRD), Ultraviolet visible absorption Spectroscopy. The diameters of QDs were calculated using Debye-Scherrer's formula. They are found to be in 3.6-3.9 nm range. The two photon absorption has been studied by the open aperture Z-scan technique using frequency double Nd:YAG laser. It has been found that the values of two photon absorption coefficients higher for doped QDs than undoped CdS QDs. Hence, they can be regarded as potential material for the development of optoelectronics and photonics devices.

## INTRODUCTION

The study of quantum confinement effects in semiconducting materials has attracted huge interest due to their structural, chemical and physical properties which are different from those of the bulk materials. Pure and doped semiconductor QDs are extensively investigate to obtain basic knowledge on impurity states in QDs and to examine their potential applications in novel optical devices. Semiconductor QDs doped with transition metal ions have attracted great attention due to their excellent luminescent properties [1-3]. The transition metal doped QDs show different optical properties corresponding to their host counterparts. These QDs have found tremendous application in optical light emitting diodes [4-6]. It is well known that the quantum confinement effect changes the electronic structure of QDs when their diameter is comparable to or smaller than the bulk exciton [7,8]. The CdS semiconductor has been widely used as an excellent phosphor to exhibit photoluminescence (PL), electroluminescence (EL), cathodoluminescence (CL) in devices due to its better chemical stability, favorable optical and electronic properties for optoelectronic applications compared with other chalcogenides such as CdSe. The bulk CdS has a direct band gap of 2.42 eV at 300K, the typical Bohr exciton diameter of CdS is around 5.8 nm consequently CdS QDs in the range 1-6 nm show sizeable quantum confinements effects with noticeably different properties. The changes in the properties of quantum dots are due to the increase in the surface to volume ratio and changes in the electronic structure of the material due to quantum mechanical effects with reduced crystal size [9]. In the present study, nonlinear absorption properties of pure and Mn doped semiconductor QDs has been studied.

## SAMPLE PREPARATION

Doped CdS collodial QDs were prepared by chemical co-precipitation method using the chemicals, Cadmium acetate, Manganese acetate, Thioglycolic acid (TGA) and sodium sulphide all of analytical grade. Thioglycolic acid (TGA) was used as the capping agent. The principle involved in this method is the precipitation of metal precursor i.e. cadmium acetate ions with sulphide ions. Cadmium acetate of desired molar concentrations was dissolved in 40ml ultra pure deionized water and stirred vigorously for 1 hour with constant heating at 60-70oC. Manganese acetate was added to cadmium acetate solution (1% by weight) again stirred for an hour with vigorous stirring, then 0.5ml TGA was added dropwise to obtain the milky white solution. After 30 min under same conditions 40ml Na2S solution of optimum molarity was added quickly to obtain coloured solution. The precipitates were collected and centrifuged to separate quantum dots from the reaction medium, washed repeatedly with ethanol followed by distilled water to remove impurities and then further characterization were carried out. QDs so obtained were stored at 4°C to prevent the agglomeration.

## RESULTS AND DISCUSSION

### XRD MEASUREMENTS

The structure of the synthesized sample was investigated by X- ray diffraction technique. The XRD patterns of the samples are shown in figure 1. All diffraction patterns were obtained using CuK $\alpha$ radiation ($\lambda$ = 1.54051 A°) at 30 kV and 15 mA. Measurements were made from $2\theta$ = 20° to 80° with steps of 0.02°.

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

Where $\lambda$ is the wavelength of X-ray used, $\beta$ is the full width at half maxima (FWHM) of the diffraction peak and $\theta$ is the diffraction angle for the (h k l) plane.

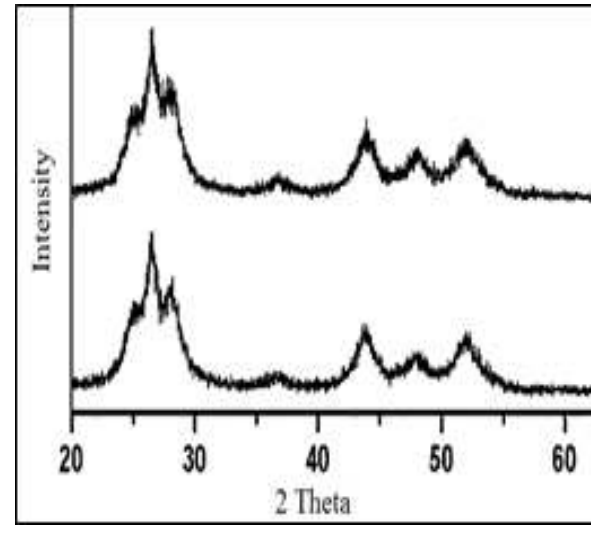


**Fig1: XRD of undoped CdS, Mn doped CdS Qds.**

The linear refractive index of undoped CdS, Mn doped CdS quantum dots were calculated through the relation [10]

$$n_{0\,CdS(QDs)} = \sqrt{1 + \frac{(\varepsilon_{bulk}-1)}{1+\left(\frac{0.75}{D}\right)^{1.2}}} \qquad (2)$$

Where, $\varepsilon$ bulk is the dielectric constant of bulk CdS and D is the average diameter of CdS QDs in units of nm. The calculated values of diameter of QDs and linear refractive index of all the samples are shown in table 1.

**Z-SCAN TECHNIQUE**

The experimental set up for the calculations of nonlinear parameters was the Z-scan technique, shown in figure 2. The laser power transmitted through the sample was measured with open and aperture in the far field region as a function of the position of the sample and read by an oscilloscope (Tektronics, TDS-2024). The cuvette was mounted in a translation stage which can translate the sample in the pre-focal and post-focal directions along the direction of propagation (Z-axis) of the transmitted laser beam. All the Z-scan measurements were carried out at room temperature. The transmission photo detector (Thorlabs, DET-110) was kept fully open, which is known as open aperture (OA) Z-scan. The Open Aperture Z-scan data were collected for both samples. From the Open Aperture Z-scan data one can measure the nonlinear absorption coefficient (β) [11].

The excitation source was frequency doubled Nd:YAG laser (Quanta System, HYL-101) at wavelength (λ=532nm) having 10 Hz repetition rate and pulse width of 5ns. The laser beam was focused by using a convex lens with focal length of 20 cm. The intensity at the focal spot is given by, I=P/π wo2; where, wo is the beam radius at the focal plane, P is the power given by P = E /t ; where, E is the energy of the pulse, t is the pulse duration. The calculated beam radius (w0) is 32.45μm which gives Rayleigh length (zR ) equal to 6.21 mm by using the relation, zR=kw02/2 , k being the wave vector. Rayleigh length was found to satisfy the basic criteria of Z-scan experiment i.e ( zR>>L), L is the sample length (1.45mm).

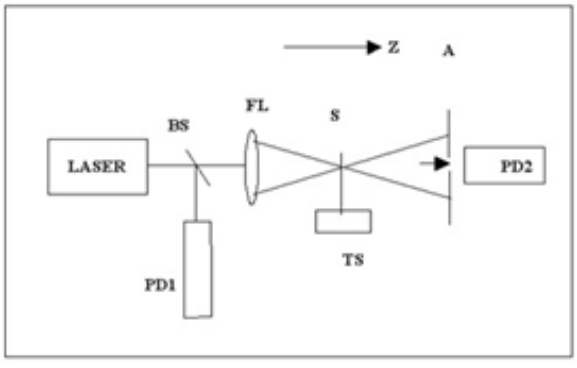


**Figure2: Schematic diagram of experimental Z-scan arrangement. BS beam splitter, FL focusing Lens, S investigated sample, TS translation stage, PD1and PD2 photodiodes, A aperture.**

The normalized transmittance of the samples for open aperture Z-scan shown in figure 3 is a function of the nonlinear absorption. By determining the normalized transmittance T(z) in the open aperture Z-scan the nonlinear absorption coefficient (β) can be evaluated through the relation by theoretically fitting with equation (3)

$$T(z) = \sum_{m=0}^{\infty} \frac{\left[\beta I_0 L_{eff} / 1+(z/z_0)^2\right]^m}{(m+1)^{3/2}} \qquad (3)$$

The two terms in the summation are generally sufficient to determine the value of nonlinear absorption coefficient.

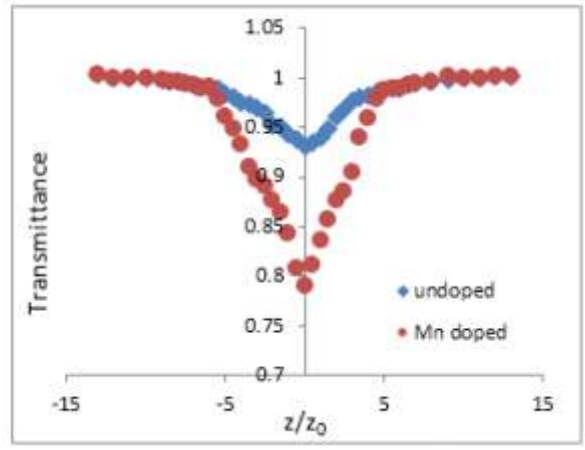


**Figure3: Open Aperture Z-scan of undoped, Mn doped quantum dots at λ =532nm.**

The two photon absorption phenomenon takes place when the laser photon energy is greater than half of the energy band gap and lower than the energy band of the investigated sample ($E_g/2 < h\nu < E_g$). Hence, the relation between the laser photon energy and energy band gap of the investigated sample allows us to determine the two photon absorption coefficient (β).

The open aperture Z-scan curve exhibits a normalized transmittance valley, indicating the presence of reverse saturable absorption in the QDs. Interestingly, Mn doped CdS QDs exhibit a larger induced absorption behaviour than undoped QDs. The increase of nonlinear absorption in doped QDs may be due to free-carrier absorption taking place from the 3d shell of $Mn^{2+}$ ions doped in CdS lattice. Thus, we can say that the observed nonlinearity is due to TPA followed by weak free carrier absorption in the doped QDs samples. Since, on doping the energy band gap increases due to accumulation of number of charges in quantum dot which cause variety of electrostatic repulsion leading to the larger band gap therefore the exciton oscillator strength also increases. Hence, in QDs the quantum confinement effect concentrates the oscillator strength of many excitons in a single excitonic state. As a consequence, the frenkel exciton obtains large oscillator strength and the optical nonlinearity is greatly enhanced [12]. Table 1 shows the normalized values of nonlinear parameters obtained by closed and open aperture Z-scan data. Results clearly indicate that the values of nonlinear parameters are higher for doped CdS QDs than undoped CdS QDs. Hence, the doped semiconductor QDs can also be used for variety of applications in the future photonics devices.

**Table1: Calculated values of optical band gap, size, linear refractive index, two photon absorption co-efficient at I0 = 0.76 TW/cm² and λ= 532 nm**

| Sample | Optical band gap(eV) | Size of QDs (nm) | Linear refractive index | Two photon absorption coefficient |
|---|---|---|---|---|
| CdS | 2.82 | 3.62 | 2.34 | 0.3941×10-8 |
| Mn:CdS | 3.22 | 3.85 | 2.24 | 0.2562×10-7 |

**CONCLUSION**

Colloidal QDs of undoped CdS, Mn doped CdS were synthesized by chemical co precipitation method. Absorption spectra of undoped, Mn doped CdS QDs exhibits a blue shift as compared to the bulk CdS which proves quantum confinement due to reduced size. The diameters of QDs are found to be in 3.6-3.9 nm range. The nonlinear absorp-

tion coefficients of the samples are calculated using nanosecond laser pulses of frequency double Nd:YAG laser. The doped QDs shows large nonlinearities which are attributed to the TPA followed by weak free carrier absorption in the doped QDs samples. Hence, we have found that the doped CdS QDs can be regarded as potential material for optics and photonics applications.

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