Preface

Semiconductor nanoparticles have been the subject of scientific interest because of their unique quantum confinement nature, which changes the optical and electronic properties of materials. The study of these properties constitutes new perspectives for basic and applied research in nanophotonics. Amongst the different semiconductors, ZnO has gained substantial interest because of its large exciton binding energy which could lead to lasing action based on exciton recombination even above room temperature. Nonlinear optics offers to these classes of nanomaterials numerous new functionalities such as spectral tunability and ultrafast nonlinear response. The thesis has seven chapters and it reports the results obtained from the systematic studies carried out on the spectral and nonlinear optical properties of ZnO nanocomposites.

Chapter 1 gives a glimpse of the potentials of the marriage between nonlinear optics and nanotechnology. Blue shift of the absorption edge, size dependent luminescence, enhanced oscillator strength and nonlinear optical properties are some of the interesting properties exhibited by most of the nanomaterials. All these properties are various manifestations of the quantum confinement effect, which arises due to the increasing proximity of electrons and holes with the diminishing size of the crystallites and the consequent changes in the electronic structure. This is an exciting area of research, which makes it possible to tune the properties of nanoparticles to suit any application by tailoring size and may find tremendous technological applications. . In this chapter, the applications of ZnO nanocomposites along with some important optical properties exhibited by them have been introduced. This chapter also includes the theory and experimental details of the z-scan technique used to study the nonlinear optical properties of ZnO nanocomposites.

Chapter 2 describes the fluorescence spectroscopy of nano colloids of ZnO. The fluorescence behaviour has been studied as a function of the excitation wavelength and there is a red shift in emission peak with excitation wavelength. In essence, the inefficient energy transfer between the upper and the lower vibrational levels of the excited state of these particles owing to short fluorescence lifetime is primarily responsible for the excitation wavelength dependent spectral shift of ZnO colloids. Fluorescence spectra consist of emissions in the UV and visible regions. Apart from the known band gap emissions at 380 nm and impurity dominated emissions at 530 nm, emissions at 420 and 490 nm are also observed with change in particle size. Systematic studies on nano ZnO have indicated the presence of luminescence due to excitonic emissions when excited with 255 nm as well as significant contribution from surface defect states when excited with 325 nm. The relevant energy levels showing the transitions corresponding to the observed peaks in the emission spectrum of ZnO of particle size 18 nm under 255 nm excitation are identified. The luminescence mechanism and a correlation analysis between the particle size and spectroscopic observations are discussed.

Chapter 3 discusses the size dependent enhancement of nonlinear optical properties in nano colloids of ZnO. ZnO nano colloids show negative nonlinearity and good nonlinear absorption behaviour at 532 nm. The observed nonlinearity is explained through two photon absorption followed by weak free carrier absorption. 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 of ZnO nano colloids, in the range of 6–18 nm, increases with the increase of particle size.

Chapter 4 presents the third order nonlinear optical properties of self assembled films formed from ZnO colloidal spheres are investigated and are compared with those of ZnO thin films deposited by sol-gel process as well as pulsed laser ablation. Both ZnO colloids and films clearly exhibit a negative nonlinear index of refraction. However there is a change in the sign of the absorptive nonlinearity of the self assembled films compared to others.

The colloids and the films developed by dip coating and pulsed laser ablation exhibit reverse saturable absorption whereas the self assembled films exhibit saturable absorption. These different nonlinear characteristics can be mainly attributed to ZnO defect states and electronic effects when the colloidal solution is transformed into self assembled films. We report our investigations on the intensity, wavelength and size dependence of saturable and induced absorption of ZnO self assembled films and colloids. Values of the imaginary part of third order susceptibility are calculated for particles of size in the range 20-300 nm at different intensity levels ranging from 40 to 325 MW/cm^2 within the wavelength range of 450–650 nm. The wavelength dependence of figure of merit, which specifies the magnitude of nonlinear absorption for unit value of linear absorption, is calculated and this helps in comparing the absorptive nonlinearities at various excitation wavelengths.

Chapter 5 explains the effect of annealing on the spectral and nonlinear optical characteristics of ZnO thin films deposited on quartz substrates by sol gel process. As the annealing temperature increases from $300\text{-}1050^0C$, there is a decrease in the band gap which indicates the changes of the interface of ZnO. In the fluorescence spectra we have observed two principal bands: UV band and visible band. Systematic studies on nano crystallites have indicated the presence of luminescence due to excitonic emissions when excited with 255 nm as well as significant contribution from surface defect states when excited with 325 nm. The intensity of UV peak remains the same while the intensity of the visible peak increases with increase in post-annealing temperature. Nonlinear optical response of these samples is studied using nanosecond laser pulses at off-resonance wavelengths for optical limiting applications. The nonlinear susceptibility increases from $2.3x10^{-6}$ to $1.3\ x10^{-5}$esu when the annealing temperature rises from 300ºC to 1050ºC, mainly due to the enhancement of interfacial state and exciton oscillator strength. We have experimentally studied the optical nonlinearity as a function of temperature and a $T^{2.5}$ dependence of nonlinear susceptibility is obtained for thin films of nano ZnO. Optical limiting response is temperature dependent and the film annealed at higher temperature and having larger particle size is a better nonlinear absorber and hence a good optical limiter.

Chapter 6 explains the spectral and nonlinear optical properties of ZnO based nanocomposites prepared by colloidal chemical synthesis. Very strong UV emissions at room temperature are observed from ZnO-Ag, ZnO-Cu and ZnO-SiO_2 nanocomposites. The strongest visible emission of a typical ZnO–Cu nanocomposite is over ten times stronger than that of pure Cu due to transition from deep donor level to the copper induced level. The optical band gap of ZnO-CdS and ZnO-TiO_2 nanocomposites is tunable and emission peaks changes almost in proportion to changes in band gap. It is possible to obtain a desired luminescence colour from UV to green by simply adjusting the composition. Nonlinear optical response of these nanocomposites is studied using nanosecond laser pulses from a tunable laser in the wavelength range of 450-650 nm at resonance and off-resonance wavelengths. The nonlinear response is wavelength dependent and switching from induced absorption to SA has been observed at resonant wavelengths. Such a change-over is related to the interplay of plasmon/exciton band bleach and optical limiting mechanisms. ZnO based nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behaviour at 532 nm. The observed nonlinear absorption is explained through two photon absorption followed by weak free carrier absoption, interband absorption and nonlinear scattering mechanisms. The nonlinearity of the silica colloid is low and its nonlinear response can be improved by making composites with ZnO and ZnO-TiO_2. The enhancement of the third-order nonlinearity in the composites can be attributed to the concentration of exciton oscillator strength. This study is important in identifying the spectral range and composition over which the nonlinear material acts as an RSA based optical limiter. These materials can be used as optical limiters and are potential nanocomposite material for the light emission and for the development of nonlinear optical devices with a relatively small limiting threshold.

Chapter 7 deals with the summary of the present work along with a brief report of the future prospects.

List of Publications

I. Journal Publications

1 **Litty Irimpan,** V P N Nampoori and P Radhakrishnan; "*Spectral and nonlinear optical characteristics of nanocomposites of ZnO-CdS*" Journal of Applied Physics [American Institute of Physics] **103**, 094914 (2008)

2 **Litty Irimpan,** V P N Nampoori and P Radhakrishnan; "*Spectral and nonlinear optical characteristics of nanocomposites of ZnO-Ag*" Chemical Physics Letters [Elsevier] **455** (4-6), 265-269 (2008)

3 **Litty Irimpan**, A Deepthy, Bindu Krishnan, V P N Nampoori and P Radhakrishnan; "*Nonlinear optical characteristics of self assembled films of ZnO"* Applied Physics B*:* Lasers and Optics [Springer] **90** (3-4), 547-556 (2008)

4 Litty Irimpan, Bindu Krishnan, V P N Nampoori and P Radhakrishnan; "*Luminescence tuning and enhanced nonlinear optical properties of nanocomposites of ZnO-*TiO_2" Journal of Colloid and Interface Science [Elsevier] **324** (1-2), 99-104 (2008)

5 **Litty Irimpan**, A Deepthy, Bindu Krishnan, L M Kukreja, V P N Nampoori and P Radhakrishnan; "*Effect of self assembly on the nonlinear optical characteristics of ZnO thin films"* Optics Communications [Elsevier] **281** (10), 2938-2943 (2008)

6 **Litty Irimpan**, Bindu Krishnan, A Deepthy, V P N Nampoori and P Radhakrishnan; "*Size dependent enhancement of nonlinear optical properties in nano colloids of ZnO"* Journal of Applied Physics [American Institute of Physics] **103**, 033105 (2008), Virtual Journal of Nanoscale Science & Technology, February 25 issue, 2008

7 **Litty Irimpan**, A Deepthy, Bindu Krishnan, V P N Nampoori and P

Radhakrishnan, '*Size dependent fluorescence spectroscopy of nanocolloids of ZnO*', Journal of Applied Physics [American Institute of Physics] **102**, 063524 (2007)

8 **Litty Irimpan**, Bindu Krishnan, A Deepthy, V P N Nampoori and P Radhakrishnan; "*Excitation wavelength dependent fluorescence behaviour of nano colloids of ZnO*" Journal of Physics D: Applied Physics [Institute of Physics] **40,** 5670-5674 (2007)

9 **Litty Irimpan**, V J Dann, Bindu Krishnan, A Deepthy, V P N Nampoori and P Radhakrishnan; "*Backscattering of laser light from colloidal silica*" Laser Physics [Springer] **18** (7), 882-885 (2008)

10 **Litty Irimpan,** Bindu Krishnan, V P N Nampoori and P Radhakrishnan; "Nonlinear optical characteristics of nanocomposites of ZnO-TiO_2-SiO_2" *Optical Materials* [Elsevier] DOI:10.1016/j.optmat.2008.05.009 (2008)

11 **Litty Irimpan,** V P N Nampoori and P Radhakrishnan; "*Enhanced luminescence and nonlinear optical properties of nanocomposites of ZnO-Cu*" Journal of Materials Research [Materials Research Society] 2008 (in press)

12 **Litty Irimpan,** D Ambika, V Kumar, V P N Nampoori and P Radhakrishnan; "Effect of annealing on the spectral and nonlinear optical characteristics of thin films of nano ZnO" Journal of Applied Physics [American Institute of Physics] 2008 (in press)

13 **Litty Irimpan,** Bindu Krishnan, V P N Nampoori and P Radhakrishnan; "*Linear and nonlinear optical characteristics of ZnO-SiO_2 nanocomposites*" Applied Optics [Optical Society of America] 2008 (in press)

14 **Litty Irimpan,** V P N Nampoori and P Radhakrishnan; "*Visible*

luminescence mechanism in nano ZnO under weak confinement regime" communicated to Optics Letters

15 Bindu Krishnan, **Litty Irimpan**, V. P. N. Nampoori and V. Kumar; "*Synthesis and nonlinear optical studies of nano ZnO colloids*" Physica E [Elsevier] **40**, 2787 (2008)

16 Bindu Krishnan, A Deepthy, **Litty Irimpan**, V J Dann and V P N Nampoori; "*Back scattering from nano-sized ZnO colloids*" Physica E [Elsevier] **35**, 23-26 (2006)

17 Annieta Philip K, Lyjo K. Joseph, **Litty M. Irimpan**, Bindu Krishnan, P. Radhakrishnan, V. P. N. Nampoori and Raghu Natarajan "*Thermal Characterization of Ceramic Tapes using Photoacoustic Effect*" Physica Status Solidi (a) [Wiley Interscience] **204** (3), 737 (2007)

18 Annieta Philip K, Lyjo K Joseph, **Litty Mathew Irimpan**, P. Radhakrishnan and V.P.N Nampoori; "*Photoacoustic study on the photostability of polymethyl methacrylate (PMMA) films doped with Rhodamine 6G-Rhodamine B dye mixture systems",* Journal of Physics D: Applied Physics [Institute of Physics] **38**, 2904 (2005)

II. Conference Publications

1 **Litty Irimpan**, Bindu Krishnan, A Deepthy, V P N Nampoori and P Radhakrishnan; "*Excitation wavelength dependent fluorescence behaviour of nano colloids of ZnO"* Proceedings of national conference on Current Trends in Chemisty, CTriC-2008, Cochin, India, 18-19 January, 2008, OP-26, P 21

2 **Litty Irimpan**, A Deepthy, Bindu Krishnan, V P N Nampoori and P

Radhakrishnan; *"Size dependent fluorescence spectroscopy of nano ZnO colloids"* Proceedings of International Conference on Materials for the Millennium, *MatCon 2007*, Cochin, India, 1-3 March, 2007, P 115

3 **Litty Irimpan**, Bindu Krishnan, A Deepthy, V P N Nampoori and P Radhakrishnan; "*Size dependent enhancement in nonlinear optical properties of nano ZnO colloids using z-scan technique"* Proceedings of Eighth International Conference on Optoelectronics, Fiber Optics and Photonics, *Photonics 2006*, Hyderabad, 13-16 December 2006, NLO 5, P 188.

4 **Litty Irimpan**, A Deepthy, Bindu Krishnan, V P N Nampoori and P Radhakrishnan; "*Nonlinear optical characterization of self-assembled 3D photonic crystals from ZnO colloidal spheres*" Proceedings of Eighth International Conference on Optoelectronics, Fiber Optics and Photonics, *Photonics 2006*, Hyderabad, 13-16 December 2006, NLO 18, P 346.

5 **Litty Irimpan**, Deepthy A, Nampoori V.P.N, Radhakrishnan P; "*Optical nonlinearities in silicon quantum dots"*; Proceedings of International Conference on Optics & Optoelectronics, *ICOL-2005*, Dehradun, Uttaranchal, India, 12-15 December 2005, NLO 17, P260.

6 **Litty Irimpan**, V.J Dann, Bindu Krishnan, A. Deepthy, V.P.N Nampoori and P. Radhakrishnan; "*Studies on backscattering of laser light in colloidal silica"*; Proceedings of Seventh International conference on Optoelectronics, Fiber optics and Photonics, *Photonics 2004*, Cochin, India, 9-11 December 2004, LTW P10, P207.

7 Bindu Krishnan, **Litty Irimpan** and V. P. N. Nampoori; "*Nonlinear optical studies in PEI-capped ZnO colloids*", National conference on photonics for advanced technology (NCPAT 2007), Thanjavur, Tamil

Nadu, March 22-25, 2007

8 Ritty J Nedumpara, Thomas K J, **Litty Mathew**, V P N Nampoori and P Radhakrishnan; "*Nonlinear absorption in dye doped polymer matrices"*; Proceedings of Eighth International Conference on Optoelectronics, Fiber Optics and Photonics, *Photonics 2006*, Hyderabad,13-16 December 2006, NLO 21, P 349.

9 Bindu Krishnan, **Litty Irimpan** and V P N Nampoori; "*Flexible nanocomposite films with selective optical filtering*"; Proceedings of International Conference on Optoelectronic Materials and Thin films for Advanced Technology*, OMTAT 2005,* Cochin, India, 24-27 October 2005, NT020, P 63.

10 Bindu Krishnan, **Litty Irimpan**,V. P. N Nampoori and V.Kumar; "*Stable nano ZnO colloid using a novel capping agent*" Proceedings of First National Conference on Nanoscience and Technology, NPL, Pune, March 2005

11 Lyjo K Joseph, **Litty Mathew Irimpan**, Dann V J, Radhakrishnan P and V P N Nampoori; "*Fluorescence Study of Lanthanum Titanate*"; Proceedings of DAE- BRNS *NLS-5*, Vellore, P181-2 (2005)

12 Bindu Krishnan, **Litty Irimpan**, Deepthy A, Dann V.J and V.P.N. Nampoori; "*Non linear optical properties of nano-ZnO colloids using z-scan technique"*; Proceedings of National Laser Symposium, *NLS-4,* BARC, Mumbai, 10-13 January 2005, F7, P-418

13 Annieta Philip K, Lyjo K Joseph, **Litty M. Irimpan**, P. Radhakrishnan and V.P.N Nampoori; "*Concentration dependent photostability of dye doped olymer films- A PA study",* Proceedings of National Laser Symposium, *NLS-4,* BARC, Mumbai, 10-13 January 2005, C3, P-300

14 Annieta Philip K, Lyjo K. Joseph, **Litty M. Irimpan**, Bindu Krishnan, P. Radhakrishnan, V. P. N. Nampoori and Raghu Natarajan "*Thermal characterization of zirconia and alumina-zirconia ceramic tapes using photoacoustic technique*"; Proceedings of National Laser Symposium, *NLS-4,* BARC, Mumbai, 10-13 January 2005, D5, P-342

15 P. Nandi, **Litty Irimpan**, P. Radhakrishnan, V.P.N. Nampoori and G. Jose; "*Spectroscopic properties of Ag-Na ion exchanged, Er-Yb codoped phosphate glasses*"; Proceedings of National Laser Symposium, *NLS-4,* BARC, Mumbai, 10-13 January 2005, G28, P515

16 Bindu Krishnan, A. Deepthy, **Litty Irimpan**, Dann V.J and V.P.N Nampoori; "Coherent b*ackscattering from nano-sized ZnO suspensions*"; Proceedings of Seventh International conference on Optoelectronics, Fiber optics and Photonics, *Photonics 2004*, Cochin, India, 9-11 December 2004, LTW P10, P208

17 Annieta Philip K, Lyjo K Joseph, **Litty Irimpan**, P. Radhakrishnan and V.P.N Nampoori; "*Photosensitivity of Laser Dye Mixtures in Polymer Matrix-A Photoacoustic Study*"; Proceedings of Seventh International conference on Optoelectronics, Fiber optics and Photonics, *Photonics 2004*, Cochin, India, 9-11 December 2004, PMR P7, P440

"Live as though you will die tomorrow,
but learn as though you live forever"
: Gandhiji