SYNTHESIS AND LASER INDUCED STUDIES OF NANOSIZED ZnO FOR PHOTONIC APPLICATIONS

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Synthesis and Laser induced Studies of nanosized ZnO for Photonic Applications

PhD thesis in the field of Photonics

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Front cover: Schematic of Random Laser. SEM -Nano ZnO synthesized as part of the thesis work by polyol method.

CERTIFICATE

Certified that the research work presented in the thesis entitled "***Synthesis and Laser induced Studies of nanosized ZnO for Photonic Applications***" is based on the original work done by Ms.Bindu Krishnan under my guidance and supervision in the International School of Photonics, Cochin University of Science & Technology, Kochi 682 022 and has not been included in any other thesis submitted previously for the award of any degree.

Kochi
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DECLARATION

Certified that the work presented in the thesis entitled "***Synthesis and Laser induced Studies of nanosized ZnO for Photonic Applications***" is based on the original work done by me under the guidance and supervision of Dr.V.P.N.Nampoori, Professor, International School of Photonics, Cochin University of Science & Technology, Kochi 682 022, India and has not been included in any other thesis submitted previously for award of any degree.

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Doing PhD in experimental work on part-time basis is no fun. One feels like an alien in the lab among lasers when one enter it once in a blue moon, with limited number of leaves in hand. But not after the arrival of the present group of research scholars. Lyjo, Litty, Dann, Ambika...thank you for being true Photonians, who spread light around just by their presence. I

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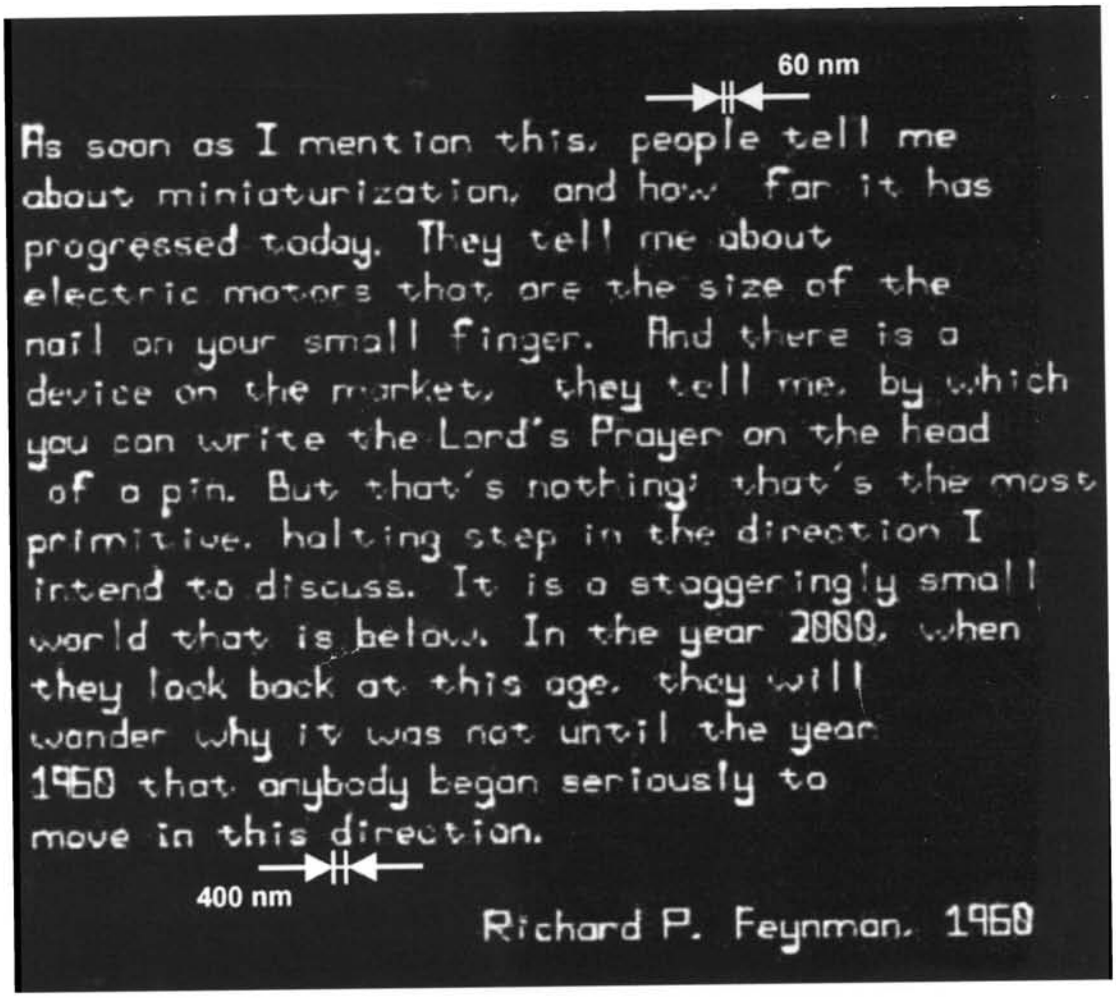

As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

Richard P. Feynman, 1960

Preface

In the nanometer regime, various new interesting physical effects, most of them quantum mechanical in nature, can be observed. Many such materials, with the possibility of tuning of electronic and optical properties by varying the size of the particles, are viewed as promising candidates for future applications. This has led to intense activity in both synthesis and experimental probing of nanocrystals in the past few decades. In particular, optical methods of study provide rich information about the band gap of nanocrystals. ZnO is a technologically important material with a wide range of applications and one of the few oxides that show quantum confinement effects in the experimentally accessible range of sizes. Keeping all these in view, this thesis is focused on the synthesis and laser induced experiments in nano sized ZnO.

First chapter of the thesis gives a bird-eye-view of nanotechnology, quantum dots, and some unique optical properties of quantum dots. It also emphasizes the significance of ZnO among a vast scenario of semiconductor materials.

Second chapter gives the details of all the experimental techniques used in the studies. After briefing about the various popular methods of synthesis of nanopowders, this chapter focuses on hydrothermal methods and capping. Then the three chemical routes of preparation used in the present study are described. Then processing techniques like screen printing technique, doctor blade process and dip coating process to produce thin films and thick films of ZnO are also described. Lastly, experimental details of characterization techniques are given, which includes XRD, BET, SEM, Absorption spectroscopy, Fluorescence spectroscopy, Coherent back Scattering technique, Z-Scan technique.

Third chapter explains how the shift of absorption edge can be effectively used to calculate the size of nanocrystals. After outlining the theory behind it, its use in characterizing the different ZnO samples are detailed. How the amount of capping agent affects the spectrum and hence the size, how the spectrum at different time intervals look like with and without the addition of capping agents etc are also discussed.

Fourth chapter describes the fluorescence spectroscopy of samples. Keeping in mind the potential of ZnO as a random lasing material, it also studies in detail how emission spectra vary with varying pump fluences. Threshold behavior and line narrowing, signature of random lasing action, is observed.

Fifth chapter is about the back scattering studies conducted in colloidal ZnO samples. Back scattering studies are well known for providing valuable information about multiple scattering and mean free path inside any random medium. The back scattering cone is measured for various samples and hence mean free path is calculated. Effect of concentration is studied.

Sixth chapter describes the Z-Scan measurements of the colloidal ZnO samples. Nonlinear optical constants of the samples are calculated. Surprisingly high fluence dependent increase of third order nonlinear susceptibility is observed. Possible explanations are discussed.

Seventh chapter gives the concluding remarks. It also envisages the future possibilities.

List of publications

Thesis related

1. ***Line narrowing effects and enhanced back scattering from ZnO colloids***
   Bindu Krishnan and V. P. N Nampoori ,
   J.Material Science, in print.
2. ***Screen printed nanosized ZnO thick film***
   Bindu Krishnan and V.P.N Nampoori,
   Bulletin of Material Science, in print.
3. ***Stabilisation of nano ZnO colloid using a novel capping agent***
   Bindu Krishnan, Litty Irimpan, V. P. N Nampoori , V.Kumar
   Applied Physics Letters (Communicated).
4. ***Backscattering from nano-sized ZnO suspensions***
   Bindu Krishnan, A. Deepthy Litty Irimpan, Dann.V.J, V.P.N Nampoori
   Journal of Optics A-Pure and Applied Optics (Communicated).
5. ***Nonlinear optical properties of nano ZnO colloids***
   Bindu Krishnan, Deepthy.A, Litty Irimpan, V.P.N Nampoori.
   Applied Physics. B (Communicated).

Conference Papers

1. ***Nano ZnO for photonic applications*, Bindu Krishnan**
   Indo-dutch workshop on current trends in photonic materials,ISP,CUSAT, 2002.
2. ***Laser Induced UV emission from ZnO colloids***
   Bindu Krishnan, K. P. Unnikrishnan, V. P. N Nampoori
   National Laser symposium, Kanpur,2003.
3. ***Back Scattering from nano-sized ZnO Colloids***
   Bindu Krishnan, A. Deepthy, Litty Mathew, Dann.V.J, V.P.N Nampoori,
   'Photonics 2004', Cochin, Dec,2004
4. ***Nonlinear Optical Properties of Nano ZnO Colloids using Z-Scan Technique***
   Bindu Krishnan, Litty Irimpan, Deepthy. A, Dann V.J, V. P. N Nampoori
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5. ***Stable nano ZnO colloid using a novel Capping agent***
   Bindu Krishnan, Litty Irimpan,V. P. N Nampoori , V.Kumar
   First National Conference on Nanoscience and Technology, NPL, Pune,
   March 2005.

Other publications

1. ***A Silicon-based Fiber Optic Temperature sensor Using Temperature-Dependent Absorption***
   Bindu Krishnan, P. K .C Pillai, C. P. G Vallabhan, V. P. N Nampoori
   Journal of Instrumentation of India. 28(1) 52-56, 1997.
2. ***Dispersion and tape casting of Silicon Carbide through aqueous route***
   Bindu Krishnan and Raghu Natarajan,
   Journal of Materials Science, in print.
3. ***Aqueous tape casting route for microwave substrates***
   Bindu Krishnan, K.Sasidharan and Raghu Natarajan
   Ferroelectrics, in print.
4. ***Studies on backscattering of laser light in colloidal silica***
   Litty Irimpan, V.J Dann, **Bindu Krishnan**, A.Deepthy, V.P.N Nampoori and
   P. Radhakrishnan.
   Photonics 2004 & communicated to *Optics communication*
5. ***Thermal Characterization of Zirconia and Alumina-Zirconia Ceramic Tapes Using Photoacoustic Technique***
   Annieta Philip K, Lyjo K. Joseph, Litty M. Irimpan, **Bindu Krishnan,**
   P. Radhakrishnan, V. P. N. Nampoori and Raghu Natarajan
   National Laser Symposium, Mumbai,2004.

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Chapter 1

INTRODUCTION

Abstract

This first chapter serves as a general introduction to what this thesis is all about. It introduces the basic concept and relevance of nano technology, giving emphasis to semiconductor nano crystals or quantum dots. It gives a bird eye view of various techniques of synthesis if quantum dots. Then the basic concepts of a few important optical properties exhibited by quantum dots are introduced. This includes quantum confinement effects, random lasing action, Coherent backscattering and nonlinear optics. At the end it justifies the selection of ZnO as the material of studies by highlighting its merits and applications

"There is a time for some things and a time for all things;
a time for great things and a time for small things."
Miguel de Cervates

Introduction

Physics of systems of reduced dimensionality is a fascinating area, from the point of view of both physicist and material scientist. How to produce high quality mono disperse nano particles is as challenging as the studies to explore what happens to the common physical phenomena when the size regime move over to a few nm. The present thesis deals with the use of various techniques to synthesize nanosized ZnO, a technologically important semiconductor material, a few processing attempts to make thin films, thick films and polymer composite films from nano ZnO. Then we will discuss the results of various laser induced optical studies in these samples. An overview of the field of nanotechnology is given in the following sections.

1.1 Nano Technology

Nanostructured materials have become a subject of intensive research for their extraordinary properties compared to their bulk counterparts. The last two decades have witnessed substantial progress in the synthesis, characterization and understanding of this class of materials. The Greek word nano (means dwarf) is one thousandth of a micron and is roughly the length occupied by around 10 atoms stacked in a straight line. Nanotechnology has been defined to be dealing with materials in the range of 0.1 to 100nm.

The root of modern nanotechnology can be traced back to a 1959 talk by Dr.Richard Feynman, titled "Plenty of room at the bottom". He speculated that future scientists and engineers would build structures of sizes comparable to those of atoms and molecules. But it was not until eighties with emergence of advanced methods of preparation and sophisticated characterization techniques that notable developments began to occur. Nano technology is described as a multidisciplinary enabling technology that will pave the way for novelty in every stream of technology.

Nanostructured materials exhibit different properties from their microstructured counterparts. For instance, mechanical properties of the material are enhanced through nanostructuring, whereas density and thermal conductivity will be reduced as schematically given in Fig.1.1. Furthermore, optical properties change due to the size confinement effects with changing particle size. For example, the color of Cadmium telluride changes from green to red with changing particle size from 2 to 5 nm. Nanotechnology will have a profound effect in all major areas of life including medicine creation and delivery, smaller and more powerful computers, cleaner energy supplies, more efficient automobiles, to name a few.

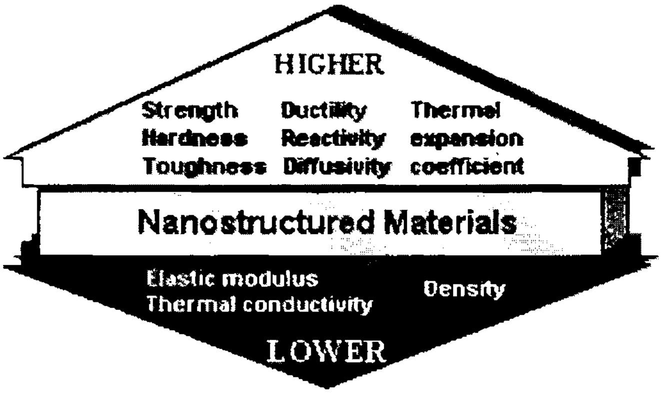

Fig.1.1.Modification of different properties of nanostructured materials when compared with the bulk

1.2 Semi conductor nanocrystals or Quantum Dots

After successfully making 2D structures by epitaxial methods, physicists tried to go one step further to decrease the dimensions to quasi 1 or 0D.Semiconductor 0D structures are called Quantum dots (Q.Dots). Its radius is larger compared to lattice constant but comparable to spatial extension of wave function of electrons, holes and excitons. Semiconductor nanocrystallies are interesting because of their size-dependent electronic and optical properties. Blue-shift of the absorption spectrum, size dependent luminescence, enhanced oscillator strength, enhanced nonlinear optical properties etc are some of the interesting properties exhibited by nanoparticles [1-3]. All these properties are various manifestations of the so-called 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. Doping various glasses, polymers and sol-gels with quantum dots alters their optical properties in useful ways.

1.3 Synthesis of quantum dots

Some of the first quantum dots were probably made many hundred years ago by people who created coloured glass by melting a certain amount of semiconductor material, such as ZnS or ZnSe together with the usual glass material. More controlled attempts to create quantum dots inside a matrix material started in late seventies and intensified during the eighties and nineties of the last century. The growth of quantum dots in glass matrix is still one of the most popular techniques [4-6]. Typically, the growth temperatures range between 550-700° C. Sol-gel technology offers an alternative way of inorganic glass fabrication that does not involve high temperatures [7-8]. Porous glasses developed in this way have nanosized pores, which can be impregnated with nanocrystals. Synthesis of quantum dots in Zeolite (al-0-Si) with regularly arranged cages of about 1 nm size is another method [9].

Besides the growth of quantum dots inside a glass matrix, the synthesis of semiconductor crystallites in liquid solvents is the second one of the currently most used techniques [10-13]. The procedures applied are typically based on near-room temperature precipitation using methods and materials borrowed from organic and polymer chemistry. Here we have the possibility of manipulating the clusters after original growth by passivating or capping the surface. [14-15].

1.4 Optical properties of nano structured random medium

There are many ways of viewing a system of semiconductor particles of nm size. One is the energy structure point of view- how quantum confinement effects come in to play. The electronic states and probabilities of optical transitions in nanocrystals give us an idea about what happens on the way as size increases from that of atom to crystal. Nanocrystals are basically clusters composed of discrete number of atoms. They begin to show size-dependent inhomogenously broadened absorption and emission spectra due to quantum confinement, distribution of sizes, defect concentrations etc. Nonlinear interaction of light with nanocrystals gives us more information about excitonic transitions and local field effects

The other possibility is viewing the system as a completely random medium. In any random medium, when the size of the particles approach the order of wavelength of light used, many interesting properties like localization, enhanced backscattering etc occur. When such a medium also happens to be an amplifying one, random lasing action is another possible interesting phenomenon to occur.

1.4.1. Quantum confinement effects

In semiconductors, local excitation of an electron, (eg. via an optical absorption process), leads to the formation of an electron-hole (e-h) pair called an exciton. The term quantum confinement, when applied to low-dimensional semiconductors, describes the confinement of the exciton within the physical boundaries of the semiconductor. This is an inherently quantum phenomenon - hence the names, "quantum well", "quantum wire", and "quantum dot", which describe confinement in 1, 2 and 3 dimensions, respectively.

The exciton Bohr radius (a_B) is often used as a meter-stick to judge the extent of confinement in a low-dimensional structure. Quantum confinement effects arise as soon as the dimension of a nanocrystal (D) becomes comparable to the Bohr radius of the exciton wave function (a_B), leading to significant changes in the electronic and optical properties. Depending on the magnitude of crystallites, one generally differentiates between different regimes of confinement-quantisation as given below and applies specific theoretical approximations.

Strongly-confined regime: $D < 2a_B$

Intermediate confinement regime: $D \sim 2a_B$

Weakly-confined regime: $D > 2a_B$

It is in the strongly-confined regime that the optical properties of the quantum dots are most affected. This is most clearly demonstrated by a marked blue shift of the optical band gap in the absorption spectrum with decreasing size [16-18]. This is an exciting area of research, which makes it possible to tune the properties of quantum dots to suit any application just by tailoring size, which may find tremendous technological applications.

1.4.2. Coherent Backscattering

Propagation of light waves in disordered, strongly scattering dielectrics is complex and full of surprises. When laser light is scattered off a colloidal suspension and the intensity of the backscattered light is measured as a function of angle, we can see an enhancement in the intensity following a Lorentzian profile. This is called coherent backscattering. Much of the interest in coherent backscattering has been related to the link between phase coherent time reversed paths and photon localization.

The simplest form of transport of light in a random dielectric medium is light diffusion. The fundamental parameter in the light diffusion model is the transport mean free path, corresponding to the distance that light travels in the medium before its direction is randomized. Surprisingly, interference effects can survive random multiple light scattering and lead to striking phenomena beyond diffusion theory. The most robust of these interference phenomena is weak localization of light [19], which originates from the fundamental concept of reciprocity. In weak localization, interference leads to a net reduction of light transport similar to the weak localization phenomenon for electrons in disordered semiconductors. It is often seen as the precursor to Anderson (or strong) localization of light [20]. It is this weak localization of light that is manifested as an enhancement of light intensity in the backscattering direction. This enhancement is called the cone of coherent backscattering. A measure of the full width at half maximum (FWHM) of the backscattered cone gives us an idea about the mean free path of the medium. Hence, backscattering experiment is a valuable tool to characterize any disordered medium.

Since the first experimental observation of coherent backscattering from colloidal suspensions [21], the phenomenon has been successfully studied in strongly scattering powders [22,23], cold atom gases [24], two-dimensional random systems of rods [25], randomized laser materials [26], disordered liquid crystals [27,28], and even photonic crystals [29].

1.4.3. Random lasers

Lasing in disordered media has been a subject of intense theoretical and experimental studies. It represents the process of light amplification by stimulated emission with feedback supplied by disorder-induced scattering. Light scattering was traditionally considered detrimental to laser action because such scattering removes photons from the lasing mode of a conventional laser cavity. However, in a strongly scattering gain medium, light scattering plays a positive role: (i) multiple scattering increases the path length or dwell time of light in the active medium, thus enhancing light amplification by stimulated emission; (ii) recurrent light scattering provides coherent feedback for lasing. First experimental observation of this phenomenon was made by Lawandy et al when they observed that upon addition of submicron TiO2 particles in a dye solution, emission spectrum narrowed down drastically and have the spectral and temporal characteristics of a multimode laser oscillator [30]. Since then, many reports have come in this area from allover the world. There are many candidates for random lasers like submicron powders of GaN [31], ZnO [32], various dye-scatterer systems[33-35], polycrystalline ZnO films [36], Polymer-semiconductor films etc[37].

1.4.4. Nonlinear optical properties

Quantum dots have the unique ability of their properties to be altered in a nonlinear fashion with respect to stimulation intensity. Specifically, they possess the ability to undergo ultrafast (less than 1pico second) changes in both their absorption coefficient and refractive index, simply by altering the power input (pumping intensity) to the dots. These non-linear features are a result of complex quantum mechanical phenomena and are inherent to the quantum confined dots. Quantum dot systems have additionally demonstrated their use in passive mode locking and as inexpensive solid-state saturable absorbers.Increased spatial confinement in nanostructured systems often leads to improved nonlinear response due to local field enhancement.. They show large third order nonlinear (NL) susceptibility. NL effects in semiconductor nanocrystals is mainly decided by the interplay of the population and depopulation of exciton states while the NL properties exhibited by metal nanoparticles like Ag, Pt etc are mainly due to surface plasmon bands [38]. Study of NL properties of nanostructures is still a comparatively new area and many interesting results are being reported They are sure to find applications in various fields like optical limiters, switches, auto correlation systems for laser pulse characterization etc.

1.5 ZnO – material of 21st century

ZnO is a unique material which combines semiconducting, piezoelectric and electromechanical properties. It is a semiconductor with direct band gap of 3.37eV and a large exciton binding energy of 60meV. It is an important functional oxide, exhibiting near-UV fluorescent emission. It shows very low dark current and high optical damage thresholds. Because of its non-central symmetry, ZnO is piezoelectric, which is a key factor in building sensors and transducers. Finally, ZnO is biosafe and biocompatible and can be used for biomedical applications without coating. A great variety of nano structures like nano belts, nano rods, nano rings etc can be made of ZnO besides quantum dots. Because of these factors, it was cited as the material of 21^{st} century in Materials Today, June 2004 [39].

Even if we consider only the photonic applications, ZnO is a versatile material. It shows efficient blue-green fluorescent emission, which can be utilized in Field emission displays. Its is an efficient UV detector and emitter. Solar cells made of ZnO is very popular. Its UV absorbing property has been utilized in UV protection films and cosmetic sunscreen lotions. It is a promising blue laser material. Efficient UV lasing has been observed at room temperature from ZnO thin films as well as ZnO nano clusters. ZnO has achieved the name of first powder laser after Cao et al demonstrated UV lasing from a submicron cluster of ZnO [40].Because of high third order nonlinearity and damage threshold, second and third harmonic generation capability etc, ZnO is predicted to become an important NL Optical material in near future.

There exist various techniques to prepare and characterize ZnO particles of nm size. The following chapters of this thesis describe the science and technology of nano ZnO systems besides their applications in the field of Photonics.

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Chapter 2

EXPERIMENTAL DETAILS

Abstract

This chapter gives the experimental details of both sample preparations and characterization techniques. Apart from the synthesis on nano ZnO by different chemical methods, the attempts made to process thin films, thick films and polymer-ceramic composite films of ZnO are also described. These include screen printing. Dip coating and tape casting techniques. Next the experimental details of different characterization techniques like XRD, BET etc, absorption and fluorescence spectroscopic techniques and back scattering and nonlinear studies carried out in these samples are described.

"Experiments are the only means of knowledge at our disposal. The rest is poetry, imagination"

Max Planck

2.1. Synthesis of nano ZnO

Nano-sized powders with uniform shape and narrow size distribution are shown to possess many interesting properties not shown by their bulk counterparts. They have larger surface area and wider band gap between valence and conduction bands. In many ways they exhibit atom-like behaviors. This can effectively enhance optical, chemical and electro-magnetic properties. They sinter to dense bodies at lower temperature, their microstructures are uniform after sintering, and they show quantum-confinement effects [1].

There are various methods for the synthesis of nanopowders. Main criteria for a good method are reproducibility in size and shape and the control over average size. Basically there are two approaches in getting submicron powders- one is ***top to bottom*** approach ie mechanical break down process by attrition etc. and the other approach, ***bottom to top***, is building up process or nucleation process. This involves a phase change from vapour or liquid to solid. These methods are broadly classified into (a) low temperature and (b) High Temperature methods. Among the low temperature techniques, chemical precipitation, and replication methods have been widely used. Chemical precipitation methods [2-5] include precipitation of solutions from room temperature to 100° C, Hydrothermal synthesis (>100° C, >1 atm pressure)[6-7], Inverse micelle method [8], Sol-Gel synthesis [9-11] etc. These methods are ideally suited for precise control of size and shape of nano particles. In addition, they are cost effective because of less energy consumption. The main drawback with precipitation technique is chemical contamination in general. The replication method has been used to produce nano oxides or metals by carrying out reactions in micropores and mesopores of either crystalline or amorphous porous materials.

The high temperature methods include Gas condensation [12], Self propagating High temperature Synthesis (SHS) [13], Spray Pyrolysis [14], Laser ablation [15] etc. In the gas condensation technique, metal is volatilized in inert atmosphere to produce nano powders. SHS is a combustion process involving an exothermic reaction during which highly porous nanosized powders are formed. Laser ablation method used pulsed laser light to evaporate metal atoms to form hot plasma, which then condenses to form nanoclusters.

Zinc Oxide finds diverse applications as UV protection, photocatalysts, Field emission displays, Varistors, random lasing medium etc [16] Accordingly, the preparation of monodisperse ZnO particles with sub micrometer size has attracted much attention. They have been prepared by Spray pyrolysis [14], aqueous precipitation [2], thermal decomposition of Zinc acetate[17], evaporative decomposition of solutions[18] and hydrolysis of alkoxides [19] calcinations of basic Zinc Carbonate samples[20], Glycothermal treatment[21] etc. etc.

In the present work, ZnO is synthesized by different chemical routes. Synthesis by chemical route has the advantage of being more economical compared to the complex epitaxial methods. In addition, various capping agents can be used to prevent growth and modify the size and shape. This in turn has direct influence in the energy spectrum. Colloidal chemistry also happens to be the stepping-stone towards developing self assembled super lattices. In the present work, ZnO is prepared by two different chemical routes and different capping agents like Poly Vinyl Pyrrolidone(PVP) and Poly Ethylene Imine(PEI) etc have been used. Stable colloids of ZnO thus prepared are studied by various optical methods.

2.1.1. Polyol Synthesis

It is basically a hydrothermal process. Hydrothermal methods, which are commonly used to produce nanosized ceramic powders, are environmental friendly because they take place in closed systems at relatively low temperatures. Low temperatures help to avoid problems like poor stoichimetric control. The combined effect of temperature and pressure force the solution to undergo transformation from solution to solid phase beyond a critical point. Small nuclei are formed throughout the solution, which act as seeds of growth of ultra fine particles [6,7].

The reactions are carried out in water or any other solvent. When other organic solvents such as methanol, ethanol, polyols etc are used, the process is termed solvothermal process. Main advantages of hydrothermal processes in general are

(a) Kinetics of reaction are greatly increases with a small increase in temperature
(b) New metastable products can be formed
(c) Generally single crystals are obtained
(d) High purity products can be obtained from impure stocks.
(e) No precipitants are needed in many cases and thus the process is cost effective.

One of the main drawbacks of hydrothermal process is slow kinetics at any given temperature. To overcome this, one can introduce microwave or ultrasonic fields in the system.

A route called glycothermal treatment has been developed for the preparation of oxides from acetates and alkoxides [21]. Polyols as solvents has high melting points and hence offer a wide range of reaction temperatures. ZnO has been first prepared in polyol medium by Collins et al [22] and Didier et al [23].

In the present study, diethylene glycol (DEG) was chosen as the medium because it is reported to give more uniform-sized powders. Zinc Acetate Dihydrate (Merck) was chosen as the salt. Desired molar concentrations of ZnAc were dissolved in DEG (Merck) by constant stirring and heating to 120° C. After complete dissolution of the salt, stirring was stopped and the solution is slowly heated to 160° C. Around 150-160° C, ZnO precipitated and a milky white colloidal suspension is formed. An aging time of 15 minutes is given to obtain high yield.

The size of the particles and hence stability of the colloidal suspension depended both on ZnAc concentration and rate of heating. Up to molar concentration of 0.05M, colloids were highly stable for a heating rate of 4° C/minute. Above this concentration, colloids were stable only for 1-2 hours. Later on, the particles aggregated and settled. But by ultrasonification, they could be dispersed again for further measurements. Even at lower concentrations, precipitation occurred if the heating rate was increased. When the solution was heated rapidly, sometimes the precipitation did not occur at all, instead the clear solution turned first yellowish and then brownish in colour. Block diagram for Polyol synthesis technique is given in Fig.2.1.

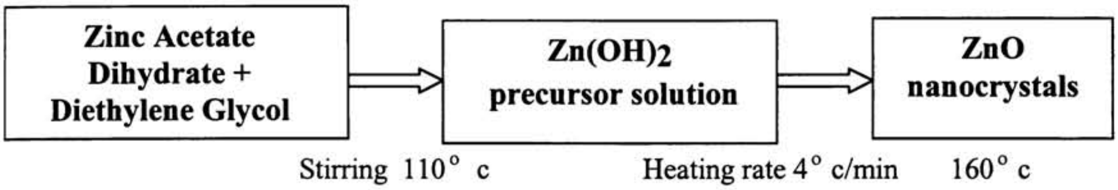

Fig.2.1. Block diagram for Polyol Synthesis

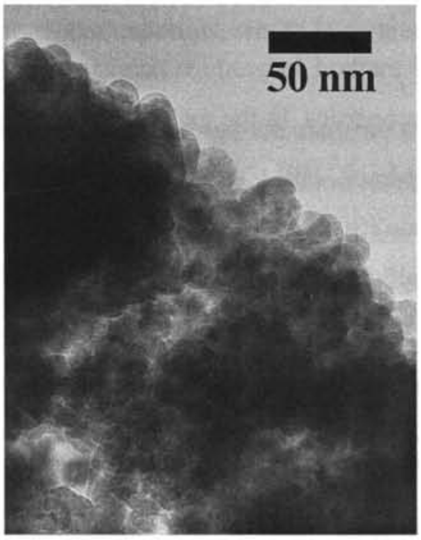

Fig.2.2.TEM photograph of ZnO particles prepared by Polyol Synthesis

Powder was extracted with much difficulty and characterized by XRD and BET measurements. TEM photograph of the powder was also taken (Fig.2.2). The ZnO Colloids were characterized by optical absorption measurements. Fluorescence studies were done and it showed line-narrowing effects, offering it as a potential random lasing medium. Coherent back scattering studies were done. It showed clear enhancement and dependence of FWHM with concentration. Nonlinear optical studies in these colloids showed surprisingly high multiphoton absorption.

2.1.2. Use of Capping agents

Two major challenges often faced in the preparation of nano crystals in solution are Oswald ripening and agglomeration. Use of capping agents prevent these by effectively shielding the surface of the nuclei as soon as they are formed and thus preventing them from coming into direct contact with the solution. Often molecules with long polymer chains are used as capping agents. Thiols[24,26], dodecyl benzene sulfonate[27] and Polyvinyl Pyrrolidone(PVP)[28,29] are some commonly used capping agents. PVP is often added in controlled amounts before reaction. Thiols are added after the reaction at specific time intervals to get specific sizes. Preparation of nano ZnO quantum dots by the use of PVP capping is also reported to give surface modification and hence enhanced UV emission and quenched green emission [28].

(a) PVP Capping

PVP capping is an accepted method to produce nanosized ZnO. This capping is also expected to give better luminescent properties. In the method we adopted, 0.5mM Zinc Acetate solution in 60ml Isopropyl alcohol (Merck, HPLC grade) was prepared with stirring at 50° C. 40ml of 0.2mM Poly Vinyl Pyrolidone (Sisco) was added with stirring. It was then hydrolysed with 1.25mM NaOH under ultrasonification for 2 hours. This gave different particles sizes according to different PVP:ZnAC ratio. Cooling both ZnAc and NaOH precursor solutions to 4° C before mixing helps in keeping the particle size minimum.

(b) Use of a novel capping agent- Polyethylene Imine

Polyethylene imine (PEI) is often used as a cationic dispersant in preparation of aqueous slurries of various powders [29]. But we have demonstrated that the addition of PEI immediately after mixing of ZnAC and NAOH followed by ultrasonification gives stable nano ZnO colloids.

The ZnO is precipitated in Isopropyl alcohol medium using NaOH, as reported earlier [30]. Zinc acetate Dihydrate is the salt used. 10 $^{-3}$ M of ZnAc solution in IPA is prepared and cooled. To this, one drop of the cationic dispersant PEI [Sigma Aldrich] added with stirring .Then 002M solution of NaOH is added to this with stirring. The mixture is ultrasonicated for 10 minutes. The same procedure is also repeated without imine addition. Here ZnO powders grow with time and settle under gravity in a few days. The growth can be clearly monitored with absorption spectrum takes in intervals of 1 hours initially and then once in every 12 hours. The pH of the capped and uncapped samples is 9 and 11 respectively.

PEI is a polyelectrolyte (i.e., it achieves dispersion by electro-streric mechanism). It is a cationic dispersant, i.e. when adsorbed to ZnO, it makes the surface positively charged. The positive charges keeps the particles repelled from each others and prevent agglomeration. The long polymeric chains of PEI on the other hand effectively cap the surface as soon as nucleation occurs and prevent growth. Thus, a polyelectrolyte can make a stable nano semiconductor crystal colloid by a dual mechanism.

2.1.3. Monodisperse ZnO

While preparing submicron powders by precipitation, there will always be a range of size distribution involved. Getting strictly uniformly sized particles is a challenge. But such monodisperse colloidal spheres are the first step for achieving 2D-3D photonic crystals by self-assembly. Under favourable circumstances, they arrange themselves into periodic structures, giving rise to photonic band gap materials, which is an area that has attracted a lot of attention in the past decade [31].

ZnO monodisperse colloidal spheres are made by a modification of polyol synthesis – a two step process.0.03M of ZnAc added to 300ml of DEG and heated. Centrifuged and supernatant collected. Same experiment was repeated and fixed amount of supernatant added just before spontaneous precipitation. Result is highly monodisperse ZnO spheres. The size of the particles depended on the amount of supernatant solution added. It can be varied from 10nm to 700nm. SEM Picture of the sample was taken at IISc , Bangalore (Fig.2.3).

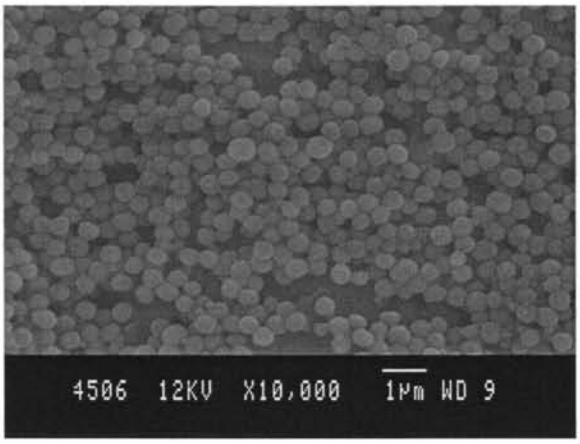

Fig.2.3. SEM photograph of monodisperse ZnO on silica substrate

2.2. Processing of nano ZnO

From applications point of view, just preparing colloidal solution of nano particles is not of much use because of difficulties in handling. Hence, it is desirable to get thin films, thick films and flexible polymer films out of these.

2.2.1 Thick films of ZnO

Screen Printing is a useful technique for producing thick films of uniform thickness and distribution. This technique is commonly used for printing electrode patterns in multilayer capacitors and actuators. Recently they are also used for making thick film actuators, display devices, alkaline batteries etc [32,33]. Screen printed ZnO thick films are also used as varistors and solar cells [34].

The first and most crucial step in screen printing is preparing a screen printable paste of optimum viscosity and uniform distribution out of the material to be screen printed. For this, optimum amounts of suitable solvents and binder are to be added. In the present study, screen printing paste of desired viscosity is prepared as follows. Nano ZnO powder extracted from colloid in DEG medium (0.09 M), washed several times with acetone and dried A known amount of Ethyl cellulose [Merck] was taken (3 wt%) and dissolved in known amount of solvent Turpinol (71 wt%) by keeping overnight and mixing thoroughly to get an agglomerate-free highly viscous solution. A known amount of the extracted ZnO was added (26 wt%) and thoroughly mixed. This paste was screen printed onto a thoroughly cleaned glass substrate using a screen printing machine (AMI Model MSP-465). The mesh size was 325 μ m. It was then dried under IR radiation. The thickness of the film was measured to be 30μm using a film Thickness monitoring gauge (Hanatek 8010).

2.2.2. Dip Coated thin films

Dip coating is a relatively simple method to get thin films of various materials on suitable substrates. Here also preparing a stable and suitable dipping solution of the given material with enough wettability is the crucial step. Usually stable sols are prepared using alkoxides [35]. But, in the present case, the nano ZnO colloid with PVP capping itself was used because PVP is also reported to be a wetting agent [36]. Once the solution is formed, the substrate is lowered into it by a motorized set up at a given rate. It is then held inside the solution for a fixed period and then slowly withdrawn at the same rate. This usually gives films on both sides of the substrate. But for optical studies, we need one-sided films. So immediately after each dip, one side was wiped with IPA. Then it is dried at 110° C for half an hour. The procedure is repeated for as many times as needed, depending upon the final thickness one needs. In the present case, a dipping rate of 5cm/minute was used and an immersion time of 30 seconds.

2.2.3. Polymer-ZnO composite flexible tapes

In general, a composite consists of one or more discontinuous phases embedded in a continuous phase. Nanoparticles embedded in a polymer matrix is considered very attractive for photonic applications since they combine the attractive features of quantum dots with the flexibility and ease of handling of polymers. ZnO-Polymer films find commercial application as UV protection films [37]. They are also reported to exhibit high luminescence and used for antistatic applications [38,39]. Hence, we have tried to disperse nano ZnO in PMMA matrix. PMMA is a transparent organic polymer which has high mechanical strength and scratch resistance. Conventional methods to produce polymer-ceramic composites are solvent casting, Spin coating and hot press techniques. We have used tape casting technique.

Tape casting is a popular method to produce uniform green sheets of ceramics, commonly used to make various multiplayer devices. It usually needs a slurry containing the powder, a suitable solvent, a dispersant, binder and plastisizers [40-41]. The binder imparts strength to the tape and the plastisizers give flexibility. In the present case, PMMA acts as the binder and DEG act as plastisizer. Since ZnO formed in DEG is a stable colloidal suspension, a separate dispersant is not needed. Nano ZnO is prepared in DEG medium as mentioned previously (0.09M). 20 Wt% PMMA crystals of MW 1200 is dissolved in the solvent MEK (Merck) by roll-milling for 24 hours. ZnO in DEG is added to PMMA solution in desired ratio and again roll-milled for half an hour. The mixed colloid is poured onto the glass plate of the tape-casting machine and the blade moves over it at fixed speed, spreading it into a film of uniform thickness determined by the blade- glass plate gap. After an hour of drying, the tape can be readily released. Average thickness of the films was 40 μ m.

2.3.Characterisation Techniques

2.3.1 X-Ray Diffraction (XRD)

X-ray diffraction is an analytical technique, which is commonly used for material characterization in diverse fields such as physics, geology, ceramics, mineralogy etc. Xray beams get reflected at each atomic plane and if they emerge out of the crystal so that they interfere positively, we get a maximum diffracted beam intensity. The Bragg's law for diffraction is

$$2d\sin\theta = n\lambda$$

Where n is an integer describing the order of reflection,

λ wavelength of X-ray,

d interplanar spacing,

θ Bragg angle at which diffraction maximum occurs

So each material gives well-defined peaks characteristic of its crystal structure.[42] Thus XRD pattern for a material is like finger print pattern for a human being- it is unique and is a sure way of identification. If the material is crystalline, it gives sharp peaks. But amorphous systems show a hallow instead. XRD is widely used for identification and characterization of nano particles. Width and shape of the measured diff lines are characteristic of crystallite size and microstrain. Very small crystallites can be considered domains, which are diffracting incoherently with respect to one another, resulting in a Lorentzian broadening. Line profile analysis of XRD data is often used for the determination of crystallite size distribution.

If the line broadening is caused only by small crystallite size, the size can be estimated from the Scherrer's equation [43]

$$D = \frac{k\lambda}{\beta\cos\theta}$$

Where θ is the Bragg angle

D mean dimension of the crystallite size

β FWHM on the 2θ scale in radian and k is a constant

If this method has to be used, a correction for instrumental broadeni9ng has to be applied. Profile fitting analysis gives even better results.

XRD studies for the present investigation were performed using an AXS Bruker D%005 Diffractometer (Germany). X-ray generator was operated at 40 KV and 30mA. CuKα ($\lambda = 1.5418 A^0$) radiation was used. The crystal structure was determined by comparing the d values with the International Centre for Diffraction Data – Powder Diffraction Files (ICDD-PDF) [44]

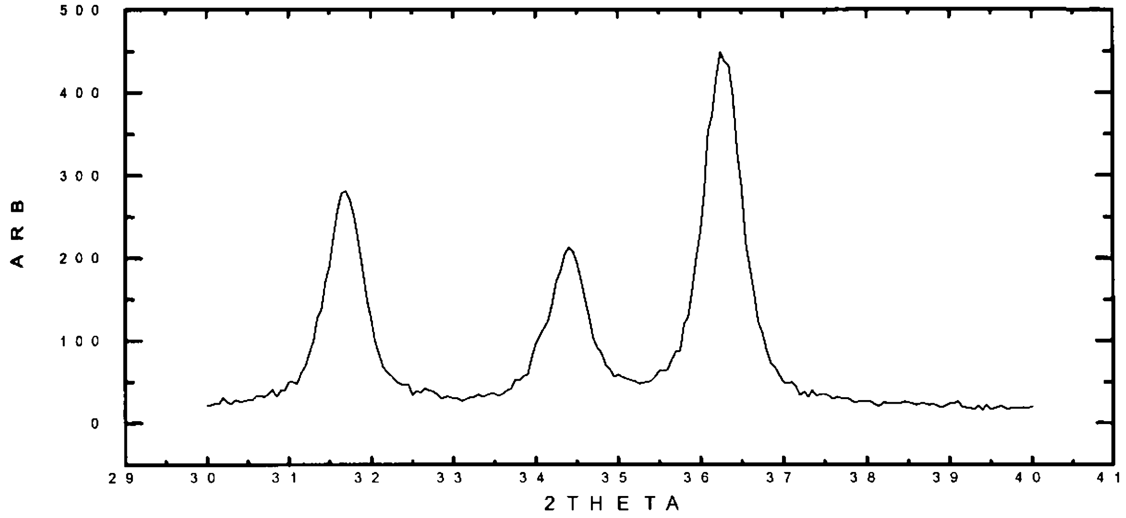

Fig.2.4. XRD pattern of nano ZnO

2.3.2. B. E. T Surface area analysis

The Brunauer-Emmet-Teller (B.E.T) method is the most widely used procedure for the determination of the surface area of solid materials [45] From the quantity of nitrogen adsorbed on the surface of a material, average surface area can be calculated. In the present study, surface area was measured by Nova 1200, Quantachrome Instruments by nitrogen adsorption at liquid Nitrogen Temperature.

Nano particles have very high surface area. If we assume that all particles are spherical and of uniform size, one can get a rough idea about particle size by relating volume, surface area and density.

$$\text{Particle diameter in } \mu\text{m} = \frac{6}{\text{Surface area} * \text{Density}}$$

In our case, the surface area of ZnO synthesized by Polyol synthesis was 30m^2/g and the average particle size calculated from this was 35nm.

2.3.3. Absorption Spectroscopy

Absorption spectra of colloidal ZnO samples, ZnO thin films, Screen printed sample and ZnO –PMMA films are measured using the spectrophotometer JascoV-570(UV/VIS/IR). Details of analysis of the same and the method of finding crystal size from the absorption spectra are detailed in chapter 3.

2.3.4. Fluorescence spectroscopy

Fluorescence spectra of pellets of the nano ZnO prepared by polyol synthesis and commercial ZnO of 5 micron size were done at MG University (Shimadzu RFPC 5301). Peak absorption was at 360nm and 255 nm as reported [46]. The emission spectra had two peaks, one in the UV and the other one in the green region.

We carried out some fluence-dependent fluorescence experiments in the ZnO-DEG colloidal samples at our Lab with the view of studying the effect of pump fluence on the emission line profile. This was to see if the colloidal medium shows any promise of showing random lasing action. More details will be discussed in chapter 4.The samples taken in glass cuvette are optically pumped by the third harmonics (λ = 355 nm) of Nd-YAG laser (DCR-11SpectraPhysics 10 Hz repetition rate , 15nm pulse width). The spectrum of emission is collected by a microscope objective onto a UV sensitive fiber which is coupled to a monochromator.(McPherson 0.2m , Model no.275). The beam is incident and collected at an angle of 30° to the cuvette surface. The pump beam intensity was measured by power meter (Coherent Lab master) and the pumping beam diameter was varied by aperture. The experimental set up as shown in Fig.2.5

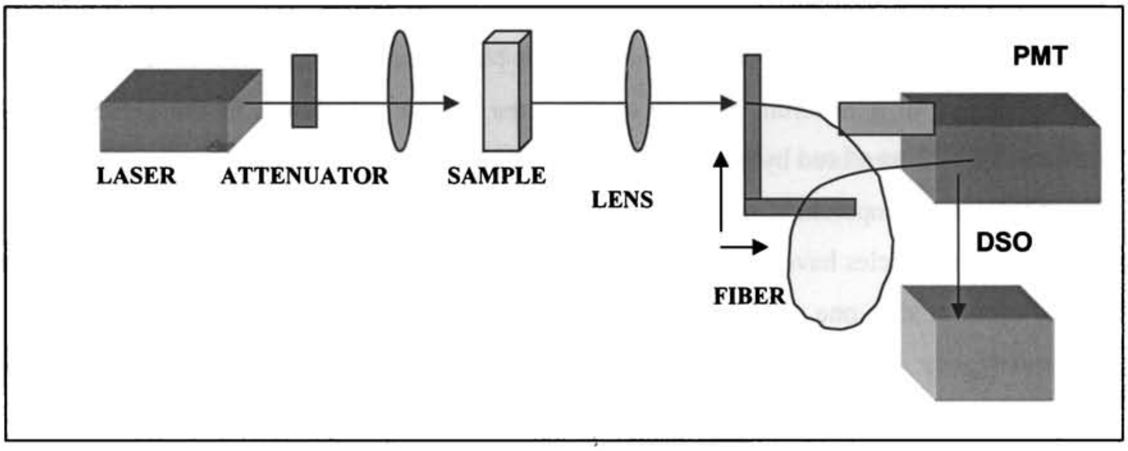

Fig.2.5.Experimental set up for the florescence studies.

2.3.5. Coherent backscattering Experiments

To characterize any random disordered medium, it is essential to have an idea of the mean free path length in the sample. An efficient way to obtain this is back scattering studies. In highly disordered systems, multiple scattering occurs and the interference between time-reversed paths gives an enhanced intensity cone in the exact backward direction. Details will be given in chapter 5. If we measure the FWHM of the back scattering cone, we can deduce the mean free path of the medium from the equation

$$\theta = \frac{0.7\lambda}{2\pi\square}$$

Our experimental setup more or less resembled the standard set ups used for backscattered measurements [47]. The source of light is a diode pumped solid state laser (DPSS BWT 50, 40mW, 532 nm). The beam expander assembly (BE) provides a collimated parallel beam. The half-silvered mirror allows observations in the exact backward direction. The sample cell is turned slightly so that specular reflection from the glass cell is kept from the detector. After passage through lens, L the beam is focused onto a fiber tip of diameter connected to a monochromator-PMT setup. The output of the DPSS was plane polarized. This together with analyzer A ensured detection in polarization preservation channel.

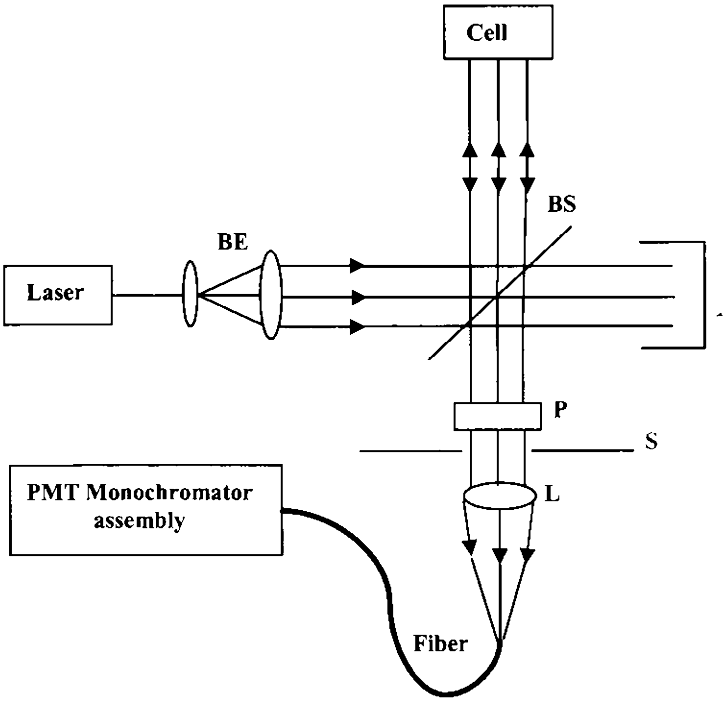

Fig.2.6. Experimental set up for back scattering studies.

2.3.6. Nonlinear Optic measurements-Z-Scan

The interaction of intense laser light with matter has opened up an exciting field of study called Non Linear Optics. Systematic studies of nonlinear properties of materials are essential for the design and fabrication of devices using them for various applications like optical limiting and logic gates. Nano particles are a rather new group of materials extensively studied for their NL properties in the past decade [48-49].

For the nonlinear optical measurements, we have employed the Open-aperture Z-scan technique developed by Sheik Bahae and his co-workers [50] which is a single beam method used in a wide variety of experiments to determine the nonlinear susceptibilities of solids, ordinary liquids, and liquid crystals and has sensitivity comparable to interferometric methods . This method is essentially sensitive to nonlinear absorption of the sample. We have studied ZnO colloids prepared by different methods using this method.

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 the focal length being 200 mm. 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 signals are interfaced with a computer and the sample, which is mounted on a translation stage, is controlled by the computer. The z-scan system is calibrated using CS_2 as a standard. The experimental set up is as shown in the figure.2.7.

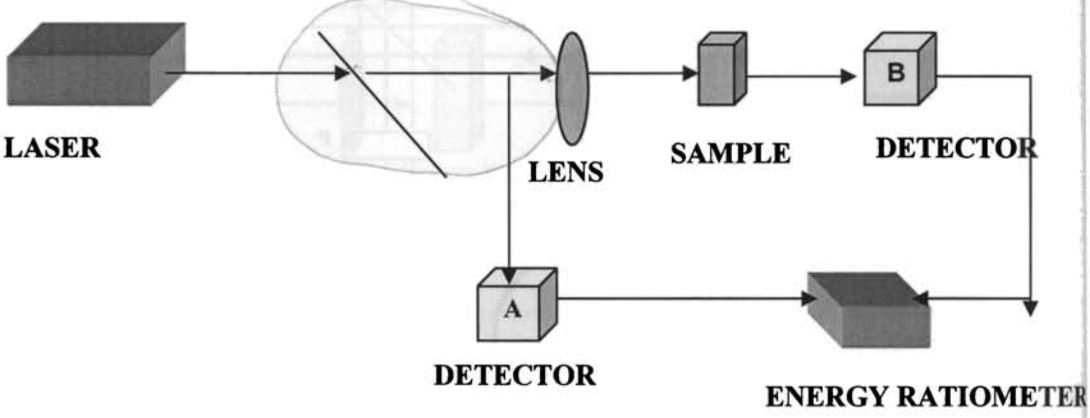

Fig.2.7. Experimental set up for Open aperture Z-Scan studies

2.4.Instrument Specifications

Pulsed Nd:YAG laser

Model and Make : Quanta Ray.GCR:170
Wavelength
  When frequency doubled : 532 nm
  When frequency Tripled : 355nm
Pulse Energy(Maximum) : 450mJ
Pulse width : 6-7ns
Pulse Repetition Frequency : 10Hz
Spatial Mode : Gaussian

Digital Storage Oscilloscope

Model and Make : Tektronix TDS 360
Rise Time : 1.75ns
Sensitivity : 2mV/Div to 10V/Div

Energy Meter : Rjp-7620 Energy Ratiometer

Detector Head : Rjp-75

Spectrophotometer

Model and Make : Jasco 570
Wavelength Range : 190nm to 2500
Resolution : 0.1nm(UV/Vis region)
: 0.5nm(NIR Region)

Diode Pumped solid state Laser DPSS

Model and Make : Uniphase BWT-50
Out put voltage : 50mW

PMT

Model and Make : Thron MI S-20 cathode
Operating Voltage : -750 V (1.7 Œ 2.1 KV).

Monochromator

Model and Make : McPherson Model No. 275
0.2m, f/2
Max.Resolution : 0.4nm
1200G/mm grating
Wavelength range : 200 nm to 600 nm.

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Chapter 3

ABSORPTION SPECTROSCOPY OF NANO ZnO

Abstract

This chapter deals with the absorption spectroscopy of nanosized ZnO in detail. Theoretical idea of how quantum confinement results in the shift of absorption edge is given in brief. Next how this shift is utilized in the present study extensively for size determination is given taking different samples prepared by different methods separately. How the amount of capping agents affects the spectra, how spectra at specific time intervals look like with and without the addition of capping agents etc are illustrated.

“I was lucky enough to look over the Lord's shoulder while He was at work."

Heisenberg on his discovery of Quantum Mechanics

Introduction

Semiconductor nanocrystals exhibit quantum confinement effects. When the dimensions of nanocrystals become very small, there are significant changes in their electronic and optical properties. This is most clearly demonstrated by a marked blue shift of the optical band gap, which can be clearly seen in the absorption spectra. This makes it possible to tune the band gap to suit any specific application by changing the size, which has tremendous applications. Absorption spectroscopy is an effective analytical tool, especially in studying dilute colloids and solutions of nanocrystals.

3.1 Quantum Confinement effects

In recent past, there has been considerable interest in the study of size effect in semiconductors in reduced dimensions due to their applications in solar cells [1], catalysis[2], light emission displays[3], resonant tunneling devices[4] and lasers[5]. Most studied nanocrystalline semiconductors belong to the II-VI group. These nanocrystallites of different sizes grown as colloidal particulates [6,7], gas evaporated particles embedded in glass matrices [8,9,10], and in Zeolite cages [11,12] have been studied by optical absorption, photoluminescence and Raman spectroscopic studies. Many studies in dilute ZnO colloids in alcoholic medium are also reported [13-15].

When quantum dots are excited with energies larger than band gap energy, electrons in the conduction band and holes from the valence bands are excited. Depending on the excitation conditions, the coulomb attraction between a hole and electron might lead to a bound state, the Wannier Exciton. Just as the hydrogen atom, the exciton states are characterized by a product wave function consisting of a plane wave part for the centre-of-mass motion and hydrogen functions for the e-h relative motion. The characteristic length scale for the relative motion is the exciton Bohr radius, which may be of the order of 1-20 nm, depending on the semiconductor material. Quantum confinement effects arise, as soon as the linear extension of the quantum dot is comparable to this exciton Bohr radius.

In the case of nanocrystallites, the electrons, holes and excitons have limited space to move and their limited motion becomes possible only for definite values of energy. The highest occupies valence band and lowest unoccupied conduction band are shifted to a more negative and positive values respectively resulting in widening of band gap. This leads to a blue shift of absorption band which be observed through optical absorption and transmission studies.

In their pioneering investigations of quantum confinement in semiconductor microcrystallites, Efros and Efros [16] introduced three confinement regimes, depending on the ratio of crystallite size to Bohr radius of electrons, holes and excitons. When the radius of the crystallite R is smaller than 2 Bohr radii, electrons and holes are considered as two confined particles, bound by an enforced Coulomb interaction where confinement energy becomes larger than Coulomb energy. This is the strong confinement limit. Here the energy band gap is given by [17]

$$E = E_g + \frac{h^2\pi^2}{2\mu R^2} - \frac{1.786e^2}{\varepsilon} - 0.248E_{ex} \qquad (3.1)$$

Where μ, ε, E_g and E_{ex} are reduced mass, dielectric constant, bulk band gap and exciton binding energy respectively.

When the crystallite radius is larger than 4 exciton radii, the ground exciton is treated as a rigid sphere, confined as quasi particle exciton. In theoretical analysis of such systems, one often introduces relative and centre of mass co-ordinates for excitons. In this weak confinement limit, the lowest energy will be

$$E = E_g + \frac{h^2\pi^2}{2MR^2} - E_{ex} \qquad (3.2)$$

Where M is the translational mass.

In between these two extreme cases, there is an intermediate confinement regime where the effective mass of holes is much larger than that of electrons. Here the influence of quantum confinement on electron and hole is substantially different.

3.2.Particle size determination from absorption spectra

There are several approaches to estimate particle size from the absorption onset. Brus[18], Henglein[19], Gaponenko[20], and Ekimov[21], and coworkers have modified the quantum mechanical treatment to explain the various experimental results of wavelength threshold as a function diameter of semiconductor nano particles. The most widely used approach is that proposed by Brus et al, who used affective mass approximation.

The absorption edge is obtained from absorption spectra as follows. We know that ZnO is a direct band gap semiconductor for which absorption coefficient α is related to the excitation energy $E = h\nu$ by

$$\alpha = Const(h\nu - E_g) \tag{3. 3}$$

So to obtain the absorption onset, one usually plots ln (I/I$_t$) Vs $h\nu$ and extrapolation of the linear part until its intercept on the hv axis gives Eg.

But the validity of EMA has been questioned by many. Nair et al [22] and Kayyanuma [23] calculated the exciton binding energy variationally and found that the finite size and deformability of exciton play a crucial role in determining the lowest exciton state s even in weak confinement regime. One important result of this calculation was that centre of mass approximation becomes accurate only at relatively large particle radii. Recently in a paper by Ranjani Srivastava et al of IISc, Bangalore [24], we see convincing arguments about how EMA approximation seriously overestimate the size of small quantum dots. In this paper, they also suggest a better method to obtain the absorption onset, which is getting the point of inflection obtained from the minimum in the first derivative curve of the absorption spectrum.

After detailed theoretical discussions based on molecular orbital theory, they argue that dependence of band gap on diameter of nano crystals is given by

$$E_g = 100(18.1d^2 + 41.4d - 0.8)^{-1} \tag{3.4}$$

3.3. Absorption spectra of ZnO colloids

ZnO colloids were prepared by 3 different techniques, as detailed in chapter 2. In each case, they were characterized by absorption spectroscopy, which gave the crystallite size and variations when experimental conditions like precursor concentrations and amount of capping agents were varied. Also, in the case of Polyethyle imine, time dependent absorption spectroscopy was performed to monitor particle growth.

3.3.1. Polyol Synthesis

In the case of Polyol synthesis, the molar concentration of Zinc acetate in dithylene glycol was varied from 0.0001 to 0.1M. In each case, the colloids were taken in a cuvette and transmission spectrum was plotted. Then from the first derivative curve of this spectrum, point of inflection was found out. This was taken as the cut off wavelength and the corresponding Eg is calculated. The deviation of this from the standard reported Eg of bulk ZnO, namely 3.2 eV was calculated. Then using the formula (3.4), the particle size was calculated. Fig.3.1. Shows the absorption spectra of ZnO colloids of various molar concentrations. Table 3.1. Gives the particle size for different concentrations.

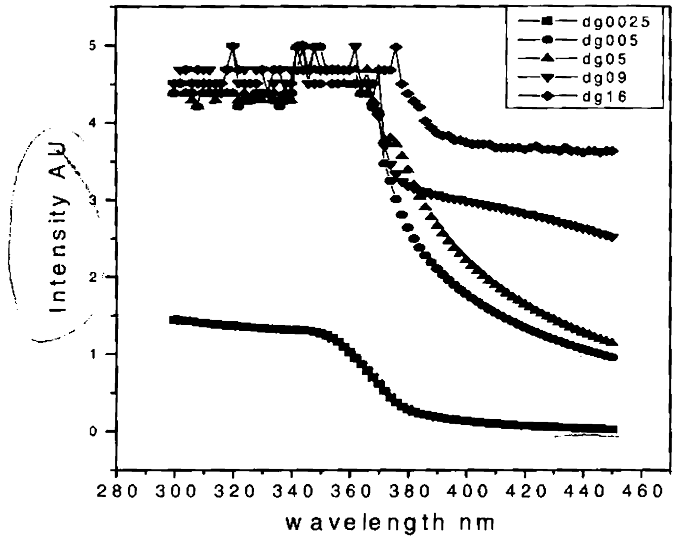


Fig.3.1 Absorption spectra of ZnO - DEG colloids of different molar concentrations

Molar Conc. **M**	**Cut off** **λ** **nm**	**Eg** **eV**	**Crystallite** **size** **± 0.5nm**
0.0025	357.75	3.473	5.05
0.05	370	3.351	12.08
0.09	372.5	3.328	18.54

Table.3.1 Particle size for ZnO-DEG colloids of different concentrations

3.3.2. Capping with PVP

Several approaches have been considered to prepare size-controlled semiconductor nanocrystallites with narrow size distribution. Many of these preparation methods control the growth by the addition of stabilizers or capping agents like Thiols, PVP etc [25,26], by restricting the growth space in matrices like Zeolites[27], reverse micelles[28], porous silica matrix [29] etc. Surface-capped CdS colloids have been prepared by different thiols, for example, Henron et al [30] have shown that CdS nanoclusters of various sizes can be prepared by adjusting the ratio of sulfide to thiophenol during synthesis. Yang et al have attempted preparing ZnO q.dots of different sizes by PVP capping [26]. We have attempted a similar approach. Fig.3.2 gives the absorption spectra of PVP capped ZnO for different PVP: Zn ratio. Table 3.2 gives the variation of particle size in this case.

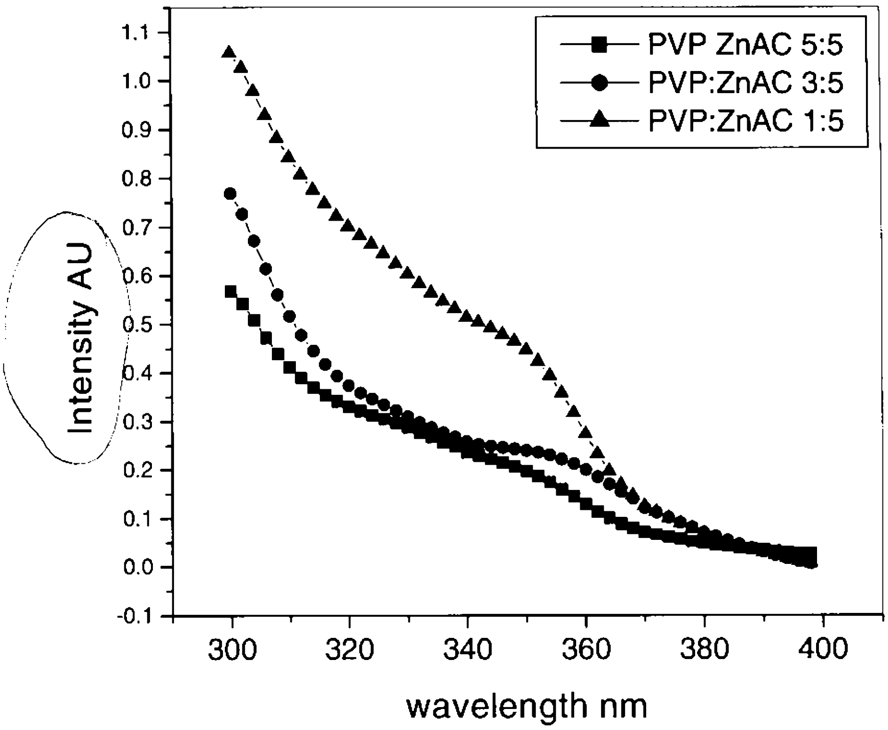


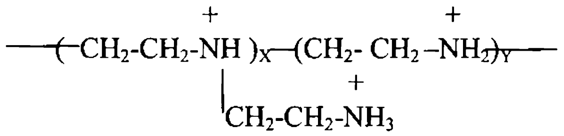
Fig.3.2. Absorption spectra of PVP capped ZnO for different PVP: ZnAc ratio.

PVP:ZnAc ratio	Eg eV	Size ± 0.5nm
5:5	3.3668	2.6
3:5	3.647	3.4
1:5	3.594	4.6

Table 3.2 Particle size variation with PVP concentration

3.3.3. Poly Etrhylene Imine- a Novel capping agent

PEI is a mixture of primary, secondary and tertiary amines after the polymerisation of the monomer. Its chemical structure can be represented below



$$-\!\left(\mathrm{CH_2\text{-}CH_2\text{-}\overset{+}{N}H}\right)_X\!-\!\left(\mathrm{CH_2\text{-}CH_2\text{-}\overset{+}{N}H_2}\right)_Y\!- \qquad \text{with branch } \mathrm{CH_2\text{-}CH_2\text{-}\overset{+}{N}H_3}$$

By virtue of the high charges on a branched polymeric structure, PEI acts as good electrosteric dispersant. It is a cationic dispersant ie when adsorbed to ZnO, it makes the surface positively charged [31]. The positive charges keeps the particles repelled from each other's and prevent agglomeration. The long polymeric chains of PEI on the other hand effectively cap the surface as soon as nucleation occurs and prevent growth. Thus, a polyelectrolyte can make a stable nano semiconductor crystal colloid by a dual mechanism.

ZnO colloid is prepared as described in 2.5., In another trial, the procedure is repeated but without imine addition. Here ZnO powders grow with time and settle under gravity in a few days. The growth can be clearly monitored with absorption spectrum takes in intervals of 1 hours initially and then once in every 12 hours. Fig.3.3 and 3.4 gives the absorption spectra of samples with and without imine addition at regular time intervals.

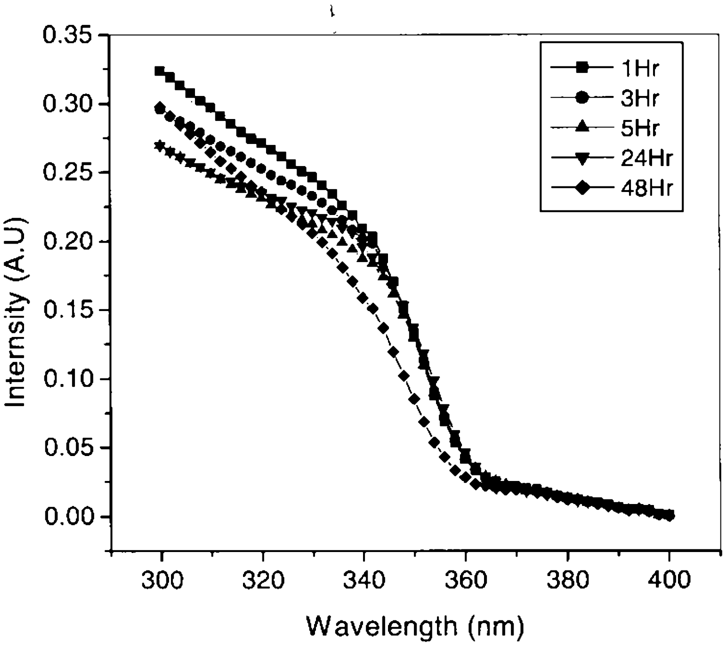


Fig.3.3 Absorption spectra at time intervals when PEI is not added

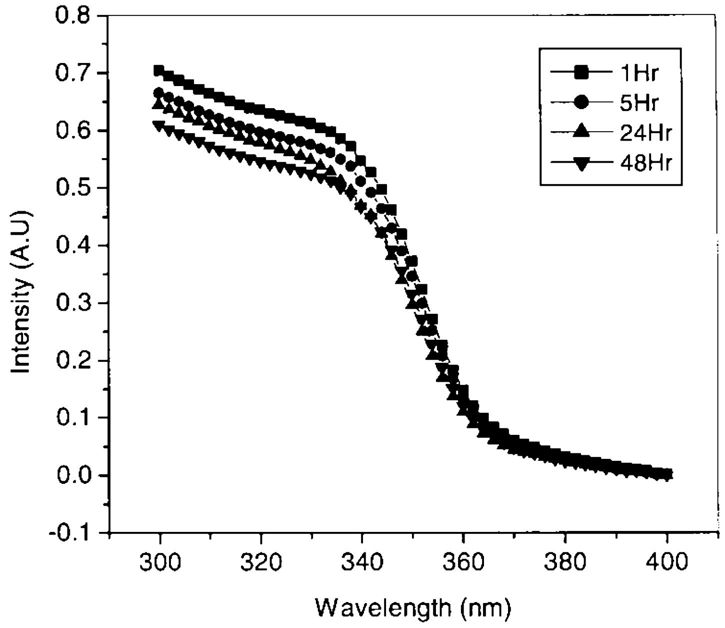


Fig.3.4.Absorption spectra at time intervals after PEI addition

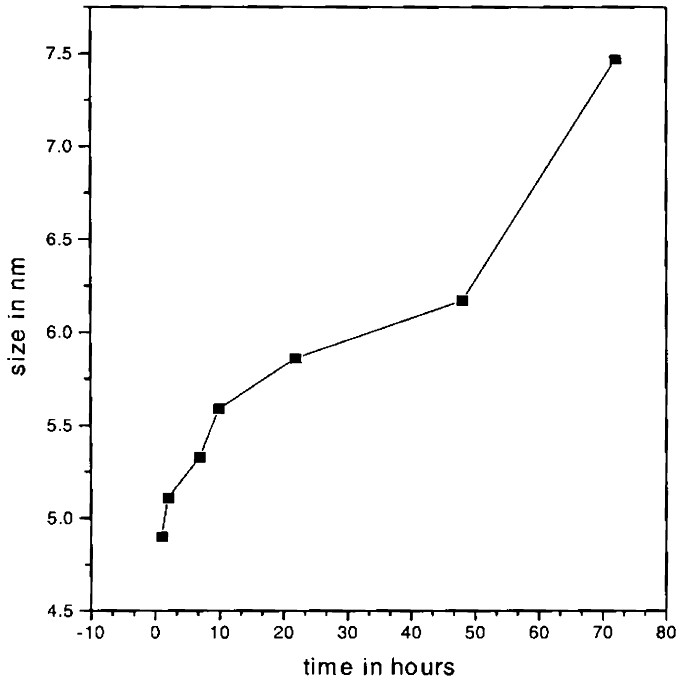


Fig.3.5 Particle size growth of uncapped ZnO over time

Time in hours	Eg eV	Size ± 0.5nm
1	3.48	4.9
10	3.45	5.59
48	3.4	7.47
72	3.35	12.08

Table.3.3. Shift of band gap and corresponding size change with evolution of time in uncapped ZnO colloid.

From the above data, we can clearly see how addition of polyethylene imine effectively arrests the growth, in which case the size remained 4.8nm even after months. This stable colloid was then used for Nonlinear Optical studies.

3.4. Absorption spectra of ZnO-PMMA thin films

The main commercial application of ZnO has been in UV protection films and sunscreen lotions. It has been realized that particle size reduction is advantageous for these applications. According to the United States Geological Survey, over 25 million kilograms of zinc oxide are used each year in products ranging from UV absorption coatings and cosmetics to anti-bacterial additives and adhesives. Smaller zinc oxide particles improve product performance in several ways. Smaller particles increase the amount of ultra-violet sunlight that is absorbed; which gives suntan lotions higher SPF ratings and keeps plastics and resins from cracking or paints from peeling after being exposed to direct sunlight.

Besides the commercial applications, many research appears are also coming on ZnO-Polymer composite films [32-33] Glen C.Irvin of Eastman Kodak Co. (USA) report their investigations on the optical properties of nano-scale zinc oxide/PMMA composites. Their films were produced by spin coating and cast coating dispersions of nanoparticle/PMMA organic solutions. It was found that the refractive index of the composite films scaled linearly with volume fraction of nanofillers. Besides the UV filtering, when the films were loaded with a high content of such semiconductor nanoparticles, the surface resistivity decreased enough for the coatings to be used for antistatic applications. Vollath et al [33] report that nanocomposites, consisting of an electrically insulating oxide core and PMMA coating exhibit strong luminescence, which they attribute to the interface, where PMMA is bond via a carboxylate bonding to the surface.

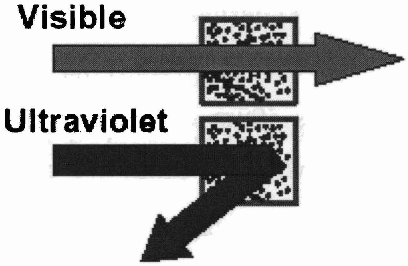


Fig.3.6. UV Filtering of ZnO films

The selective optical filtering property of ZnO films is illustrated by Fig.3.6, which is transparent for light in visible rang while blocking the UV rang of the incident light. The ZnO filler can evenly block the UVA and UVB range, which is its advantage over the other UV absorber not mention its excellent stability.

One of the main challenges in making such polymer-ZnO films is getting uniform dispersion of particles. In our case, the growth medium diethylene glycol is a known plastisizer for tape casting. So without extracting the powder, the stable colloid itself can be mixed with PMMA, which also happens to be a good binder. Hence the missed slurry could be easily tape casted and free films could be obtained.

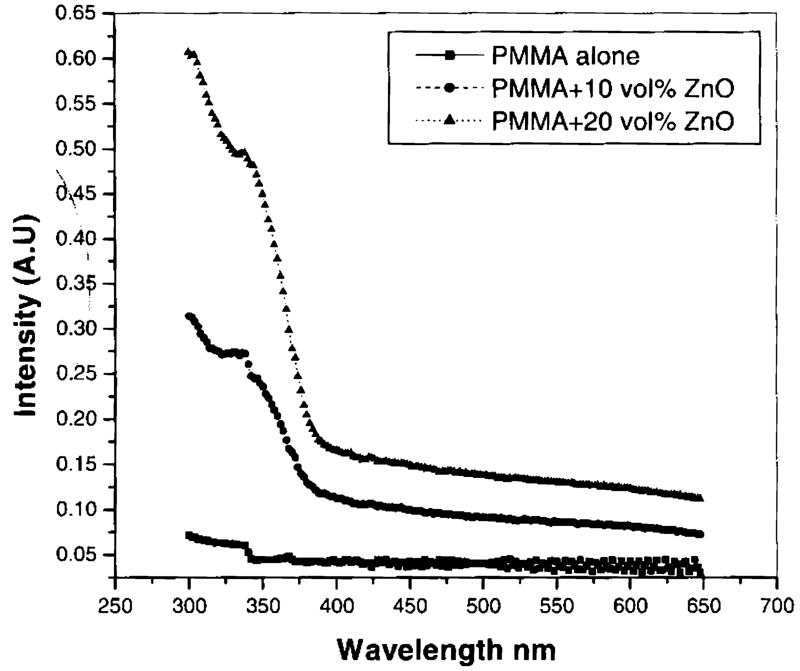


Fig.3.7. Absorption spectra of PMMA-ZnO flexible films with different soild loading

The thickness of the films was 40μm on average. Fig.3.7 shows the absorption spectra of pure PMMA as well as PMMA-ZnO films. We can see that as ZnO content is increased, absorption increases.

3.5. Conclusions

We have seen that absorption spectroscopy is a powerful tool in characterizing nanocrystal colloids. Even without sophisticated tools like TEM, one can get an idea about the size range from the shift of absorption edge. Time dependent absorption spectroscopy gives us an idea about particle growth over time and the effect of capping in the prevention of growth.

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Chapter 4

FLUORESCENCE SPECTROSCOPY OF ZnO

Abstract

ZnO is reported to show two emission bands, a UV emission band and one band in the green region. The relative intensities of these two bands are different for nano and bulk ZnO. This fact is discussed and studied in the beginning of this chapter. Then we have concentrated on the UV emission only. Keeping in mind the possibility of Random lasing action, we have attempted pumping nano ZnO colloidal samples at different laser intensities and the emission is studied. A clear threshold behaviour and line narrowing is observed.

"The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It is something in principle can be done, but has not been done because we are too big"

Richard Feynman, 1959

Introduction

Semiconductor nanocrystals show remarkably different optical properties compared to their bulk counterparts. We have seen the shift of absorption edge in the last chapter. In the present chapter, we focus on the fluorescence. Systematic studies by different groups on nano crystallites has indicated the presence of luminescence due to excitonic emissions as well as significant contribution from surface states on the lower energy side of the PL spectrum [1-3]. It has been observed that as the particle size decreases, visible emission is observed to dominate. For example, J.Nanda et al has observed that for CdS nanocrystals, red emission dominates as size decreases [4].Another observation is the increase in quantum efficiency of luminescence for nanocrystals in comparison to bulk. This is explained on the basis of quantum confinement [5,6]. Surface passivation and doping strongly affects PL spectra of quantum dots [7]. On the other hand, when we consider ZnO nanoparticles as disordered medium and study the influence of pumping energy on the fluorescence, drastic line narrowing effects beyond a threshold can be observed [8]. Keeping in view of these observations, we present our results in two separate sections. Section 4.1 describes the comparison of fluorescence spectra of ZnO in nanostrucured form as well as in bulk form. Section 4.2 deals with colloidal ZnO as a potential gain medium.

4.1. Fluorescence in nano ZnO

It has been observed by many that in ZnO quantum dots, green emission (490-530nm) dominates in comparison to UV emission (390nm) unlike in the case of bulk ZnO in which the UV emission dominates [9,10]. This observation is predominant mainly in ZnO prepared in alcoholic medium [10]. Many have tried to explain this. Van Dijken et al [9] explains the green emission involves as due to deeply trapped charge carrier. H. Zhou [11] et al attributes the green emission to the core-shell structure of Zn-OH group. It has been observed that there is difference in the spectra of ZnO of same size prepared by different methods [12]. Surface passivation using capping agents like PVP is reported to quench the green emission resulting in strong UV peaks [7]. Modified Preparation methods like pyrolitic synthesis [13], electrochemical deposition [14] etc also has been reported to give ZnO with quenched green emission. The effect of method of preparation and surface passivation itself is an indication that the green emission is due to surface states. Following sections give detailed analysis of the experimental results of the fluorescence studies of nano and bulk ZnO.

Fig.4.1.a shows the fluorescence spectrum of bulk and nano ZnO, when excited with 360nm, recorded using Shimadzu RFPC 5301. Pellets were made of both powders by cold pressing, using PVA as binder. Commercial ZnO (Merck) of particle size of around 5 micron was used as the bulk sample. ZnO prepared by Polyol synthesis and extracted from diethylene glycol medium was used for the nano sample.

In the fluorescence spectrum, we can see that in bulk, UV emission dominates as expected. In the case of nano ZnO, it is the green emission that is predominant. But UV emission is not as subdued as reported for those grown by chemical precipitation in alcoholic medium [15]. We can see that surface states are not fully quenched as in the case of PVP capped ZnO.

Fig.4.1.b gives the energy band diagram of ZnO. We can see that the UV band corresponds to the transition from conduction band edge to the valence band and the green emission is either conduction band to or from to the valence band.

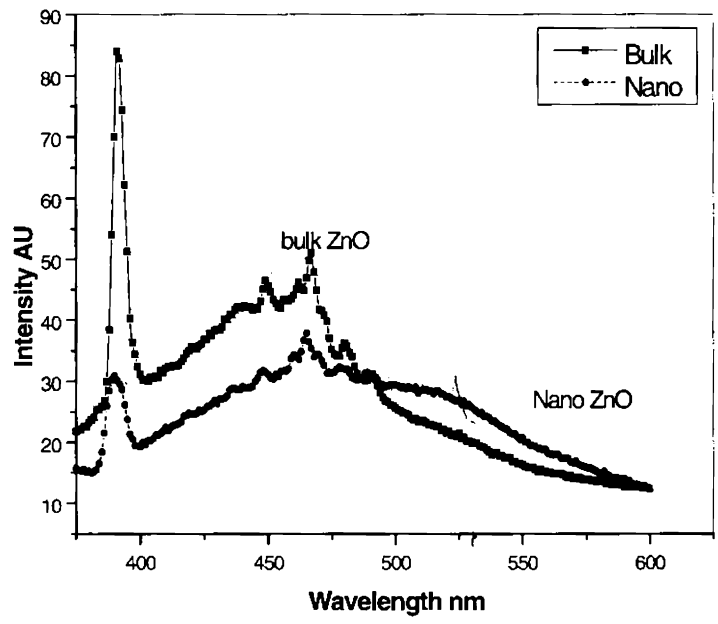

Fig.4.1.b. Fluorescence spectra of nano and bulk ZnO when excited with 360nm source

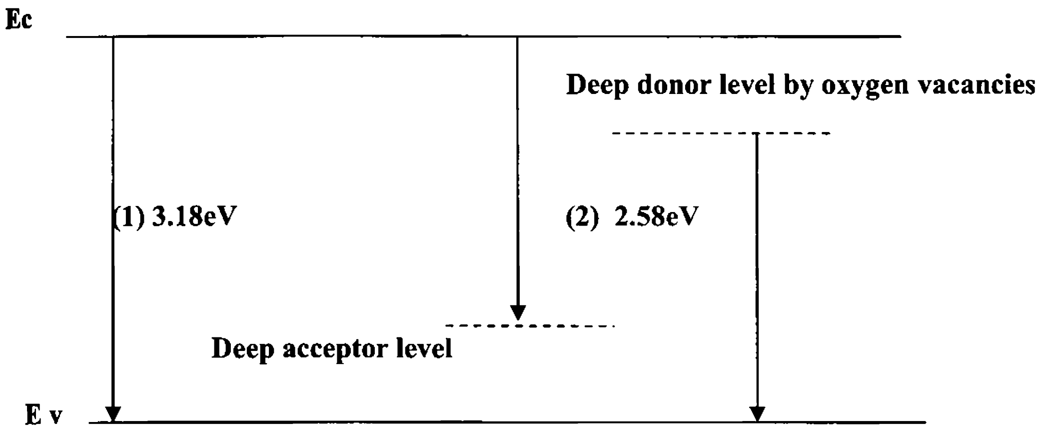

Fig.4.1.c. The UV and green photoluminescence mechanisms of ZnO. (1) Transition from conduction band edge to valence band (2) The transition from deep donor level to valence band or from conduction band to donor acceptor band.

4.2.Amplifying Random medium

The mention of the term laser evokes the picture of a highly ordered system. But the conjunction of lasing and disorder has been of interest for a long time. It was Letokhov who first proposed in 1968 [16] the theory of self-generation of light in an active medium filled with scatterers. But only much later an experimental verification came when Lawandy et al [17] made the discovery that placing random scatterers in a gain medium could enhance the frequency stability of laser emission. The observation of lasing action in rare earth doped powders and in colloidal suspensions of submicron Titania particles in dye solutions [18,19] have renewed interest in amplifying random media. A dramatic narrowing of spectrum [20,21] and shortening of emission time [22,23] is observed above a threshold in pumping energy. These results have raised the prospects of utilizing the phenomenon for a variety of display, sensing and switching applications [24].

4.2.1.Random Lasers – basic mechanism

A random laser is a non-conventional laser whose feedback mechanism is based on disorder induced light scattering. Light scattering was traditionally considered detrimental to laser action because such scattering removes photons from the lasing mode of a conventional laser cavity. However, in a strongly scattering gain medium, light scattering plays a positive role (i) Multiple scattering increases the path length or dwell time of light in the active medium, thus enhancing light amplification by stimulated emission; (ii) recurrent light scattering provides coherent feedback for lasing. There are two kinds of feedback: one is *intensity* or *energy* feedback; the other is *field* or *amplitude* feedback. The former feedback is incoherent and non-resonant, while the latter is coherent and resonant. Based on the feedback mechanisms, random lasers are classified into two categories: (1) random lasers with non-resonant feedback, (also called incoherent random lasers) (2) random lasers with resonant feedback (also called coherent random lasers).

4.2.2. Random lasing in ZnO

It was Cao et al who first demonstrated laser like emission in a 1 micron sized cluster of ZnO, thereby earning the name of first powder laser. Here they called it a microlaser because they individually pumped 1 μm sized ZnO clusters consisting of several 10000 of nanosized crystals. The term microlaser means to confine light in a small volume with dimensions of the order of wavelength of light. The same group also has observed random lasing with resonant feedback in ZnO films on silica substrates(25) and powder films of ZnO which is electrophoretically deposited (26). They have also studied gradual transition from incoherent to coherent type of lasing in ZnO nanoparticles suspended in dye solutions (27). In all the studies mentioned above, some common observations were made which are listed below

1. At low excitation intensity, a broad spontaneous emission spectrum was observed.
2. As the pump power increased, narrow emission peaks emerged beyond a threshold value.
3. The frequencies of the spectral peaks depended upon the sample position. This means that light is trapped by multiple scattering and light returns to the original scatterer and this interference is constructive only at certain frequencies. In a different region of the sample, the particle configuration may be different and this gives different peaks.
4. Lasing threshold depends on pumping area.
5. Emission pulse also shortened drastically above a threshold.

In our studies, we have attempted to see if dilute colloids of ZnO itself without dye can act as random lasing medium.

4.3. Experimental Results

We measured intensity-dependent emission from ZnO in ditheylene glycol (DEG) medium using frequency-tripled output (355nm) of Nd:YAG laser as pump radiation. The experimental set up and details are as shown in chapter 2. (Fig.2.5)

The direction of the incident pump light makes an angle 30^o with the cuvette surface. Emission occurs in all directions and this was collected by a large area short focus length lens and focused onto the tip of a UV sensitive fiber tip. We recorded the emission spectrum with a monochromator-PMT assembly.

When the spectrum was charted, we could get a broad and strong emission peak in the green region and a relatively weak UV peak, as expected. But in the present study, we focused only on the excitonic UV peak. At low pump intensities, we got a broad spontaneous emission spectrum. But as the pump power was gradually increased, beyond a threshold, line narrowing began to manifest. The FWHM reduced from 6nm to 3 nm. The intensity of the peaks also increased considerably beyond the threshold. Fig.4.2. shows the emission spectrum of a 0.0025M ZnO colloid at different pump intensities. Fig.4.3 shows the plot of pump power against emission

Cao et al (27) describes an experiment where they observed a transition between an incoherent random laser to coherent mode in ZnO –Dye solution in which they observe two thresholds. Beyond the first threshold, the line width collapses to 5nm and when the pump intensity increased further and reached a second threshold, discrete peaks of line width of <0.2nm emerged similar to those occurred in ZnO powder (28). In our case, most probably we have reached only the first threshold. We could not increase the pump power further because of the lack of appropriate UV optical components.

Fig.4.4 shows the emission from 0.09M colloid. The difference is due to the change in the number of scatterers. This will affect the mean free path and multiple scattering, which actually leads to the line narrowing.

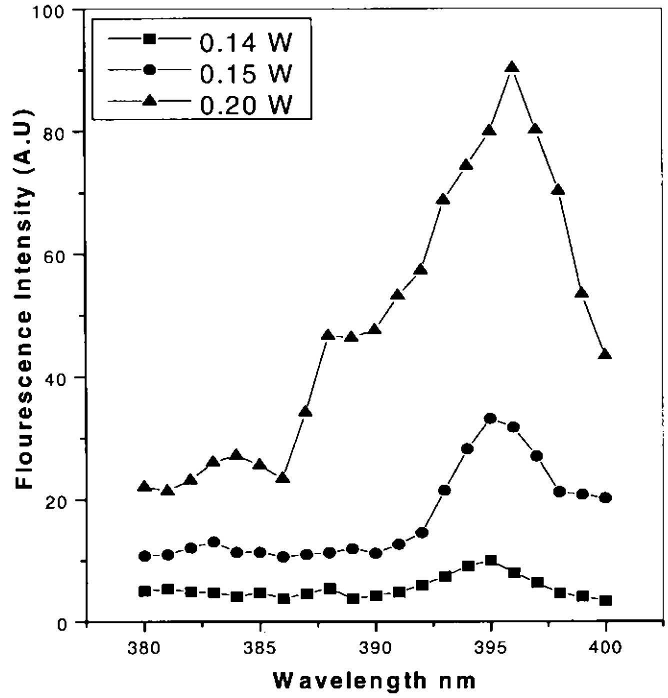

Fig.4.2. Fluorescence spectrum of colloidal ZnO (0.0025 M conc.) for various pump power

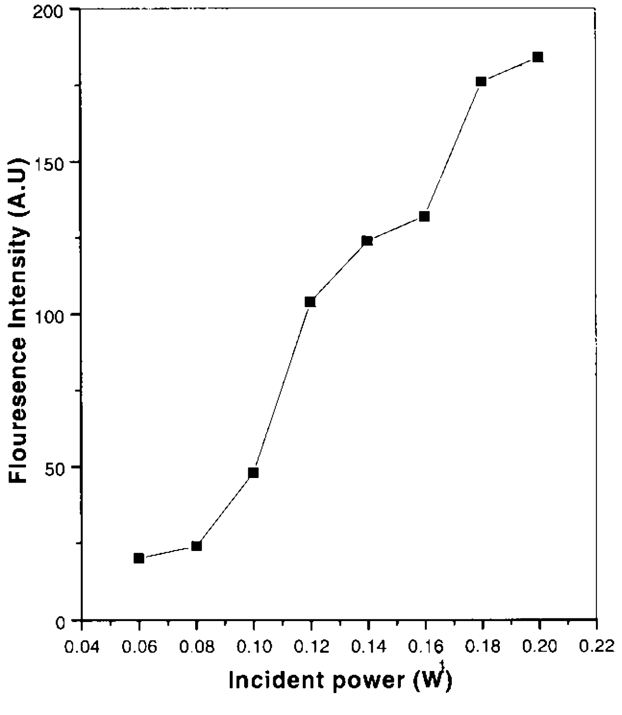

Fig. 4.3. Variation of fluorescence intensity with pump power of colloid of ZnO

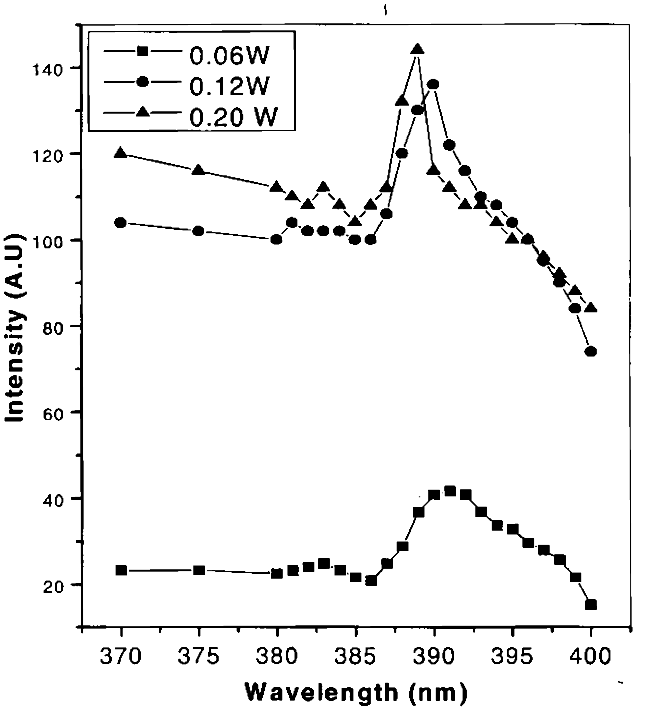

Fig.4.4. Fluorescence spectrum of colloidal ZnO (0.009 M conc.) for various pump power.

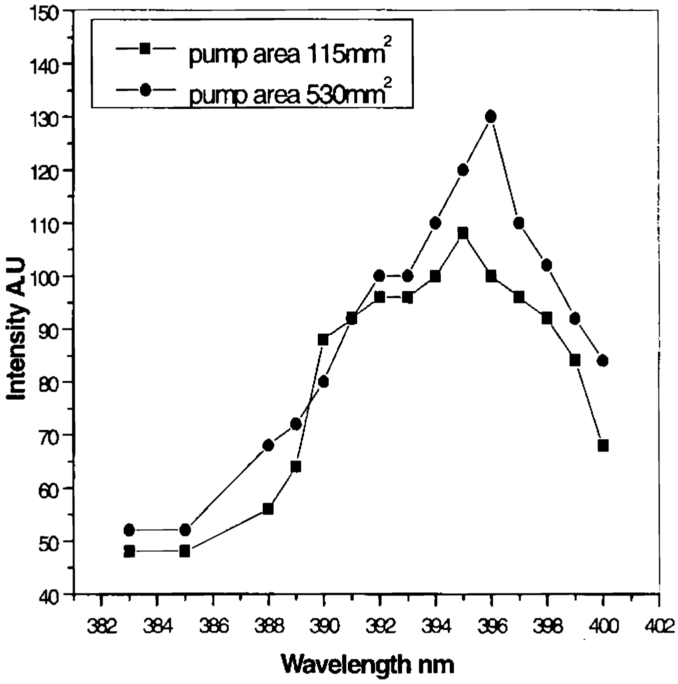

Fig.4.5. Variation of fluorescence when pump area is varied

The most striking characteristic of random lasing is the area-dependence. We cold also observe changes in the spectrum, when we limited the pumping area with an aperture. The area was changed from $530mm^2$ to $115mm^2$.Fig.4.5 compares the spectrum with and without aperture. We can see a small but definite shift as expected.

4.3.Conclusions

To conclude, we compared the fluorescence spectra of ZnO in nano structured and bulk form. We could observe that in nano ZnO, green emission dominates. From the fluence-dependent fluorescence, studies conducted in colloidal ZnO sample in DEG medium proved that it shows promise of being a good random lasing medium. Further studies with better experimental conditions and possibly imaging the spots with a CCD camera could yield more information.

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Chapter 5

STUDY OF BACKSCATTERING FROM ZnO

Abstract

Backscattering experiments give valuable information about any random media. Here we study backscattering in ZnO colloids of a few nm in size, prepared in two different media, by different methods. The intensity profile of backscattered cone gave Lorentzian profile as expected, indicating coherence. The FWHM of the backscattered cone and hence the mean free path varied with concentration in ZnO. The output also showed clear power dependence.

“Where the world ceases to be the scene of our personal hopes and wishes,
where we face it as free beings admiring, asking and observing,
there we enter the realm of Art and Science"

Einstein

Light scattering experiments have enjoyed renaissance after the invention of lasers and have gained prominence as potential applications of quantum optics and photon localization are conceived. Coherent backscattering is the hottest topic in this area. Most of the work done in this fascinating area, where localization effects begin to be manifested, has been concentrated in particles of sizes comparable to the wavelength of light used. In this chapter, we describe the results of backscattering studies of ZnO of a few nm in size, much less that the wavelength of light used.

5.1. Localization of light

Traditionally the theory of conductance of electrons was built on the picture of an electron being multiply scattered by impurities and diffusing through the solid. A cardinal concept in the description of this scattering process is the mean free path, the average length the electron travels before it suffers an elastic collision. In the theory of localization the main question is: *does a lower limit to the mean free path exist*? Will a monotonic increase of the degree of disorder be accompanied by a monotonic decrease of the mean free path? This issue was raised and solved, by Philip Anderson (1] in 1959 1958 He conceived the idea of electron localization: Beyond a critical amount of impurity scattering the diffusive motion of the electron will come to a halt. This will occur if the mean free path becomes smaller or on the order of wavelength (divided by 2π). There is not much to 'wave' anymore for a wave if its mean free path has become that short. Anderson localization of electrons in a disordered system has become a prominent part of condensed matter physics and remains an active subject of theoretical and experimental research.

Anderson localization is completely based on interference and interference is a common property of all wave phenomena, it is natural to extend electron localization to photon localization in disordered dielectric media. The idea of the light localization started to evolve in the beginning of the 1980's. Standard diffusion theory is obtained when neglecting all interference effects. In the localization regime this neglect is absolutely wrong. The probability for a wave returning to its point of origin can never be well described by neglect of all interferences. Every returning path can also be traversed in opposite direction and these paths have the same phase and interfere constructively. This means that interference will enhance the return probability (this is already a begin of localization). An enhanced returning probability translates in light scattering into *enhanced backscattering* or Coherent backscattering (CBS). The observation of enhanced backscattering of light together with the exposure of the close analogy with electron localization was reported by in 1985 and independently by M. van Albada and A. Lagendijk [2] and Maret and Wolf [3]. This is also known as ***weak localization of light***.

CBS in light can be detected experimentally since it is manifest as an enhancement in the intensity of light scattered in the exact backward direction. Moving away from this exact backward direction, phase differences will develop and average out the interference effect. The result is a cone on top of diffuse background. The width of this cone will be inversely proportional to the mean free path and hence is a measure of the amount of scattering inside the sample. The backscattering cone contains information about parts deep inside the sample, regions that cannot be accesses with normal optical techniques.

Furthermore, the increase in intensity in the backscattered intensity means a reduction in the amount of transmitted light. If we make l shorter and shorter, for instance by increasing the density of scatterers, transmission would be considerably reduced due to interference. In theory, it should be possible to decrease l so much that all light will be trapped inside the sample, similar to Anderson localization of light. This is known as ***strong localization***. A clean undisputed observation of Anderson localization of light has not yet been reported.

It is of tremendous interest to study the enhanced backscattering in detail, both theory and experiment, as there is intimate relation between this and strong localization.

5.2.Coherent backscattering – basic theory

The enhancement of intensity of light in the exact backward direction was first observed by A. Ishimaru and Y. Kuga [4] but it was not until the observations of M. van Albada and A. Lagendijk [2] and Maret and Wolf [3] that its connection with photon localization was made clear. Since then the phenomenon has been successfully studied in colloids strongly scattering powders [5,6], cold atom gases [7], two-dimensional random systems of rods [8], randomized laser materials [9], disordered liquid crystals [10,11], and even photonic crystals [12].

Fig.5.1 gives the schematic representation of a CBS experiment. Backscattered intensity from a colloidal suspension is recorded as a function of backscattering angle. The characteristic cusp shaped intensity profile with the theoretically predicted cone enhancement of two is illustrated.

In order to understand the origin of this enhanced intensity cone, the nature of the photon scattering within the colloidal suspension must be examined [13]. The simplest model describing this process is that the photons are undergoing a diffusion-like random walk with an average step size given by the transport mean-free-path length. However, since light in this experiment behaves as an electromagnetic wave, and not a classical particle, interference between scattering paths must be considered. It is just this interference between time-reversed (momentum-reversed) paths that gives rise to the CBS intensity cone. Figure 5.2 shows a prototypical scattering path and its time-reversed mate and also illustrates the existence of a path length difference (PLD) between the two.

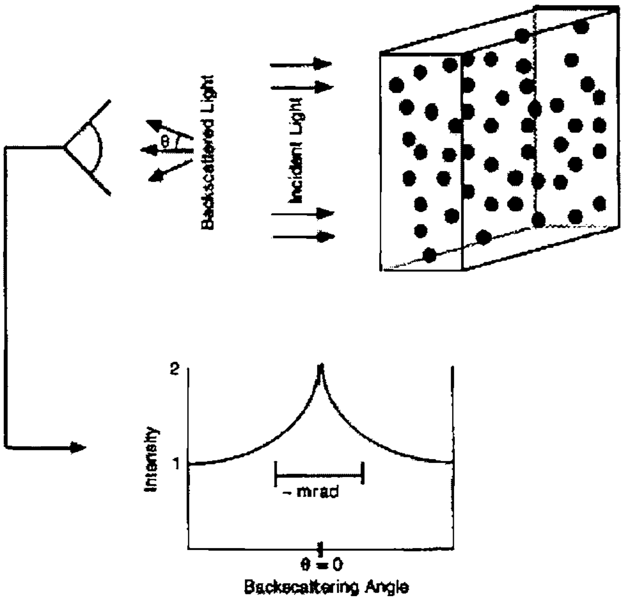

Fig.5.1. A schematic representation of a CBS experiment

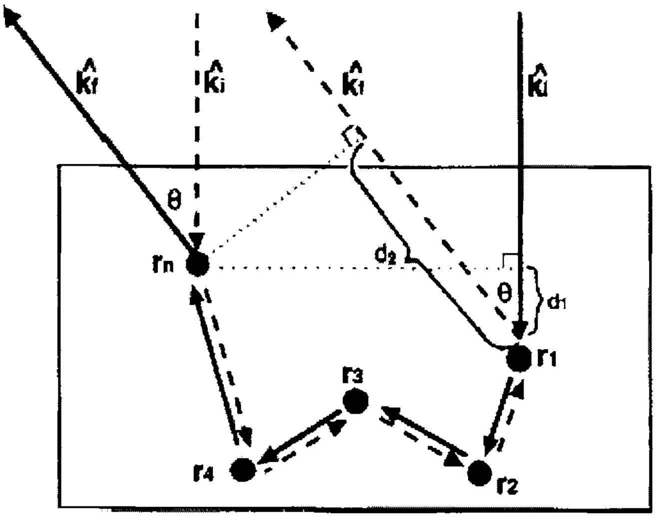

Figure 5.2. A prototypical scattering path (solid line) and its time-reversed mate (dashed line) with incident light direction and final direction.

Incident light direction and final direction are $\mathbf{k}_i$ **and** $\mathbf{k}_f$. Five scattering centers are shown with positions given by $\mathbf{r}_1$ through $\mathbf{r}_n$ relative to an arbitrary origin. The last scattering center is labeled $\mathbf{r}_n$ since the results of the analysis hold for any scattering order beyond single scattering.

The nature of the time-reversed scattering path interference depends on the phase difference between the two scattered waves. This phase difference is given as

$$\Delta\phi = \frac{2\pi}{\lambda}[d_2 - d_1] \tag{5.1}$$

For light scattered exactly in the backward direction $k_f = -k_i$

$$\Delta\phi = \frac{2\pi}{\lambda}(k_f + k_i)(r_n - r_i) \tag{5.2}$$

By evaluating the dot product, the phase difference becomes

$$\Delta\phi = \frac{2\pi}{\lambda}2\sin\left(\theta/_2\right)R\cos\alpha \tag{5.3}$$

where is the scattering angle measured from the backward direction R is $r_1 - r_n$ and α is the angle between $k_f + k_i$ and $r_1 - r_n$

For experimentally realized situations of small and assuming for a dense colloid, $r_1 - r_n$ will be nearly parallel to the sample surface and $k_f + k_i$, yielding $\cos\alpha \approx 1$

$$\Delta\phi \approx \frac{2\pi}{\lambda}\theta R \tag{5.4}$$

From photon diffusion theory we have

$$R^2 = 6Dt = 6\left(\frac{cl}{3}\right)t \tag{5.5}$$

Where D is the photon diffusion coefficient, t is the random walk time and c velocity of light. Substituting for R, s=ct we get

$$\Delta\phi \approx \frac{2\pi}{\lambda}\theta\sqrt{2ls} \tag{5.6}$$

In order for the two partical waves to add constructively, the phase difference should be small. So there is a critical angle θ_c below which this condition is maintained. The critical angle is given by

$$\theta_c = \frac{\lambda}{\sqrt{2ls}} \tag{5.7}$$

From this equation we can see that the coherent cone width varies inversely with mean free path length.

In the backscattering direction, the waves are coherent so we sum then square but if they are incoherent than we square then add. This gives an enhancement factor of two. The intensity profile can be derived within a diffusion approximation. [2]

$$I(q) = \frac{3}{16\pi}\left[1 + 2\frac{z_0}{l} + \frac{1}{(1+ql)^2}\left(1 + \frac{1-e^{-2qz_0}}{ql}\right)\right] \tag{5.8}$$

The dominating feature in this profile is the cone term. It gives a Lorenzian profile.

FWHM of the backscattered cone is related to the mean fee path by the relation

$$\text{FWHM} = \theta = \frac{0.7\lambda}{2\pi\square} \tag{5.9}$$

5.3.Experimental results

The experimental set up is described in chapter two. We have carried out backscattering experiments in ZnO in DEG medium, ZnO capped with PVP and screen printed ZnO.

Fig.5.3 shows the result of backscattering cone profile from ZnO in DEG medium. The concentration of the colloid is varied by adding different amounts of pure DEG. We can see that as conc. Is varied, the mean free path varies and accordingly the FWHM of the backscattered cone varies. The intensity profile is Lorentzian as predicted by the theory, confirming the coherent nature of scattered light.

Fig.5.4 gives the plot of FWHM of backscattering cone Vs Concentration. Relationship between backscattered cone width (θ) and mean free path ($\square$) is

$$\theta_c = \frac{0.7\lambda}{2\pi\square}$$

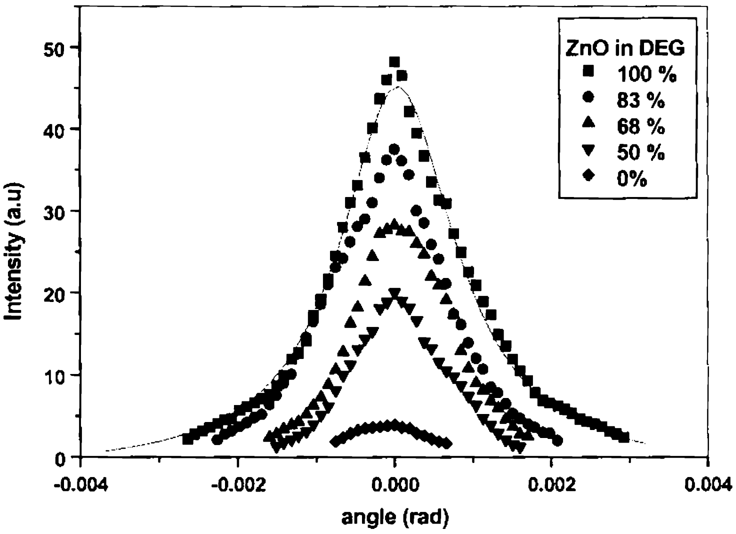

Figure 5.3. Backscattering profile for ZnO in DEG for various ZnO concentrations

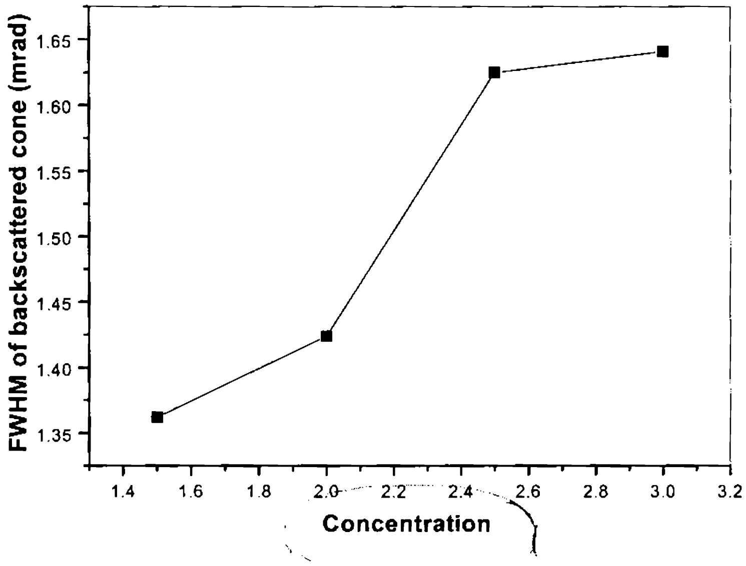

Fig.5.4. Variation of backscattered cone width with concentration

In the present case, magnitude of mean free path varies from 36.14, 36.43, 41.64, to 43.61μm as the concentration of ZnO in DEG decreases from 100 %, 83 %, 68 % to 50 %. The fact that the mean free path of half dilution is almost 1/1.414 of that of undiluted sample, matches with the diffusion approximation.

Fig.5.5 gives the result of backscattering from PCVP capped ZnO. Here the amount of capping agent is varied which in turn varies the particle size in the range 3-5nm. As the amount of capping agent is increased, the particle size is reduced which inturn reduces the particle-particle interaction.As per theory, mean free path *l* varies inversely with square of particle size.Hence, FWHM decreases. This fact is clearly seen in Fig.5.5.

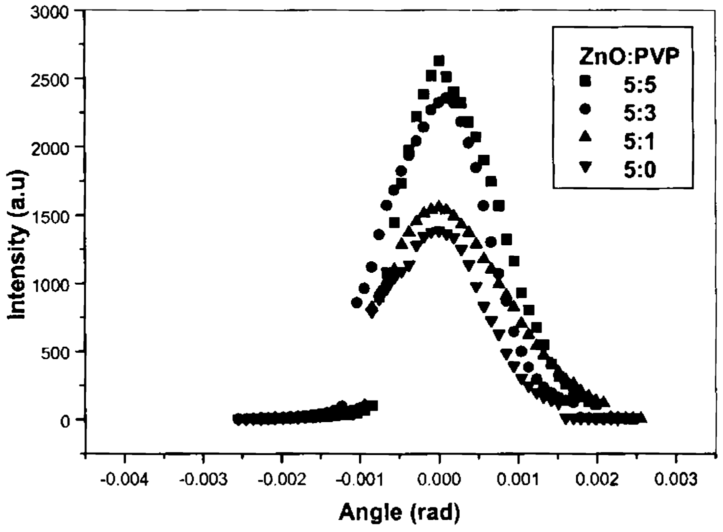

Figure 5.5: Backscattering profile for PVP capped ZnO sample for various ZnO:PVP ratio.

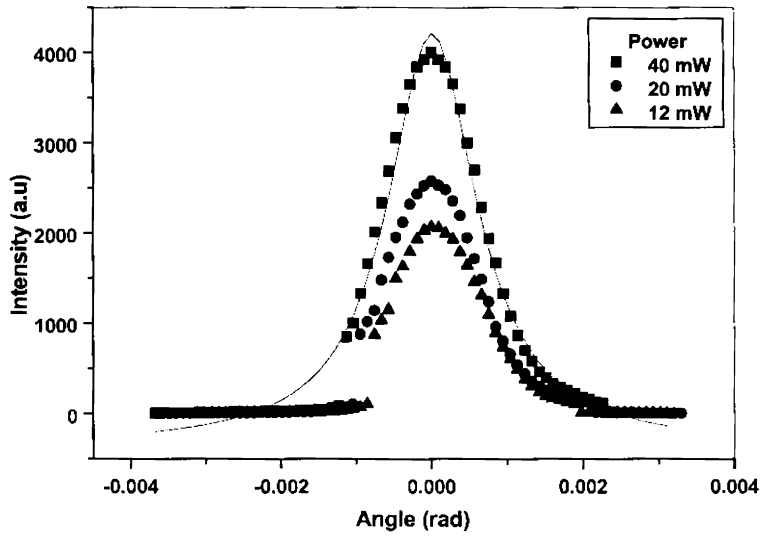

Figure 5.6: Pump power dependence of the backscattering profile from ZnO capped with PVP

In both colloidal samples, there is clear power dependence as can be seen in Fig.5.6. At higher pumping powers, multiple scattering events become predominant and the backscattered cone narrows down. The narrowing down of scattering cone is characteristic of coherent nature of scattered phenomenon. Hence we are observing the enhancement of backscattering better at higher pump levels.

Similar experiments were carried out thick film ZnO samples .ZnO powder extracted from Diethylene glycol was screen printed on glass substrates. Here also there was clear power dependence in the backscattering profile. The results are shown in Fig.5.7

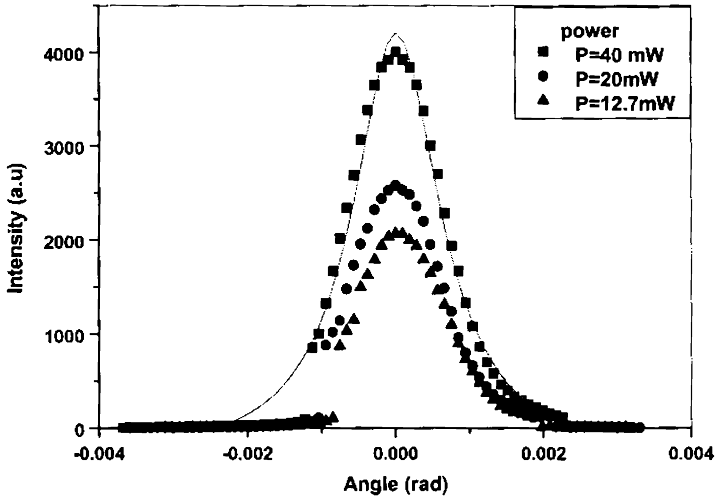

Figure 5.7: Pump power dependence of the backscattering intensity profile for Screen printed ZnO Sample.

Conclusions

Backscattering of light from colloidal suspension ZnO particles of nanometer size has been investigated. The width of the scattering cone decreases with the concentration of ZnO in DEG as well as with particle size of ZnO in PVP as per theory. The profile exhibits Lorentzian one, which characterizes the coherent nature of BS light. Power dependence is shown by screen printed sample also. We are modifying the experimental setup to get better resolution in the scattering cone with respect to coherent and incoherent scattering.

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Chapter 6

NONLINEAR OPTICAL STUDIES BY Z- SCAN TECHNIQUE

Abstract

In the present chapter, we focus on the evaluation of nonlinear optical susceptibility of nano ZnO colloids employing the technique of single beam z-scan, at a wavelength of 532 nm. Open-aperture curve exhibits a normalized transmittance valley, indicating the presence of nonlinear effect resulting from intensity dependent absorption. Nonlinear absorption coefficient and third order susceptibility is calculated. It has been observed that the samples display large third order nonlinearity with pronounced fluence dependence. The Enhanced absorption at higher input intensity can be attributed to free carrier absorption following two photon absorption (TPA). These studies show that colloidal nano ZnO medium is a promising Nonlinear Optical material.

"The man of science observes what nature offers with the eye of understanding, but her beauties are not lost on him for that reason. More truly it can be said that understanding refines our vision and heightens our appreciation of what is striking and beautiful"

C.V.Raman

Introduction

For many optoelectronic applications like optical limiting and switching, the knowledge of the nonlinear optical properties of materials is necessary. There are number of nanosized organic nonlinear optical materials and semiconductor structures of low dimension are a new entry into the field of NL optics. There are many methods to study the NL properties of materials. Z-Scan is a fairly accurate and convenient method to study transparent samples. In this chapter, we will discuss the Z-Scan measurements carried out in nano ZnO colloids.

6.1. Nonlinear optics

NL Optics is essentially concerned with the study of phenomenon that result from field induced modifications in the optical properties of materials. Measurements using conventional light sources give a polarization P which is linearly dependent on electric field strength E

$$P = \varepsilon \chi E \qquad (6.1)$$

Where ε is the susceptibility of vacuum This domain of interaction of electric field with matter is called linear optics. With the invention of lasers, which has high degree of spectral purity, coherence, intensity and directionality, it became possible to irradiate atoms and molecules with radiation of intensity that corresponds to E which is comparable to inter atomic field. Consequence is that, induced polarization becomes a function of higher powers of electric field showing nonlinear (NL) dependence on electric field. In such cases, polarization is expressed as

$$P = \varepsilon \left[\chi_1 E_1 + 2\chi_2 E_2 E_3 + 4\chi_3 E_1 E_2 E_3 + ... \right] \qquad (6.2)$$

Here χ_2 and χ_3 are called second order and third order susceptibilities respectively.

In the NL optical regime, a number of interesting phenomena like second harmonic generation, third harmonic generation, optical limiting emerge that are absent in linear regime. Many of these NL effects have important scientific and technological significance .The magnitude and response of third order nonlinear susceptibility is one of the important parameters of NL materials and several techniques exist for measuring these parameters. Z-scan[1], Degenerate Four Wave Mixing (DFWM)[2], Third Harmonic Generation (THG)[3], Time resolved optical Kerr effect[4], three wave mixing[5], ellipse rotation[6], beam distortion measurements[7] etc. are different techniques used for this purpose. Using z-scan, the sign and magnitude of the third order susceptibility tensor can be calculated. Degenerate Four Wave Mixing can give both the magnitude and response of the third order nonlinearity. Similarly, THG is another technique used for the measurement of the magnitude of the third order susceptibility tensor. Electro absorption is used for the dispersion studies of third order nonlinearity and the time resolved optical Kerr effect is used for the photo physical processes determining the nonlinearity.

6.2. Nonlinear absorption

The amount of light absorbed in most of the absorbing, materials increases linearly with input irradiance, giving rise to a constant transmittance. This is referred to as linear absorption and is independent of intensity of light. In such cases, absorption in the sample can be fully explained by Beer-Lambert law. If α is the linear absorption coefficient, transmitted intensity I_t is related to input intensity Io by

$$I_t = I_0 e^{-\alpha\lambda} \tag{6.3}$$

Where λ is the sample length. Any deviation from the behaviour in the above equation is called nonlinear absorption. Here α can increase or decrease with respect to incident intensity so that α becomes a function of wavelength as well as I.

The intensity dependent absorption arises due to third order optical nonlinearity in which the complete refractive index can be written as $n(I) = n_1 + n_2 I$.Both n_1 and n_2 are complex quantities. For a given wavelength, if α increases with intensity, the effect is called Reverse Saturable absorption (RSA).On the other hand, if α decreases with intensity, it is called Saturable absorption. In RSA, sample becomes more and more opaque as intensity is increased due to enhanced absorption at higher intensities. This phenomenon is exploited in passive optical power limiting to protect optical sensors, including human eye, from intense laser pulses.

Optical limiting is achieved primarily by materials, which absorb strongly at high intensities i.e. Reverse saturable absorption (RSA). A number of compounds have been found to possess such a property [8].

At sufficiently high intensities, enhanced absorption of radiation in the normally transparent region of the spectrum is observed due to multiphoton absorption process. The probability of absorption of N photons by such a process at a given λ is proportional to $\sigma_N I^N$ where σ is the N photon absorption cross-section, I the intensity of radiation and N is the no. of photons absorbed in a single multiphoton absorption event. When N is 2, it is called two photon absorption (TPA). In the process of TPA, an atom makes a transition from its ground state to the excited state by the simultaneous absorption of 2 laser photons (Fig.6.1).

Another reason for RSA to occur is the absorption cross section σ_{12} from the first excited molecular state to the higher state being greater than σ_{01} from ground state to first excited state. As the optical excitation intensity increases, more molecules are promoted to the excited state, thus giving rise to higher absorption (Figure 6.1).

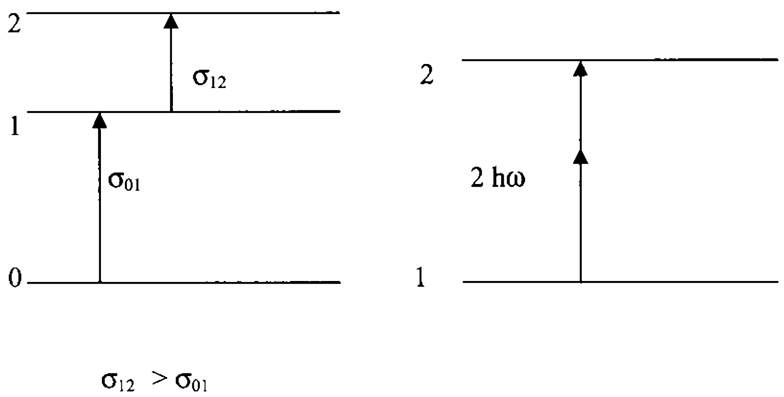

Fig.6.1. Energy level diagram showing (a) Excited State absorption ESA (b) Two Photon Absorption(TPA)

The nonlinear dependence on intensity implies that such a process can be localized to a chosen region of the absorbing material by focusing the radiation. This has served as the basis of a host of new technologies like 2 and 3 photon microscopy [9], fluorescence correlation spectroscopy in live cells etc in biology[10], optical data storage[11], lithography[12], optical limiting [13]etc.

6.3. Nonlinear optical properties of quantum dots

Nanometer sized semiconductor materials are good NL candidates because they exhibit large third order NL effect due to quantum confinement effects and interfacial effects. Two important discoveries in the early eighties awakened the current interest in the NL properties of quantum dots. Quantum confined stark effect [14] and large and relatively fast NL response in colour glass filters containing CdS:Se nanoparticles by Jain and Lind [15]. To avoid the masking of quantum size effects by inhomogeneous broadening, the particles must be strictly of uniform size. In spite of the limited control available in the preparation of semiconductor-doped glasses, they have come to occupy an important place in the family of NL optical materials [16].

Apart from quantum confinement effects, the optical properties of quantum dots are also influenced, sometimes strongly, by the fact that the field seen by the electrons in QD differs from the applied field. Much work has been done on the local field effects of nano composite materials in terms of Maxwell-Garnet theory [17]. When the size of the constituents is comparable to the wavelength of light in any composite material, the most important effect is the enhancement of local field due to interference. The starting point of the theory for this is that for a dielectric sphere of radius smaller than wavelength of light, the field inside the sphere is given by

$$\frac{E_S}{E_0} = \frac{3}{2+\varepsilon(\omega)} \tag{6.4}$$

where $\varepsilon(\omega)$ is the dielectric constant relative to the embedding medium. Clearly the field would be resonantly enhanced at a frequency ω given by $\varepsilon(\omega) = -2$. In metals, this corresponds to the excitation of surface plasmon mode and occurs in visible region. In semiconductor nanoparticles it is obtained on higher frequency side due to excitons [18].

Another important factor determining the NL effects of quantum dots is the major role played by surface states. Due to large surface area, there are large number of atomic vacancies or defects on its surfaces that can become trapped states for electric charge. When excited by external radiation, these trapped states would cause nonradiative transfer for photo excited carriers and can contribute to NL effects. For semiconductor nanoparticles coated by a layer of organic molecules on their surfaces, great enhancements of third-order optical nonlinear susceptibility have been predicted and observed in the single-photon resonance region [19,20].

Optical nonlinearities in the transparent spectral region of semiconductors can be classified into two main categories, viz (1) third order nonlinearity arising from bound-electronic effects and Two photon absorption (TPA) and (2) Free Carrier absorption (FCA) due to the photo excitation of free carriers [21]. It is known that TPA is important in femtosecond time domain while free carrier effects are important in the nanosecond region and longer.

Justus and Tonucci [22] investigated the nonlinear optical properties of quantum-confined GaAs and InP microcrystallites deposited in vycor glass, and significant enhancement of nonlinear optical response were observed. Baolong Yu et al [23] observed the same kind of enhancement in coated Bi_2O_3 nanoparticles when studied using Z-Scan technique. K.S.Bindra et al has studied the nonlinearity of nanosized semiconductor doped glasses using femtosecond pulses to distinguish between 3rd order and 5the order nonlinearities [24]. More and more papers are appearing in literature dealing with the topics related to this exciting area [25-28].

6.4. ZnO as a new nonlinear optical (NLO) material

In recent years, wide-gap semiconductors, in general and ZnO in particular, have been subjected to intense studies because these materials can be used to develop laser diodes and optoelectronic devices operating in the short wavelength regions. For all these applications, a thorough understanding of the third order nonlinearity and response time and basic mechanism responsible for the nonlinearity is needed.

Recently, ZnO is being considered as a possible candidate for optical limiting applications as well. Relatively little work has been done on exciton dynamics and optical nonlinearities of ZnO. Z-Scan technique has been used to measure the third order nonlinearity in bulk ZnO [29,30]. and in ZnO microcrystalline thin films by many [31-33].Second harmonic[34] and third harmonic[3] generation in ZnO thin films have also been observed and is due to second order optical nonlinearity. However, in ZnO colloids relatively little work has been done. For example, Guo et al [35] reports enhancement in third order nonlinear susceptibility in PVP capped ZnO colloid by DFWM technique.

6.5. Z-Scan technique

The Z-scan technique is a simple and effective experimental method to measure intensity dependent nonlinear optical susceptibilities of materials. Z-scan technique was originally introduced by Sheik Bahae *et.al* [1]. In this method, the sample is translated in the Z-direction along the axis of a focussed Gaussian beam, and the far field intensity is measured as function of sample position. This technique helps us to measure the sign and magnitude of both real and imaginary part of the third order nonlinear susceptibility coefficient $\chi^{(3)}$ of materials.

Z-Scan technique exploits the light matter interaction in which an incident beam propagating inside a NL medium induces a self phase change thereby producing a wavefront distortion of the beam. Thus a laser beam propagating through a nonlinear medium will experience both amplitude and phase variations. If we measure the transmission intensity of a focused laser beam as a function of distance from the sample, we will get information about nonlinear refraction and nonlinear absorption by the medium respectively.

This technique has several *advantages*, some of which are

- Simplicity: No complicated alignment except for keeping the beam centered on aperture.
- Simultaneous measurement of both sign and magnitude of nonlinearity.
- Data analysis is quick and simple except for some particular conditions.
- Possible to isolate the refractive and absorptive parts of nonlinearity unlike in DFWM.
- Close similarity between the geometries of Z-Scan the Optical Power Limiting techniques.

Some of the *disadvantages* include

- Stringent requirement of high quality Gaussian TEM_{00} beam for absolute measurements
- For non-Gaussian beams the analysis is completely different. Relative measurements against a standard samples allows relaxation on requirements of beam shape
- Beam walk-off due to sample imperfections, tilt or distortions

6.6. Theory of open aperture Z-scan technique

There are two techniques employed in Z-Scan studies (1) Open aperture Z-Scan and (2) Closed aperture Z-Scan. Nonlinear absorption of the sample is manifested in the open aperture Z-scan measurements. For example, if nonlinear absorption like two-photon absorption (TPA) is present, it is manifested in the measurements as a transmission minimum at the focal point [8]. On the other hand, if the sample is a saturable absorber, transmission increases with increase in incident intensity and results in a transmission maximum at the focal region. A straight-line z-scan graph is obtained in the case of samples with linear absorption. These three cases are represented graphically in Fig.6.2.

All three curves in Fig.6.2.are normalized to give a transmittance of one in the linear region (i.e. regions of large $|z|$). Sample positions are presented in units of z/z_0 where z_0 is the diffraction length.

In the case of an open aperture z-scan, the transmitted light measured by the detector is sensitive only to the intensity variation. Therefore the phase variations of the beam can be neglected safely. The theory of Z-scan experiment outlined below is same as that given by M Sheik Bahae et. al. in reference [1].

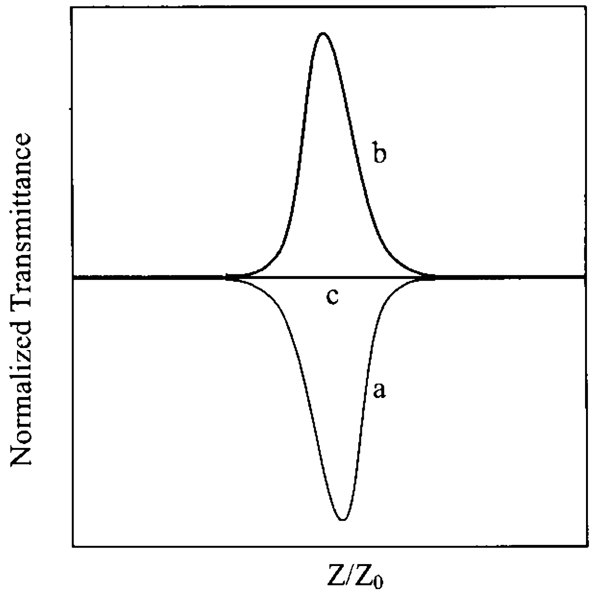

Fig. 6.2. Open aperture z-scan curves for
a) Excited State Absorption b) Saturable absorbers and c) linear absorption.

The intensity dependent nonlinear absorption coefficient α(I) can be written in terms of linear absorption coefficient α and TPA coefficient β as [1]

$$\alpha(I)=\alpha+\beta I \tag{6.5}$$

The irradiance distribution at the exit surface of the sample can be written as

$$I_r(z,r,t) = \frac{I(z,r,t)e^{-\alpha l}}{1+q(z,r,t)} \tag{6.6}$$

where

$$q(z,r,t) = \beta I(z,r,t)L_{eff} \tag{6.7}$$

L_{eff} is the effective length and is given, in terms of sample length l and α by the relation

$$L_{eff} = \frac{(1-e^{-\alpha l})}{\enclose{circle}{\alpha}} \tag{6.8}$$

The total transmitted power P(z, t) is obtained by integrating Eq. (6.6) over z and r and is given by

$$P(z,t) = P_l(t)e^{-\alpha l}\frac{\ln[1+q_0(z,t)]}{q_0(z,t)} \tag{6.9}$$

$P_l(t)$ and $q_0(z, t)$ are given by the equations (6.10) and (6.11) respectively.

$$P_l(t) = \frac{\pi\omega_0^2 I_0(t)}{2} \tag{6.10}$$

$$q_0(z,t) = \frac{\beta I_0(t)L_{eff}z_0^2}{z^2+z_0^2} \tag{6.11}$$

For a pulse of Gaussian temporal profile,(6.9) can be integrated to give the transmission as

$$T(z) = \frac{C}{q_0\sqrt{\pi}}\int_{-\infty}^{\infty}\ln(1+q_0e^{-t^2})dt \tag{6.12}$$

Nonlinear absorption coefficient is obtained from fitting the experimental results to the (6.12).

If $|q_0| < 1$, (6.10) can be simplified as

$$T(z,S=1) = \sum_{m=0}^{\infty}\frac{[-q_0(z,0)]^m}{(m+1)^{3/2}} \tag{6.13}$$

Once an open aperture z-scan is performed, nonlinear coefficient β can be unambiguously deduced.

6.7. Experimental results and Discussions

Details of the experimental set up are as described in chapter 2. Z-Scan measurements were carried out in ZnO colloids prepared by polyol synthesis and those capped by PVP an PEI. Result of the measurements from ZnO colloid in DEG medium which corresponds to the far-field normalized transmittance as a function of the distance is shown in Figure 6.3. for three different input energies. The open-aperture curve exhibits a normalized transmittance valley, indicating the presence of nonlinear effect resulting from intensity dependent absorption. The parameter q in Fig.6.4.is the depth of the valley obtained from the theoretical fit and is a measure of intensity dependent absorption and I is the irradiance at focus.

The data were analyzed by using the procedure described by Sheik Bahae *et. al* and the nonlinear absorption coefficient β is obtained by fitting the experimental z-scan plot with the theoretical plot from which susceptibility is calculated. The values of nonlinear absorption coefficient β and $\operatorname{Im}\chi^{(3)}$ obtained from the present studies at different energy levels are given in Table I.

We have observed very strong fluence-dependence of absorption in this sample. A laser pulse can cause interband or intraband excitations.In the present case of ZnO, a two photon absorption can take the excitons to the conduction band and once this has occurred, cascaded multiphoton induced intraband excitations within the conduction band is possible

Fig.6.5 gives the Z-Scan traces of PEI capped ZnO samples. Figure 6.6 gives the Z-Scan traces in PVP-capped ZnO samples. Fig.6.7 gives the loq vs log I plot of PEI capped sample. Both samples show photon absorption effect after the occurrence of two photon absorption. But fluence-dependence in ZnO:PEI system is not as pronounced as in the case of ZnO-DEG samples. The reason for this could be the fact that the volume fraction of ZnO in the DEG sample is one order higher than the capped samples. However, the exact mechanism can be explained only after Z-Scan measurements are made using femto second pulses. Our plans include such studies and time - resolved Z-Scan measurements in these samples.

Table.I gives the comparison of nonlinear optical susceptibilities and absorption coefficients of the three samples.

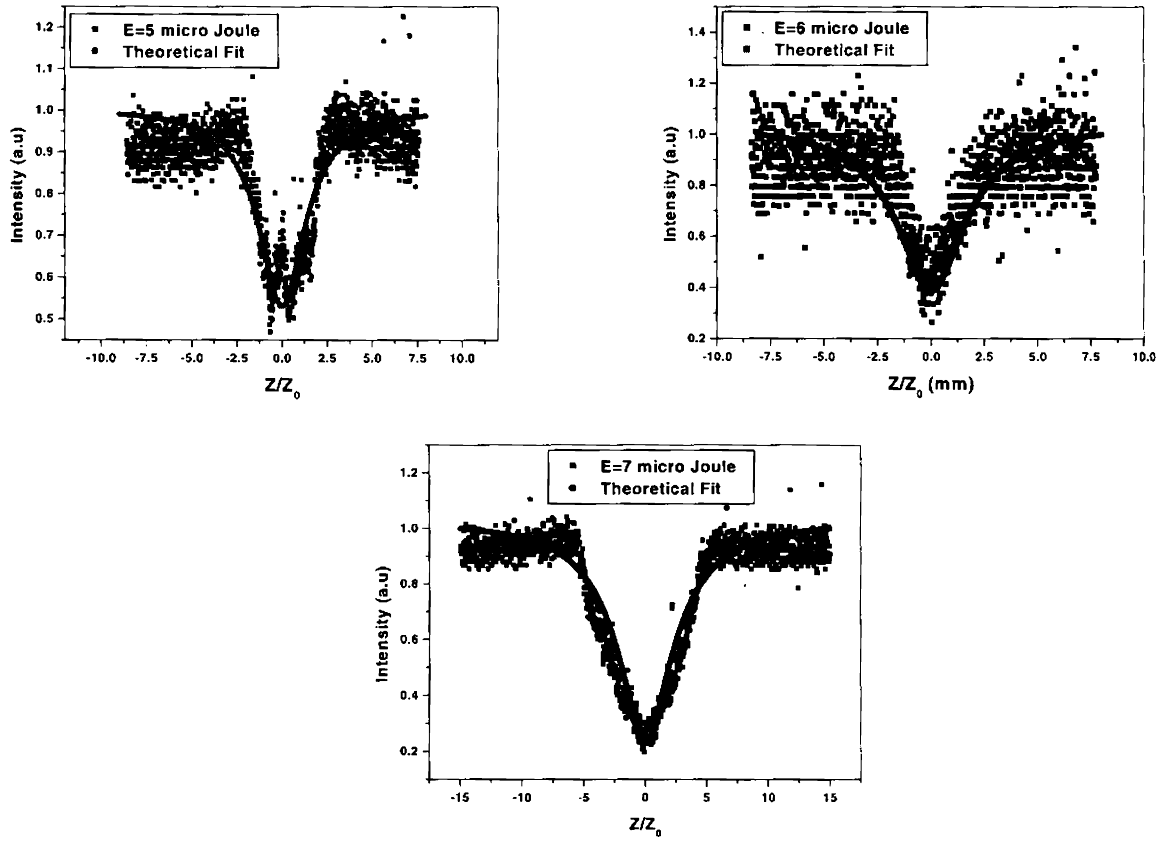

Fig.6.3. Z-Scan traces of ZnO-DEG system for various pump power along with theoretical fit

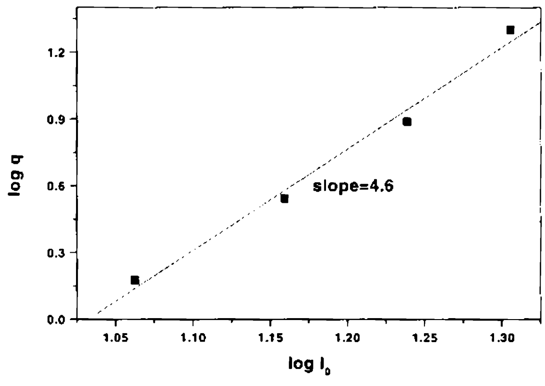

Fig.6.4. Plot of log q versus log I of ZnO-DEG system where q is the depth of valley in the open aperture Z-Scan

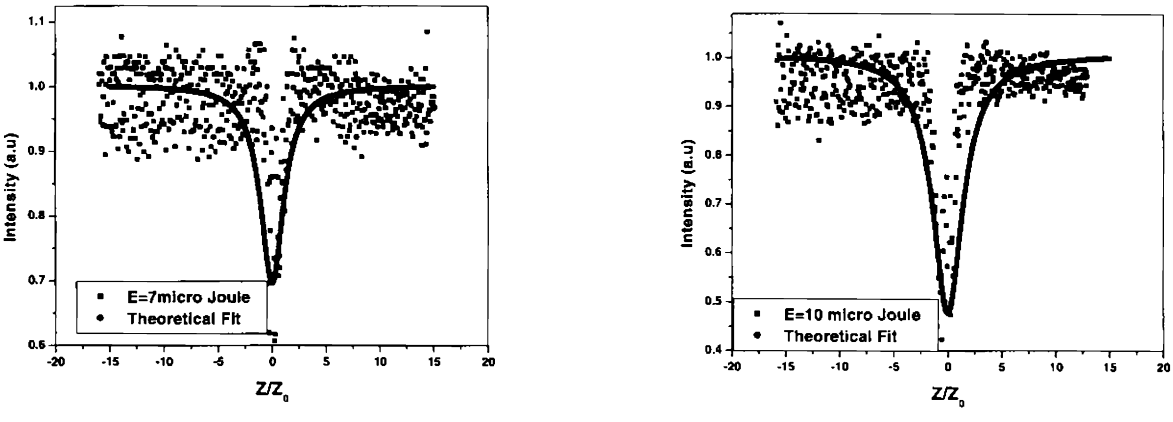

Fig.6.5 Z-Scan traces of PEI capped ZnO samples for two pump powers along with theoretical fit

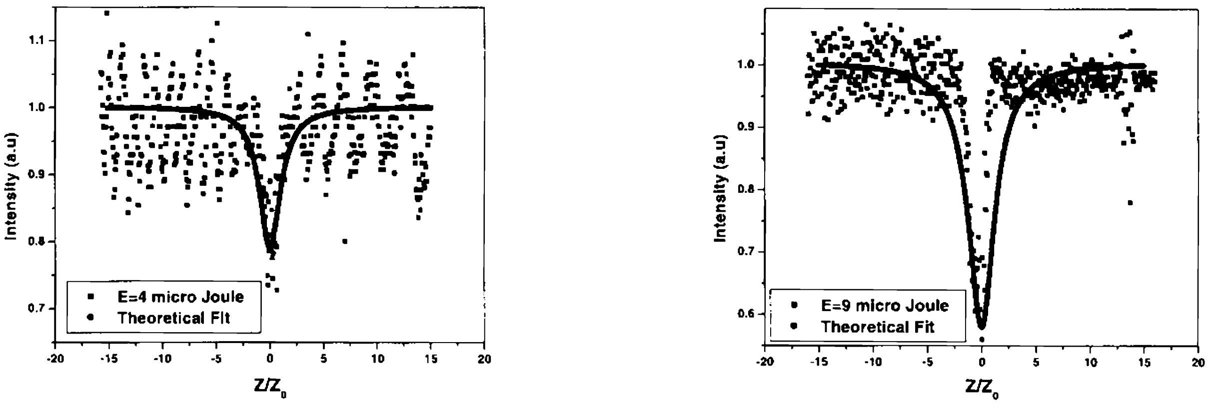

Fig.6.6 gives the Z-Scan traces of PVP capped ZnO samples for two pump powers along with theoretical fit.

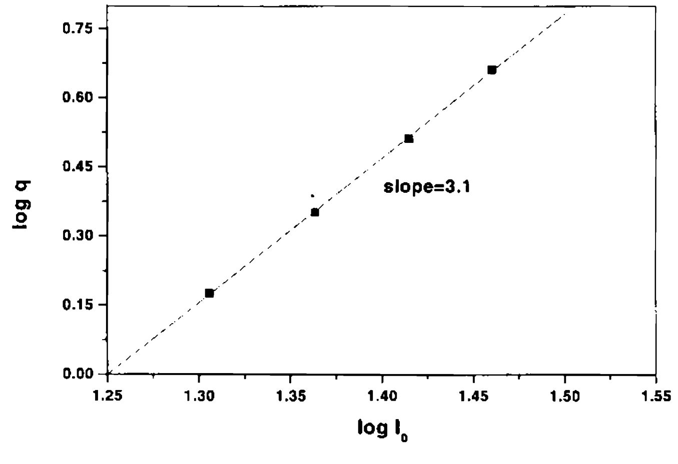

Fig.6.7. Plot of log q versus log I of PVP capped ZnO system where q is the depth of valley in the open aperture Z-Scan

	E μJ	β cm/GW	$\mathrm{Im}(\chi)$ $*10^{-20}\ \mathrm{m^2V^{-2}}$
ZnO-DEG	4	8.7	7.89
	5	16.2	14.73
	6	30	27.18
	7	66.3	60.12
ZnO-PEI	7	5	4.51
	8	6.5	5.92
	9	8.4	7.60
	10	10.7	9.68
ZnO-PVP	4	4.9	4.47
	6	5.2	4.74
	7	5.3	4.81
	9	7.1	6.43

Table I. Comparison of Nonlinear absorption coefficients and susceptibilities of the three ZnO samples

6.8. Conclusions

The Z-Scan studies conducted in colloidal ZnO samples of different preparation histories showed large nonlinear third order susceptibilities. Strong fluence-dependence which could be attributed to free carrier absorption following two photon absorption is observed. However, time -resolved Z-Scan studies in pico and femto second regimes are essential for the exact determination of various contributions to the enhancement in nonlinear susceptibility.

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Chapter 7

GENERAL CONCLUSIONS AND FUTURE PROSPECTS

Abstract

In this final chapter, a summary of the thesis and the conclusions drawn are given. Also some thoughts about what more can be done in this area...

"When you want something, all the world conspires to help you to achieve it"

Paulo Coelho, in 'The Alchemist'

Nanosized semiconductor structures exhibit many fascinating properties and have a multitude of potential applications. ZnO is one of such material which is undoubtedly a technologically important one. Nanosized ZnO in the form of quantum dots, nanorods, nanobelts and nanorings are expected to revolutionize the future. In the field of photonics also, the interest in ZnO has intensified dramatically after the demonstration of random lasing action in ZnO clusters. Keeping these in mind, this thesis focused on the synthesis of nanosized ZnO, a few attempts at processing thick and thin films of nano ZnO and various laser induced studies in these samples.

For synthesis of nano sized ZnO, different chemical routes were adopted. Growing semiconductor nanocrystals in solutions by chemical methods has many advantages- Relatively low precipitation temperature, Scope of capping the surface by various organic ligands, thus providing a way to control the surface states and relatively low cost are some of them.

In the present study, the first method was polyol synthesis, a hydrothermal method in diethylene glycol medium. ZnO colloids of relatively high volume fractions could be obtained by this method, which proved to be an asset later during nonlinear optical studies. This method was also found to be highly suitable to produce flexible polymer-ZnO films. The medium of growth, diethylene glycol, happens to be a known plastisizer in tape casting, imparting flexibility to the tapes. Hence the colloid as such could be mixed with the polymer PMMA and good transparent films were obtained by tape casting technique. This avoided the common problems of agglomeration and coagulation often encountered when trying to introduce a powder into a viscous polymer. ZnO- Polymer films are commercially much in demand as efficient UV protection filters.

A slight modification of the polyol synthesis by the addition of supernatant proved to be very effective in giving strictly uniform sized ZnO particles arranged in a regular manner. Only some preliminary attempts were made in this direction and there is much scope for future works. Such studies are important since it could be used to produce photonic band gap materials by self-assembly technique.

The other methods involved capping the surface by different organic ligands. Here we have found a new capping agent, Polyethylene Imine, for producing stable ZnO colloids with arrested growth. PEI is commonly used as a dispersant in aqueous processing but our time dependent absorption spectroscopic studies proved that it is acting as an efficient capping agent by a dual mechanism.

Nano crystals in the form of colloidal suspensions are good for conducting basic studies to understand physical phenomena but are of little use from the point of view of practical applications. Hence attempts were made to get thin and thick films from the synthesized ZnO. The capped colloids could be readily used for getting thin films by dip coating method since the capping agent PVP is also a known wetting agent which can give good quality films on glass substrates. Powder extracted from DEG medium was used to make thick films by screen printing technique. Screen printed ZnO is popular for solar cell applications.

Absorption spectroscopy is the main characterizing technique used in the present study to assess crystal size in the absence of in-house SEM/TEM facilities. We used a relatively new analytical formula for calculating the size from the shift of absorption edge.

Fluence-dependent fluorescence studies in ZnO colloids proved that they are good candidates for random lasers. There was clear line narrowing effects beyond a certain pump threshold. Our back scattering studies also confirm multiple scattering and weak localization in ZnO samples. Besides the pure academic interest in random lasers because of the exciting possibility of photon localization, random lasers may find many future applications, such as Field Emission Displays and super radiant LEDs. ZnO is at present the best candidate in this promising area.

Nano materials are a relatively new entry into the world of nonlinear optical materials. Quantum confinement effects and local field enhancement are expected to contribute to large third order effects. Everyday new results with widely varying explanations are coming up in this area. In our case, Z-Scan studies in ZnO colloids prepared by different routes gave interesting results. All showed highly fluence-dependent third order optical nonlinearity. This can be attributed to Free carrier absorption following two photon absorption.

Nonlinear studies in quantum dots offer a fascinating area where much work can be done. Nanocomposites are especially worth mentioning. This includes both polymer-ZnO composites and ZnO surface coated with different organic and inorganic materials. How different surface modification affects photoluminescence is another interesting area. When the spherical particles are converted into nano rods by changing the solution conditions like pH, how the luminescence and nonlinear optical properties are altered is another possible direction for future studies. For ZnO, the future is bright and for nano ZnO, it is even more so...This is an area where little means more. The smaller we can get, the higher we can go.