STUDY OF NONLINEAR OPTICAL PROPERTIES ON ZINC OXIDE NANORODS

PROJECT REPORT

Submitted by

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DEPARTMENT OF PHYSICS

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CERTIFICATE

This is to certify that the project report entitled "**STUDY OF NONLINEAR OPTICAL PROPERTIES ON ZINC OXIDE NANORODS**" is an authentic work done by **AADIYA SALBI (AM22PHY001)** under my guidance at Department of Physics, St. Teresa's College (Autonomous), Ernakulam for the partial fulfillment of the requirements for the award of the Degree of Master of Science in Physics during the year 2023-24. The work presented in this dissertation has not been submitted for any other degree in this or any other university.

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DECLARATION

I, AADIYA SALBI, final year MSc. Physics student of the Department of Physics and Centre for Research, St. Teresa's College (Autonomous), Ernakulam, do hereby declare that the project report entitled "**STUDY OF NONLINEAR OPTICAL PROPERTIES ON ZINC OXIDE NANORODS**" has been originally carried out under the guidance and supervision of **Dr. SANTHI A,** Assistant Professor, Department of Physics, St. Teresa's College (Autonomous), Ernakulam in partial fulfilment for the award of the Degree of Master of Physics. I further declare that this project is not partially or wholly submitted for any other purpose and the data included in this project is collected from various sources and are true to the best of my knowledge.

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Aadiya Salbi

STUDY OF NONLINEAR OPTICAL PROPERTIES ON ZINC OXIDE NANORODS

ABSTRACT

This work focuses on the nonlinear branch of optics wherein the investigation of nonlinear absorption coefficient of Zinc Oxide Nanorods of approximately 200 nm has been found out. Zinc Oxide nanorods for this work has been prepared using the Hydrothermal method and characterised using UV-Visible Spectroscopy, FTIR and SEM imaging. The nonlinear property of the prepared Zinc Oxide Nanorods were then studied using the Z Scan technique.

CONTENTS

CHAPTER 1

INTRODUCTION

Abstract: This chapter provides an insight on the branch of optics which deals with the nonlinear behaviour of optical media which is the nonlinear optics. Through this chapter an introduction to Z Scan technique, the technique to measure the nonlinear absorption coefficient and refractive index of a material has also been done. Along with these the advantages and application of the nonlinear optics are also being discussed upon.

1.1 HISTORY

The development of nonlinear optics began when Arthur L. Schawlow and Charles H. Townes in 1958 proposed a laser device. Later in 1960 Theodore Maiman developed the first operational laser, an acronym for "Light Amplification by Stimulated Emission of Radiation". These lasers produced highly monochromatic and coherent light with very high intensities. Later in 1961 a group led by Peter Franken demonstrated second harmonic generation, a prominent nonlinear effect where frequency doubling of light occurred. In the second harmonic generation light came in at one frequency and came out at twice the frequency.

But things had already started developing in the field of nonlinear optics as early as in the nineteenth century, i.e., even before the invention of laser when two other noteworthy discoveries occurred. These discoveries were made by John Kerr and C. A. Pockels. While Kerr in 1875 described a quadratic field effect which later on was called Kerr Effect, Pockels in 1883 described a linear effect which got the name Linear Pockels Effect. The Kerr Effect and the Linear Pockels Effect was later on understood to be the third order nonlinear effect and second order nonlinear effect respectively. Later on, various processes including nonlinear coupling between acoustic and optical waves in a medium (Leon N. Brillouin), Raman effect (Chandrasekhara V. Raman and Kariamanickam S. Krishnan) and many more were identified to be third order nonlinear effects.(1)

But the nonlinear branch of optics grew enormously when laser came into existence. The property of laser which played crucial role in changing the nonlinear optics were that it could amplify light and hence produce high intensity beam of light which is highly directional and coherent. The powers of lasers varied from 10^{-9} to 10^{20} W with frequencies ranging from 10^{11} to 10^{17} Hz (which corresponds from microwave region to soft X ray spectral region).

Along with this, nonlinear optical effects like second harmonic generation (SHG), sum-frequency generation (SFG), difference- frequency generation (DFG), optical parametric oscillation and third harmonic generation all were observed. Furthermore, the introduction of lasers played a crucial role in accelerating the synthesis of various new nonlinear optical materials which demonstrated the frequency conversion and parametric oscillation properties and hence led to the development of new tunable laser systems. Later in 1961 Franken published the paper reporting the use of a quartz crystal as nonlinear material to observe second harmonic generation which became the turning point in the research field of nonlinear optics (2).

1.2 NONLINEAR OPTICS

Nonlinear optics thus is defined as the branch of optics which deals with the nonlinear behaviour of light in nonlinear optical media. In nonlinear optical media the polarization density, P responds nonlinearly to the applied electric filed, E of the light. This understanding of how polarization induced in a material changes the optical nature of a medium is necessary to understand what nonlinear optics is. The change in refractive index which occurred in a material when the electric field is applied to it is called electro-optic effect. But this electric effect must be high enough to bring out the nonlinear activity of a material. (3)

In a primary glance the nonlinear optical effects manifest themselves as second harmonic generation, optical parametric amplification, sum and difference frequency mixing, third harmonic generation and self-focusing (intensity dependent refractive index). Of all these, the third harmonic generation is the prominent one in centrosymmetric and isotropic materials (i.e., materials with an inversion symmetry) as they do not produce second order nonlinear effects. Centrosymmetric materials include liquids, gases and amorphous solids like glass. While third order nonlinear optical effects can be exhibited by both centrosymmetric and non-centrosymmetric crystals, second order nonlinear optical effects can only be exhibited by non-centrosymmetric crystals. Some of the non-centrosymmetric crystals include KDP crystals, CaCoSO, CaZnSO nanocrystals, etc. (4)

1.3 Z- SCAN TECHNIQUE

Z scan technique is a simple yet powerful technique which is based on the principle of spatial beam distortion. Originally proposed by Sheikh Bahae (5), this method is widely used to study third order nonlinear optical activity. The third order nonlinear optical activity is induced in a

material because the high intensity laser beam passing through the material can change the induced refractive index due to the self-focusing and defocusing of the laser beam. It can investigate the response of materials to intense laser radiation. In the Z scan technique, the sample is moved along a focused Gaussian laser beam. The sample then experiences different intensities according to its position as the intensity of the laser beam changes due to its Gaussian beam profile. The technique measures the transmitted or reflected light as a function of position. By analysing the resulting data, valuable information about the material's absorption, scattering, and nonlinear optical properties can be extracted. The technique is mainly of two types- open aperture Z-scan technique for nonlinear absorption and closed aperture Z-scan technique for nonlinear refraction.

The Z Scan Technique offers several advantages over other NLO characterization methods. It is highly sensitive, capable of detecting subtle changes in the material's optical properties. Additionally, it can be used with a wide range of materials, including liquids, solids, and thin films. This enables researchers to explore the nonlinear behavior of materials across different intensity regimes and obtain comprehensive insights into their optical properties.

The Z Scan Technique, while a valuable tool for characterizing nonlinear optical properties, does have some limitations that should be considered. The Z Scan Technique relies on a single laser beam for measurement, which may not capture the full complexity of the nonlinear optical response. Some materials may exhibit different behaviours under multiple excitation beams or in the presence of complex optical fields, which cannot be fully characterized using the Z Scan Technique alone. Depending on the intensity and duration of the laser used in the Z Scan Technique, there is a risk of sample damage. High laser powers can lead to heating effects and potential structural changes in the sample, which may affect the accuracy of the measurements or even cause irreversible damage to the material. The Z Scan Technique assumes that the sample is homogeneous. However, if the sample contains variations or non-uniformities in its composition or structure, the measurements may not accurately represent the overall nonlinear optical properties. The accuracy of Z scan measurements can be affected by the quality and uniformity of the samples. Variations in sample characteristics may lead to unreliable results. High-power laser sources are required for Z scan experiments, imposing constraints on the energy levels and potential sample damage. The analysis of Z scan data often involves complex nonlinear fitting procedures, requiring expertise in data processing and interpretation.

1.4 ADVANTAGES AND APPLICATIONS

Nonlinear optics proved to have diverse and impactful applications across various fields, including medical imaging, laser technology, optical computing, and quantum information processing. The unique properties of nonlinear optical materials and effects have revolutionized these areas, enabling advanced technologies and scientific discoveries. By utilizing nonlinear effects, such as two-photon fluorescence and second harmonic generation, researchers and medical professionals can visualize biological structures at the cellular and molecular levels. This enables more accurate diagnostics, better understanding of disease mechanisms, and advancements in medical research.

Nonlinear optical materials and effects play a crucial role in the development of advanced laser systems. Nonlinear frequency conversion processes, such as harmonic generation and parametric amplification, enable the generation of laser beams with different wavelengths, powers, and pulse durations. These powerful and efficient lasers find applications in various fields, including industrial manufacturing, medical procedures, scientific research, and telecommunications. Nonlinear optics is also a key component in the development of optical computing technologies. By utilizing nonlinear effects, such as all-optical switching and nonlinear wave mixing, researchers aim to harness the unique properties of light for faster and more efficient computational systems. Optical computing offers potential advantages over traditional electronic computing, including higher processing speeds, lower power consumption, and increased parallelism. The ability to manipulate light at the nonlinear level opens up exciting possibilities for developing novel technologies with improved speed, precision, and energy efficiency.

Despite all these, nonlinear optics research faces several challenges, including the development of new materials with enhanced nonlinear properties, managing optical losses, and achieving high conversion efficiencies. Additionally, precise control and manipulation of nonlinear effects pose significant research challenges. In terms of material limitations nonlinear optical materials with high nonlinearity and low absorption even though are essential for efficient nonlinear optical processes their development poses significant material science challenges. Nonlinear effects can induce signal distortion and degradation, impacting the fidelity and stability of optical communication and data transmission systems. Also, the implementation of nonlinear optical devices in practical systems requires advanced engineering and integration techniques due to the complexity of nonlinear effects.

CHAPTER 2

SYNTHESIS AND CHARACTERISATION

Abstract: In this chapter the synthesis of ZnO nanorods of approximately 200 nm using hydrothermal method has been explained. The various characterisation techniques like UV-Visible Absorption Spectroscopy, FTIR Spectroscopy and SEM imaging were done in order to confirm the presence of ZnO nanorods. The results obtained from these techniques has also been discussed in this chapter.

2.1 Introduction

Nanorods are a fascinating subject within nanoscience and nanotechnology, undergoing significant advancements in recent years. Their unusual physical properties have attracted considerable research attention. Nanorods are nanoscale structures with dimensions ranging from 1 to 100 nm, synthesized from metals or semiconductor materials through direct chemical synthesis. A mixture of ligands acts as shape regulation agents, binding with varying strengths to specific aspects of the nanorod, allowing for controlled expansion at different levels and creating elongated objects known as solid nanofibers.

Nanoscale materials, such as fullerenes, quantum dots, and metallic nanoparticles, possess special properties due to their high surface area to volume ratio. Nanorods exhibit enhanced fluorescence compared to bulk metals and nanospheres. Many nanomaterial characteristics, including catalytic, magnetic, electrical, chemical, and physical properties, depend on their size and shape.

2.2 Zinc Oxide Nanorods

Zinc oxide nanorods, also known as nanowires, have emerged as popular materials for electronic devices such as solar cells, light-emitting devices, transistors, and sensors. The diverse structures of ZnO nanorod arrays offer unique characteristics suitable for high-performance system development. ZnO nanorods possess a direct bandgap energy of 3.37 eV, a high excitation binding energy of 60 meV at room temperature, and effective ultraviolet luminescence. Different types of ZnO nanorods have been grown, and the effects of growth conditions have been studied by several groups. (6)

The photodetection and photo response of zinc oxide nanorods depend on various factors such as surface condition, structure quality, production methods, and the rate of oxygen adsorption and photo desorption. Enhancing the photo response and photosensitivity can be achieved through the use of appropriate dopants, structural improvements, surface passivation, and other methods.

Zinc oxide (ZnO) is a compound semiconductor from group II-VI, with an ionic character between covalent and ionic semiconductors. Among its crystal structures, including wurtzite, zinc blende, and rock salt, only the wurtzite phase is thermodynamically stable. Techniques such as thermal vapor deposition, metal-organic chemical vapor deposition, molecular beam epitaxy, and top-down approaches by etching can be used to cultivate zinc oxide nanorods with various shapes and orders. Vapor deposition and chemical methods are commonly used for their controllability, repeatability, efficiency, and mass production.

2.3 Synthesis of ZnO Nanorods

Various synthesis techniques are employed in nanotechnology to produce nanoparticles with specific properties. These techniques are broadly classified into two methods i.e., top down and bottom up. The top-down approach starts with a solid mass and makes it into smaller nanosized particles through mechanical methods (e.g., mechanical grinding), followed by stabilization to the required size. The bottom-up approach begins with atomic-sized materials, which are fabricated to the required nanoscale using chemical methods. Examples of Bottom-Up approaches include Physical Vapor Deposition, Chemical Vapor Deposition, Molecular Beam Epitaxy, Wet Chemical methods, and Pulsed Laser Deposition. Top-Down methods include Nano-lithography and Ball-milling techniques.

ZnO nanorods are commonly synthesized using hydrothermal methods. The hydrothermal technique is one of the most promising methods for controlling particle size, morphology, and size distribution by adjusting the reaction temperature, time, and additives.

Reagents used in this method are $ZnCl_2$, NaOH and HCl. The synthesis procedure involves taking $ZnCl_2$ and NaOH with molar ratio of 1:2 and dissolving them in deionized water so that a white $Zn(OH)_2$ precipitate forms. After filtration and washing with deionized water, the white precipitate is dispersed in deionized water and the pH value is adjusted to 6 by HCl. After stirring for about 3 h, the homogeneous sol is poured into a Teflon-lined autoclave and hydrothermally heated at 160° C for 6 hours. Then, the autoclave is cooled to room temperature

and the product is filtered using a grade 1 filter paper of mesh size 11 µm. The filtered product is washed with deionized water multiple times and then dried at room temperature. (7)

Fig. 2.1 Reagents used for synthesis

Fig. 2.2 Placing the white precipitate in teflon-lined flask for heating it for 6 hours at 160℃

Fig. 2.3 Stirring of precipitate dissolved in deionized water for 3 hours in a magnetic stirrer

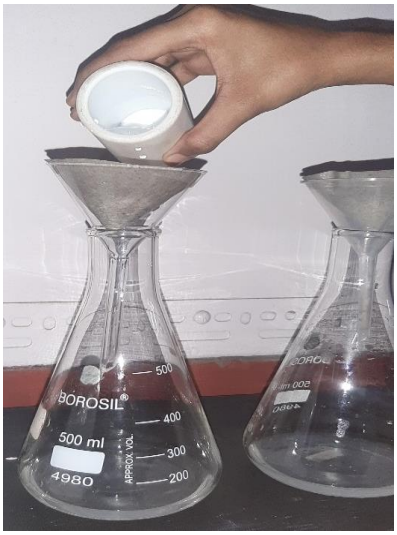

Fig. 2.3 Filtration and washing with deionized water

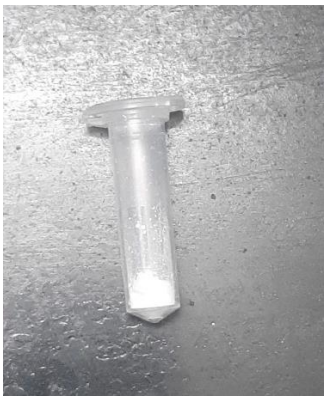

Fig. 2.4 Synthesised sample in a microtube

In the precipitation and hydrothermal process, the ZnO Nanorods form via two reactions:

$$ZnCl_2 + 2NaOH \rightarrow Zn(OH)_2 + 2Na^+ + 2Cl^-$$

$$Zn(OH)_2 \underset{-H_2O}{\rightarrow} ZnO$$

The above results indicate that the $Zn(OH)_2$ precipitate can lose water at 100°C under the hydrothermal conditions.

If the reaction temperature for which the sample is kept in Teflon lined autoclave is changed from 160°C to 220°C, the particle morphology from bullet-like and rod-like shapes to a crush stone-like shape. This change is attributed to the differing growth speeds between various

crystallographic planes. At high temperatures, the growth speeds of different crystal faces become similar, leading to a transformation in particle morphologies from a 1D rod-like shape to a 2D sheet-like shape, and eventually to a 3D crush stone-like shape.

2.4 Characterization of ZnO Nanorods

Materials characterization is a crucial process that involves probing, measuring, and determining the chemical, microstructural, and physical properties of a material using various analytical methods, techniques, and tools. Modern characterization techniques offer high accuracy in measuring and analysing the structure, chemical composition, optical properties, thermal properties, and electrical properties of materials.

2.4.1 Optical Characterizations

Optical characterization techniques utilize light or photons of electromagnetic radiation to probe the properties of materials non-destructively. These techniques provide insights into the structure, morphology, physical, chemical, and electronic properties of materials based on their optical properties. For this work the two optical characterisation techniques that has been adopted are:

1. Fourier Transform Infrared Spectroscopy (FTIR) and

2. UV-Visible Absorption Spectroscopy

The results and their analyses of each these techniques are discussed as follows.

1. Fourier Transform Infrared Spectroscopy (FTIR): FTIR is used to measure electromagnetic radiations in the mid and far regions of the spectrum. These radiations interact with vibrations and rotations of molecules, providing information about the molecular structure of the material. FTIR spectra are unique for each material and can be used to identify unknown materials and confirm known ones.

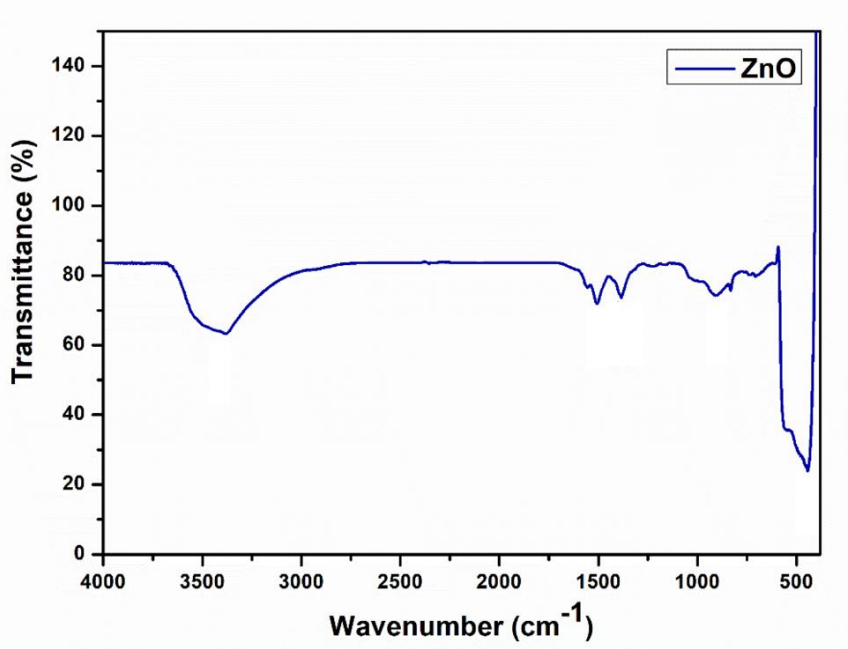

Fig. 2.5. FTIR of synthesised ZnO Nanorods

From this spectrum it can be noticed that there are peaks at 3436.935 cm^{-1}, 1508.89 cm^{-1}, 1383.31 cm^{-1}, 509.98 $cm^{-1}$and 440.21 cm^{-1}. The peak at 3436.935 cm^{-1}corresponds to O-H stretching vibrations, indicating the presence of hydroxyl (alcohol) groups. This can be attributed to the presence of sodium hydroxide which is a strong base that generates hydroxyl ions in the solution. During the synthesis process, hydroxyl groups may have been introduced onto the surface of the zinc oxide nanorods, leading to the observed O-H stretching vibration peak. The peak at 1508.89 cm^{-1} indicates C=C stretching vibrations, suggesting the presence of aromatic compounds or conjugated systems while the peak at 1383.31 cm^{-1} corresponds to C-H bending vibrations, typically seen in alkanes or methyl groups. Also, the peak at 509.98 cm^{-1}indicates the presence of chlorine atoms bonded to carbon, suggesting the presence of chloroalkanes or similar compounds. The usage zinc chloride ($ZnCl_2$) as a precursor in the synthesis process lead to the incorporation of C-Cl bonds in the resulting sample. Finally, the peak at 440.21 cm^{-1}potentially indicates bending vibrations in metal-halogen bonds, which in this case is the Zn-O bonds.

2. UV-Visible Absorption Spectroscopy

   This technique measures the absorption and transmission of light by a material for varying energies of incident photons. It detects the energies of photons that cause

electron transitions within the material, such as band gap energies and other transition energies. In the present work we have done the UV- Visible absorption spectra of the synthesised sample and the absorption spectra was obtained.

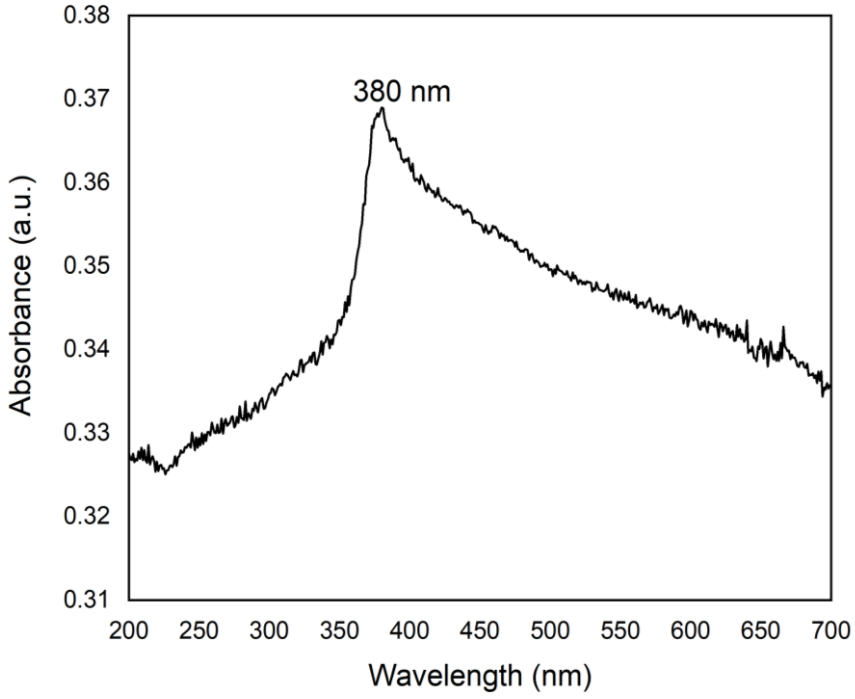

Fig. 2.6 Absorption Spectrum of synthesised ZnO Nanorods

From the obtained absorption spectra, it was noticed that the absorption occurs at 380 nm, i.e., light is most strongly absorbed at around 380 nm in a range of 200 nm to 700 nm. The absorption peak observed at 380 nm is the typical absorption behaviour noticed in ZnO materials.

2.4.2 Structural Characterizations

Various structural characterization techniques reveal information about the structural properties of synthesized materials. Scanning Electron Microscopy (SEM) is one of the structural characterisation techniques which produces detailed, magnified images of an object's surface, showing its composition and physical features in three dimensions. In this study, the obtained ZnO nanorods were analysed using SEM, and the obtained images provide detailed information about their morphology and structure.

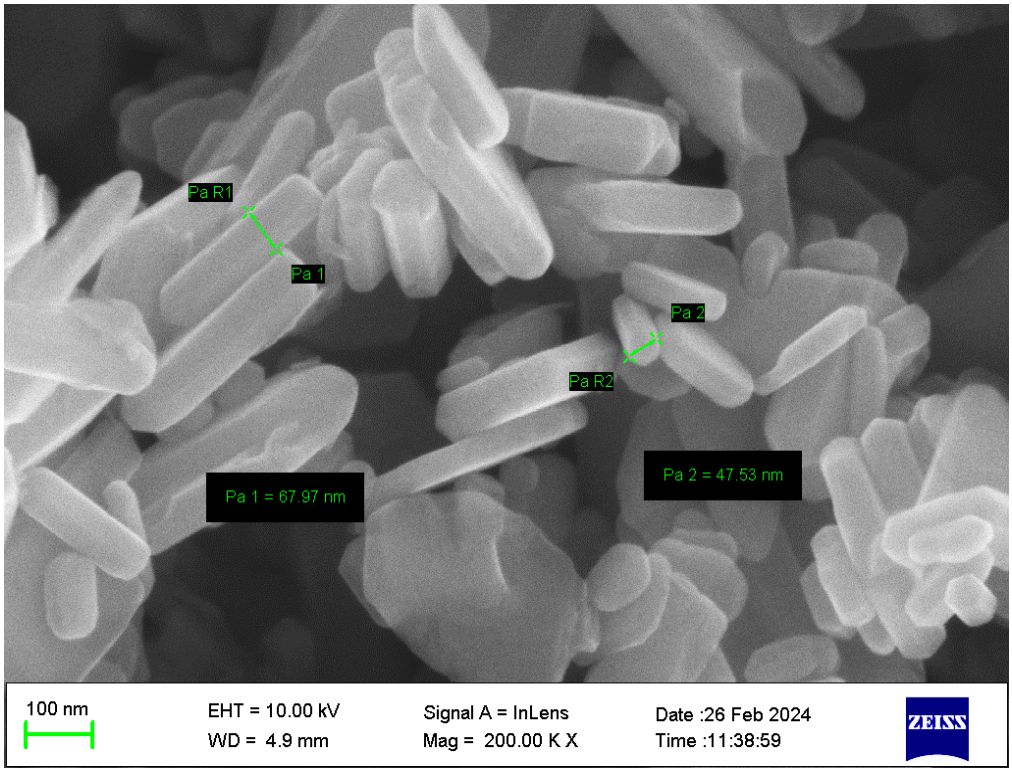

Fig. 2.7. SEM image of synthesised ZnO Nanorods showing that the width of the synthesised nanorods is in the range 50 nm

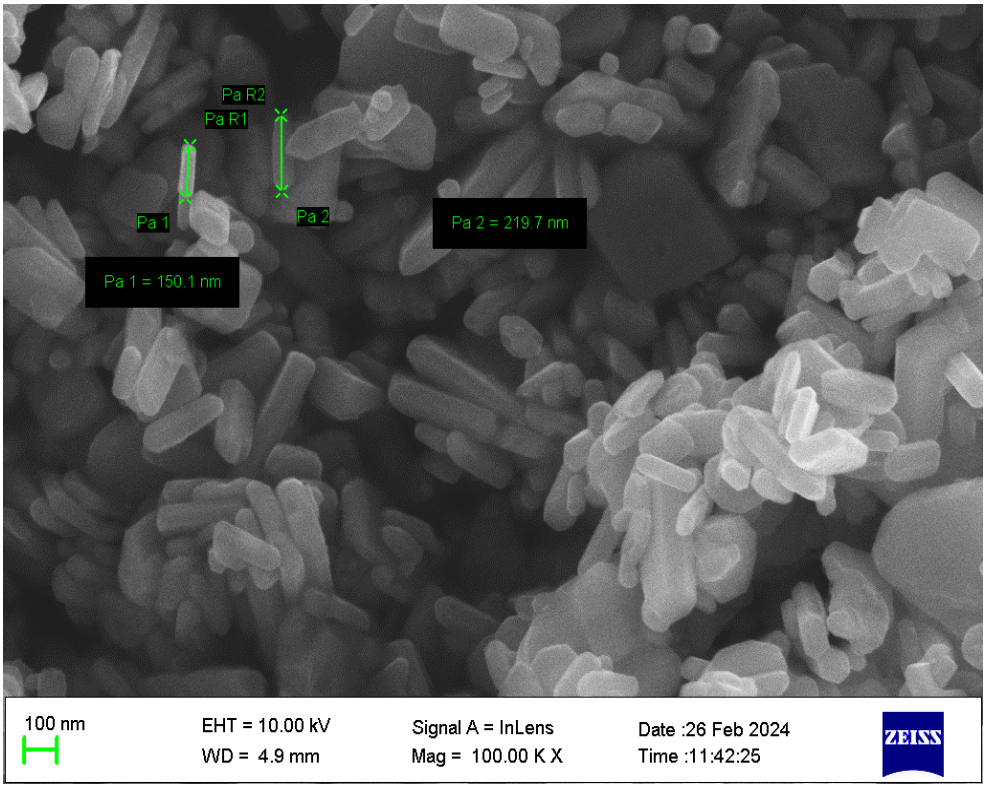

Fig. 2.8. SEM image of synthesised ZnO Nanorods showing that the length of the synthesised nanorods is in the range 200 nm

From the figures 2.7 and 2.8 it can be seen that the synthesised Zinc oxide compound has a rod structure and has an average length of 200 nm and breadth of 50 nm which further confirms that their morphology corresponds to that of a nanorod.

CHAPTER 3

Z SCAN TECHNIQUE FOR NONLINEAR OPTICAL STUDIES

Abstract: Through this chapter a detailed explanation of Nonlinear Optics and Z Scan setup is discussed. Various nonlinear optical effects like second harmonic generation, sum and difference frequency generation, optical parametric oscillation, third harmonic generation, optical Kerr effect and four wave mixing has also been discussed in detail in this chapter. The different types of Z Scan setup like Open Aperture Z Scan Setup and Closed Aperture Z Scan Setup have also been shown along with their bock diagram representation.

3.1 Laser and their Gaussian Profile

The invention of lasers in 1960 was what played a crucial role in the development of nonlinear optics into what it is now. The basics of laser beam is hence also an important factor in understanding nonlinear optics. The output of laser can either have a Gaussian beam profile or a Lorentzian beam profile. For nonlinear studies mostly, a Gaussian beam profile is used.

Consider a laser beam with Gaussian beam profile travelling along the z axis. The beam has the amplitude spatially varying away from the beam axis and also along the beam axis. In a gaussian beam profile the various parameters that can be defined are the beam diameter, waist radius, spot size, beam divergence, Rayleigh range and beam parameter factor.

The following diagram (fig. 3.1) presents a Gaussian beam profile.

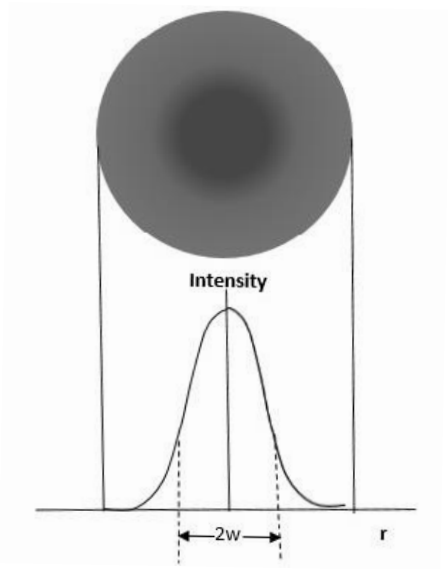

Fig. 3.1. Light intensity across a beam cross section along with light intensity vs. radial distance r from beam axis (z). (8)

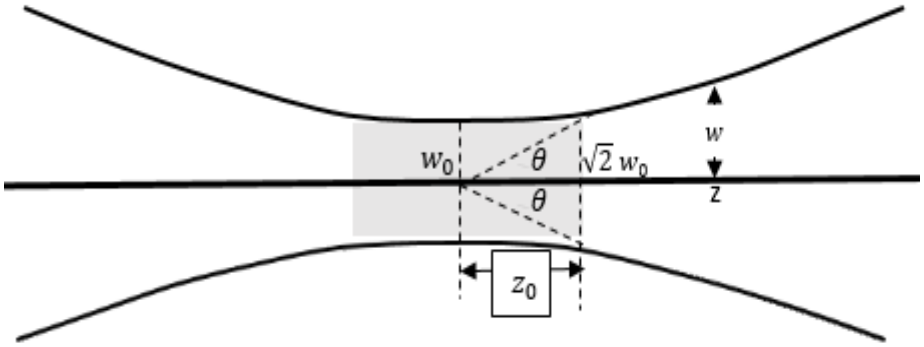

Fig. 3.2. Gaussian Beam Profile (8)

The beam diameter 2w at any point is the area where the power of the beam is 86%. Along the 2w which is also the spot size, the wave fronts of the beam remain parallel to each other and w is the spot size. As the beam diameter i.e., 2w increases the 2θ also increases. This 2θ is the beam divergence. The Rayleigh distance, z_0 or the depth of focus is the distance at which the beam diameter becomes $\sqrt{2}(2w_0)$. Along with all these parameters, beam parameter product or M^2, which is given as $w_0\theta$, is also an important parameter as it is a well-defined constant for a given wavelength.

Thus, the transversal intensity distribution in the case of a Gaussian beam profile can be given as:

$$I(z,r) = \frac{2P}{\pi w(z)^2} e^{-\frac{2r^2}{w(z)^2}} \quad (3.1)$$

These peculiarities of the gaussian beam profile of the lasers played a crucial role in the development of nonlinear optics branch. (8)

3.2 Nonlinear Optics

Nonlinear optics played a crucial role because of the ability of a nonlinear optical medium to undergo a change in its refractive index. The refractive index of a material can be changed by changing the structure of the material. The structure of the material can be changed using electric field, mechanical stress or even light. The change in structure of the material obtained by applying electric field to it is called electro-optics but the applied electric field must be relatively very large. This applied electric field can shift the positively and negatively charged particles which are sensitive to electric fields and hence bring about a change in refractive index.

The relationship between polarisation of a material and an incident field is as follows:

$$P = \varepsilon_0 \chi E \quad (3.2)$$

where P is polarization, E is the electric field, χ is the susceptibility and ε_0 is the vacuum permittivity.

Nonlinearities are taken into account in the expression (3.2) in order for energy transfers between optical levels to occur at different frequencies. By conceptualising the susceptibility as a tensor, the relationship between polarisation (P) and electric field (E) can be expanded.

Susceptibility is therefore expressed as a power series expansion with the following formula:

$$\chi = \chi^{(1)} + \chi^{(2)} E(t) + \chi^{(3)} E_2(t) + \cdots \quad (3.3)$$

Here E represent the real field.

For (3.3) to be valid

$$\left|\chi^{(1)}\right| >> \left|\chi^{(2)}\ \mathrm{E(t)}\right| >> \left|\chi^{(3)}\mathrm{E_2(t)}\right| > \cdots$$

Thus, real polarization,

$$P = \varepsilon_0\chi^{(1)}E(t) + \varepsilon_0\chi^{(2)}E^2(t) + \varepsilon_0\chi^{(3)}E^3(t) + \cdots \quad (3.4)$$

where $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$ are the primary (linear), quadratic (nonlinear), and cubic (nonlinear) polarizabilities of the medium, respectively, and in general, they are the coefficients of the tensor form.

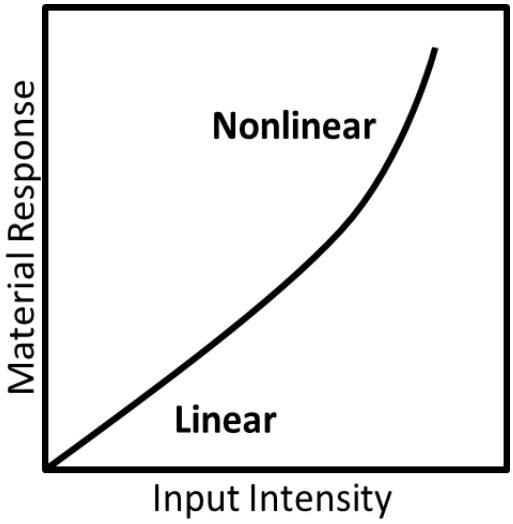

Fig.3. 3. The response of material as the intensity of the input light increases.

Thus, the nonlinear effects can be mainly divided into $\chi^{(2)}$ and $\chi^{(3)}$ effects. Of these $\chi^{(2)}$effects are further divided into second harmonic generation, sum and difference frequency generation and optical parametric amplification while $\chi^{(3)}$effects are further divided into third harmonic generation, optical Kerr effect and four wave mixing.

3.3 Nonlinear Optical Effects

3.3.1 Second Harmonic Generation

Second harmonic generation is a nonlinear optical process in which two photons with the same frequency interact with a nonlinear material. This interaction results in the generation of a new photon with twice the energy.

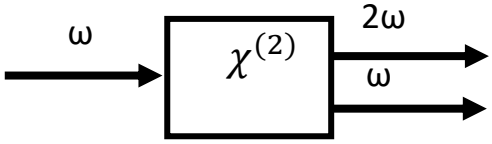

Fig.3.4. Second Harmonic Generation (9)

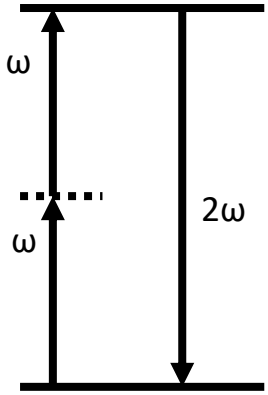

Fig. 3.5. Second Harmonic Generation shown as an energy level diagram (9)

The process in second harmonic generation can be easily explained by taking a laser beam as $\tilde{E}(t) = Ee^{-i\omega t} + c.c$, where c.c is the complex conjugate. Then as

$$P^{(2)}(t) = \varepsilon_0 \chi^{(2)} \tilde{E}(t)^2 \tag{3.5}$$

we get $$\tilde{P}^{(2)}(t) = 2\varepsilon_0 \chi^{(2)} EE^* + \left(\varepsilon_0 \chi^{(2)} E^2 e^{-i\omega t} + c.c\right) \tag{3.6}$$

From (3.6) it can be understood that in the second order polarization term there is a contribution of the ω and 2ω frequencies.

3.3.2 Sum and Difference Frequency Generation

In the case of sum and difference frequency generation the second order nonlinear optical medium is incident with two distinct frequency components changing the electric field component as $\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c.c$ and hence the nonlinear polarization terms will have various frequency components given by:

$$\left.\begin{aligned} P(2\omega_1) &= \varepsilon_0 \chi^{(2)} E_1^2 (\text{SHG}), \\ P(2\omega_2) &= \varepsilon_0 \chi^{(2)} E_2^2 (\text{SHG}), \\ P(\omega_1 + \omega_2) &= 2\varepsilon_0 \chi^{(2)} E_1 E_2 (\text{SFG}), \\ P(\omega_1 + \omega_2) &= 2\varepsilon_0 \chi^{(2)} E_1 E_2^* (\text{DFG}), \end{aligned}\right\} \tag{3.7}$$

$$P(0) = 2\varepsilon_0 \chi^{(2)} (E_1 E_2^* + E_1^* E_2) \text{ (OR)}$$

where SHG is the second harmonic generation, SFG is the sum frequency generation, DFG is the difference frequency generation and OR is the optical rectification.

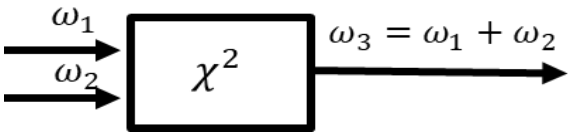

Fig. 3.6. Sum Frequency Generation

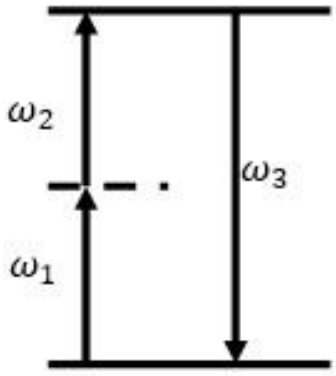

Fig. 3.7. Energy Level Diagram of Sum Frequency Generation

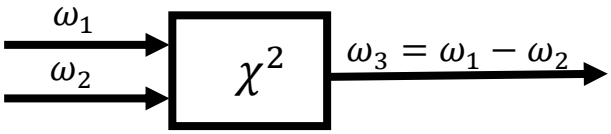

Fig. 3.8. Difference Frequency Generation

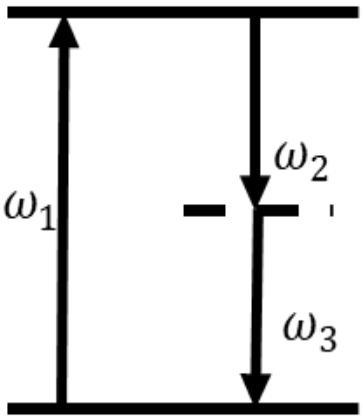

Fig.3.9. Energy Level Diagram of Difference Frequency Generation

3.3.3 Optical Parametric Oscillation

Optical Parametric Oscillation is the process by which an applied frequency ω_1, called the pump frequency can be used to generate the desired output frequency ω_2 called the signal frequency and another frequency ω_3 called idler frequency.

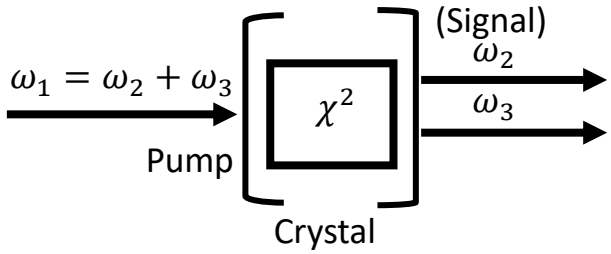

Fig.3.10. Optical Parametric Oscillation

3.3.4 Third Harmonic Generation

Third harmonic generation involves the production of a new photon with three times the energy of the incident photon. Typically, this process occurs for centrosymmetric materials (i.e., material with inversion symmetry) where $\chi^{(2)}$ vanishes. Thus, polarization becomes:

$$P = \varepsilon_0 \chi E + \varepsilon_0 \chi^{(3)} E^3 \tag{3.8}$$

i.e., $$P_{nl} = \varepsilon_0 \chi^{(3)} E^3 \tag{3.9}$$

In this case the electric field term will contain three frequency components and E^3 will contain 3ω and ω term.

Now, $P_{nl}^3 = P_{nl}^{\omega} + P_{nl}^{3\omega}$ where $P_{nl}^{3\omega}$ will contain 3ω (3^{rd} harmonic generation) and P_{nl}^{ω} will contain ω (self-phase modulation)

Due to this $n(\omega) \neq n(3\omega)$ and we can obtain the equation for refractive index as

$$n \approx n_0 + \frac{3}{4n_0}\chi^3 |E_0|^2 \tag{3.10}$$

or $$n = n_0 + n_2 I$$

In equation 3.10 n_2 is the Kerr coefficient and I is the intensity of the light.

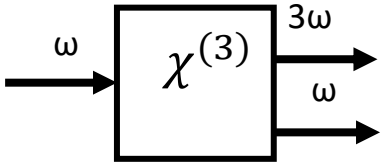

Fig.3.11. Third Harmonic Generation

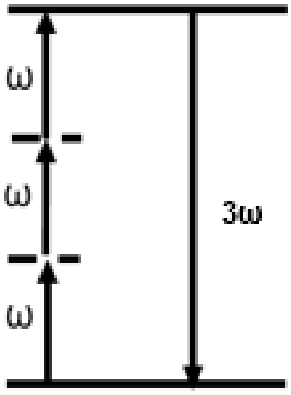

Fig. 3.12. Energy Level Diagram of Third Harmonic Generation

3.3.5 Optical Kerr Effect

The change in the refractive index due to the nonlinearity is given by the equation (3.18) where n_0 is the usual refractive index and $n_2 = \left(\frac{3}{4n_0^2\varepsilon_0 c}\right)\chi^{(3)}$ is an optical constant that characterises the strength of the optical nonlinearity. Gaussian beam profile of laser beam causes the refractive index of the material to also have Gaussian behavior i.e., the refractive index will be maximum at centre leading to bending of light to a point.

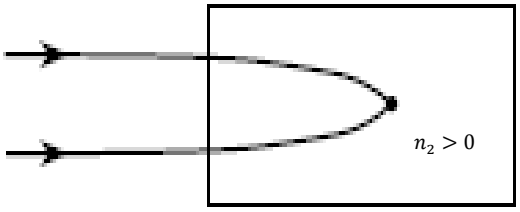

Fig. 3.13. Self-Focusing of Light

3.3.6 Four-Wave Mixing

Four-wave mixing is a nonlinear process that involves the simultaneous interaction of multiple optical waves within a material to generate new frequencies through constructive and destructive interference. This phenomenon results in the creation of new frequencies.

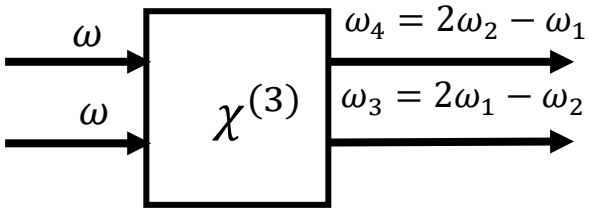

Fig. 3.14. Four Wave Mixing

3.4 Z Scan Technique

Z Scan Technique is a technique which is a simple and highly sensitive measurement technique, generally used for measuring the third order optical nonlinearities. Other techniques like degenerate four-wave mixing, nearly degenerate three- wave mixing, optical Kerr effect, ellipse rotation, interferometric methods, beam self-bending and third harmonic generation are complex even though are sensitive techniques. The complexity of all these methods were overcame when Mansoor Sheik-Bahae (5) introduced the Z Scan Technique.

The Z scan technique based on the principle of spatial beam distortion involves the movement of a sample taken in a cuvette (preferably 1mm pathlength, to satisfy the thin lens approximation used in its theory) in the z direction along the tightly focused Gaussian laser beam. Through this technique the magnitude of nonlinear absorption and the sign and magnitude of nonlinear refraction could be determined simultaneously. The name z scan is due to the fact that when the sample is translated through the beam waist of a focused beam in order to measure the transmitted power it is along the z axis.

Z scan experiments are of two types mainly namely open aperture and closed aperture z scan experiments. The difference between the two experiment techniques is that in the closed aperture setup we place an aperture in front of the detector while in open aperture no aperture is placed. Using closed aperture z scan experiments nonlinear refractive index, n_2 can be determined while using open aperture z scan experiment nonlinear absorptive coefficient, β.

3.4.1 Open Aperture Z Scan

Using this technique nonlinear absorption, which is the change in transmittance of the beam as a function of intensity, can be computed. Through this technique the output trace is expected to be symmetric with respect to the focus i.e., at z = 0.

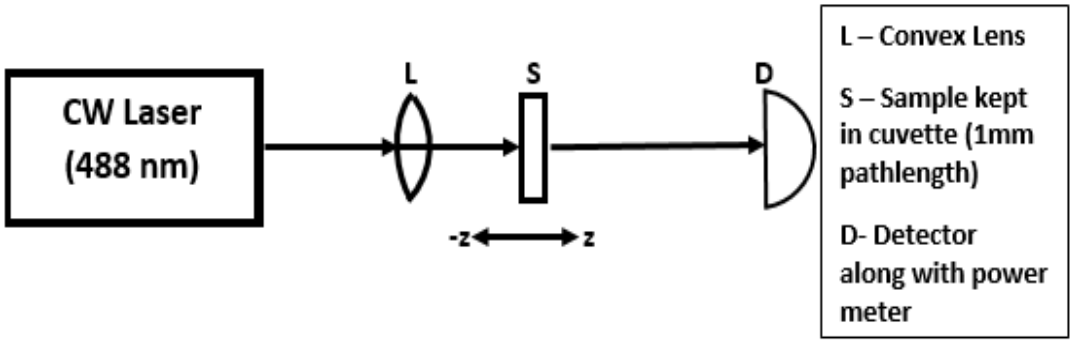

Fig. 3.15. Open Aperture Z Scan Scheme Diagram

The main components of an Z Scan setup include laser, convex lens, translation stage, cuvette and a power detector. The laser taken should have a Gaussian beam profile with the magnitude of E given as:

$$E(z,r,t) = E_0(t)\frac{w_0}{w(z)}\exp\left[-\frac{r^2}{w^{2(z)}} - \frac{ikr^2}{2R(z)}\right].\exp\left(-i\phi(z,t)\right) \qquad (3.11)$$

where w(z) is the radius of the beam at z, E_0 is the electric field at the beam waist where z = 0 and r = 0. The sample length is taken very thin so that there are no changes in the beam diameter within the sample. The phase shift is taken as:

$$\Delta\phi(z,r,t) = \frac{\Delta\phi_0(t)}{1+\frac{z^2}{z_0^2}}\exp\left[-\frac{2r^2}{w^2(z)}\right] \qquad (3.12)$$

Here $$\Delta\phi_0(t) = kn_2I_0(t)L_{eff} \qquad (3.13)$$

where $I_0$is the irradiance at the focus z = 0 and $L_{eff} = (1-\exp(\alpha L))/\alpha$ is the effective propagation length inside the sample with the sample length L and α as the linear absorption coefficient.

In order to find the value of nonlinear absorption coefficient, β we first consider the equation of nonlinear absorption given by the equation:

$$\alpha(I) = \alpha + \beta I \qquad (3.14)$$

Thus, the irradiance distribution for the light coming out from the sample's surface is:

$$I(z, r, t) = \frac{I(z, r, t)e^{-\alpha L}}{1 + q(z, r, t)} \tag{3.15}$$

In equation (3.15), $q(z, r, t) = \beta I(z, r, t) L_{eff}$.

Integrating (3.15) over the limits z and r total transmitted power can be obtained as:

$$P(z, t) = P_i(t)e^{-\alpha L} \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)} \tag{3.16}$$

Also normalized Z-scan transmittance T(z) is:

$$T(z) = \frac{\int_{-\infty}^{\infty} P_T\left(\Delta\phi_0(t)\right) dt}{s \int_{-\infty}^{\infty} P_i(t)\, dt} \tag{3.17}$$

where P_T is the transmitted power and $P_i(t) = \pi w_0^2 I_0(t)/2$ is the instantaneous power (within the sample).

Again, integrating equation (3.17) over time for a Gaussian pulse we get the formula for normalized energy transmittance as:

$$T_{Z,S=1} = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^m}{(m + 1)^{3/2}} \tag{3.18}$$

In equation 3.18 m is an integer and $q_0 = \frac{\beta I_0(t) L_{eff}}{1 + \frac{z^2}{z_0^2}}$ which can be obtained from the fitting of Open Aperture Z Scan experimental data using equation (3.18).

In the open aperture Z scan technique, as the sample approaches focus it can be noticed that the transmittance measured either decreases or increases i.e., a valley or peak is obtained at the focus. When a peak is obtained at the focus it is known as saturable absorption (also known as negative type of absorption nonlinearity) and if it is a valley it is reverse saturable absorption (also known as positive type of absorption nonlinearity).

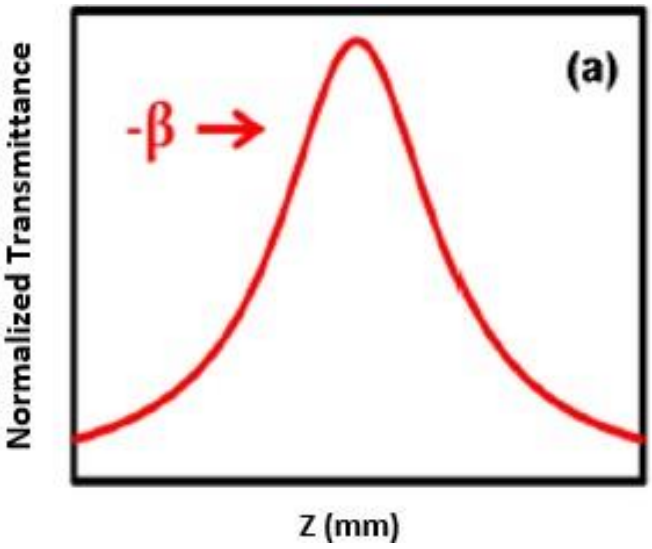

Fig. 3.16(a). Open aperture Z Scan outputs Saturable Absorption Curve (10)

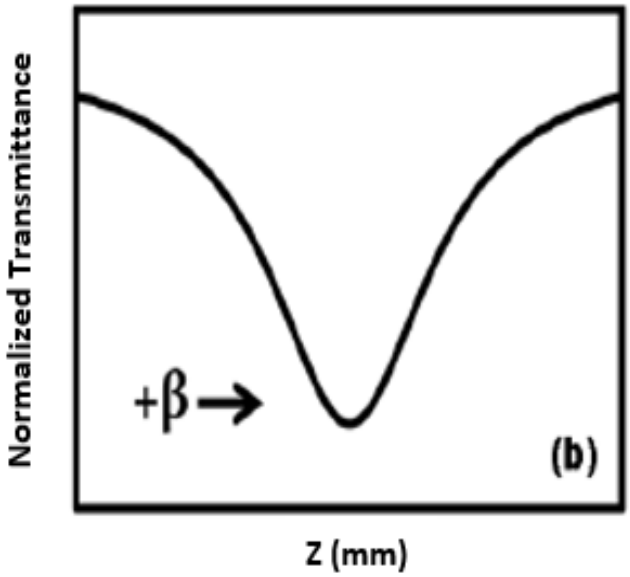

Fig. 3.16 (b). Open aperture Z Scan outputs Reverse Saturable Absorption Curve (10)

3.4.2 Closed Aperture Z Scan

This technique helps in measurement of nonlinear refractive index, n_2. In this technique, an aperture is placed in front of the detector. The Gaussian laser beam when

passing through the medium makes it an intensity dependent lens whose effective focal length of medium changes due to the variation in input intensity.

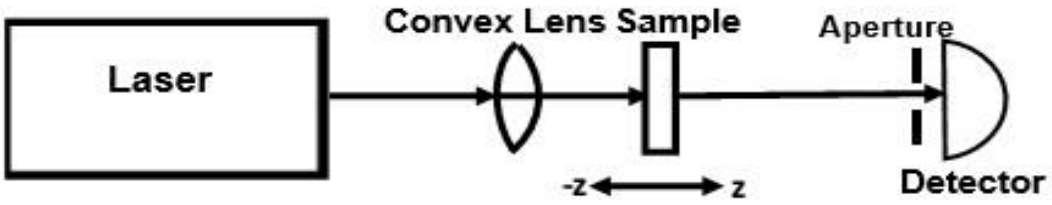

Fig. 3.17 Closed Aperture Z Scan Schematic Diagram

In the closed aperture Z scan the intensity of the beam will not be strong enough to cause any nonlinearity within the sample when it is far from the focus. Due to this the measured power will be constant. But as the sample approaches the focus, the nonlinear absorption and refraction enhances making the sample act line a variable lens diverging the beam passing through it and hence a small amount of light falls on the detector increasing the measured transmittance. At focus the lensing effect becomes maximum and as the sample moves away from the focus, the refraction strength decreases due to lower intensity. The sample then again moves very far from the focus causing the power to again remain constant.

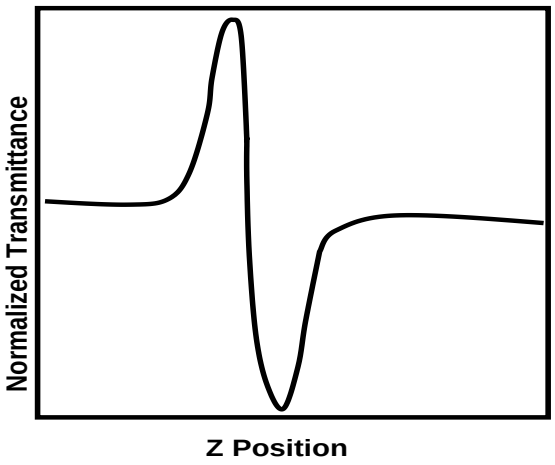

Fig.3.18 Closed Aperture Z Scan Transmittance Curve

3.5 Z Scan Setup

In the present work, the open aperture Z scan technique has been performed on the synthesised ZnO Nanorods (approx. 200 nm). The experimental has been done using a continuous wave laser of wavelength 488 nm. A convex lens of 20 cm focal length has been placed in front of

the laser. 20 cm away from the lens a translational stage has been set up and on top of it the sample is taken in a 1 mm pathlength cuvette. A power detector has also been placed at 20 cm (approx.) away from the focal point at which the cuvette has been placed. The reading on the detector is read in mA using a digital power meter. The laser is then switched on and the sample is moved in the z direction over a range of 5 cm and the reading corresponding to each z has been noted.

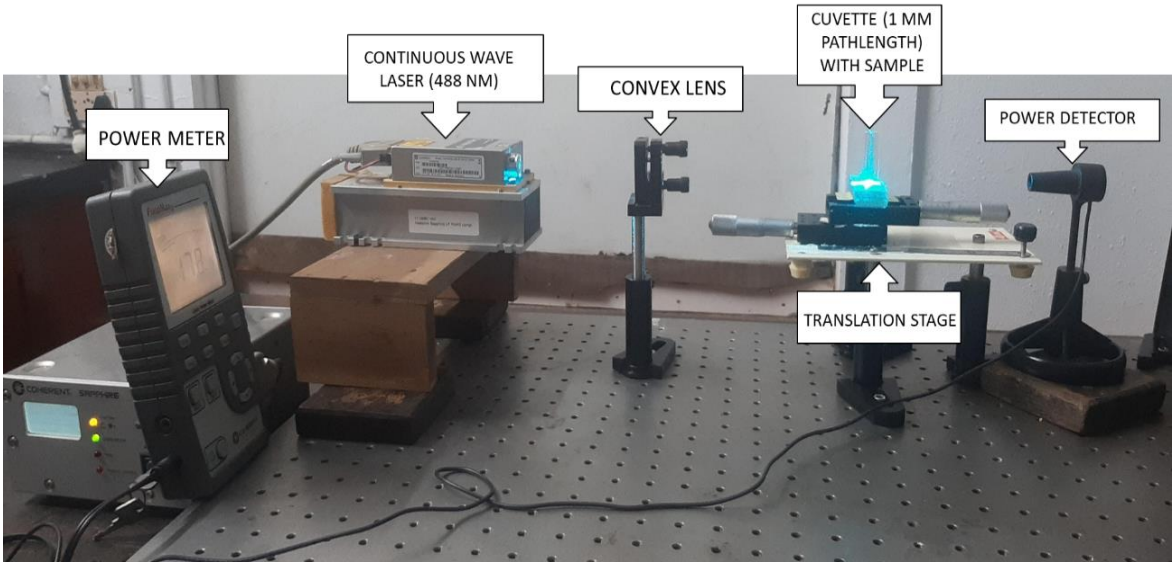

Fig. 3.19 Open Aperture Z Scan Setup used in the present work

CHAPTER 4

RESULTS AND ANALYSIS

Abstract: In this chapter the results obtained from the Z Scan experiment are presented and discussed about. Theoretical fitting of the experimental data has been done and the nonlinear absorption coefficients are estimated.

4.1 Experiment

In the Z scan experiment performed the ZnO nanorods were taken as the sample in a 1 mm pathlength cuvette. About 0.14 g ZnO nanorods is taken in powder form and dispersed in 16 ml of distilled water in order to obtain a 0.1075 mM solution. For the experiment a 488 nm COHERENT laser was used. The peak power of the laser was 27.3 mW and the spot size of the laser beam was found to be 195.3 μm. From the data sheet of the laser the Rayleigh length, z is found out to be 3.72 cm. The experiment is repeated by changing the concentration of ZnO nanorod solution.

About 1.15 ml of 0.1075 mM ZnO nanorod solution is dissolved in 3 ml distilled water. The obtained solution was ultrasonicated in order to make the solution have a homogenous dispersion of the sample. The concentrations were changed by changing the amount of ZnO nanorod solution in the distilled water. The concentrations were taken as 0.0298 mM, 0.03225 mM and 0.0347 mM.

4.2 Results

The results from the Z Scan experiment is obtained translating the sample past the focal plane and measuring the transmitted intensity as a function of sample position.From the resultant intensities the transmittance is found out which is then normalized. This data is then analysed using a suitable curve fitting program.

The results for different concentrations are obtained as:

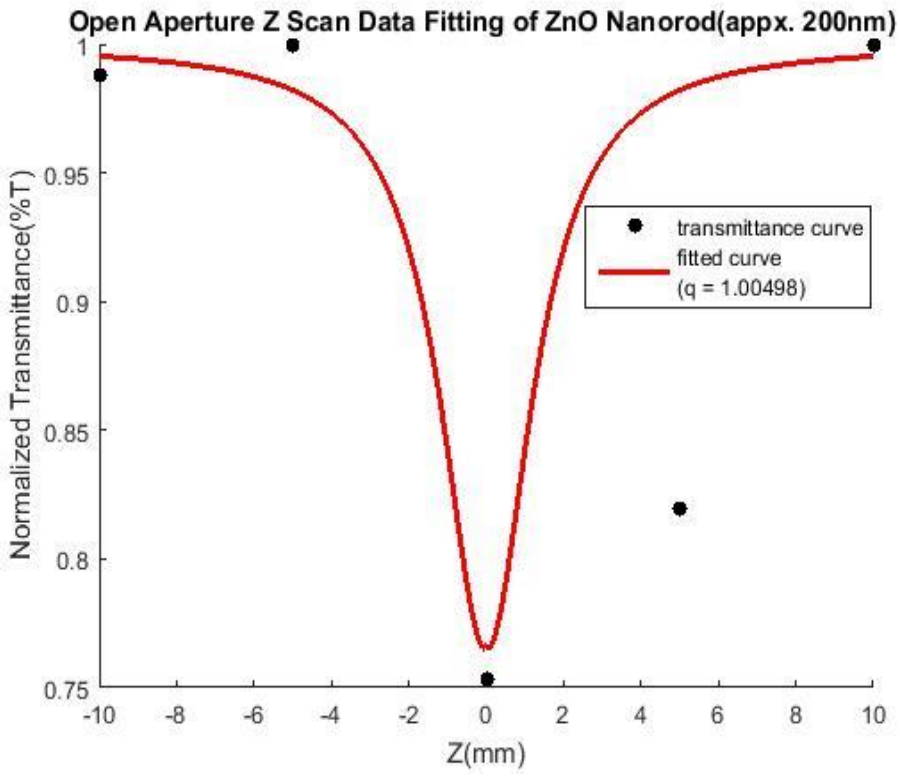

Fig. 4.1 Reverse Saturable Absorption Curve for 0.0298 mM ZnO nanorod solution

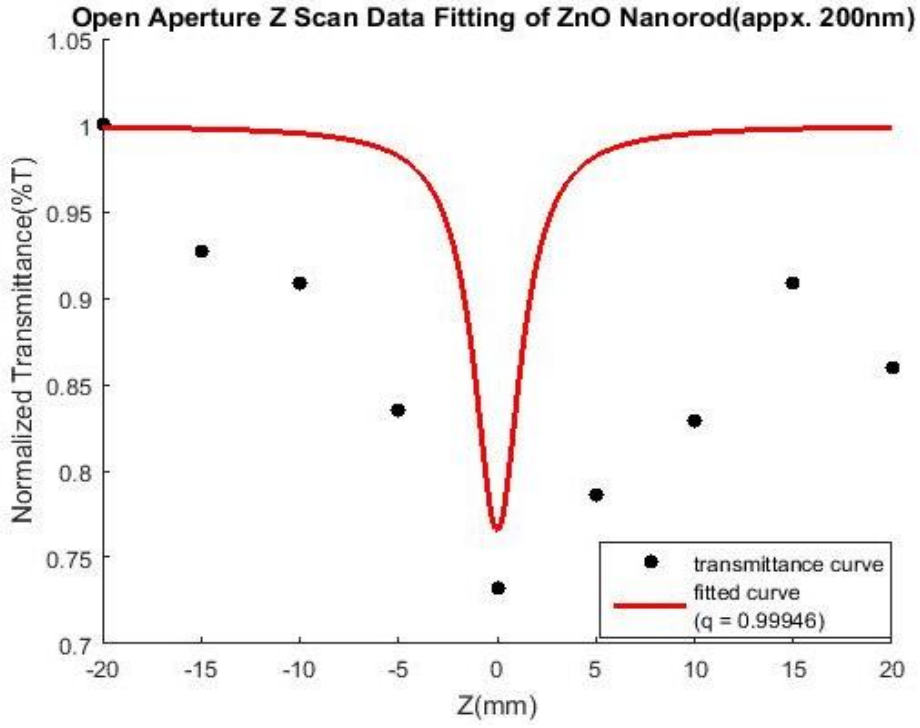

Fig. 4.2 Reverse Saturable Absorption Curve for 0.03225 mM ZnO nanorod solution

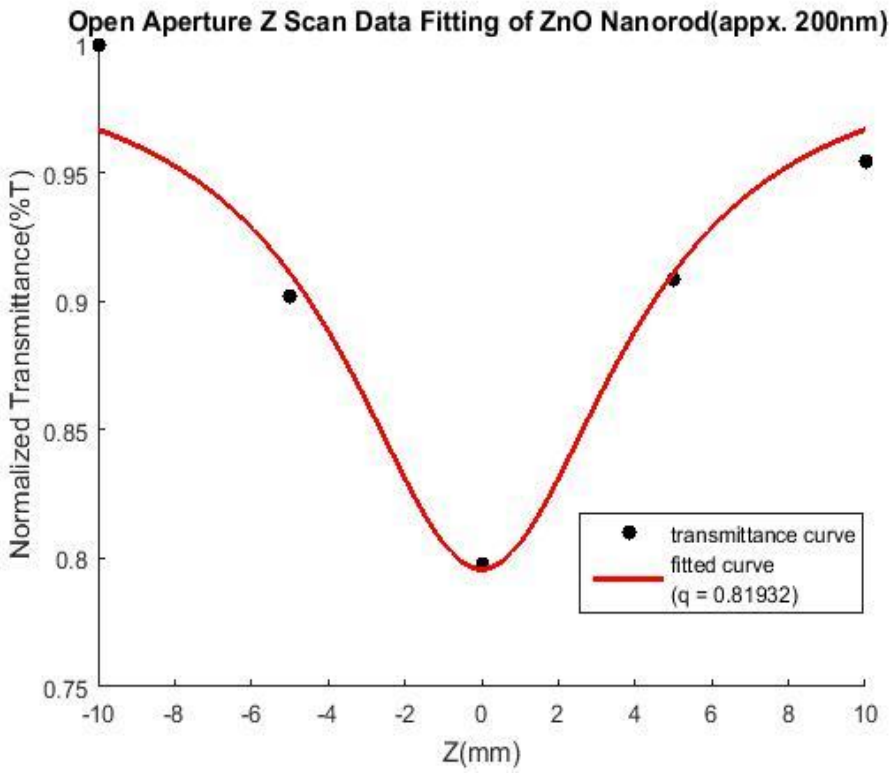

Fig. 4.3 Reverse Saturable Absorption Curve for 0.0347 mM ZnO nanorod solution

4.3 Analysis

The results for q_0 obtained for different concentrations at 23.7 mW can be tabulated as following:

Concentration (mM)	**q_0**	**Nonlinear Absorption Coefficient, β (cm/W)**
0.0298	1.00498	4.2404×10^{-6}
0.03225	0.99946	4.2171×10^{-6}
0.0347	0.81932	3.457×10^{-6}

From the results it can be understood that the nonlinear absorption coefficient, β of ZnO nanorods (approximately 200 nm) decreases as the concentration increases. The beta values obtained above which is approximately in the range of 4.2×10^{-6} cm/W which is comparable

to the nonlinear absorption coefficient of zinc oxide nanoparticles which is found to be around 0.8×10^{-6}cm/W. (11)

The reverse saturable absorption property shown by the Zinc Oxide Nanorods show that the optical transmittance decreases at intense laser irradiation. The photons are absorbed by the material when exposed to intense laser radiation which causes the excitation of electrons from the valence band to the conduction band and hence the transmittance decreases. Due to this a material exhibits reverse saturable absorption property. Reverse saturable absorption results in an increase in absorption as the laser intensity rises, causing a decrease in transmittance and potentially protecting against laser damage. Reverse saturable absorption is of interest for optical limiting applications, where the material can protect sensors or human eyes from high-intensity laser beams. (12)

CHAPTER 5

CONCLUSION

Nonlinear optics which is a vastly growing field of optics is explored through this project. Through this work we attempted to study the nonlinear optical properties of Zinc oxide nanorods using Z-Scan technique. Zinc oxide has wide range of applications due to its piezoelectric and semiconducting properties. They play a crucial role in the optoelectronic application due to their wide bandgap and also in lasing mechanism due to its large exciton energy. They have novel application in sensors and transducers. They also prove to be a biosafe material and hence find applications in the field of biomedical science.

Zinc oxide nanorods were synthesised for this work using wet chemical method. Various characterisation techniques such as UV-Visible absorption spectrum analysis, Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscope (SEM) image analysis were employed to study about the optical, chemical and morphological properties of the synthesised product. From the UV-Visible spectrum, the synthesised product was found to have an absorption peak at 388 nm while FTIR spectrum confirmed the presence of several chemical bonds present in the sample. Thus, the synthesised product was confirmed to be Zinc oxide. The SEM image later confirmed that the synthesised Zinc oxide has the nanorod structure with approximately 200 nm length and 50 nm width.

This prepared ZnO nanorods were used to study the nonlinear optical properties using the Open Aperture Z-Scan Technique. Various concentrations such as 0.0298 mM, 0.03225 mM and 0.0347 mM of Zinc oxide were taken for this purpose. A COHERENT Sapphire SF 488 nm laser was used for this work. The sample was taken in a 1 mm pathlength cuvette and the experiment was repeated for above mentioned three different concentrations. Using the theoretical fitting, the results were analysed and the nonlinear absorption coefficient were found to have a decreasing trend with increasing concentration of Zinc Oxide Nanorods. The plot obtained from the Open Aperture Z Scan technique with distance (z) in X-axis and normalized transmittance (%T) in Y-axis shows that the Zinc Oxide Nanorod shows a Reverse Saturable Absorption Curve. This reverse saturable trend found in Zinc Oxide Nanorods suggest that they can be used as optical limiters and also in lasers for obtaining mode locking.

The work can be further elaborated by varying the power of the laser source and also using lasers of different wavelength. The experiment can be performed using the closed aperture Z-Scan technique in order to obtain the nonlinear refractive index changes also. All these variations may help in finding further extensive application of Zinc oxide nanorods in the nonlinear optic regime.

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