Non-linear characteristic of copper oxide (CuO) through Z-scan technique

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Abstract

Z-Scan technique has been used to study the nonlinear characteristics of nano CuO. The results of the experiment show that there is an excellent agreement between experimental and theoretical analysis of the three photon absorption (3PA) spectrum of CuO.

Keywords: Nanocrystals, Z-Scan Technique, Three Photon Absorption.

Resumen

La técnica Z-Scan se ha utilizado para estudiar las características no lineales de nano CuO. Los resultados del experimento muestran que existe un excelente acuerdo entre el análisis teórico y experimental de los tres fotones de absorción (3PA) espectro de CuO.

Palabras clave: Nanocristales, técnica Z-Scan, tres fotones de absorción.

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I. INTRODUCTION

Transition metal oxides have attracted much attention in recent years because of their size dependent optical properties and electronic structure [1, 2]. Copper oxide is a transition-metal oxide with a monoclinic structure [3, 4]. It is a covalent semiconductor having an indirect band gap between 1.2eV and 1.5eV. Controlling the size, shape and structure of nanocrystals is technologically important because it will have strong effect on the optical, electrical, and catalytic properties. With the decreasing crystal size, CuO nanocrystals exhibit some unique properties like change in ionic character, ferromagnetic response etc. Investigation of electronic properties of CuO nanocrystals will provide more insight into the electronic correlation and also the electronic coherent states. As Copper oxide has more industrial applications like solar energy storage, semiconductors and catalysis, it attracts researchers to study its behavior at various size regimes. Copper(II) oxide or Cupric oxide (CuO) is the higher oxide of copper. As a mineral, it is known as tenorite. Copper oxide belongs to the monoclinic crystal system, with a crystallographic point group of 2/m or C_{2h}. The space group of its unit cell is C2/c, and its lattice parameters are a = 4.6837(5), b = 3.4226(5), c = 5.1288(6), $\alpha = 90°$, $\beta = 99.54(1)°$, $\gamma = 90°$. The copper atom is coordinated by 4 oxygen atoms in an approximately square planar configuration as shown in the Fig. 1 and Fig. 2.

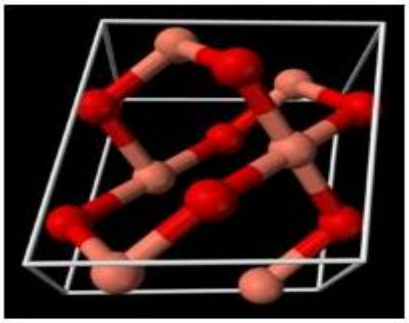

FIGURE 1. The unit cell of copper(II) oxide.

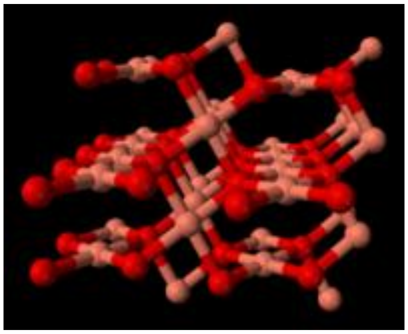

FIGURE 2. Part of the crystal structure of CuO.

We have also investigated the characterization of nano CuO by XRD analysis [5]. Further we have characterized ZnS quantum dot by UV-VIS absorption spectroscopy and compared with CuO nanocrystal [6]. Now we have made an humble effort to study the nonlinear character of nano CuO. Though experimental techniques have been developed to measure the magnitude and dynamics of third order nonlinearties. The Z-Scan is the simplest method to measure the intensity dependent nonlinear susceptibility of the materials [7, 8]. It is a single beam technique to measure the nonlinear refractive index and nonlinear absorption coefficients for wide variety of materials [9]. The Z- Scan utilizes the self-focussing effect of the propagating beam to measures the nonlinear refractive index. The nonlinear transmittance method is utilized to measure the photon absorption co-efficent (β) value from the transmittance. In Z- Scan the sample is translated along the axis of the focused gaussian beam in and out of the focal region of an incident laser beam thereby varying the intensity of light falling on the sample and the far field intensity is measured as a function of sample position. Analysis of the intensity versus sample position the Z- Scan curve gives the real and imaginary part of third order nonlinear susceptibility. By varying the aperture placed in front of the detector one can make the Z- Scan transmittance more or less sensitive to real or imaginary part of the nonlinear response of the material. There are two types of Z-Scan techniques namely closed aperture and the open aperture Z-Scan.

A. Closed Aperture Z-Scan

This method gives quantitative information on the nonlinear refraction of the samples. In this setup there is a possibility for either of the effects like negative lensing and positive lensing, which happens is a case of material with negative nonlinear refractive index and positive nonlinear refractive index respectively. A material with a negative nonlinear refractive index and thickness smaller than diffraction length of the focused beam, is regarded as a thin lens of variable focal length. Starting the scan the sample is moved from a distance far away from the focus close to the lens (negative Z direction) the beam irradiance on the sample is low and negligible nonlinear refraction occurs resulting in relatively constant transmittance. Now, the sample is moved closer to the point of focus the beam irradiance on the material also starts increasing leading to self lensing in the sample. As the width of the beam decreases towards focus the entire energy of the beam is concentrated into a small area in the sample. A negative self-lensing will collimate the beam causing narrowing of beam at the aperture resulting increase in measured transmittance. Now, when the sample is moved towards positive Z direction self de focusing will come into play where the beam reaching the aperture gets diverged more resulting in decreased transmittance as shown in the Fig. 3. This suggests that there is null as the sample crosses the focal plane. This is analogous to placing a thin lens at or near the focus. A prefocal transmittance maximum (Peak) followed by a post focal transmittance minimum (Valley) is the Z-Scan signature of negative refractive index nonlinearity.

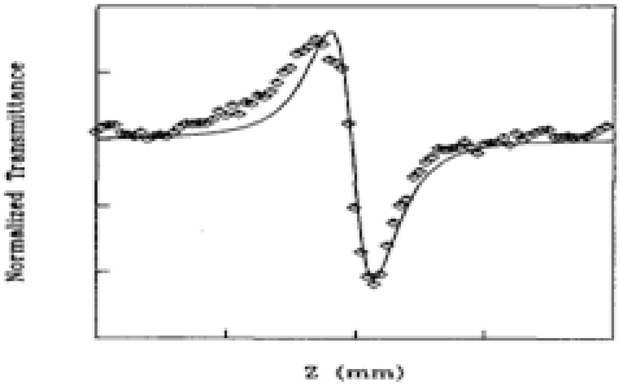

FIGURE 3. A Typical closed aperture Z scan curve.

Positive nonlinear refraction gives rise to the opposite valley-peak configuration. The sensitivity to nonlinear refraction is due to the presence of the aperture and removal of aperture will completely eliminate the effect. For a transparent nonlinear medium the Z-Scan curve will be symmetrical about Z=0. However if some absorptive nonlinearties are present the symmetry will be lost. Example, multiphoton absorption suppresses the peak and enhances the valley while saturable absorption enhances the peak and suppresses the valley.

B. Open Aperture Z-Scan

The nonlinear absorption in a nonlinear medium may arise due to multiple photon absorption, saturation of single photon absorption or free carrier absorption. In case of open aperture Z-Scan technique the aperture placed close to the detector is removed and the sample transmission for different Z values is measured as before as shown in the Fig. 4. The transmittance will be minimum in case of two-photon absorption and maximum for saturable absorption.

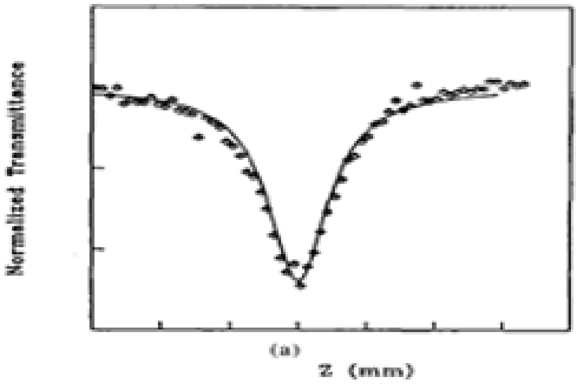

FIGURE 4. A Typical closed aperture Z scan curve.

II. THEORY

The necessary theory to study the fluence calculation and nonlinear characteristics of CuO nanocrystal is given below

A. Curve Fitting Equation

Two photon absorption transmission equation

$$T = \left((1-R)^2 \exp(-\alpha_0 L)/\sqrt{\pi} q_0\right)\int_{-\infty}^{+\infty} \ln\left[\sqrt{1+q_0 \ \exp(-t^2)}\right]dt, \tag{1}$$

where T is the net transmission of the samples. L and R are the sample length and surface reflectivity respectively, and α_0 is the linear absorption coefficient. q_0 in Eq. (1) is given by $\beta(1-R)I_0L_{eff}$, where I_0 is the on-axis peak intensity, L_{eff} is given by $[1-\exp(-\alpha_0 L)]/\alpha_0$, α and β is the effective nonlinear absorption coefficient.

Three-photon absorption equation

$$T = \frac{(1-R)^2\exp(-\alpha L)}{\sqrt{\pi}\,p_0}\int_{-\infty}^{+\infty}\ln\left[\sqrt{1+p_0{}^2\exp(-2t^2)}+p_0\exp(-t^2)\right]dt, \tag{2}$$

where $p_0 = [2\gamma(1-R)^2I_0{}^2L_{eff}]^{1/2}$. Here R is the Fresnel reflection coefficient at the sample-air interface, α is the absorption coefficient, L is the sample length, and I_0 is the incident intensity. L_{eff} is given by $[1-\exp(-2\alpha L)]/2\alpha$.

B. Fluence calculation

For a Gaussian beam, each z position corresponds to an input fluence of $4\sqrt{\ln 2}E_{in}/\pi^{3/2}\omega(z)^2$, where E_{in} is the input laser pulse energy and ω(z) is the beam radius. ω(z) is the beam radius given by $\omega(0)/[1+(z/z_0)^2]$, where ω(0) is the beam radius at the focus, and $z_0 = \pi\omega_0{}^2/\lambda$ is the Rayleigh range.

III. EXPERIMENT

To study the nonlinear transmission of nano CuO We have made the Z-Scan experimental set up at Raman Research Institute, Banglore The description are given below.

A. Experimental setup

In a typical experimental setup initially the input high intense laser beam is passed through a 50:50 beam splitter. Here part of the beam, which is transmitted through the beam splitter reaches a detector that measures the intensity of this direct beam and the other part of the beam, which is reflected from the beam splitter reaches a lens which focuses the incident transverse Gaussian beam towards the sample (nonlinear medium) mounted on a sample holder as shown in the Fig. 5. The thickness of the sample for the study should be less than the Rayleigh range. The sample holder is mounted over a stepper motor arrangement, which is helpful to move the sample in and out of the focal region of the beam along the axial direction of the focused beam. The sample experiences the maximum intensity at the point of focus, which progressively decreases in either direction of motion from the focus. A suitable detector is placed in the far field to measure the transmitted intensity as a function of sample position, which is an open aperture setup. In case of closed aperture Z-Scan an aperture of suitable "S" value is placed closely in front of the detector and the experiment is repeated as before. The Photograph of experimental set up as shown in the Fig. 6.

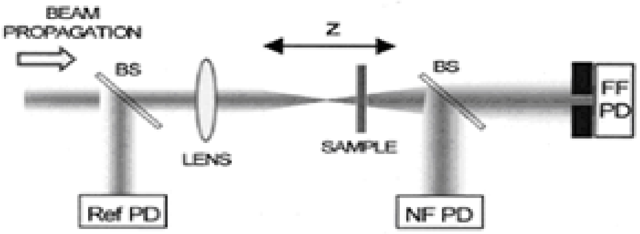

FIGURE 5. Schematic diagram of Z-Scan experiment.

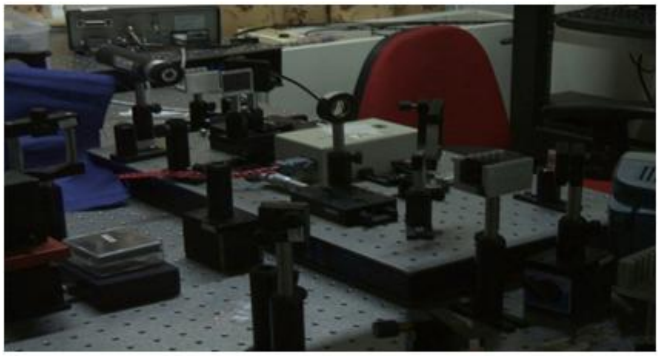

FIGURE 6. Photograph of Z-Scan experimental setup.

B. Synthesis CuO Nanocrystall

The synthesis of Copper oxide nanocrystals is done by a combined precipitation-pyrolysis method, which involves initially preparing precursors and finally decomposing the precursors in a furnace with different annealing temperatures, which lead to the final products of copper oxide nanocrystals.

C. Procedure for Preparing Precursor A

Preparation of precursor A involves the following reaction. 0.3M of aqueous ammonium carbonate is prepared by dissolving 4.714g of ammonium carbonate in 100ml distilled water. Similarly, 0.05M of aqueous copper acetate is prepared by dissolving 4.991g of copper acetate in 500ml of distilled water. Now, 50ml of freshly prepared aqueous ammonium carbonate is rapidly added to 300ml of aqueous copper acetate, and precipitate is formed. After a reaction time of 1minute, the precipitate formed is separated by a centrifuge process. Then they are washed with distilled water and ethanol to remove possible remnant ions in the final products, which are dried in air at 60^0C and kept ready for further reaction

D. Procedure for Preparing Precursor B

0.3M of aqueous sodium hydroxide is prepared by dissolving 4.714g of sodium hydroxide in 100ml distilled water. Similarly, 0.05M of aqueous copper acetate is prepared by dissolving 4.991g of copper acetate in 500ml distilled water. 50ml of prepared aqueous sodium hydroxide is mixed rapidly with 300ml of aqueous copper acetate. After a reaction of 1 min the precipitate is formed which is separated by centrifuge process, and then washed with distilled water and ethanol. It is then dried in air at 60^0 C.

E. Thermal Decomposition of Precursors

Thermal decomposition of the precursors in a furnace with different annealing temperatures led to the final product of CuO nanocrystals and nanorods. Sample (S2) was prepared at 200^0C by using precursor A under constant nitrogen flow. Annealing at temperatures 300^0C, 400^0C, and 500^0C, samples (S3), (S4), and (S5) are prepared respectively from precursor A. without nitrogen flow the final product obtained was copper oxide nanocrystals. Sample (S6) was prepared by using precursor B with the reactant copper sulphate at an increased concentration 0.15M, which is obtained by dissolving 3.742g of copper sulphate in 100ml of distilled water and at an annealing temperature of 300^0C.

F. Z-Scan Measurement

The Z-Scan results of CuO nanocrystals and nanorod are shown below, which shows the Six nonlinear transmission curves at excitation wavelength of 532nm.All the six curves fit to a three photon absorption process.

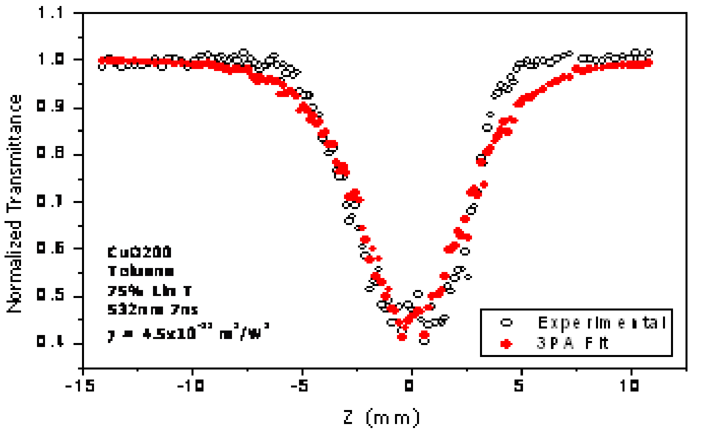

FIGURE 7(a). Fluence fit for CuO nanocrystal under 532nm irradiation.

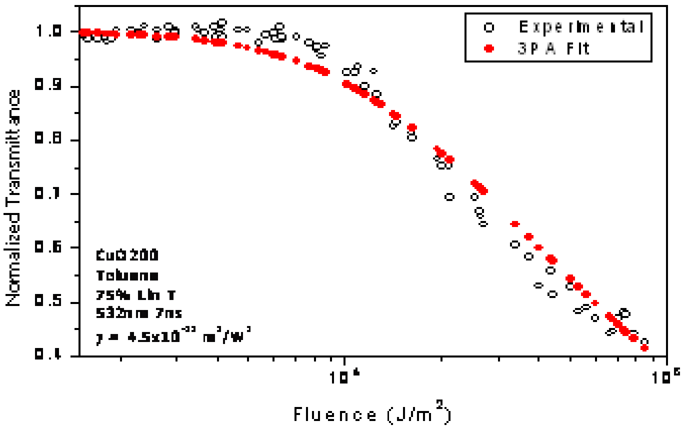

FIGURE 7(b). Fluence fit for CuO nanocrystal under 532nm irradiation.

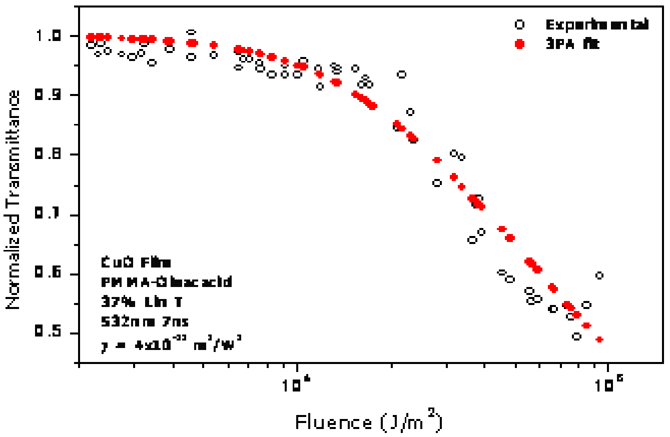

FIGURE 7(c). Fluence fit for CuO nanocomposite under 532nm irradiation.

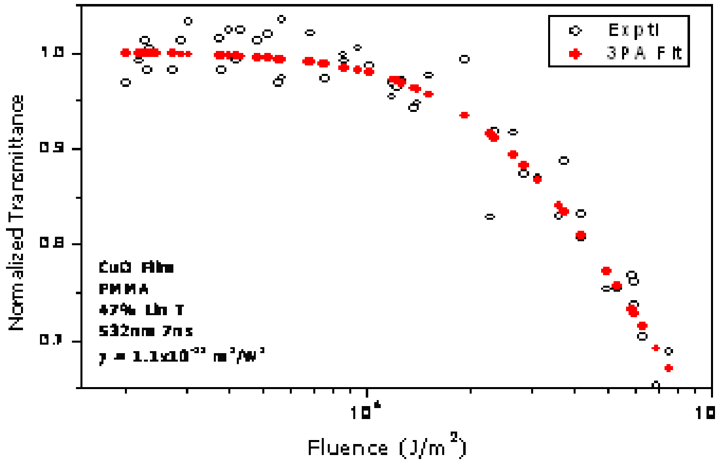

FIGURE 7(d). Fluence fit for CuO nanocomposite under 532nm irradiation.

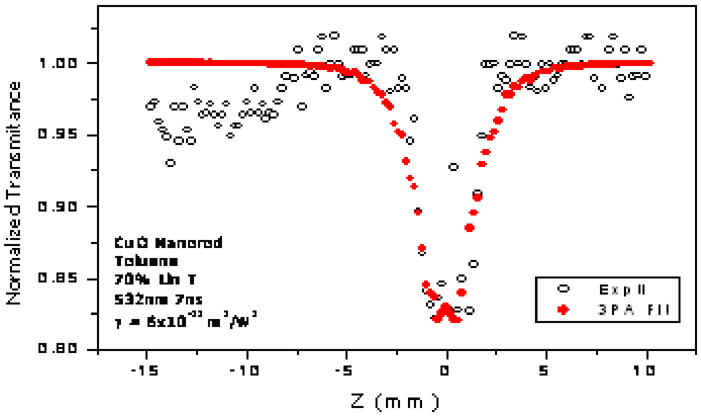

FIGURE 7(e). Fluence fit for CuO nanorods under 532nm irradiation.

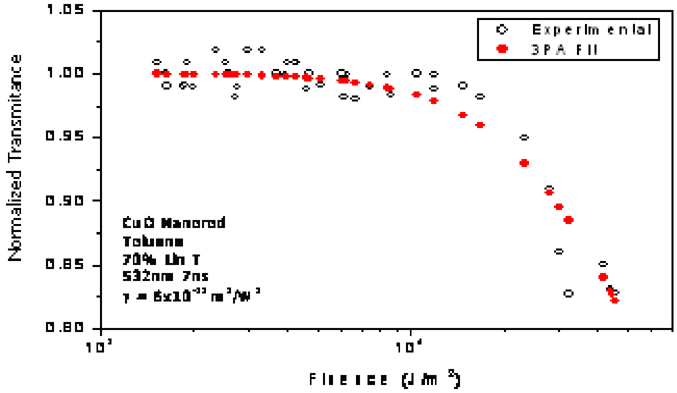

FIGURE 7(f). Fluence fit for CuO nanorods under 532nm irradiation.

It is observed from the Fig. 7(a) to 7(f) that there is an excellent agreement between experimental results and theoretical calculation for 3PA spectra of nano CuO. Michaela Balu *et al.*, while demonstrating a sensitive and broad band characterization technique for nonlinear absorption achieved good agreement between experimental results and theoretical calculations for the 2PA spectra of ZnSe, a well characterized semiconductor.

IV. CONCLUSIONS

We have demonstrated a sensitive and broadband characteristics technique for nonlinear absorption while achieving excellent agreement between experimental results and theoretical calculations for the 3PA spectra of CuO a well characterized semiconductor.

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