Dopant Effect on The Nonlinear Optical Properties of TiO_2-PMMA Nano Composites for Optical Limiter Applications

Aya H. Makki
Laser and Optoelectronics Engineering Department, University of Technology/ Baghdad
Email: au.alani@gmail.com
Dr. Ali H. AL-Hamadani
Laser and Optoelectronics Engineering Department, University of Technology/ Baghdad
Dr. Mohammed Abdulridha Husien
Laser and Optoelectronics Engineering Department, University of Technology/ Baghdad

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ABSTRUCT

In this paper the effect of ZnO dopant on the nonlinear optical behavior of TiO_2-PMMA Nano composites films was studied. TiO_2-PMMA Nano composites films were prepared using solution casting method then doped with different amounts of ZnO nanoparticles. Z-Scan measurements were performed to obtain the nonlinear optical response of these samples at 1064nm using CW Nd-YAG laser. The addition of ZnO nanoparticle into the Nano composites showed a great enhancement in the nonlinear optical response and decreasing in limiting threshold (10 mW) as the dopants concentration increased.

Keywords: TiO_2-PMMA Nano composites, Tow photon absorption, optical limiter.

INTRODUCTION

In recent years organic/inorganic nan composites have attracted the attention of many researchers due to their great enhancement in the mechanical, electrical, optical, magnetic, thermal and nonlinear optical properties[1].Nano composites containing titanium dioxide have gained interest for their potential applications in optoelectronic devices [2],which benefit from the development of fast, low optical loss materials with large values of third order nonlinear susceptibility $\chi^{(3)}$[3].

TiO_2-PMMA nan composites are promising as nonlinear optical materials, since they exhibit a very fast recovery time of 1.5 picosecond and large optical nonlinearity up to 1.93×10^{-9}esu as observed by Z-scan technique using 250 femto-second laser pulses at 780 nm [4].

Zinc oxide (ZnO) has attractive properties, such as a wide band gap (3.37 eV) and a large excitation binding energy (60 meV)[5].

In this paper the effect of adding ZnO nanoparticles on the nonlinear optical properties of TiO_2-PMMA nan composites films was studied using Z-scan technique.

Experimental Part

TiO_2-PMMA nan composites were prepared using solution casting method[6] where poly(methyl methacrylate) (PMMA, Veracril , Colombia) was first dissolved in chloroform ($CHCl_3$, 99% , BDH chemicals Ltd Poole England) in beaker 1 meanwhile 2 wt% of titanium peroxide nanoparticle (TiO_2, 99.8%, particle size = 50 nm , Hongwunanometer , China) were dispersed in

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chloroform in beaker 2 . Both beakers were stirred for 4 hours then sonicated for 30 minutes , finally both solutions were mixed together and stirred for 10 hours then sonicated for 20 min to obtain the homogenous mixture. The mixture of the solutions were poured into Petri dish and left at room temperature for 24 hour to evaporate the solvent. The same procedure was followed to prepare zinc oxide (ZnO , 99.8%, particle size = 80 nm , Hongwunanometer , China) dopedTiO_2-PMMA where ZnO nanoparticle were dispersed with TiO_2 nanoparticles in beaker 2. ZnO doped TiO_2-PMMA films with ZnO concentration of (0.2 ,0.3, 0.4)wt% were prepared with thickness of 125µm measured with coating thickness gauge (SonacoatIII , Sonatest, England).The films were labeled as Z1, Z2, Z3 and Z4 referring to (0,0.1, 0.2, 0.3)wt% of zinc oxide in the nan composites respectively.

The UV-visible spectrum of these samples was measured using (Metertech SP8001, Taiwan). The nonlinear optical properties of the nan composites were measured using Z-scan Technique. The excitation source of this system is CW Nd-YAG laser (MIL-111, Changhun new industry, china) with wavelength of 1064 nm. The output beam is focused onto the sample by using a convex lens with a focal length of 15 cm, giving a spot size of ~ 60 µm. Open aperture Z-scan is used to determine the two photon absorption coefficient (β) by assuming the total nonlinear absorption effect as $\alpha = \alpha_o + \beta I$ and for Gaussian laser beam the normalized change in transmittance ΔT(z) for open aperture is describe by [7]

$$\Delta T(z) \approx -\frac{q_o}{2\sqrt{2}} \frac{1}{[1+Z^2/Z_o^2]} \qquad ...(1)$$

Where: $q_o = \beta I_o L_{eff}$,z_o is the diffraction length of laser beam, I_o is the intensity of laser beam, L_{eff} is the effective thickness.

The closed aperture Z- Scan is used to obtain the nonlinear refractive index (n_2)by using[8]

$$\Delta T_{pv} = 0.406(1-S)^{0.27}|\Delta\Phi_o| \qquad ...(2)$$

Where $\Delta\Phi_o = \frac{2\pi}{\lambda} n_2 I_o L_{eff}$,

ΔT_{pv} is the normalized difference of the maximum (peak) and minimum (valley) transmission in the closed aperture scheme, $\Delta\Phi_o$ is the induced phase shift in focus due to nonlinear refraction, S is the aperture transmission.

The imaginary and real parts of the third order nonlinear optical susceptibility of nonlinear optical material can be calculated using the relations [9]

$$\mathrm{Im}(\chi^{(3)}) = (n_o^2 \varepsilon_o c\lambda/2\pi)\beta \qquad ...(3)$$

and$$\mathrm{Re}(\chi^{(3)})(esu) = \frac{n_o^2}{0.0395} n_2 (cm^2 W^{-1}) \qquad ...(4)$$

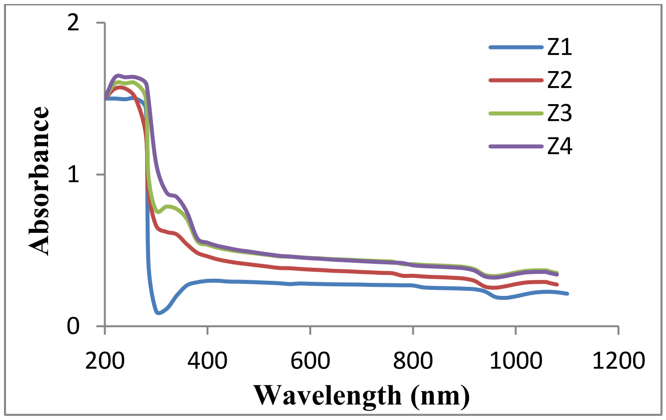
Where: $n_o = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - K^2}$ is the linear refractive index,ε_o is the vacuum permittivity and c is the light velocity

The value of the third order nonlinear optical susceptibility of these films were calculated [9] using

$$\chi^{(3)} = \left[(\mathrm{Re}\chi^{(3)})^2 + (\mathrm{Im}\chi^{(3)})^2 \right]^{1/2}$$

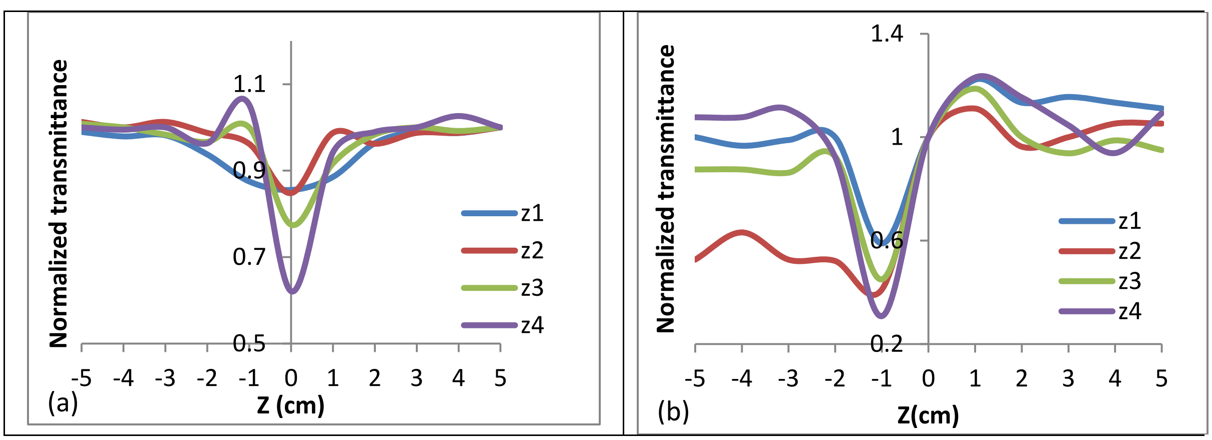
Characterization

Fig (1) shows the absorption spectrum of these films over the range from (200-1100) nm, the increasing in the absorbance peak is due to the increasing in ZnO concentration [10]. The broadband of weak absorption region causes the optical limiting behavior of these films to extend to visible and IR region [11].



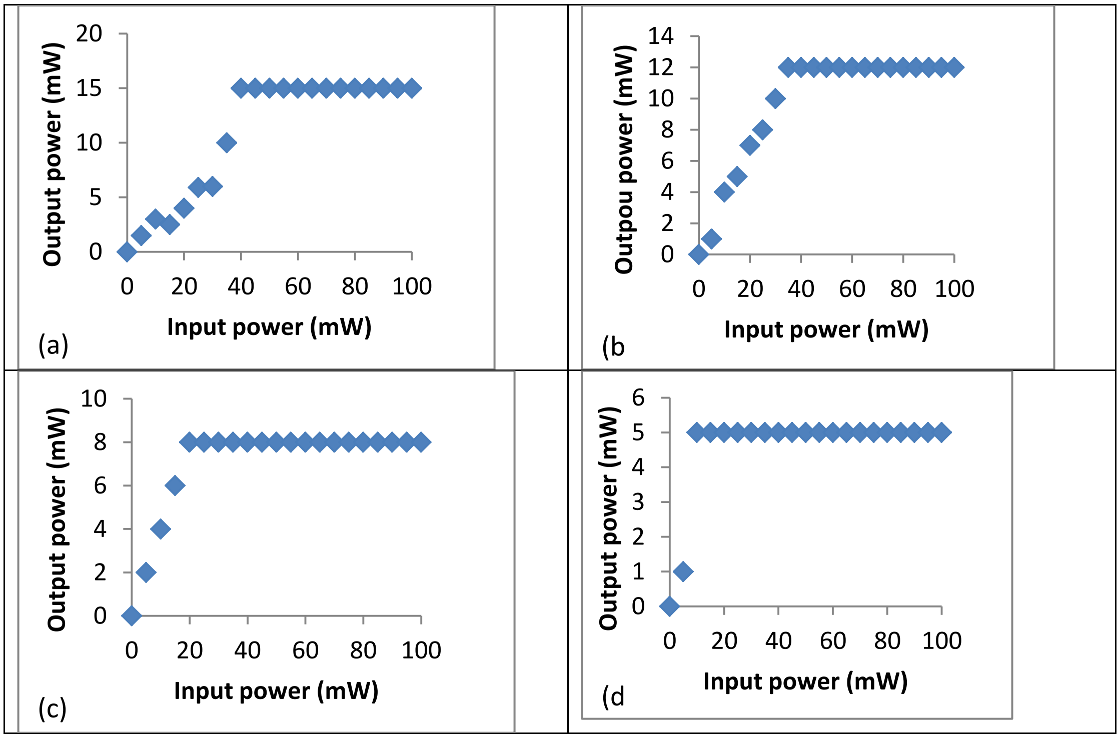
Figure(1):UV-Vis absorption spectrum of Z1,Z2,Z3 and Z4.

The nonlinear optical properties of films as a function of ZnO concentration is shown in Figure (2).Figure (2.a) shows symmetrical and have minimum values at Z=0 which corresponds to $\beta>0$. It also shows that β increased as ZnO concentration increased. Figure (2.b) shows that all the films possess positive nonlinearity ($n_2> 0$), the normalized transmission exhibit minimum " valley" followed by maximum "peak", it also shows that n_2 increased as the ZnO concentration increased. The increasing in nonlinearity as the ZnO concentration increased can be explained by the enhancement in excitation oscillation strength [12].The values of β,n_2,$\chi^{(3)}$for all transparent films are shown in table (1).



Figure(2):Open aperture and (b) Closed aperture Z-scan measurements results for Z1,Z2,Z3, and Z4 films, performed with 1064nm. The input irradiance was 2.12×10^{-3} MW/cm^2 and beam waist 60µm.

Figure (3) show the optical limiting behavior of Z1, Z2, Z3, and Z4.



Figure(3):Optical limiting curve for (a) Z1 , (b) Z2, (c) Z3, and (d)Z4.

The results show decreasing in the limiter threshold as the concentration increased.

Table(1):nonlinear optical properties of Z1,Z2,Z3 and Z4 films.

Sample	n_2 (cm^2/MW)	β (cm/GW)	$\chi^{(3)}$ (esu)	optical limiting threshold (mW)
Z1	1.32	7.43×10^{3}	2.05×10^{-4}	40
Z2	1.55	8.83×10^{3}	2.64×10^{-4}	35
Z3	1.77	1.13×10^{3}	3.13×10^{-4}	20
Z4	2.22	1.24×10^{4}	3.93×10^{-4}	10

CONCLUSION

The nonlinear optical response of ZnO doped TiO_2 – PMMA Nan composites prepared via solution casting method are investigated using Z-scan technique. It was found that the nan composites exhibit increasing in optical nonlinearity as the ZnO concentration increased which can be attributed to the enhancement of excitation oscillator strength. The observed nonlinear absorption is explained by two photon absorption and the nonlinear refraction is explained by self-focusing. The nan composites are found to be good optical limiters and the optical limiting threshold of 0.4 wt% of ZnO is found to be 10 mW. These dopants greatly reduce the limiting threshold and enhance the optical limiting performance of the nan composites making it suitable for nonlinear optical devices with a relatively small limiting threshold.

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