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Determination of Non-linear Refractive Index of Pure SnO_2 and TiO_2 Doped SnO_2 Thin Films Using Z-scan Technique

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Abstract

In this research work the non-linear refractive indices n_2 was determined for the pure SnO_2 and TiO_2 doped SnO_2 thin films by using the Z-scan technique. We have used a continuous wave Ar-ion laser with incident wavelength of 514 nm as the source. n_2 was measured by varying three quantities: the incident laser intensity, thickness of the pure SnO_2 films and doping concentration of TiO_2 in SnO_2 films. From the experimental results, the values of n_2 were found to be increasing with the increase of thickness of the pure SnO_2 films and also with the increase of doping concentration of TiO_2 in SnO_2 thin films.

Keywords: Z-scan; Ar-ion laser; non-linear refractive index; thin films.

I. Introduction

Materials with large optical nonlinearities have changed into the topic of a great scientific interest, because of their inclusive applications in high speed optical switching devices[1]. Z-scan method is one of the easiest methods to determine the nonlinear optical properties of materials. It has been developed for boundless applications like optical limiting[2], Multi-photon polymerization[3], as well as optical switching[4].Many thin films have shown non-linear properties that may use in developing the high speed optical switching devices and other electrical devices.

Among them SnO_2 is one the important films that have high non-linear properties as well as highly transparent[5]. By doping various metal ions or nanoparticles, one can able to enhance the nonlinearities in SnO_2 thin films[6,7].There are many techniques, for example chemical vapor deposition[8], sputtering[9], sol-gel[10], reactive evaporation[11], pulse laser ablation[12], screen printing technique[13], and spray pyrolysis[14] by which one can prepare SnO_2 thin films with smooth surface. In this experimental work, SnO_2 was deposited on sodalime glass by spray pyrolysis process. Sodalime glasses have fascinated much research attention due to better glass-forming nature compared with many other traditional systems. This type of glass has excellent optical and mechanical properties, good chemical stability, high UV transparency, strong thermal resistance, low non-linear refractive index, high surface damage threshold and good durability[15,16]. The thickness of the films can be controlled by deposition time, that means with the increase of time, the thickness of the films also increases. In this research work, the SnO_2 thin films were prepared for different time duration via spray pyrolysis process. The doping of TiO_2 with different metal ions has frequently been tried to enhance the absorption of visible light by giving faulty states in the band gap[17].

W. M. Mat Yunus et al.[6] investigated the non-linear optical properties of phosphate glasses based on ZnO by using Z-scan technique. They used a continuous-wave laser with a wavelength of 405 nm and estimated the values of the non-linear refractive index and the absorption coefficient. They found that the nonlinear refractive index was increasing with the increase of the ZnO concentration in the glass samples. They also calculated the real and imaginary parts of the third-order nonlinear susceptibility. A. M. Yahya et al.[18] observed the optical properties of CuS thin films by Z-scan system. The films were prepared by spray pyrolysis process. They used Q-switched Nd:YAG laser with 1064 nm wavelength to perform the experiment. They observed that n_2 values were decreasing with the increase of incident laser beam intensity and thicknesses of the films. P. Kockaert et al.[19] investigated the values of non-linear refractive index of graphene using Z-scan technique. They varied the input intensity of source and estimated the nonlinear refractive index for varying intensity. From the result it was seen that the nonlinear refractive index n_2 was decreasing with the increase of peak input intensity.

Nonlinearity of films has become more important for developing the high speed switching devices as well as many other electrical devices. This can be played a vital role to enhance the optoelectronics devices. In our present research work, we have investigated the variation of non-linear refractive index for different thickness of Pure SnO_2 thin films and also for different doping concentration of TiO_2 doped SnO_2 thin films. We also have investigated the variation of nonlinear refractive index with respect to the input power of the continuous wave Ar-ion laser source.

II. Experimental Details

In this experiment, pure SnO_2 thin films for different thickness and TiO_2 doped SnO_2 films with different doping

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concentrations were prepared by Spray pyrolysis process, using a homemade spray pyrolysis system. At first 10 mL ethanol was mixed with 90 mL distilled water and made 100 mL solution. Then 2.0 gm of $SnCl_2.2H_2O$ was dissolved in the the previous 100 mL solution to aquire the precursor solution of strength 0.1 M. After that we added 1 mL HCl in the solution to make it more transparent. The solution was stirred for 2.5 hours in a magnetic stirrer[20].

The ultrasonically cleaned soda-lime glass was used as a substrate. We prepared different thickness of the SnO_2 films by changing the time duration of the Spray. Films were made for 5 min, 10 min, 15 min & 20 min and as for higher spray time, the thickness was also developed. We also used different percentage of TiO_2 with this pure SnO_2 solution for producing SnO_2 films of different doping concentrations.

The optical Thin-Film measurement instrument (Model TF-166) was used to measure the thickness of the films.

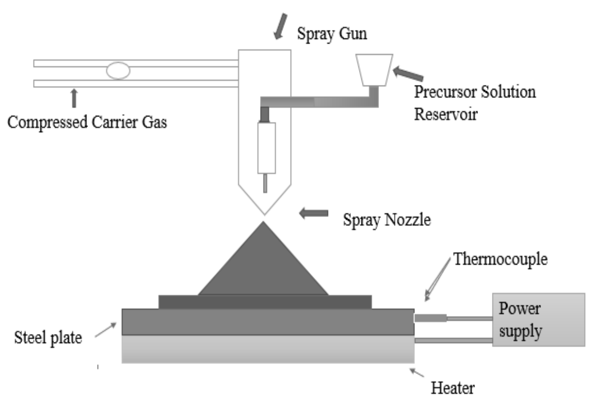

Fig. 1. Schematic diagram of homemade Spray Pyrolysis System

In this Z-scan technique, a Gaussian laser beam was focused by a convex lens to scan third order nonlinear materials. The samples were moved through the focal point of the lens. In general, non-linearity comes from the non-centrosymmetric structure of the sample. For centrosymmetry media, the properties of the medium are not change by the transformation $\vec{r} = -\vec{r}$, so the second-order nonlinear susceptibility is zero means $\chi^{(2)} = 0$. Therefore the third-order term becomes more important[21]. An interesting and important effect that can be seen in the third order nonlinear medium is known as self-focusing.

The variation of transmittance depends on the non-linear phase shift and the phase shift $\Delta\phi_0$ is related to the non-linear refractive index n_2. The total refractive index n for cubic non-linearity can be expressed as[21],

$$n = n_0 + n_2 I \tag{1}$$

where n_0 is the linear refractive index.

We used a continuous wave Ar-ion laser as the source to measure the n_2 of thin films. A convex lens of 100 mm focal length was used for focusing the laser beam.

We also used LabVIEW programming (2015 version) to control the translation motor and tracking the positions of the sample and corresponding power simultaneously.

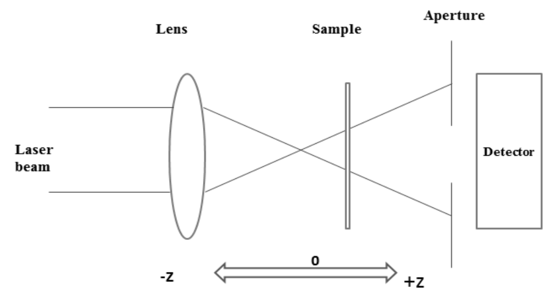

Fig. 2. Schematic diagram of the set up of the Z-scan experiment

III. Results and Discussion

From the peak-valley differences of close aperture z-scan curve, the nonlinear refractive index for different peak intensities was estimated and verified.

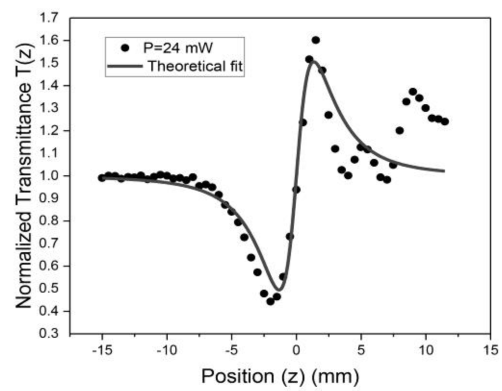

Fig. 3. Close aperture curve with theoretical fitting for SnO_2 thin films with input power $P = 24\ mW$ at fixed wavelength 514 nm

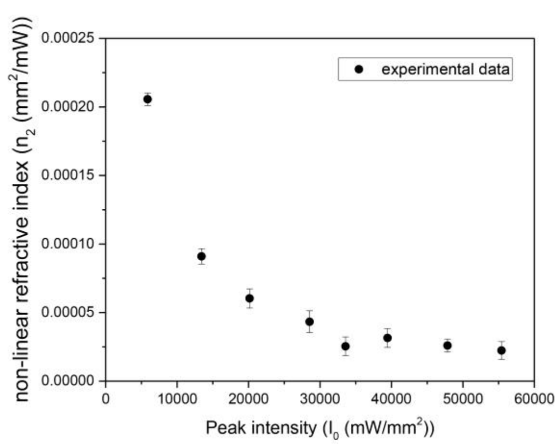

Fig. 4. Non-linear refractive index vs peak intensity at focus for SnO_2 thin films at 514 nm wavelength

So from the graph (in Fig.4), it can be said that the non-linear refractive index decreases with the increment of the peak intensity for a certain wavelength.This above variation for n_2 vs I_0 has been in well agreement with the result of P. Kockaert et al.[19].

For a TEM_{00} Gaussian laser beam with waist radius ω_0 propagating in the +z direction, the electric field can be written as[22,23],

$$\mathrm{E}(r,z) = E_0 \frac{\omega_0}{\omega(z)} exp\left[-i\left\{kz + \tan^{-1}\left(\frac{z_0}{z}\right)\right\}\right] \quad (2)$$

The parameters are $\omega(z) = \omega_0\left\{1+\left(\frac{z}{z_0}\right)^2\right\}^{\frac{1}{2}}$, ω_0 is the beam waist at $z = 0$, $z_0 = \frac{k{\omega_0}^2}{2}$ is the Rayleigh length, $k = \frac{2\pi}{\lambda}$ is the wave number, λ is the wavelength of laser source and *r*(*x*, *y*) is the transverse radial distance[22,24].

The normalized transmittance for open aperture calculations is given[22,23],

$$T(z) = -\frac{q_0}{2\sqrt{2}}\frac{1}{\left(1+\frac{z^2}{z_0^2}\right)} + 1 \quad (3)$$

The far field condition a geometry-independent normalized transmittance for a thin sample is found to be[22,23],

$$T(z,\Delta\phi_0) = 1 + \frac{4\Delta\phi_0\frac{z}{z_0}}{\left(1+\left(\frac{z}{z_0}\right)^2\right)\left(9+\left(\frac{z}{z_0}\right)^2\right)} \quad (4)$$

where at the laser focus, the on-axis phase change can be given as[24],

$$|\,\Delta\phi_0| = \frac{\mathbf{2\pi}}{\boldsymbol{\lambda}} n_2 I_0 L_{eff}$$

and $$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\,\Delta\phi_0|$$

The non-linear index n_2, can be determined from the phase shift using,

$$n_2 = \frac{\Delta\phi_0}{kI_0L_{eff}} \quad (5)$$

where, $L_{eff} = \frac{(1-e^{-\alpha L})}{\alpha}$, L_{eff} is the effective sample thickness, L is the thickness of the samples and α is the linear absorption coefficient.

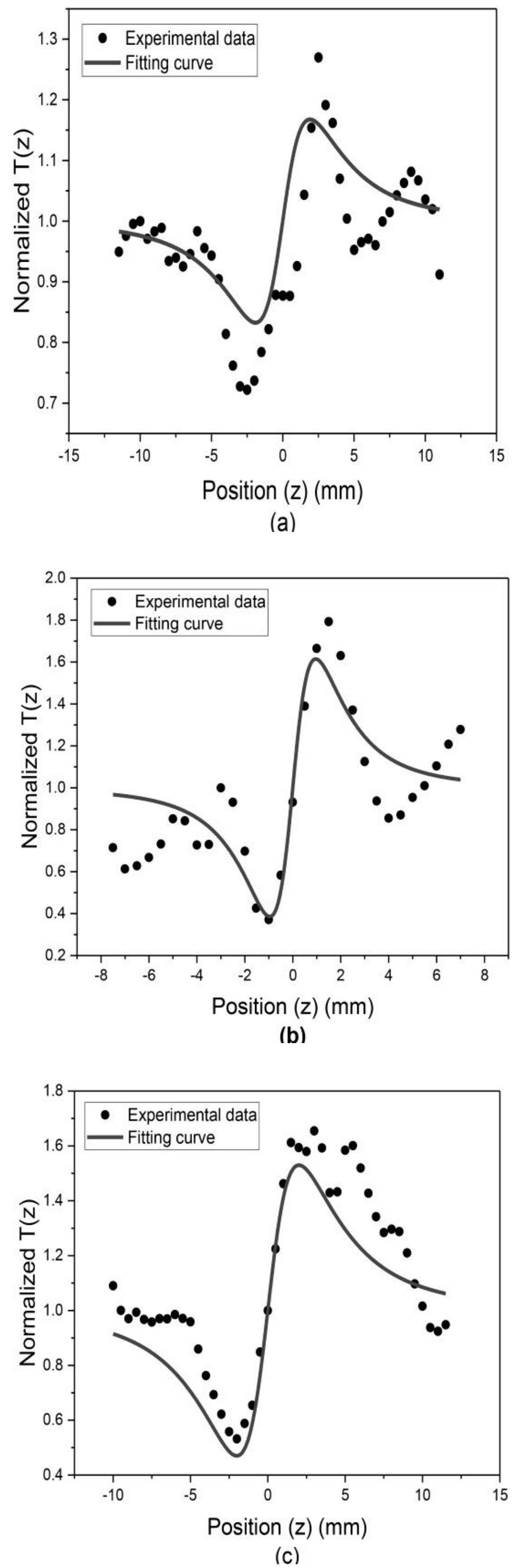

Fig. 5. Close aperture curves with theoretical fit for (a) thickness 209.9 nm (b) thickness 216.6 nm (c) thickness 217.2 nm

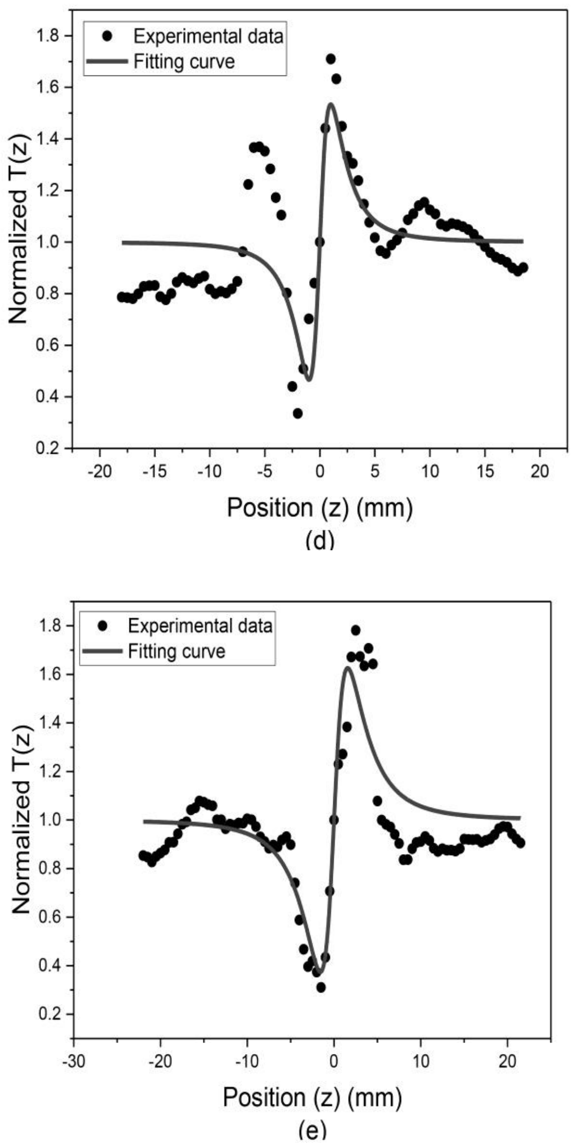

Fig. 5. Close aperture curves with theoretical fit for (d) thickness 218.0 nm and (e) thickness 219.4 nm of SnO_2 thin films at peak intensity $I_0 = 60158.72\ mW/mm^2$ and 514 nm wavelength

From the close aperture Z-scan curves (in Fig.5), the nonlinear refractive index n_2 is calculated from the peak-valley differences of the curves and is tabulated in table 1. It shows that the nonlinearity increases with the increase of the thickness of SnO_2 thin films for a certain peak intensity or input power.

Also from the Open aperture curves (in Fig.6), the Rayleigh length z_0 was found almost same for all SnO_2 samples and so the average value of z_0 was calculated 2.13 mm & beam waist w_0 was found 18.68 μm.

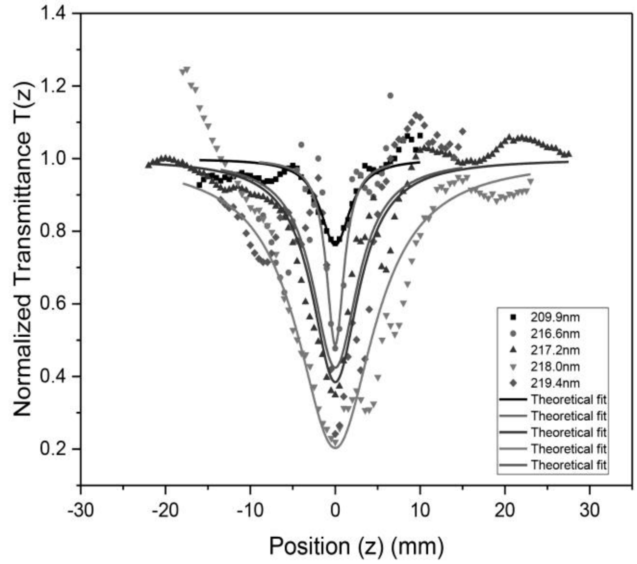

Fig. 6. Open aperture data fitting for different thickness of SnO_2 thin films at peak intensity $I_0 = 60158.72\ mW/mm^2$ and 514 nm wavelength

From the close aperture curves (in Fig.5), it is observed that the values of peak-valley difference ΔT_{p-v} increase with the increase of the thickness of the films. As the thickness increases, the amount of the material also increases that may enhance the electronic polarizability and magnifies the nonlinearity of the films. The result shows a good agreement with that of H. M. Shanshool et al.[25].

Table 1. The following table describes the results of non-linear refractive index for SnO_2 thin films of different thickness.

Thickness of the SnO_2 thin film samples (L) nm	Non-linear refractive index with std. $(\boldsymbol{n_2 \pm \sigma})$ $\boldsymbol{10^{-5} \times mm^2/mW}$
209.9	0.9771 ± 0.0239
216.6	2.186 ± 0.1320
217.2	1.821 ± 0.0973
218.0	2.308 ± 0.0416
219.4	2.457 ± 0.0510

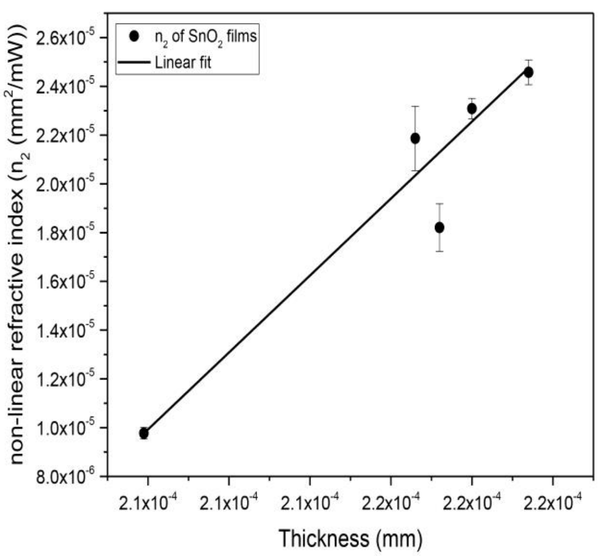

Fig. 7. Nonlinear refractive index vs thickness of the SnO_2 thin films.

From the close aperture curves (in Fig.8), the important parameter ΔT_{p-v} values are calculated to determine the values of non-linear refractive index of the films for different doping concentrations and are tabulated in table 2.

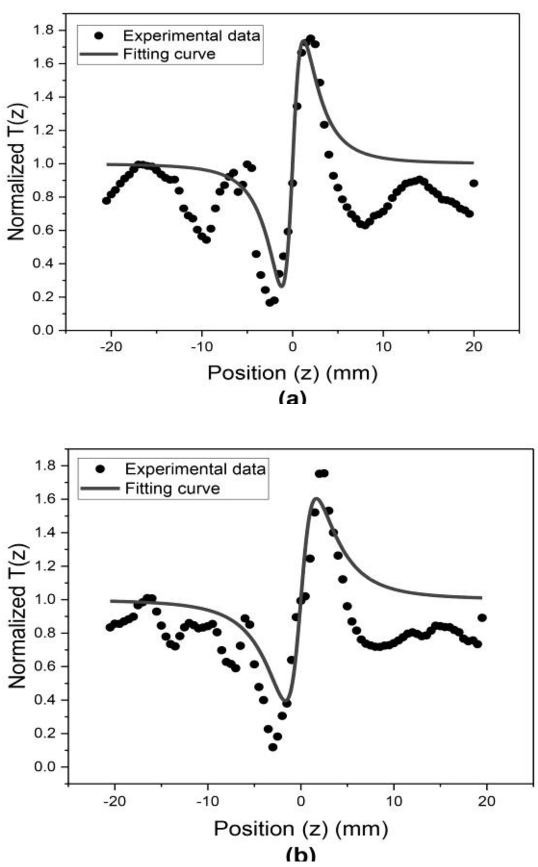

Fig. 8. Close aperture curve with theoretical fitting for a) 12.5% doping (b) 25% doping

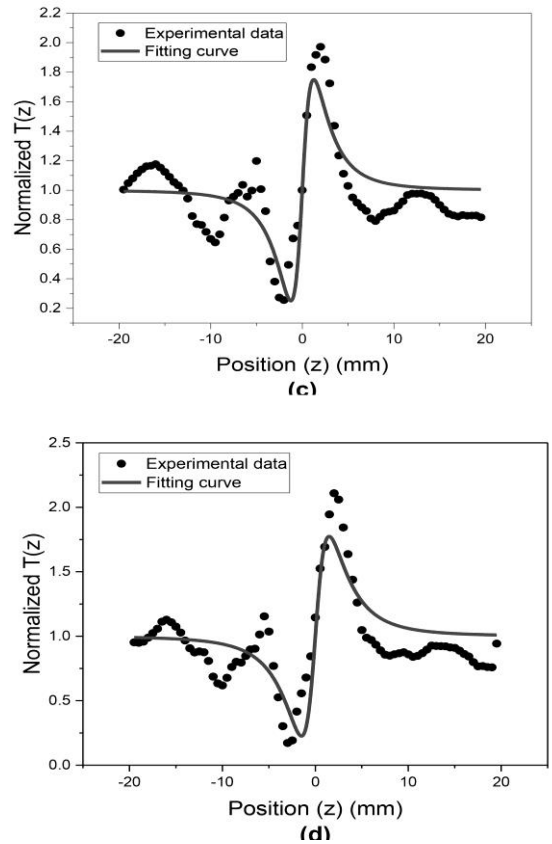

Fig. 8. Close aperture curve with theoretical fitting for (c) 50% doping (d) 75% doping concentrations of TiO_2 at peak intensity $I_0 = 55403.799\ mW/mm^2$ and 514 nm wavelength of Laser beam.

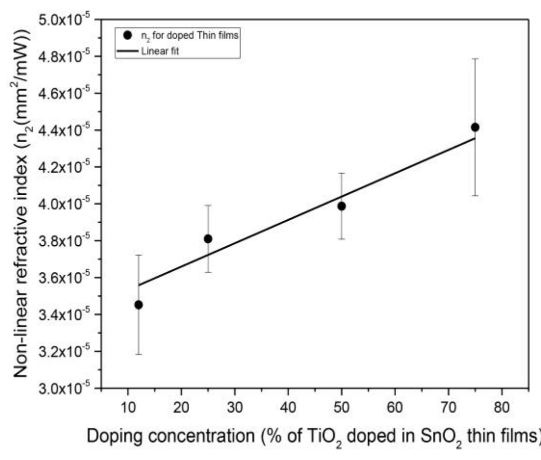

Fig. 9. Non-linear refractive index vs different doping concentrations of TiO_2 in SnO_2 thin films

From the close aperture curves (Fig.8), it is determined that with the increase of the doping concentration of the films the peak-valley difference ΔT_{p-v} increases and effective thickness L_{eff} reduces. The more doping concentration makes the films more absorptive. With the increase of Ti^{4+} in SnO_2 films the electronic polarizability highly enhances.

Table 2. The following table describes the results of non-linear refractive index for different doping concentration of TiO_2 in SnO_2 thin films.

Doping concentrations of TiO_2 , %	Thickness of thin films, L (nm)	Effective thickness of films, L_{eff} (nm)	Non-linear refractive index with std, $(\boldsymbol{n_2} \pm \boldsymbol{\sigma}) \times \mathbf{10^{-5}}\, \boldsymbol{mm^2/mW}$
12.5	209.6	187.00	3.4525 ± 0.0269
25.0	209.6	170.05	3.8100 ± 0.0181
50.0	211.6	161.66	3.9875 ± 0.0179
75.0	212.5	158.33	4.415 ± 0.0371

So on the whole, the increase of numerator ΔT_{p-v} and decrease of denominator L_{eff} in equation (5), magnifies the values of n_2. So the refractive index increases with the increment of doping concentrations of TiO_2 in SnO_2 thin films.This result indicates that the light energy is absorbed as much as the number of TiO_2 molecules increases. This same result for varying doping concentration was found similar with that of W.M . Mat Yunus et al.[6], L. Irimpan et al.[7], H. M. Shanshool et al.[25].

IV. Conclusions

We have found that the non-linear refractive index n_2 decreases with the increase of input intensity and the values of n_2 saturate when the input intensity is very high ($I_0 > 30000\, mW/mm^2$).We also determined that the non-linear refractive index increases with the increment of the thickness of the SnO_2 thin films as well as the doping concentrations of TiO_2 in SnO_2 thin films due to the electronic polarizability. The values of n_2 show that these materials have enough non-linearity for its applications in the photonics.

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