Nonlinear Characterization of Rhodamine $_{610}$ dye-doped PMMA Thin Films Under 650 nm CW Laser Light Excitation

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Abstract

In this work the nonlinear optical properties for Rodamine 610 (R610) in PMMA doped films with different concentrations with the solvent Chloroform by using a high sensitive method known as Z-Scan technique were studied.

Z-scan experiment was performed using CW diode laser at 650 nm with the power output of 45 mW, in two parts. The first part was done using a closed-aperture placed in front of the detector to measure the nonlinear refractive index. In the second part; the aperture in front the detector was removed (open aperture) to measure the nonlinear absorption coefficient. The experimental results for closed aperture show that the dye doped films exhibit negative refractive index (self_defocusing) for the films of concentration $10^{-5}$and 10^{-4} M, while the film of concentration 10^{-6}M exhibits positive refractive index (self-focusing), The results show also that the nonlinear refractive index and the third order nonlinear susceptibility increased with the increasing of the concentration due to the increasing of the film thickness which caused increasing the nonlinear phase shift in the samples. With open aperture z-scan the samples exhibit two photon absorption under the experimental conditions. The effective values of the nonlinear refractive index n_2, the nonlinear absorption coefficient β, real and imaginary parts of the third-order optical nonlinearity, $\chi^{(3)}$ were evaluated. The results imply that R610 films can be used as a potential medium for various optoelectronic applications including that in optical power limiting.

Keywords: Nonlinear optics, z-scan technique, Dye doped polymer films.

Introduction

Rapid technological advancements in optics have placed great demand on the development of nonlinear optical (NLO) materials with prominent applications in optical limiting and all optical switching. Extremely large number of organic compounds with delocalized electron and conjugated double bond systems and a large dipole moment have been synthesized to realize the susceptibilities far larger than the inorganic optical materials [1].

Dye chromophores are a class of organic molecules with multiple π-conjugated bonds, which can exhibit large optical nonlinearities and fast response time, as a result of the ease of polarization of their extended mobile π-electron clouds over large molecular distances. Strong absorption of dyes in the visible region makes them particularly suited for nonlinear optical investigations .It has also been shown that embedding dye chromophores in suitable host matrices enhances the lifetime and stability of the dyes entrapped within it [2]. Dye doped polymers find applications in the fields of modern photonic technology apart from its use as an alternative to solid state laser media. [3].

Z-scan technique based on the spatial distortion of a laser beam passed through a NLO material is widely used in material characterization because of its simplicity, high sensitivity and well-elaborated theory. The opportunity to conduct simultaneous measurements of various NLO parameters in one set of experiments also makes this technique attractive and applicable for different materials. This different materials .This method yields both the sign and the magnitude of the nonlinearity, and the value of the nonlinear refractive index n_2 may be easily extracted from experimental data with a minimum of analysis [4, 5].

There were two parts of the Z-scan: closed aperture and open aperture. Closed aperture Z-scan helps to measure the sign and magnitude of both real & imaginary part of third order (NLO) and nonlinear refractive index (n_2) .Open aperture Z-scan either two types: saturable absorption (SA) and reverse

saturable absorption (RSA). Depending on the pump intensity and on the absorption cross section at the excitation wavelength. Open aperture Z-scan helps to measure the nonlinear absorption coefficient $ß_2$ [6].

In this paper, the optical nonlinearity of dye thin films doped with PMMA at 50 mW cw diode laser power at wavelength of 650 nm was studied. The experiment was repeated for different dye concentrations, the third order nonlinear refractive index and the nonlinear absorption coefficient were found to be linearly dependent on the dye concentration within the range studied.

Experimental Section:

R 610 is from Xanthene family with fluorescence emission in the yellow -red region of the electromagnetic spectrum are well known for their excellent laser performance in liquid solutions as well as in solid matrices [6]. Fig. (1) shows its molecular structure.

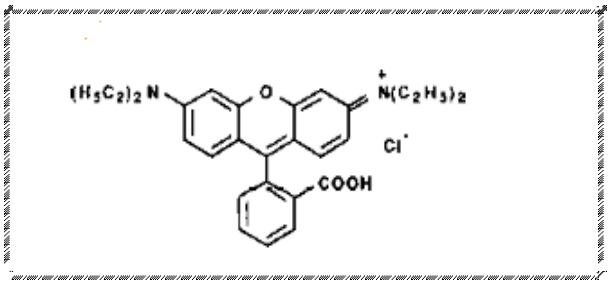

Fig. (1) The molecular structure of R 610, [7].

Polymethylmethacrylate (PMMA) is from ICI Company. The spectroscopic grade solvent Chloroform is from Lab-Scan LTd., Analitical Science HPLC Ireland-Dublin.

Samples Preperation

Solution of concentrations (10^{-6}, 10^{-5} and 10^{-4}) M in Chloroform where prepared by weighting amount of the material by using a matter balance having a sensitivity of 10^{-4} gm. To enhance the solubility of the dye in the solvent, the dye firstly dissolved in Methanol with ratio (20%).

Dye doped polymer films were fabricated by the free casting technique_(FC). Polymer solution was prepared by dissolving the required amount of polymer (7 gm. in 100 ml of the used solvent).

The free casting (FC), involves casting a polymer solution in a flat bottomed glass cup (Petri dish) without imposing hydrodynamic stress on the liquid .The dishes were arranged on a glass plate in order the dishes have a plan situation, then the dishes were covered with a heavy paper box to be protect from light and dust. .Solvent is allowed to evaporate under ambient conditions (30 cº) until the films hardens. The hardend films were then removed from the Petri dish by washing it off with distilled water and placed in the oven (50 cº) for 10 minutes to dry .The thickness of the films produced by this method is dependent in straight forward way on concentration and the volume of the liquid in the dish. In this study the liquid volume was (10) ml, yielding film thicknesses in the range (171_191)µm for different cocentrations. The thicknesses of the films were measured with an electrical device (Mini-test 3000 microprocessor coating thickness) from electro, phyisk, Germany (ERICHSEN).

UV-Visible absorption spectra of the lasing dye were carried out by using UV-Visible Shimadzu spectrophotometer. (UV 160), which operates in wavelength range of 200 nm to 1100 nm and with scanning speed of 1500(nm/min), carried out UV-Visible spectroscopy measurements.

The nonlinear optical properties were investigated employing the standard Z-scan technique schematically shown in Fig.(2), and the photographic picture shown in Fig.(3).

The *Z*-scan experiments were performed using a 650 nm CW diode laser, max.power is 50 mW, beam diameter: 1.5 mm, beam divergent 1.5 mrad, which was focused by 10 cm focal length lens. The laser beam waist ω_o at the focus is measured to be 0.015 mm and the Rayleigh length to be 0.0138 cm.

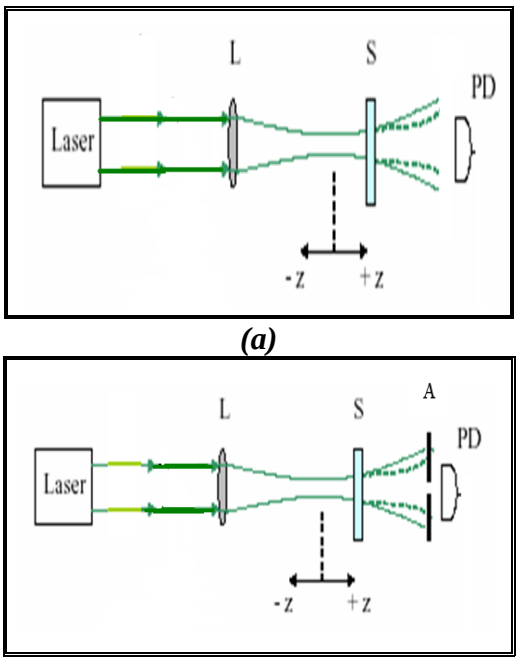

Fig. (2) (a) Open Aperture Z-Scan, (b) Closed Aperture Z-scan. [8].

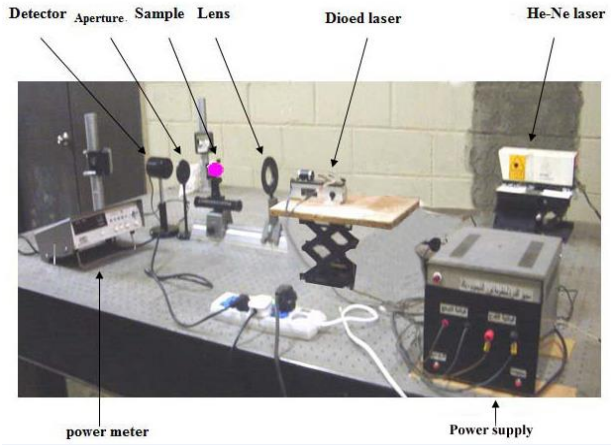

Fig. (3) Photographic picture for the experiment setup.

For this, the transmittance through the sample is monitored as a function of the incident laser light intensity, with and without an aperture in the far field, while the sample is gradually translated along the optical axis of a convex lens. The intensity dependent transmission through the sample measured as a function of sample position with respect to the focal plane, without an aperture (open aperture (OA), Fig.(2a)) gives information about purely absorptive nonlinearity; whereas the transmission measured through an aperture inserted in the far field (closed aperture (CA), Fig.(2b) includes the effect of both nonlinear refraction and nonlinear absorption, if any, the division of the normalized closed aperture Z-scan data by the open aperture Z-scan data generates a Z-scan profile pertaining to the purely dispersive (refractive) nonlinearity [9]. Z-scan method provides a direct measurement of the real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$.

The sign of the nonlinearity is an important parameter for practical realization of optical signal processing devices [10]. This information cannot be obtained from any other techniques such as degenerate four waves mixing or third harmonic generation. In general, the manifestation of strong nonlinear absorption enhances the optical limiting properties, whereas that of strong nonlinear refraction facilitates the switching properties of organic molecules [11].

Closed aperture Z-scan technique is based on the transformation of phase distortions to amplitude distortions during beam propagation. A qualitative physical argument that explains the transmittance variations in the Z-scan experiment can be given as follows: Starting the scan from a distance far away from the focus (negative z), the beam irradiance is low and negligible nonlinear refraction occurs leading to linear transmittance. As the sample is brought closer to the focus, the beam irradiance increases leading to self-lensing in the sample. A negative self-lensing (self-defocusing) prior to focus tends to collimate the beam and reduce the diffraction leading to a smaller beam at the aperture and an increased transmittance. As the scan continues and the sample crosses the focal plane to the right (positive z), the same self-defocusing effect will tend to augment diffraction and reduce the aperture transmittance. A prefocal transmittance maximum (peak) and a post focal transmittance minimum (valley) will be, the z-scan signature of a negative nonlinearity as shown by the dote line Fig.(3), while a positive one, following the same analogy, will give rise to an opposite valley-peak configuration, as shown by Solid line Fig. (4). [9].

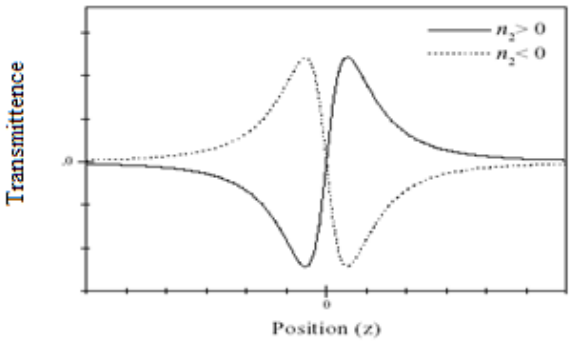

Fig.(4) Calculated Z-scan transmittance curves for a third order nonlinearity [8].

Self Focusing and Defocusing

Self-focusing (or Kerr-lansing) is a consequence of the non-uniform spatial profile of the laser Gaussian beam. If the intensity of a transmitted light beam is sufficiently high, the refractive index change will modify the light propagation not only with respect to the polarization but in its geometrical properties too [12].

For a Gaussian beam of radius ω_o (beam waist) the Kerr-lens focal length is:

$F = a\,\omega_o^2/4tn_2I$ .....(1)

Where t is the thickness of the nonlinear medium (sample), I is the irradiance and a is a correction term.

When n_2 is negative, the above equation shows there will be a negative focal length and thus self de-focusing of the incident beam [8].

Results and Discussion

The absorption spectra of dye doped polymer films for various dye concentrations 10^{-6} M, 10^{-5} M, and 10^{-4} M are illustrated in Fig.(5). The spectra of the dye molecule exhibit a wide absorption band with distinct peaks, which are located at 560 nm.

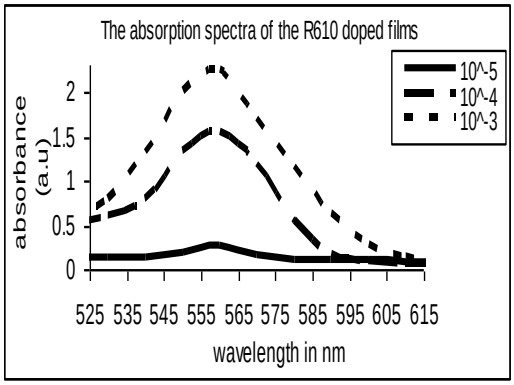

Fig.(5) Linear absorption spectra of R610 Doped films.

The third-order nonlinear refractive index n_2 and the nonlinear absorption coefficient β, of the R610 dye doped polymer films in PMMA at various concentrations for the incident intensity I_0= 509.6 W/cm^2 were evaluated by the measurements of Z-scan. Fig.(6) shows the typical OA Z-scan profiles of the solid films for the three different concentrations of the dye.

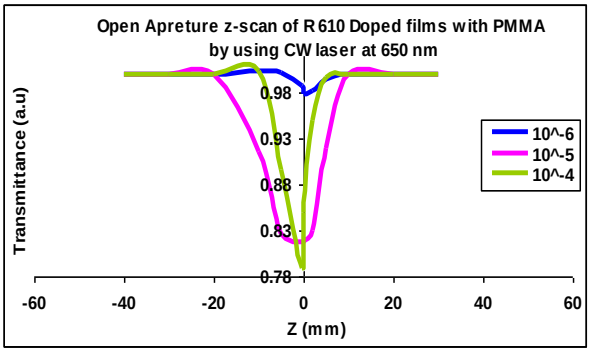

Fig.(6) OA Z-scan profile of R610 solid films of concentration 10^{-6} M, 10^{-5} M, and 10^{-4} M at I_0=509.6watt/cm^2.

The linear transmittance is normalized to unity. When the sample is away from the focus Z=0, the incident laser intensity is low and the normalized transmission is close to 1; when it moves close to the focus, the OA Z-scans exhibits a reduction in the transmission which is symmetric about the focus Z=0 for all concentrations studied. This is typical of an intensity dependent enhanced absorption termed reverse saturable absorption (RSA) or positive nonlinear absorption exhibited by a nonlinear material [13], and can be exploited for protection of eyes and sensors against radiation induced damage.

Measurements of β_2 are performed using the following equation [8]:

The total transmittance is given by:

$$T(z) = \sum_{m=0}^{\infty} \frac{\left[\frac{\beta I_o L_{eff}}{1+(Z/Zo)^2}\right]^m}{(m+1)^{3/2}} \quad \text{.....(2)}$$

Where,

Z: - is the sample position at the minimum transmittance, *m*: - integer.

T (z):- the minimum transmittance. The two terms in the summation are generally sufficient to determine β.

$L_{eff.}$: - the effective length of the sample, can be determined from the following formula: [11]

$$Leff = [1-\exp(-\alpha_0 L)]/\alpha_0 \quad \text{.....(3)}$$

Where, L is the sample length, α_o is the linear absorption coefficient,

$$\alpha_o = \frac{1}{L \ \ln(\frac{1}{T})} \quad \text{.....(4)}$$

Where T: linear transmittance

$$I_o = 2P_{peak} / \pi\omega_o, \quad \text{..... (5)}$$

where, ω_o: - the beam radius at the focal point, $P_{peak:-}$ the peak power,

$$Z_0 = k\omega_0^2/2 \quad \text{.....(6)}$$

Z_0 is the diffraction length of the beam, $k=2\pi/\lambda$, the wave number, and λ, the wavelength of the laser light [14].

For closed aperture z- scan we define the change in transmittance between the peak and valley in a Z-scan as:

$$\Delta T_{pv} = T_p - T_V \quad \text{.....(7)}$$

Where T_p and T_v are the normalized peak and valley transmittances as seen in Fig.(3). The empirically determined relation between the induced on axis phase shift, $\Delta\Phi_0$, and ΔT_{pv} for a third-order nonlinear refractive process in the absence of nonlinear absorption (NLA) is, [2]

$$\Delta T_{pv} \cong 0.406(1-S)^{0.27}|\Delta\phi_o| \quad \text{.....(8)}$$

S: the size of the aperture.

The size of the aperture is signified by its transmittance. In most reported experiments, $0.1<S<0.5$ has been used for determining nonlinear refraction. S the aperture linear transmittance is given by [13]:

$$S = 1 - \exp(-2 r_a^2/\omega_a^2) \quad \text{.....(9)}$$

with r_a denoting the aperture radius(it is 0.5 mm),and, ω_a denoting the radius of the laser spot before the aperture (it is 0.015 mm). In our experiment S= 1.12E-4 then $(1-1.12E-4)^{0.27} = 0.999999999 \approx 1$) so:

$$\Delta T_{pv} \cong 0.406|\Delta\phi_o| \quad \text{.....(10) [15]}$$

and this analogy with Mansoor Sheik-Bahae, 2007[15].

The nonlinear refractive index is calculated from the peak to valley difference of the normalized transmittance by the following formula: - [6, 8 and 15]

$$n_2 = \Delta\phi_o / I_o L_{eff}\ k \quad \text{.....(11)}$$

Closed aperture Z-scan profile (The defocusing effect) of R610 solid film at concentration 10^{-6}, $10^{-5}$and 10^{-4} M for Io= 509.6 GW/cm^2 are shown in Fig.(7).

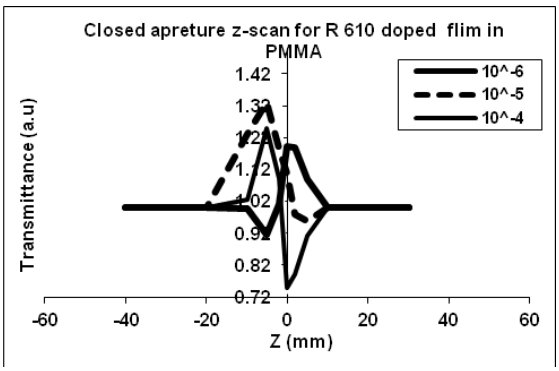

Fig. (7) CA Z-scan profile of R610 solid film at concentration 10^{-6}, 10^{-5}, 10^{-4} M for Io= 509.6 GW/cm^2 indicates to positive refractive index for film of concentration (10^{-6}) M ,and negative refractive index for films of concentration ($10^{-5}$and 10^{-4})M.

Fig (7) indicates to positive refractive index for film of concentration (10^{-6}) M, and negative refractive index for films of concentration (10^{-5}and10^{-4}) M is attributed to a thermal nonlinearity resulting from the absorption of radiation at 650 nm. Analogy to the theoretical behavior of the dotted line in Fig.(4).

Experimentally determined nonlinear refractive index n_2 and nonlinear absorption coefficient β can be used in finding the real and imaginary parts of the third-order nonlinear optical susceptibility [χ^{3}] according to the following: [15]

$$\text{Re}\,\chi^{(3)}\,(\text{esu}) = 10^{-4}\,\varepsilon_0 c^2 n_0^{\,2}\, n_2/\pi \ (\text{cm}^2/\text{W}) \quad \text{.....(12)}$$

$$\mathrm{Im}\chi^{(3)}(\mathrm{esu}) = 10^{-2}\,\varepsilon_0 c^2 n_0{}^2 \lambda\beta / 4\pi^2 \ (\mathrm{cm/W}) \quad \text{.....(13)}$$

Where ε_0 is the vacuum permittivity, and c is the light velocity in vacuum. [16]

The absolute value of the third-order nonlinear optical susceptibility is given by the relation:

$$|\chi^3| = \left[(\mathrm{Re}(\chi^3))^2 + (\mathrm{Im}(\chi^3))^2\right]^{1/2} \quad \text{.....(14)}$$

The experimentally determined values of Tp–v, n_0,n_2, Δφo and Rχ3 are given in Table (1). The experimentally determined values of β, Im χ^3, χ 3 . are given in Table (2).

Table (1)
Nonlinear parameters for PMMA Films Doped with R610 in Chloroform with various Concentrations of dye by using CW diode laser at 650 nm for closed aperture.

C (M)	*Tp–v*	*n_o*	*n_2 [cm²/W]*	*Δφo*	*R χ^3 esu*
10^{-6}	0.343	1.56	1.813E-06	0.844	1.12E-02
10^{-5}	0.290	1.55	3.067E-06	0.715	1.88E-02
10^{-4}	0.714	1.94	4.628E-06	1.758	4.42E-02

Table (2)
Nonlinear parameters for PMMA Films Doped with R610 in Chloroform with various Concentrations of dye by using CW diode laser at 650 nm for open aperture.

C (M)	*T(z)*	*β (cm/watt)*	*Im χ^3 (esu)*	*χ 3 (esu)*
10^{-6}	0.289	0.405	1.639	1.280
10^{-5}	0.678	1.085	2.814	1.678
10^{-4}	0.844	1.305	3.413	1.848

From Fig.(8 a and b), there is an increasing trend for the values of n_2 and β as the concentration increases. This may be attributed to the fact that the number of dye molecules increases as the concentration increases, more particles are thermally agitated resulting in an enhanced effect.

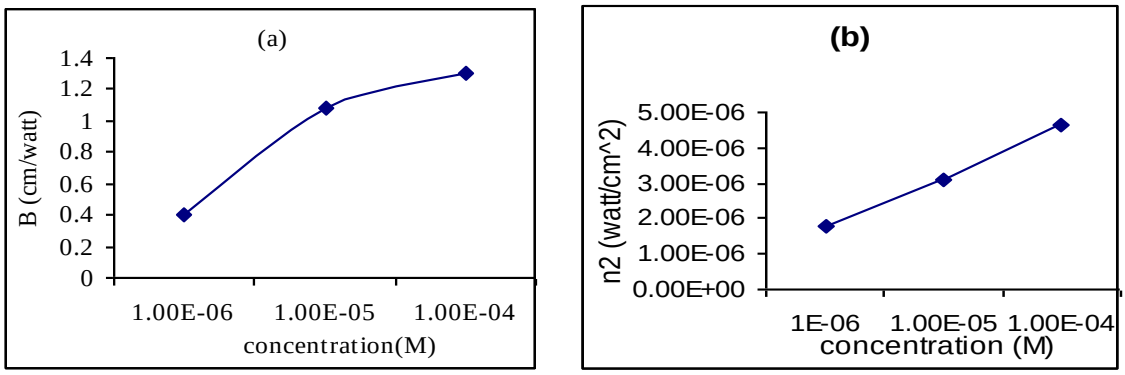

Fig. (8) Concentration dependence n2(a) and β (b) of R 610 dye in polymer film.

With cw pumping we expect major contribution to the observed third-order nonlinearities to be thermal in nature. The energy from the focused laser beam is transferred to sample through linear absorption and is manifested in terms of heating the

medium leading to a temperature gradient and there by the refractive index change across the sample which then acts as a lens. The phase of the propagating beam will be distorted due to the presence of this thermal lens. The peak–valley separation of more than 1.7 times the Rayleigh range of ~ 0.0138 cm also suggests the presence of thermal component in our case. It is well established that a separation of ~ $1.7z_0$ indicates Kerr-type of nonlinearity [1 and 16].

It is worth noting that the value of $\chi 3$ for the dye studied is larger than those of some representative third-order nonlinear optical materials such as safranin O [1] dye and its derivatives and organic dyes like Mercurochrome [2].

Conclusion

The third order nonlinear optical properties of R 610 dye have been studied. Both NLA and NLR contribute to the large third-order nonlinearity of the dye. The origin of optical nonlinearity observed in the cw regime is attributed to the thermal variation of refractive index in the medium. The aperture limited designs based on thermo-optic nonlinearity such as the one studied here can be used as efficient limiters in the CW regime. There is an increasing trend for the values of n_2 and β as the concentration increases. This may be attributed to the fact that the number of dye molecules increases as the concentration increases, more particles are thermally agitated resulting in an enhanced effect.

These samples will find potential applications in optical limiting and signal processing applications.

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وذلك لزيادة سمك الغشاء الذي يؤدي الى زيادة إزاحة الطوراللاخطي في النماذج. عند إزالة الفتحة من أمام الكاشف اظهرت النتائج إمتصاص فوتونين Two photon absorption .أوحت النتائج أن أ فلام R610 بإمكانها أن تكون أوساط لمختلف التطبيقات الكهربائية الضوئية تشتمل على المحددات البصرية للقدرة.

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الخلاصة

نقدم في هذه الورقة البحثية دراسة للصفات اللاخطية لأغشية الصبغة الليزرية رودامين ٦١٠ R والمطعمة مع البوليمر (PMMA) بتراكيز مختلفة بأستخدام المذيب الكلوروفورم و ذلك باستخدام طريقة ذات حساسية عالية تعرف بتقنية المسح على المحور الثالث Z-scan. تم أجراء تجربة المسح على المحور الثالث باستخدام ليزر الدايود ذو الموجات المستمرة عند طول موجي ٦٥٠ نانومتر و قدرة خارجة ٤٥ ملي وات على جزئيين: الجزء الأول تم وضع فتحة أمام الكاشف لغرض دراسة معامل الانكسار اللاخطي. في الجزء الثاني أزيلت الفتحة من أمام الكاشف (open aperture) لغرض قياس معامل الامتصاص اللاخطي. أظهرت التجارب في حالة وضع الفتحة أمام الكاشف إن أغشية الصبغة المطعمة تظهر معامل انكسار لاخطي سالب (self-defocusing) للتراكيز (10^{-5} M, &10^{-4} M)، بينما الغشاء الذي تركيزه 10^{-6} M أظهر إنكسار موجب (self-focusing).أظهرت التجارب ايضا ان معامل الإنكسار اللاخطي وقابلية التأثراللاخطية من الدرجة الثالثة (third order susceptibility) تزداد بزيادة التركيز