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Shaymaa Jabbar Abdulrazzaq
Department of Physics, Faculty of Education for Girls, University of Kufa, Iraq

Corresponding Author:
Shaymaa Jabbar Abdulrazzaq
Department of Physics, Faculty of Education for Girls, University of Kufa, Iraq

Enhancing the optical limiting characteristics for thin film of azure a dye by doping with PVA polymer and Ag nanoparticles

Shaymaa Jabbar Abdulrazzaq

Abstract
The objective of this research endeavour is to analyse the spectrum, linear and nonlinear optical characteristics, and the utilization of condensation (10^{-5}M) doped with polymer and nanomaterials in (Azure-A) organic laser dye. Polymer and nanoparticle compounds have the potential to develop various features of organic dyes, which has practical uses. The spectral optical characteristics of every prepared sample were investigated by means of a spectrophotometer. The Z-Scan method was employed to measure the nonlinearity in two sections (open and close aperture) in order to obtain the nonlinear absorption factor (β) and refract tile index (n_2). The studies were conducted using a solid-state laser with a wavelength of (457 nm). The study found that as the nonlinear refractive index rose, the absorption coefficient decreased, and as (n_2) increased, (β) increased in all samples. It was discovered that the doped samples containing the polymer had enhanced nonlinear properties, and that the nonlinear refractive index of every sample rose when the laser's power was raised. In contrast, when sample power rises, the nonlinear absorption coefficient decreases for all samples.

Keywords: Z-Scan device, linear optical properties, Non-linear optical properties, PVA Polymer

1. Introduction
Hydrocarbons and the materials derives from them are categorized as organic substances. Moreover, it is possible to isolate the saturated and unsaturated elements. Due to the wide range of chemical compounds present and their considerable concentrations, organic matter can exhibit exceptionally high nonlinear coefficients.

Thus, recently various theoretical and emperical investigation concerning the nonlinear optical (NLO) properties have been conducted [1]. Z- Scan is a fundamental instrument employed for determining the nonlinear optical properties. It represents a common emperical approach applied to identify the nonlinear optical properties of materials.furthermore, it can rapidly measure the conductivity of nonlinear absorption and refraction and refraction in solids and liquids, in addition to identifying the optical limited conduct [2].

The Z-Scan method has been applied for identifying optical nonlinearity of different organic compounds. It is a useful device for clear and rapid measurement of the optical materials' nonlinear refractive index. An on-axis broadcast signal is determined by a detector behind a small aperture in the distant area inspired by a guided laser beam's z-axis power pattern. For determining the refractive index modifications resulted from optical nonlinearities in the sample as a function of the model refractive index shift, typical intensity fluctuations in the transmitted signal are utilized. To recognoze the nonlinear shift index, the intensity sample position variations was employed. Furthermore, Z-Scan method was employed for detecting small linear absorption that uses low-power CW lasers. As organic componds, the transmission of optical limiters materials are decreased when the intensity of light is increased for protecting the eyes and sensors [3]. Hydrocarbons and their products are organic compounds. Accordingly, saturated and unsaturated materials can be distiguished [4]. The light-emitting particles known as organic laser dyes have long conjugate double bond systems and a high molecular weight. In most cases, their absorption spectrum is rather wide [5]. Because of their diverse ring configurations, laser dyes exhibit a broad spectrum of absorption and emission, making them a complex and perplexing chemical. It can be categorised into various classifications according to the degree of chemical similarity between their structures. Pyrromethene, xanthene, and coumarin are three fundamental examples.

The spectral emission is significantly influenced by the configuration and properties of the molecules [6].

This work investigated whether the nonlinear optical features of an organic laser dye at condensation concentrations (10^{-5}M) may be used as a limiter device for various purposes. A (CW) solid-state diode laser with a wavelength of 457 nm and a power of (56, 70, 84, 102) mW are employed for conducting the current investigation.

2. Theory

Z-scan technique

Using the z-scan technique, (n_2) and (β) are calculated for each sample. For the closed aperture Z-scan procedure, a solid-state (457 nm) continuous wave diode pump laser served as the light source. The laser intensity and a Gaussian CW laser beam with clearly evident vertical polarization (56 mW). A convex lens with a 15 cm focal length focused the laser beam at the stimulated sample under normal incidence geometry. By continuously scanning the sample along the z-axis, transmittance was determined as a function of sample position. Figure displays the z-scan experiment's configuration diagram (1).

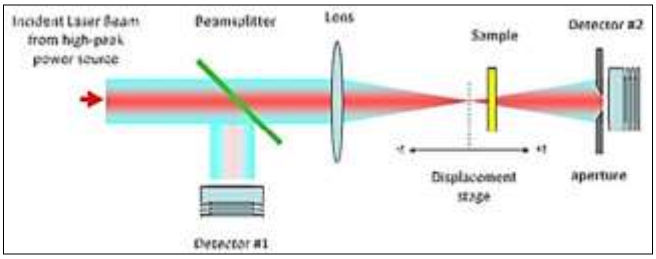

Fig 1: The empirical setup for closed aperture z-scan device

3. Employed Materials

A- Azure A

The central ring of the thiazine molecule Azure A contains sulfur and nitrogen atoms, making it a type of organic color. The molecular weight is 291.8 g/mol and the structural formula is $C_{14}H_{14}N_3SCl$. It is soluble in water and has low ethyl alcohol content, causing it to appear blue in colour. Its peak absorption ranges from 620 to 634 nm. Figure illustrates the Azure-A dye's molecular structure (2) [7, 8].

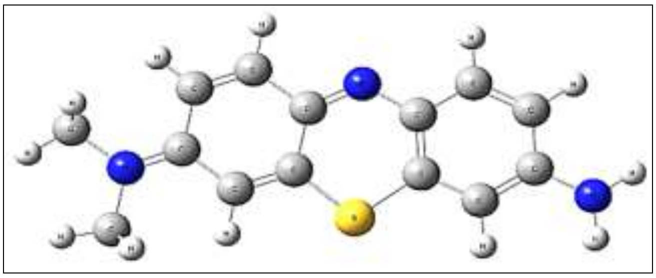

Fig 2: Molecular composition of Azure-A organic dye.

B- Ethanol Solvent

In its refined form, ethanol is a colourless liquid that is made up completely of alcohol. It is also usually referred to as ethyl alcohol. When consumed, ethanol has the potential to induce a state of intoxication similar to that of alcohol. As a result, a blue flame is produced that burns. The length of the carbon chain and the presence of the hydroxyl group are the primary factors that determine the physical properties of ethanol. A colourless, volatile liquid with a molecular weight of (46.07 gm/mol) and a density of (0.789 gm) per cubic centimetre [9].

C. Polyvinyl alcohol (PVA)

The synthetic semi-crystalline polymer PVA, often known as poly (vinyl alcohol), has the chemical formula $[CH_2CH(OH)]_n$. PVA is white and has no smell. PVA is normally sold as a powder, though rarely it can also be obtained in beads or solutions. The molecular weights of PVA products range from 20,000 to 400,000 Da. Due to its fascinating physical characteristics, polyvinyl alcohol (PVA) is extremely helpful in both material science and technical applications.. PVA has many applications as a binder in Dyes, ceramics, fibers, plastics, cement, and cork compositions etc. [10, 11].

D- Silver nanoparticles (Ag NPs)

Depending on the application of the study, there are numerous shapes that can be created for nanoparticles. The supplier of the silver nanoparticles was Laboratory Reagent LTD. The size range of silver nanoparticles is between 1 and 100 nm. Several materials have a high surface-to-bulk silver atom ratio, despite being referred to as "silver" and containing a considerable quantity of silver oxide. Silver nanoparticles (Ag-NPs) are widely employed for their remarkable optical, electrical, mechanical, catalytic, and antibacterial properties [12, 13].

4. Preparation the Samples

Dissolving a mass of (0.0029) gm of dye powder in ethanol solvent of (10 cm^3) is needed to get a concentration of (10^{-5}) M for the Azure-A. A German electronic balance with a sensitivity of four digits (BL 210 S) was used to measure the concentration of dye powder employing an equation [14].

$$W = \frac{M_W \times V \times C}{1000} \quad (1)$$

The major parameters are the substance's weight (g), molecular weight (g/mol), solvent volume (mL), and concentration (M). The dilution relationship that follows from the concentration is used to produce a solution with a lower concentration of (10^{-5}) M [15].

$$C_1V_1 = C_2V_2 \quad (2)$$

In this context, (C_1) is the starting concentration and (C_2) is the current concentration in this context. The volume before dilution is represented by (V_1), while the volume after dilution is represented by (V_2).

Azure-A thin films were drop cast on a sterilized glass slide. Each thin film was dried at room temperature for three days after being made from a (10^{-3}) M solution [16]. These thin films come in a range of thicknesses ranging from 150 to 250 nm. A dye-doped thin film Michelson's interferometer uses partial reflection to divide a paralleled beam of light into two parts. For produsing the dye-doped polymer films with a concentration of (10^{-3}) M, drop casting was employed. Polymer must be dissolved to form the solution ("2 mg in 50 mL of Ethanol solvent"). A unique method measured dye-doped thin film thickness [17].

4. Discussions

A. The Optical Characteristics of Nonlinear

It was possible to calculate the nonlinear absorption coefficient of (Azure-A) in ethanol solvent for different powers (56, 70, 84, 102) mW by employing the open-aperture Z-Scan method and applying the resulting relationship [18]:

$$\beta = \frac{2\sqrt{2}}{I_o L_{eff}} \Delta T$$

Io denotes the intensity of the laser beam at the focal point (Z=0), and (ΔT) represents the normalised transmittance difference between the baseline and the peak at the focal point (Z=0) in the open-aperture Z-scan normalised transmittance curve.

$$I_o = \frac{2P_o}{\pi \omega_o^2} \qquad (2\text{-}26)$$

Where (P_o) is the laser input power, (ω_o) is the beam radius at the focal point, (L_{eff}) is the effective length of the sample and given by:

$$L_{eff} = 1 - \frac{\exp(-\alpha_o L)}{\alpha_o} \qquad (2\text{-}27)$$

Where (L) is the true sample length.

Increased transmission around the focal point of the lens is seen during the Z-Scan with an open aperture. Figures (3) show open-aperture Z-scans of samples in ethanol solvent at a wavelength of 457 nm. We have seen the two-photon absorption phenomenon. Transmission begins to behave linearly (-Z) when the sample location is altered, depending on how far the model point is from the far-field. In the near field, transmittance curve steadily decreases until it reaches (Tmin) at the focal point (Z=0 mm). In the far field (+Z), it increases linearly.In this particular instance, two photon absorptions take place as the model traverses the beam waist, leading to a modification in the intensity level. Using a Z-scan with an open aperture, fluctuating transmittance measurements may be used to calculate the absorption coefficient. The focus plane has the greatest intensity and most nonlinear absorption [19, 20].

Figures (4) and (5) demonstrate saturable absorption in thin films of the compounds examined using an open-aperture Z-Scan. Transmission curves are linear (-Z) from the model site's distant field. The near-field transmittance curve reaches to

(T_{max}).

Following that, transmittance decreases linearly in the direction of the far-field (+Z) of the sample point until it reaches zero. Nonlinear absorption causes the transmittance to grow in direct proportion to the applied power. The intensity shift happens because the sample undergoes saturation absorption as it passes through the beam waist. Maximum intensity and nonlinear absorption occur in the focal plane. Nonlinear events are only visible in a Gaussian beam's far field owing to its low intensity. The asymmetric peak value increases the negative nonlinear absorption coefficient as a result of the sample's bleaching-like characteristics (Absorption saturation). This conduct was consistent with [21].

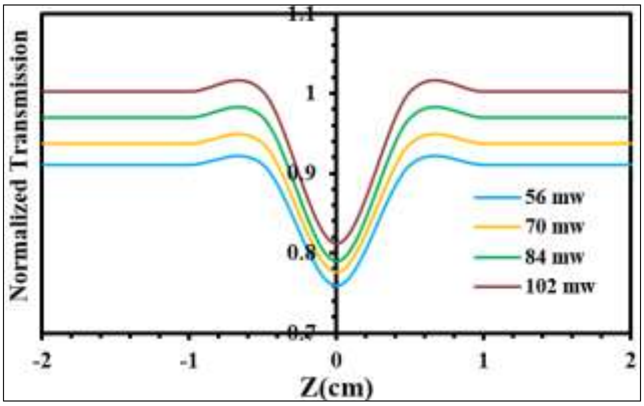

Fig 3: Open-aperture Z-Scan data of Azure-A as solution.

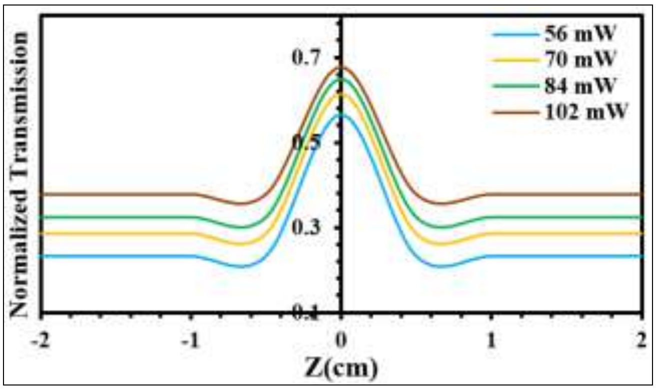

Fig 4: The results of an open-aperture Z-scan of a thin layer of (Azure-A + PVA) with several laser powers.

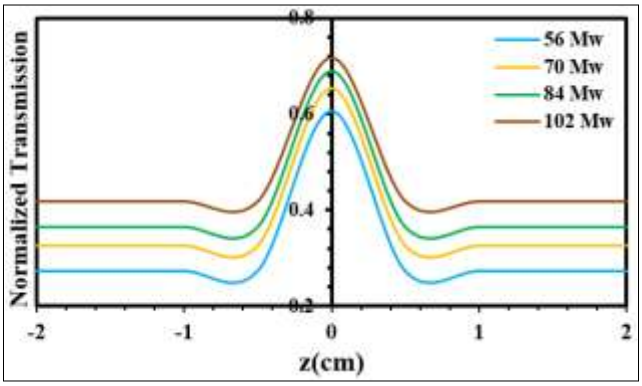

Fig 5: The results from an open-aperture Z-Scan for thin layer of" (Azure-A +PVA+ Nano) with several laser powers.

B. Nonlinear Refractive Index

The dye's nonlinear refractive index at (10^{-5}) M in ethanol solvent was measured using the Z-Scan closed-aperture technique. On the right are Z-Scan-normalized transmissions. For identifying the nonlinear refractive index (n_2), the subsequent standard relationships were applied [22]:

$$n_2 = \frac{\Delta\Phi_o}{I_o L_{eff} K}$$

Where (K) is the wave number ($K=2\pi/\lambda$) and (λ) is the laser wavelength.

$\Delta\Phi_o$) represents the laser beam's on-axis phase shift as it travels through the medium. The phase shift is proportional to the difference between (T_p and T_v) for the closed-aperture Z-Scan ($\Delta T_{P\text{-}v}=T_p-T_v$) using the equation below:

$$\Delta T_{P-V} = 0.406(1-s)^{0.25}|\Delta\Phi_o| \quad (2\text{-}30)$$

Where (S) denotes aperture linear transmittance, and given by:

$$s = 1 - \exp\left(\frac{-2r_o^2}{\omega_o^2}\right) \quad (2\text{-}31)$$

In the linear region, (r_o) is the diameter of the slit.

The data for (Azure-A) dye at a concentration of (10^{-5}) M are depicted in Figure 6 as a function of distance. This figure shows the extending of the nonlinear effect zone from -2 cm to 2 cm. Figures (7) and (8) show stabilised Z-Scan transmissions for thin films of (Azure-A) dye at concentration (10^{-3} M). Z-Scan data analysis reveals a peak and valley in the transmission curve at closed apertures, suggesting negative (n_2<0) nonlinearity and self-defocusing lensing. This conduct is consistent with [23].

Doped dye exhibits more nonlinearity than solution dye. These non-linear characteristics, obtained as in table (1), show that (n_2) values rise with power and decrease with (β). Variable transmittance values may be generated by employing the closed-aperture Z-scan. The nonlinear phase shift $\Delta\Phi_o$ may be estimated using these numbers.

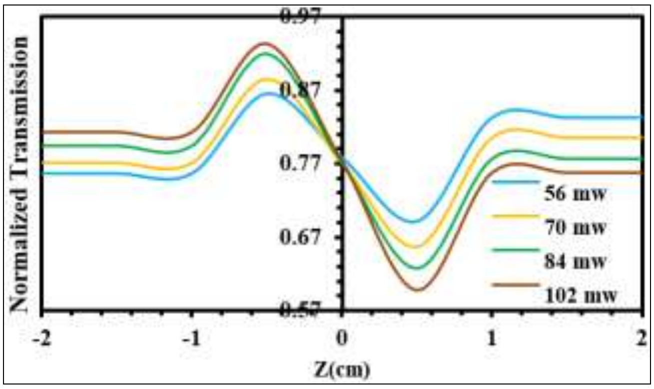

Fig 6: Azure-A data from a closed-aperture Z-Scan as a solution.

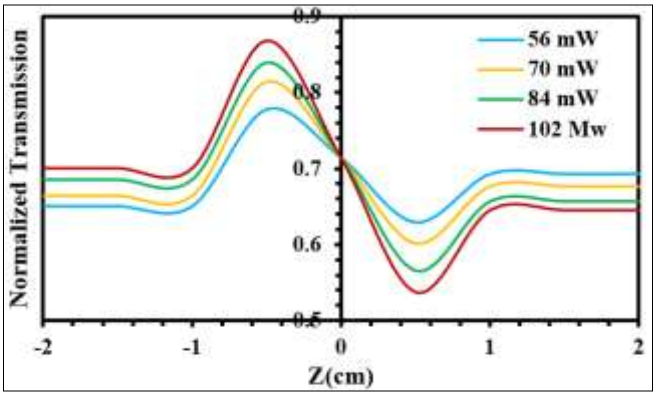

Fig 7: The results of an closed-aperture Z-Scan of a thin layer of (Azure-A + PVA) with several laser powers.

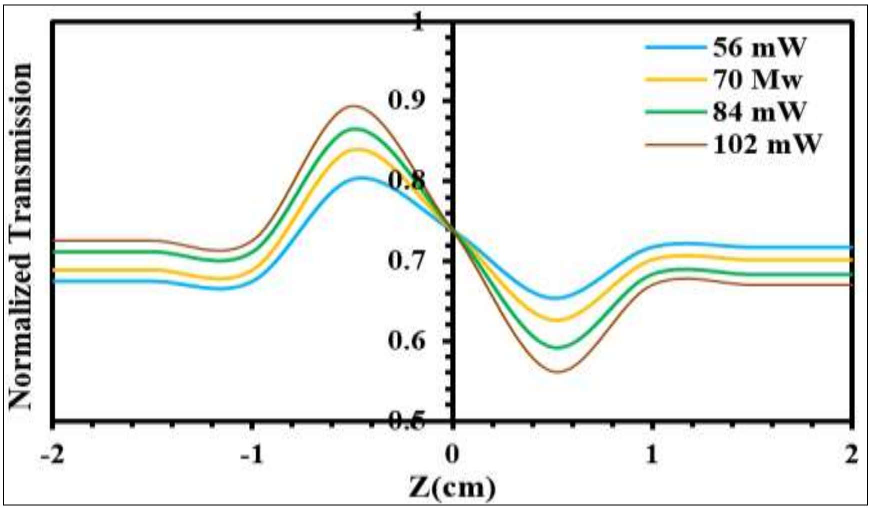

Fig 8: The results of an closed-aperture Z-scan of a thin layer of (Azure-A +PVA+ Nano) with several laser powers.

Table 1: The nonlinear optical properties of Azure-A at λ = 457nm with several laser powers.

Material	Power (mW)	$\Delta T_{P\text{-}V}$	$\Delta\Phi_o$	n_2 (cm²/mW)	T (z)	B (cm/mW)
Azure-A	56	0.1499	0.4284	5.5791×10^{-9}	0.4566	0.388×10^{-3}
	70	0.2157	0.6329	5.8786×10^{-9}	0.4237	0.328×10^{-3}
	84	0.2345	0.6983	5.9129×10^{-9}	0.5453	0.278×10^{-3}
	102	0.3312	0.7439	6.1995×10^{-9}	0.6123	0.238×10^{-3}
Azure-A + PVA polymer	56	0.1989	0.5521	4.9840×10^{-6}	0.5766	0.2163
	70	0.2727	0.6861	4.9549×10^{-6}	0.6142	0.1964
	84	0.3631	0.8415	5.0643×10^{-6}	0.6301	0.1939
	102	0.3812	0.9471	5.0397×10^{-6}	0.6777	0.1505
Azure-A + PVA polymer + Ag NPs	56	0.2189	0.6007	9.871×10^{-6}	0.5416	0.4197
	70	0.2726	0.7353	9.645×10^{-6}	0.5892	0.3833
	84	0.3631	0.8908	9.746×10^{-6}	0.6551	0.3193
	102	0.4712	0.9963	9.628×10^{-6}	0.6547	0.2886

C. Limiting Optical Behavior

The optical limiting behaviour was studied using a Z-Scan methodology and a laser closed gap, which are comparable methods. Figure (9) depicts the sample's optically limiting properties. When a threshold is reached, samples defocus the beam, increasing output power according to input power. This indicates that the optical limiting behaviour of modified polymer and nanoparticle dyes in general, and thin films in particular, has been considerably optimised in comparison to liquid specimens. Threshold and amplitude are both reduced in Azure-A thin coatings compared to Azure-A solutions. Such behaviour is in accordance with [24, 25, 26]. As demonstrated in Table (2), Azure-A thin films have a lower optical power limiting threshold and amplitude than dyes in solution.

Table 2: The optical limiting response of thin films doped with PVA polymer and Ag NPs containing (Azure-A) dye.

Case of organic dye	Limiting threshold	Limiting amplitude
Dye solution	91	9.12
Dye +PVA polymer	85	8.14
Dye+ PVA polymer + Ag NPs	82	6.52

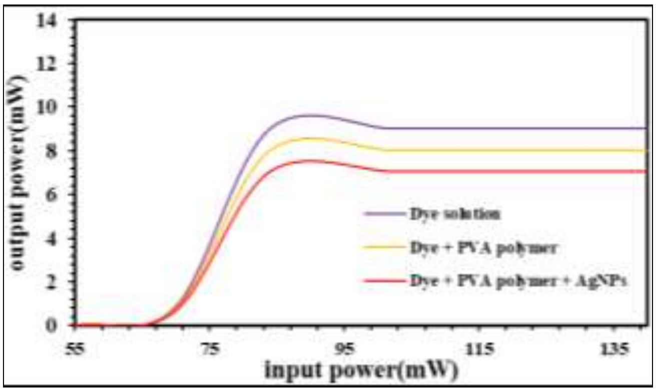

Fig 9: Optical limiting of Azure-A dye (solution, PVA, Nano).

5. Conclusions

The Z-Scan technique was used to study an ethanol solvent with an organic laser dye solution of (Azure-A) at a condensation point of 10^{-5} M using a (457 nm) continuous-wave laser. According to the findings, extraordinarily strong nonlinear optical properties are associated with the materials. The nonlinear absorption factor may be caused by a two-photon absorption process, whereas (n_2) might be caused by self-focusing. Improved optical limiter qualities and an increase in nonlinear features are seen in dye films that have been grafted with polymer and nanomaterials, according to the results.It has been studied how optical limiting behaves. These exploration findings show that this dye has potential use in optical power limiting and nonlinear optical systems.

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