Nonlinear Optical Characteristics of Thin Films Made from Mixed Organic Laser Dyes Doped with Metal Nanoparticles and PMMA Polymer

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This study examines the non-linear optical characteristics of thin films made of an organic laser dye combination of Malachite Green and Nile blue doped with PMMA polymer and Au, Ag, and Cu nanoparticles that have been dissolved in chloroform solvent. Samples of thin films made by drop-casting dye solutions at a concentration of 10^{-3} M. the absorption spectra for all samples in the (430–700) nm region. The Z-scan method, which has two kinds of closed and open apertures, has been used to investigate the non-linear absorption coefficient (β) and non-linear refractive index (n_2). Each thin film sample has an aperture that is open, allowing for saturable absorption. The outcomes demonstrated that extremely significant nonlinear characteristics are present in all thin films. According to the findings, there was a linear rise in the nonlinear refractive index with the nonlinear phase shift. According to the results, every sample has the potential to be employed as an active laser medium and in a variety of optoelectronic applications.

***Keywords*:** Organic dyes; Laser dyes; Nonlinear optics; Optical limiting
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1. Introduction

Researchers have been working hard in recent years to create novel composites based on insulators and large gap semiconductors, which include metal nanoparticles. These composites are thought to be promising materials for nonlinear optics and optoelectronics. Nonlinear optical effects and selective optical absorption in the same spectral area are explained by the phenomenon known as surface plasmon resonance (SPR). It is produced when electromagnetic (light) waves in such nanoparticles simultaneously stimulate the conduction electrons within them [1]. Free electrons in the conduction band fluctuate in response to light stimulation of the noble metal, occupying energy levels around the Fermi level, which creates the SPR. The nonlinearity of noble metal nanoparticles (NPs) such as gold (Au), silver (Ag), and copper (Cu) is enhanced by the UV-visible range of their surface plasmon resonance band (SPRB) when exposed to lasers [2,3]. Therefore, noble metal nanoparticles have drawn a lot of attention in photonics research. Optical limiters are necessary to prevent laser sources from harming sensors or the eyes by limiting the energy that may be transferred [4]. This theory requires at least one nonlinear optical (NLO) event to function. Many studies have been conducted on silver, copper, and other elements to be used in nonlinear optical (NLO) and optical linear (OL) applications in semi-continuous thin films, colloids, and other glass matrices [8–10]. The Z-scan method is a sensitive and straight forward technique that may be used to find the nonlinear refractive index and the nonlinear absorption coefficient. Numerous research organizations have adopted the approach because to its ease in both data processing and experimental setup [11]. Electronic cloud distortion or population redistribution are two possible sources of the electronic nonlinearity. A molecule transitions from its ground state to its excited state upon absorption of a photon. During this kind of transition, the dipole moment of the molecule shifts. Electronic nonlinearity will arise from the shift in the dipole moment [12,13]. It is commonly known that altering the duration or wavelength of a laser may significantly change the nonlinear optical behavior of materials [14]. Because of their optical, catalytically, mechanical, and electrical qualities, silver, cold, and copper-based nanomaterials are very desirable and have a plethora of uses in the fields of metallurgy, catalysis, nanotechnology, and optoelectronics [15–18]. In thin films prepared from mixtures of two organic laser dyes, Nile Blue (NB) and Malachite Green (MG), doped with PMMA polymer and gold (Au), silver (Ag), and copper (Cu) nanoparticles dissolved in chloroform solvent, the optical nonlinearity and optical limiting response were investigated in this work. At 457 nm wavelength and 84 mW power, a CW diode laser was employed.

2. Theory

The refractive index (n) and optical absorption (α) may be found as functions of the incident laser beam's intensity (I) using Maxwell's equations as [19]:

$$\alpha = \alpha_0 + \beta I \qquad (1)$$

where β is the linear absorption coefficient and α_0 is the intensity-related nonlinear absorption coefficient

Furthermore, the refractive index has changed when there is a powerful electric field surrounding everything. In reality, the electric field's intensity starts to affect the index of refraction. When the light is intense, the refractive index is determined by [19,20]:

$n = n_0 + n_2 I$ (2)

here, the nonlinear refractive coefficient is n_2 and the linear refractive index is n_0

The nonlinear refractive index may be calculated by using the formula below by dividing the peak to valley difference of the normalized transmittance [21]:

$$n_2 = \frac{\Delta\Phi_0}{I_0 L_{eff} k} \quad (3)$$

where I_0 is the incident laser intensity, k is the incident laser beam's wavenumber and equals k=2π/λ since λ is the incident laser beam's wavelength, and $|\Delta\Phi_o|$ denotes nonlinear phase shift and equals to [21]:

$$\Delta T_{p-v} = 0.406\ |\Delta\Phi_o| \quad (4)$$

where ΔT_{p-v} is the normalised transmittance difference, which can be computed using a closed aperture Z-scan setup, between the transmittance values at the top and the valley

The following equation can be used to compute the nonlinear absorption coefficient (β) [20]:

$$\beta = \frac{2\sqrt{2}T(Z)}{I_0 L_{eff}} \quad (5)$$

$T(Z)$ denotes the lowest normalized transmittance that may be achieved using an open aperture Z-scan configuration

Equation (4) may be used to determine the effective length (L_{eff}) of an optical medium as shown below [20,21]:

$$L_{eff} = \frac{(1-exp^{-\alpha L})}{\alpha_0} \quad (6)$$

where L is the length of a sample and α_0 is the linear absorption coefficient

3. Experimental Part

The Nile Blue (NB) dye that used in this research was supplied by Sigma-Aldrich (Germany) with high purity (99.9%), chemical formula of $2C_2OH_2ON_3O.SO_4$, and molecular weight of 732.85 g/mol. Malachite green (MG), which serves as an active medium in dye lasers, is the dye selected in this study because of its significance in a variety of applications. An organic substance belonging to the Xanthene group is malachite green. Malachite green is traditionally used as an antibacterial in aquaculture as well as a dye for textiles like silk, leather, and paper. It looks like metallic-looking green crystals [19].

Chloroform was utilized as a solvent. It is relatively unreactive, miscible with most organic liquids. The molecular structure of chloroform solvent is $CHCl_3$, molar mass of 46.07 g/mol, and polarity of 0.5771 [22]. PMMA (polymethyl methacrylate) polymer has named as acrylic or the acrylic glass and it has the trade names such as Plexiglas. Molecular structure of PMMA polymer is $CH_2{=}C(CH_3)COOR$, and its molecular weight is 84000 g/mol [22,23].

Silver (Ag) nanoparticles vary in size from 1 to 100 nm. Despite being referred to as "silver", some actually include a sizable quantity of silver oxide due to their high surface-to-bulk ratio. The shape of the nanoparticles may vary depending on the goal of the investigation. Sigma-Aldrich produces nanopowders with surface area larger than 40 m^2/g [24,25]. The gold (Au) tablet that is used in this research was obtained by the Central Bank of Iraq with high purity (99.9%). The diameter of this tablet is 2 cm and its thickness is 2 mm. The copper (Cu) nanoparticles were supplied from Laboratory Reagent, Ltd. Because of their excellent thermal conductivity and other heat transfer characteristics, copper nanoparticles are very desirable. Comparing copper nanoparticles (CuNPs) to precious metals like gold (Au), silver (Ag), or palladium (Pd), they also exhibit higher surface area-to-volume ratios, lower manufacturing costs, antibacterial potency, catalytic activity, and optical and magnetic qualities. The primary challenge is to their preparation and preservation, since they quickly oxidized upon exposure to oxygen. The circumference was ranging in 40-70 m^2/g and the layer thickness within the range of 10-100 nm [23].

Using the drop casting method, thin films were made for a combination of NB+MG with PMMA polymer, gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs) on a clean glass slide. Each solution was generated at a concentration of 10^{-3} M, and the films were dried at ambient temperature (25-30°C) for two days. These thin films range in thickness from 110 to 200 nm. Using an optical approach and an optical thin film measuring model, the thickness of the thin films was measured (LIMF-10). The required quantity of polymer (2g in 30ml of chloroform solvent) is dissolved to prepare polymer solution and a uniform mixture, the polymer solution was mixed with the appropriate amount of dye solution at room temperature (25–30°C) using a magnetic stirrer. A 0.01g weight of gold (Au), silver (Ag) and copper (Cu) nanopowders were added and mixed using a magnetic stirrer to obtain a homogenous mixture, as shown in Fig. (1).

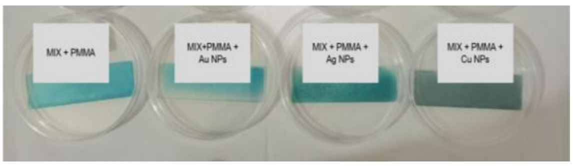
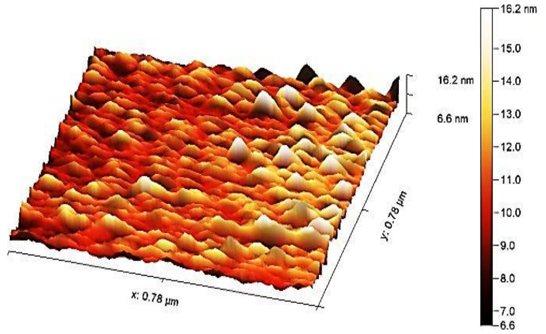


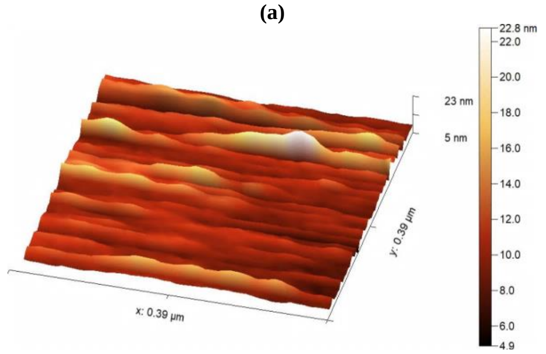
Fig. (1) Thin films of mixture NB+MG with PMMA polymer doped with gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs)

4. Results and Discussion

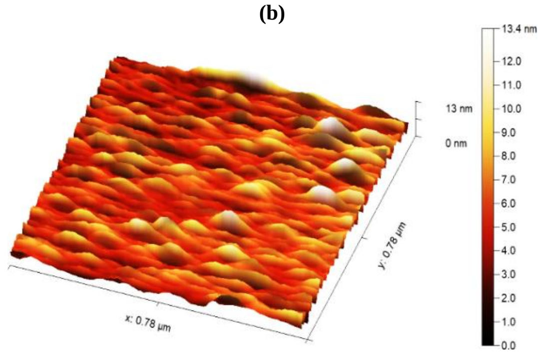
Figure (2) shows 3D AFM images of thin films prepared from the mixture of two organic laser dye (NB+MG) doped with PMMA polymer and gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs) at 10^{-3} M. The average diameters of the particles in these thin films are displayed in table (1). It is observed that the root mean square (r.m.s.) value of surface roughness and the average diameters increase with thickness when pure and doped PMMA polymer and nanoparticles are mixed to prepare thin films [25].



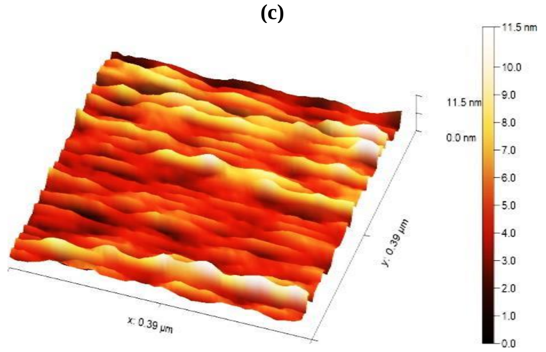
(a)



(b)



(c)



(d)

Fig. (2) 3D AFM images of thin films made from mixture of organic laser dyes doped with polymer and nanoparticles (a) Mix+PMMA, (b) Mix+PMMA+AuNPs, (c) Mix+PMMA+CuNPs, (d) Mix+PMMA+AgNPs

At room temperature, an Aquarius-7000 UV-Visible spectrometer was used to record the absorption spectra of the organic laser dyes combinations. Figure (3) shows the linear absorption spectra of PMMA- and nanoparticle-doped dye thin films at concentration of 10^{-3} M. Based on these findings, pure mixed dye including PMMA polymer and gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs) caused the absorption peaks to shift towards longer wavelengths. The electronic and vibrational states of the interfacial molecules are attributed to the shift in absorbance seen in all nanocomposite samples. Electrons in these states are driven from the lowest-occupied molecular orbital (LUMO) to the highest-occupied molecular orbital (HOMO). Equations (1) and (2) yield the linear absorption coefficient (α_0) and linear refractive coefficient (n_0) for each sample, which are shown in table (2). According to the current data, the mixture's maximum absorption wavelength was 620 nm.

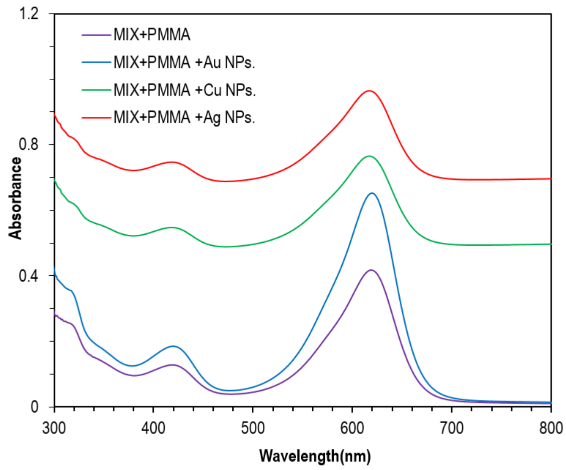


Fig. (3) The absorbance spectra for thin films of mixture organic laser dye doped with PMMA polymer and gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs)

Applying the Z-scan approach to the open and closed gaps yields the nonlinear refractive index and nonlinear absorption coefficient, respectively. Z-Scan transmittance normalized as a function of distance for organic laser dye thin films doped with gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs) and PMMA polymer. There is a -2 to 2 mm variation in the nonlinear impact region. The specimen may have self-defocus lensing because of a negative sign of refraction nonlinearity (n_2<0), as indicated by the transmittance curve of the Z-scan data for closed apertures, which displays a peak followed by a valley [26] as demonstrated by Fig. (4). Figure (5) illustrates the saturable absorption phenomena for combination organic laser dye thin films based on open-aperture Z-scan data.

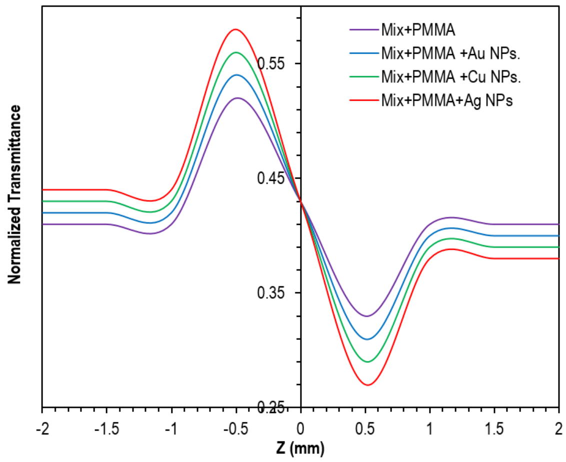


Fig. (4) Closed-aperture Z-scan data for thin films of mixture organic laser dye doped with PMMA polymer and gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs)

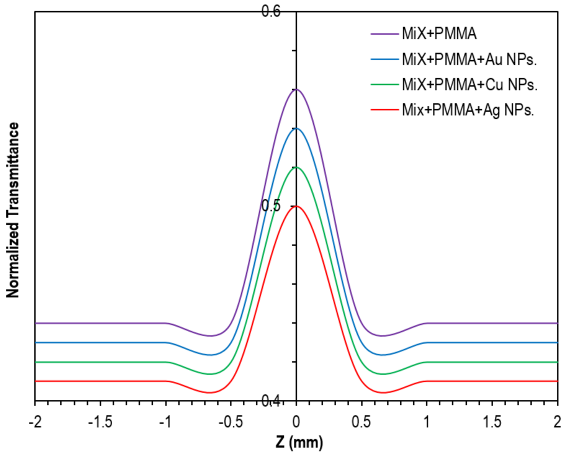


Fig. (5) Open-aperture Z-scan data for thin films of mixture organic laser dye doped with PMMA polymer and gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs)

The optical limiting behavior of mixture of NB+MG organic laser dyes as thin films doped with PMMA polymer and gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs) at concentration of 10^{-3} M were performed with a similar laser utilized in Z-scan procedure. The optical limiting features and linear and nonlinear optical parameters for a combination of NB+MG organic laser dye are displayed in table (2). Similar to dyes treated with polymers and nanoparticles, the negative correlation between concentration and the optical power limiting threshold indicates that the optical limiting properties improve with increasing concentrations as shown in Fig. (6). The basis for this connection is each sample's optical limiting threshold intensity [27]. Compared to the materials as solutions, thin films of NB+MG mixtures offer a lower optical power limiting threshold and limiting amplitude as listed in table (2).

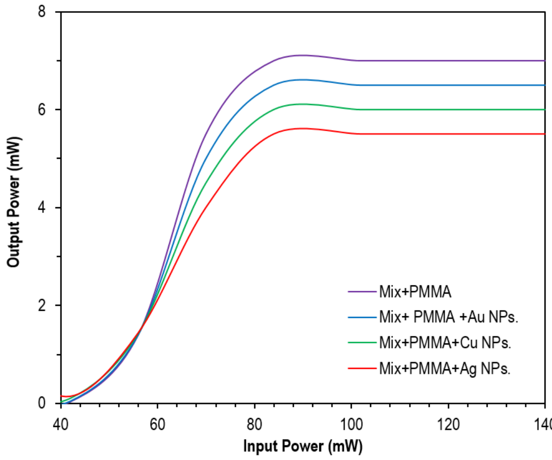


Fig. (6) Optical limiting for thin films of mixture organic laser dye doped with PMMA polymer and gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and copper nanoparticles (CuNPs)

5. Conclusions

The findings demonstrated that, for a given wavelength, absorbance rose along with concentrations of nanoparticles. Each sample's closed aperture produces self- defocusing occurrences. Every thin-film sample has an open aperture that provides saturable absorption. The findings demonstrated that all thin films had extremely significant nonlinear characteristics, with a linear rise in nonlinear refractive index with nonlinear phase shift. Because combination laser dyes doped with polymer PMMA and silver nanoparticles have superior optical limiting qualities than thin films doped with gold and copper nanoparticles, they may be utilized as more effective optical limiting in electro-optical systems. The findings also suggest that all of the samples have promise for use as active laser media and as media for other optoelectronic applications this is compatible with [28].

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Table (1) Result of AFM parameters of thin films of mixture with PMMA polymer doped with Au, Ag, and Cu NPs

Sample	Roughness r.m.s (nm)	Average Roughness (nm)	Average Diameter (nm)	Thickness (nm)
Mix + PMMA	1.74714	1.33225	81.16	142
Mix + PMMA + Au NPs	1.93094	1.35660	84.25	145
Mix + PMMA + Cu NPs	2.12119	1.51975	86.48	173
Mix + PMMA + Ag NPs	2.64687	2.70453	89.59	200

Table (2) Result of linear, nonlinear optical parameters and optical limiting response for thin films of mixture with PMMA polymer doped with Au, Ag, and Cu NPs at λ=457nm

Sample	T	($\alpha_\circ$) cm^{-1}	$n_\circ$	n_2 (cm^2/mW)	β (cm/mW)	Limiting Threshold (mW)	Limiting Amplitude (mW)
Mix + PMMA	0.9720	196.9.946	1.078	10.9×10^{-8}	5.67	7.0	88.1
Mix + PMMA + Au NPs	0.9630	220.316	1.271	14.3×10^{-8}	5.27	6.5	86.5
Mix + PMMA + Cu NPs	0.7530	2168.95	2.102	21.8×10^{-8}	4.22	6.2	85.6
Mix + PMMA + Ag NPs	0.6710	3246.2	2.203	28.9×10^{-8}	3.48	5.5	84.2