The Study of A Linear and Non-Linear Optical Property for PMMA Thin Films Doped with the Rhodamine B Laser Dye and Ag Nano Particles are Used in Medicine

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Abstract

Four different mixtures of ( 10⁻³ mol/l Rhoda mine B laser dye , 0.1 gm PMMA and one of Ag nano particles weights ( 0.02 gm ,0.04 gm , 0.06 gm and 0.08 gm ) ) had been prepared using chloroform solvent .Four different thin films had been made from these mixtures using drop casting method .The absorption spectrums of these thin films had been taken . The absorption spectral properties as (peak wave length, peak absorbance and frequency difference at half absorbance maximum) had been measured depending on the absorption spectrums for thin films. The non-linear optical properties as (Transmittance difference ∆𝑇𝑝−𝑣, Non –linear phase shift ∆Φo, Non-linear Refractive index 𝑛2, Minimum normalized transmittance 𝑇(𝑍) and Non-linear absorption coefficient β) were calculated according to normalized transmittance data obtained from 𝑍—scan setup with closed and open aperture .The main conclusion is that the Ag nano particles causes a shift of the absorption wavelengths to longer wavelengths ( red shift ) , so this helps in choosing the medium and nano particles with appropriate excitation wavelengths .

Keywords: Rhoda mine B laser dye, Ag nano particles, Linear, Non-linear, Properties.

Introduction

Many studies had been achieved on the Rhoda mine B , where some of optical and electrical characteristics had been studied on a solid dye [1] , and on a liquid dye [2].Rhoda mine B is used for quantum counters [3] , and it had been successfully works as an active medium for lasing [4] . The absorption and fluorescence spectrums had been taken to a four different concentrations of Rhoda mine B dye dissolved in a different solution [5].

The absorption and fluorescence spectral properties of a Rhoda mine B dye in ethanol had been theoretically and experimentally studied and the red shift to a longer wavelengths had been discovered at 10⁻² and 10⁻⁵ mol/l dye concentrations [6].This dye had been used in sensor applications , where it doped in different transparent polymers as ( PMMA and PVAc) and made as a thin film and the changes in absorption and fluorescence spectrums had been noticed [7].

The effect of solvent type in the absorption and fluorescence spectral properties of a Rhoda mine B dye had experimentally studied [8]. The effect of Rhoda mine dye type and the change in mixing ratio for three different types of this dye in the spectral properties ( absorption and fluorescence) had been experimentally studied [9].The effect of chloroform solvent on the absorption and fluorescence spectral characteristics for the liquid Rhoda mine B dye had been studied [10].

Rhoda mine B laser dye has red to violet color. It had the molecular formula of C₂₉H₃₁ClN₂O₃ and 479.02 gm/mol molecular weight. The laser emission by Rhoda mine B is tunable about 610 nm, while it has quantum yield of about (0.49-1.0) dependent on the temperature .When it is excited by a 514 nm of argon laser and 532nm of Q-switched Nd: YAG laser, the quantum yield...
of absolute fluorescence had been appeared [11-16]. The chemical structure of a Rhoda mine B dye had been drawn in Fig.1 [17].

Fig. 1: The molecular structure of Rhoda mine B laser dye [17]

Poly (methyl2-methylpropenoate) is the polymer of meth acrylic acids esters (PMMA), which has C5H8O2 form. It is rear, colorless polymer. It had been used in many fields as ( Dust covers , sunglasses , lenses , rear lights in vehicles , lamp covers and switch parts in electrical circuits , pills and capsules in medicine .... etc [18] . The molecular structure of PMMA polymer had been shown in Fig.2.

Fig. 2: The molecular structure of PMMA polymer [18]

PMMA has the long , thinner as well as smoother chains of essentially carbon atom .It is hardest polymer which has highly mechanical resistant .Moreover , the highly strength of it doesn't sever more changes when it exposure to UV radiation . It had less absorption peak capacity in water , high dielectric constant and thermal stability of PMMA ,for that it can be used in electrical fields .Because of it has a good transmittance for visible light , highly appropriate with human tissue[19] . An important property of PMMA had been shown in Table (1).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>(1.15 – 1.19 ) g/cm³</td>
</tr>
<tr>
<td>Peak absorption in water</td>
<td>(0.3 -2)%</td>
</tr>
<tr>
<td>Transmission , visible</td>
<td>(80-93) %</td>
</tr>
<tr>
<td>Refractive index</td>
<td>(1.49-1.498)</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>(10^14-10^15)Ω .cm</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>(2.8-4)</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>(1.46-1.47) J/g.°C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>(0.19-0.24) W/m.K</td>
</tr>
<tr>
<td>Melting point</td>
<td>130 °C</td>
</tr>
</tbody>
</table>

Table 1: An important properties for PMMA polymer [19]

The study of non-linear optical properties for a non-linear medium is very important due to it provides a knowledge of molecular response to incident laser beam energy and the possible changes related with it , so this project aims to study the non-linear optical properties for a four different thin films of \( 10^{-3} \) mol/l Rhoda mine B laser dye , 0.1 gm PMMA and one of Ag nano particles weights (0.02 gm ,0.04 gm , 0.06 gm and 0.08 gm ).
Theory

Absorption Spectral Properties

Absorption process can be happened when an incident photon crash the dye molecule in its lower energy state, the dye will be excited due to that the photon is absorbed and its energy is utilized in the dye excitation. This process can be occurred only if the incident photon energy equals to the energy difference between the two states the absorption take place at them. Absorbance $A$ can be defined as the logarithmic relative decrease of intensity. So the wavelength at the maximum absorbance may be called as peak wavelength ($nm$), while the maximum absorbance can be named as peak absorbance (arb. unit) and the width of absorption (curve at the half value of maximum absorbance is termed as $(\Delta \nu)^{1/2}$ sec') which is calculated from the absorption spectrum[20].

Linear Optical Properties

The linear optical properties related with linear optical response, had been formulated as below: The absorbance (A) describes the amount of absorbed photons by molecules, can be written as [21]:

$$A = 1 - \log\left(\frac{I_0}{I}\right) \quad \text{.......................... (1)}$$

Where $T$: is the transmittance of medium which is related with refractive index $n$ as [21]:

$$T = \frac{2n}{n^2 + 1} \quad \text{.......................... (2)}$$

The absorbance coefficient $\alpha$ of an optical medium can be related to the $A$ absorbance according to eq. (3) [22& 23]:

$$\alpha = \frac{1}{\Delta \nu A} \quad \text{.......................... (3)}$$

The effective length $L_{eff}$ of an optical medium can be calculated by eq.(4) as below [22 & 23]:

$$L_{eff} = \left(1 - \exp^{-\alpha L}\right) \quad \text{............. (4)}$$

Where $L$ is the Length of a Sample and $\alpha$ is the Absorption Co Efficient.

Non-Linear Optical Properties

Some of materials severe from the nonlinear effects as non-linearity which is a change in the refractive index of a material in response to an applied electric field. The z-scan technique is used to measure the non-linear refractive index and the non-linear absorption coefficient using the closed and open aperture, respectively. The closed aperture form helps in determining the small distortions in the incident beam on the nonlinear medium which behaves as a small non-linear lens and in measuring the non-linear refractive index, as shown in Fig. (3-a) where illustrates the construction of a closed aperture and the diagram of the possible measured data of the normalized transmittance using it.

The open –aperture Z-scan is used for measuring the non-linear absorption coefficient as the whole laser beam may be allowed to incident on the detector and the small distortions can be neglect. Fig. (3-b) illustrates the construction of a Z-scan with open aperture and the diagram of the possible measured data of the normalized transmittance using it. There are some of the changes must be taken into account in the study of the non-linear coefficients as: the non-linear response of the medium due to the laser beam in limited region (laser spot area on the medium) may be affected by the laser beam intensity in the surrounding regions. This effect can be named as (Nonlocal response). The other effect appears in the liquid samples of the colloid non-linear medium in the dielectric solution, the photonic incident field in the non-local points of a medium induces many changes as reorientation of the molecular dipoles due to the changes in the electric fields in different parts of a non-linear medium [24].
The non-linear refractive index can be calculated using eq. (5) as follow [22]:

\[ n_2 = \frac{\Delta \Phi_o}{I_0 L_{eff} K} \] \hspace{1cm} (5)

Where \( I_0 \) is the incident laser intensity, \( K \) is the wavenumber of the incident laser beam, equals to \( K = \frac{2\pi}{\lambda} \), since \( \lambda \) is the wavelength of the incident laser beam, while \( \Delta \Phi_o \) refers to nonlinear phase shift and equals to \[ \Delta \Phi_o = 0.406 |\Delta \Phi_o| \] \hspace{1cm} (6)

Where \( \Delta T_{p-v} \) is the normalized transmittance difference between the top and the valley transmittance values which can be calculated using closed aperture Z-scan setup. The nonlinear absorption coefficient \( \beta \) may be calculated using eq. (7) as follow [22 & 25]:

\[ \beta = \frac{2 \Delta T_{p-v}}{I_0 L_{eff}} \] \hspace{1cm} (7)

Since \( T(Z) \) means the minimum normalized transmittance obtained using open aperture Z-scan setup.

**Experimental Setup**

A 10^{-3} mol/l molar concentration of Rhoda mine B laser dye (R 6626-25G, product of USA, Sigma –Aldrich) had been prepared by weighting (0.001 gm) using digital balance (model- HR-200, made in Japan) from laser dye. This weight had been dissolved in (10 ml) of chloroform solvent (D- 30926 seelze, Sigma-Aldrich Labor chemikalien Gmbh, Germany). A 0.1 gm of PMMA polymer (Sc-255435, Santa Cruz Biotechnology, Dallas) had been added to the dye solution. A four different weights of Ag nano particles (MW= 107.87 g/mol , mp= 960 C, product of USA , Sigma – Aldrich , CAS= 7440-22-4) as (0.02 gm , 0.04 gm , 0.06 gm and 0.08 gm) had been weighted using the same balance and added to the dye mixtures. So a four different mixtures were obtained, contain (10^{-3} mol/l Rhoda mine B, 0.1 gm PMMA and Ag nano particles). To perform a homogeneous solution, A magnetic stirrer (model – HP-3000, Lab. companion) had been used. These mixtures had been prepared as a thin films using drop casting method. The following figure (4) shows the pictures for the prepared thin films.

The absorption spectrum for thin films samples had been recorded using UV-Vis spectrophotometer (Scinco, Mega-2100, made in Korea) and the Fig. (5) shows the absorption spectrum for these samples.

![Absorption Spectrum](image)

**Fig 5:** The absorbance spectrum of the thin films of (10^{-3} mol/l Rhoda mine B, 0.1 gm PMMA and four different weights of Ag nano particles)
The used Z-scan set up as described in paragraph (2-c), contained from SHG-Nd: YAG laser at 532 nm (green light) as a laser source had been focused to a sample using a lens of (15 cm) focal length, where the radius of laser spot was (0.05 cm) and the incident laser intensity on the sample of (778 Watt / m²). The normalized transmittance can be measured using a laser power meter (LP1-mobiken).

The normalized transmittance data for the prepared thin film samples of (4 cm) length and (1 mm) thickness, contained from (10³Rhodamine B, 0.1 gm PMMA and different weights of Ag nano particles), had been measured using Z-Scan setup of Closed aperture and Open aperture with aid of laser power meter (LP1-mobiken) and had been plotted in Fig (6): (a) Closed aperture and (b) Open aperture.

Results

According to the absorption spectrums shown in Fig.(4), the absorption spectrum characteristics for thin films of (10³ Rhodamine B, 0.1 gm PMMA and different types of nanoparticles), like (Peak wavelength nm, Peak absorbance (arb. unit) and (Δν)½ (Sec⁻¹), had been listed in table (2).

Table 3: Absorption spectrum characteristics for thin films of (10³ Rhodamine B, 0.1 gm PMMA and different types of nanoparticles)

<table>
<thead>
<tr>
<th>Weights of Ag nano particles</th>
<th>Peak wavelength nm</th>
<th>Peak absorbance (arb.unit)</th>
<th>(Δν)½ (Sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 gm</td>
<td>558</td>
<td>0.15</td>
<td>12×10⁻¹⁹</td>
</tr>
<tr>
<td>0.04 gm</td>
<td>560</td>
<td>0.3</td>
<td>10.7×10⁻¹⁹</td>
</tr>
<tr>
<td>0.06 gm</td>
<td>563</td>
<td>0.375</td>
<td>2.5×10⁻¹⁹</td>
</tr>
<tr>
<td>0.08 gm</td>
<td>569</td>
<td>0.425</td>
<td>2×10⁻¹⁹</td>
</tr>
</tbody>
</table>

The linear optical parameters for thin film samples of (10³ Rhodamine B, 0.1 gm PMMA and different types of nano particles) had been calculated according to the absorption spectrum had been taken to these samples and drawn in above paragraph in this chapter, and listed in table (4) to exploit them in the calculation of the Non-linear optical coefficients.

Table 4: The linear optical parameters for thin film samples of (10³ Rhodamine B, 0.1 gm PMMA and different types of nanoparticles) are dependent in nonlinear optical coefficients

<table>
<thead>
<tr>
<th>Nano Particle</th>
<th>Weights of particles</th>
<th>Absorbance A</th>
<th>Transmittance T</th>
<th>Absorption coefficient $\alpha$</th>
<th>Refractive index n</th>
<th>Effective length $L_{eff}$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$ Nano particles</td>
<td>0.02 gm</td>
<td>0.15</td>
<td>0.707</td>
<td>2.896</td>
<td>2.414</td>
<td>0.0377</td>
</tr>
<tr>
<td></td>
<td>0.04 gm</td>
<td>0.3</td>
<td>0.501</td>
<td>1.448</td>
<td>3.723</td>
<td>0.0388</td>
</tr>
<tr>
<td></td>
<td>0.06 gm</td>
<td>0.375</td>
<td>0.421</td>
<td>1.158</td>
<td>4.530</td>
<td>0.0390</td>
</tr>
<tr>
<td></td>
<td>0.08 gm</td>
<td>0.425</td>
<td>0.375</td>
<td>1.022</td>
<td>5.138</td>
<td>0.0391</td>
</tr>
</tbody>
</table>
The Non-linear optical parameters such as (Transmittance difference (\(\Delta T_{p-v}\)), Non-linear phase shift (\(\Delta \Phi_o\)), Non-linear Refractive index (\(n_2\)), Minimum normalized transmittance \(T(Z)\) and Non-linear absorption coefficient (\(\beta\)) for thin film samples of \((10^{-3})\) Rhoda mine B, 0.1 gm PMMA and different weights of Ag nano particles had been calculated according to the measured data of normalized transmittance using Z-Scan setup of both Closed aperture and Open aperture and the equations of non-linear optical properties mentioned in paragraph (2- Theory). These Non-linear optical coefficients had been listed in table (5).

<table>
<thead>
<tr>
<th>Nano Particle</th>
<th>Weights of particles</th>
<th>Transmittance difference (\Delta T_{p-v})</th>
<th>Non-linear phase shift (\Delta \Phi_o)</th>
<th>Non-linear Refractive index (n_2) ((x10^{-9}))</th>
<th>Minimum normalized transmittance (T(Z))</th>
<th>Non-linear absorption coefficient (\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag Nano particles</td>
<td>0.02 gm</td>
<td>0.95</td>
<td>2.3399</td>
<td>6.76</td>
<td>0.85</td>
<td>0.0819</td>
</tr>
<tr>
<td></td>
<td>0.04 gm</td>
<td>0.96</td>
<td>2.3645</td>
<td>6.638</td>
<td>0.79</td>
<td>0.0740</td>
</tr>
<tr>
<td></td>
<td>0.06 gm</td>
<td>0.96</td>
<td>2.3645</td>
<td>6.604</td>
<td>0.7</td>
<td>0.0652</td>
</tr>
<tr>
<td></td>
<td>0.08 gm</td>
<td>0.98</td>
<td>2.3687</td>
<td>6.599</td>
<td>0.62</td>
<td>0.0576</td>
</tr>
</tbody>
</table>

Discussion

It is shown from table (3) that \((\Delta \nu)_{1/2}\) values are decreased and both of maximum wavelength and peak absorbance are increased with the increasing of Ag nano particles weight.

This behavior can be interpreted by that the high concentration of nano particles causes an increasing in film absorbance (the ability of absorption is increased with the increasing of molecules in the ground energy state). Because of the high absorption in film, the film energy decreased and this induces the peak wavelength to longer wavelengths. The decreasing of \((\Delta \nu)_{1/2}\) with the increasing of Ag nanoparticles weights, means that the modes of absorption frequencies are decreased because of the high absorption in high Ag nanoparticles in these films.

The increasing of each of (absorbance \(A\), refractive index \(n\) and effective length \(L_{eff}\)) and the decreasing of both of (Transmittance \(T\) and Absorption coefficient \(\alpha\)) with the increasing of Ag nano particles weights as illustrated in Table (4), may be caused by that the nano particles in any medium, as well as it is considered as a highly absorption centers, they are contributed in increasing the absorption sample distance and makes the medium with high optical density, so this increases the difference between air and that medium.

The strongest absorption medium as more nano particles weights, becomes high transmission to the same absorption wavelengths and it has less absorption coefficient due to the same reason.

Fig (6) shows the behavior of the normalized transmittance using closed aperture, had the top-valley shape, while it has a cone shape using open aperture. It is obvious that the normalized transmittance data for samples of Rhoda mine B and Ag nano particles are suitable with the published data in Ref. [26]. The resulted data of the normalized transmittance had been decreased with increasing of nano particles weights. This behavior can be attributed to that the nano particles act as a scattering centers in the sample, so the increasing of Nano particles consolidates the scattering upon the transmittance of that sample.

The increasing of both of (Transmittance difference \(\Delta T_{p-v}\) and Nonlinear phase shift \(\Delta \Phi_o\)) and the decreasing of each of (Nonlinear Refractive index \(n_2\), Minimum normalized transmittance \(T(Z)\) and Nonlinear absorption coefficient \(\beta\)), with the increasing of Ag nano particles weights as shown in table (5), can be caused by that the nano particles act as a scattering centers, so the changes of incident waves phase becomes more possible and makes the sample more transmittance in one side (against the incident wave) and less transmittance in other side (reverse side to the incident laser photons).

Due to highly absorption to the media which is having more nano particles, each of (Nonlinear Refractive index \(n_2\), Minimum normalized transmittance \(T(Z)\) and Nonlinear absorption coefficient \(\beta\)) having less values. The nonlinear responses from other points of sample and the reorientation of
electric dipole moments causes the changes in nonlinear absorption and refractive A coefficients.

Conclusions

It can be concluded that the nano particles are the main reason to more nonlinear response to laser fields. The two photon or reverse saturation absorption or the saturation absorption, are main nonlinear effects controlled the less values of nonlinear absorption coefficient. While the negative nonlinearity is clearly appeared in the samples contained Ag nano particles which are the main indicator to occur the self-defocusing effect as shown in less values of nonlinear refractive index. The main conclusion is that the Ag nano particles cause a shift of the absorption wavelengths to longer wavelengths (red shift), so this helps in choosing the medium and nano particles with appropriate excitation wavelengths.

References