Linear and nonlinear optical properties of I and NaBH₄ doped Malachite green thin films

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ABSTRACT

The optical properties and spectral behavior for pure and doping thin films of Malachite green were studied using Cecil Reflecta-Scan CE-3055 Reflectance Spectrometer measurements of the transmissivity and reflectivity at normal incidence of light in the wavelength range 300–1000 nm in steps of 2 nm. The refractive index, n, and absorption index,k, were calculated and it was found that they are dependent on film doping in the thickness 1 μm. The absorption spectra in the UV–VIS region has been analyzed in terms of both molecular orbital and band theories. The direct energy gap was obtained and equals to 2.667 eV , 2.672eV, 2.678 eV , 2.638 eV and 2.627 eV for pure , Sodium borohydride (S2 and S3) and Iodine (S4 and S5) doping thin films, respectively. The real ε_1 and imaginary ε_2 parts of the dielectric constant, the optical conductivity σ_{opt}, electrical conductivity σ_e the third-order nonlinear optical properties $\chi^{(3)}$ and nonlinear refractive index were calculated for doping and pure Malachite green thin films.

*Keywords***:** organic dye, energy gab, nonlinear properties, thin films

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INTRODUCTION

The application of Malachite green in any one of technological devices will certainly be provided as thin films. The optical constants of thin films provide us with information concerning microscopic characteristics of the material and its determination is very important for using it in any one of such devices. Davidson [1] investigated the effect of the central metal atom on the absorption spectra of thin films.The production of the majority of modern optoelectronic devices are based on the semiconducting behaviour of these materials in thin film form such as organic solar cells [2,3], in organic field effect transistors [4], in organic light emitting diodes in which Malachite green can be used as a hole transport layers [5,6] or emitting layers [7] and in gas sensors [8,9].

The nonlinear effects can be found also in many crystals [10,11], but the glasses have advantages over crystals in lower coast, better processing, very often in larger refractive non-linearity and in the possibility to include them easily into optical fiber and planar waveguide.

The aim of this study, is to investigate the optical constants of MG thin films such as real and imaginary parts of the dielectric constant, optical band gap E_g , optical conductivity σ_{opt} and third-order nonlinear optical properties. The effect of film doping on these quantities was studied.

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MATERIALS AND METHODS

The preparation of the thin films

Malachite green (MG) was supplied from Aldrich Company with purity 96% , with molecular weight 927.03, has been selected for our experiments as shown in Fig. 1. Malachite green is a basic dye. Basic dyes are salts of the colored organic bases containing amino and imino groups and also combined with a colorless acid, such as hydrochloric or sulfuric.

We made the thin films by doing Sodium borohydride ($NaBH_4$) into MG and doping Iodine into MG. The Malachite green (MG) pure film was prepared as follows: 0.1854 gm of the MG crystal was dissolved in 50 ml of ethanol, the concentration of the resulting MG dye 0.004M, then the solution was stirred at room temperature for 50 min and then filtered through a 0.2 mm syringe filter and kept in temperature below $20\,^0C$ .The film was prepared by the spray method on a clean glass slide substrate of 75mm x 25 mm x 1mm in a size that is heated up to 80K. A smooth film without dust and solvent residues were obtained. The thickness of all the films were measured to be 1 μm. The weight of MG, iodine and Sodium borohydride are listed in the Table 1.

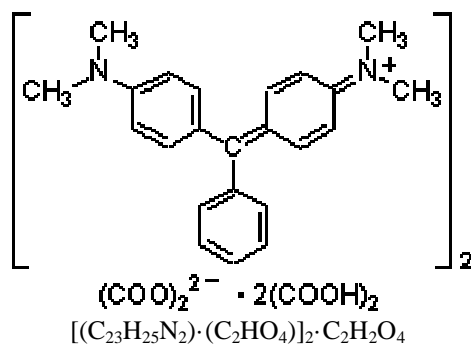$$[(C_{23}H_{25}N_2)\cdot(C_2HO_4)]_2\cdot C_2H_2O_4$$
Fig.1: The chemical structure and formula of MG.

RESULTS AND DISCUSSION

1. UV–visible Spectroscopic studies

In order to study the effect of the films doping on optical properties the absorbance, transmission and reflectance spectra of thin films with different doping materials are shows in Figs.2,3 and 4 respectively. A UV–visible spectroscopy has been used to characterize the azo dye film in the spectral range (300–1000nm). Fig. 2 shows the spectral distribution of absorbance sample in the spectral range (300–1000 nm) and the peaks of absorption for pure MG, Sodium borohydride and Iodine are located at 670 nm.
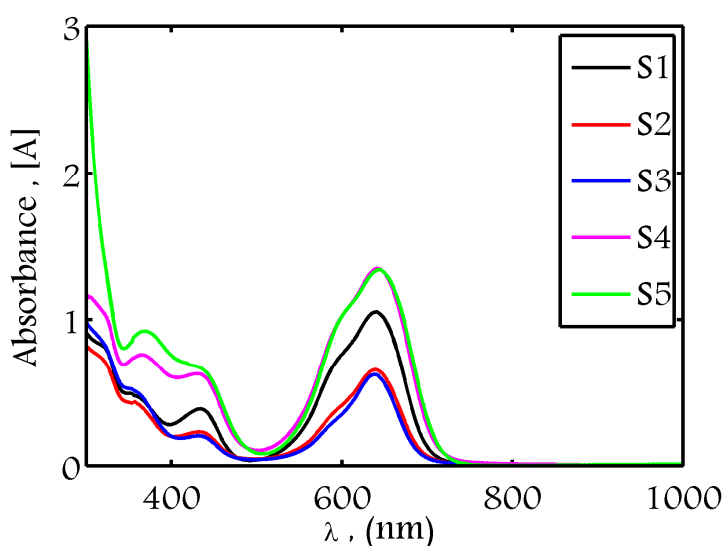

Fig.2: Absorption spectra of MG films with different doping materials at 1μm thickness.

In case of pure MG film with 1μm thickness, transmittance (T) is as low as 79% at wavelength (550 nm) and gradually rises towards shorter wavelength until it reaches its maximum value of 94% at 780 nm. At shorter

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wavelengths, transmittance decreases rather quickly, and approaches near zero at around 300 nm. The wavy nature of the curve between 300 nm and 700 nm is connected with the film thickness and consequently with the interference between MG film and the substrate. On the other hand a sharp decrease toward UV region (below 350 nm) is due to the fundamental absorption of light caused by the excitation of electrons from valence band (VB) to conduction band (CB) of MG. Similar type of behaviour is observed for other foure samples. From these spectra it is seen that average transmittance of the films increases with increasing the doping materials (Reductase materials ,NaBH$_4$ and oxidizing materials ,I) of the film.
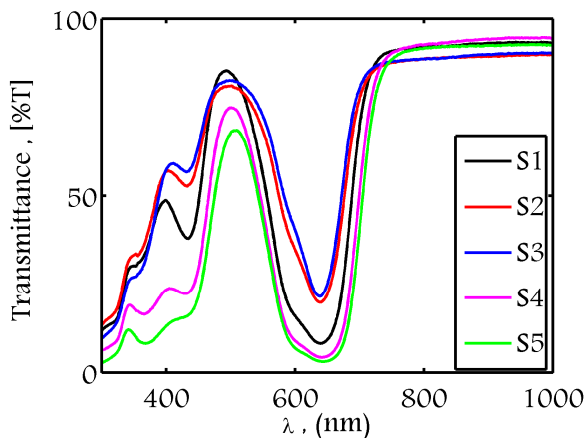

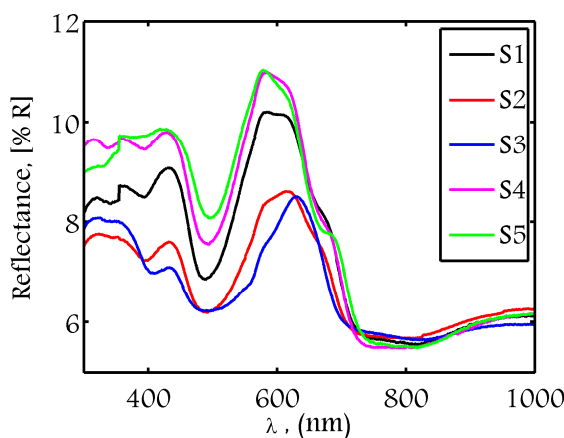| Fig.3: Transmittance spectra of MG films with different doping materials at 1μm thickness. | Fig.4: Reflectance spectra of MG films with different doping materials at 1μm thickness |

2. Determination of the optical band gap

The absorption coefficient α of the thin films was taken from the optical absorption spectrum using relation [12]:

$$\alpha = 2.303A/d \qquad (1)$$

where A and d are the absorbance and thickness of the films. Analysis of the optical absorption spectra can reveal the optical energy gap E_g between the conduction band and the valence band due to direct and indirect transitions for both crystalline and amorphous materials. The absorption coefficient α is a function of photon energy and obeys Mott and Davis model [13]:

$$\alpha h\nu = B(h\nu - E_g)^m \qquad (2)$$

where hν is the energy of the incidence photon, E_g is the optical energy band gap, B is a constant known as the disorder parameter which is nearly independent of photon energy parameter, m is the power coefficient with the value that is determined by the type of possible electronic transitions, m=1/2 or 2 for direct and indirect allowed transition, respectively [14]. The energy gaps were determined by the intercept of the extrapolations to zero absorption with the photon energy axis are taken as the values of the direct energy gaps E_g. Fig. 5 shows the variations of $(\alpha h\nu)^2$ and vs. $h\nu$. The values of band gaps calculated from the graph are listed in the Table 1.

Table 1: doping ratio and direct energy gaps E$_g$

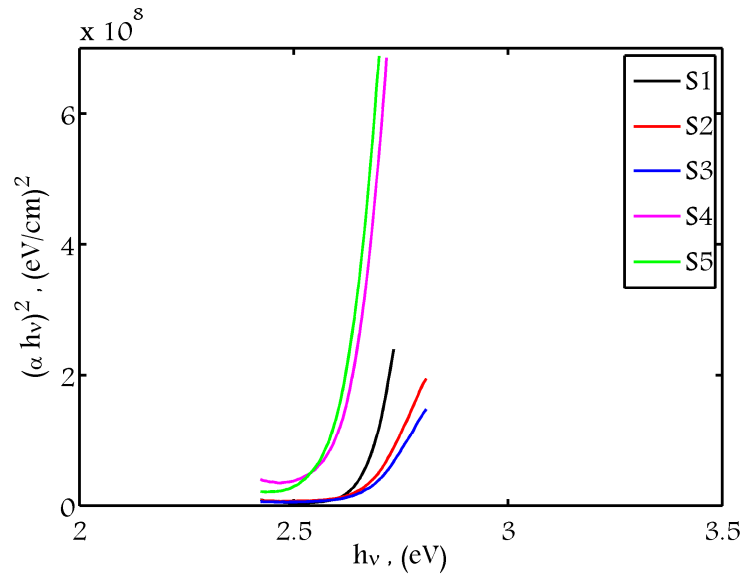| Doping type	Doping ratio	Ethanol Solvent (ml)	Weight of MG (gm)	Doping weight (gm)	Film Thickness μm	Energy gap (eV)
Pure	-	50	0.1854	-	1	S1=2.667
Sodium borohydride	0.01	50	0.1854	0.0019	1	S2=2.672
Sodium borohydride	0.04	50	0.1854	0.0077	1	S3=2.678
Iodine	0.12	50	0.1854	0.0253	1	S4=2.638
Iodine	0.18	50	0.1854	0.0407	1	S5=2.627

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Fig.5: $(\alpha h v)^2$ **vs. photon energy for different doping materials**

This can be interpreted in terms of the elimination of defects in the amorphous structure [15,16]. The insufficient number of atoms deposited in the amorphous film results in the existence of unsaturated bonds. These bonds are responsible for the formation of some defects in the films which produce localized states in the band gap, and thus the optical gap increases.

3. Optical dispersion characteristics:

The refractive index (*n*) of the films at different doping materials are determined by reflection spectra in the wavelength range 300–1000 nm by Reflctophotometer at room temperature and we calculated the refractive index values of the films using the following equation [17].

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - k} \qquad\qquad (3)$$

where *R* is the reflectance and $k = (\lambda \alpha / 4\pi)$ is the extinction coefficient. The refractive index and extinction coefficient *k* dependence of the wavelength are shown in Figs. 6 and 7. As seen in Figs. 6 and 7 *n* and *k* values are influenced by the doping concentrations and decrease with increasing the wavelength up to 670 nm. Therefore, they show the normal dispersion.
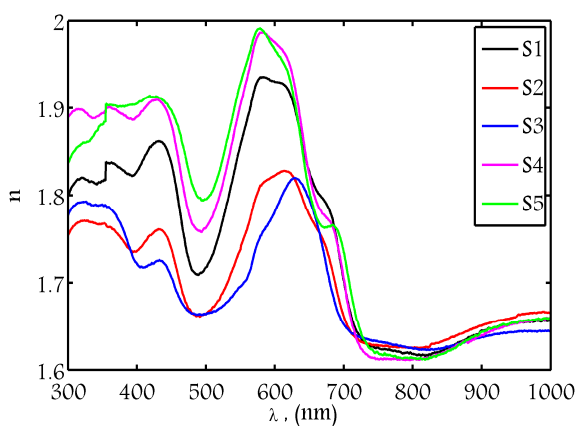

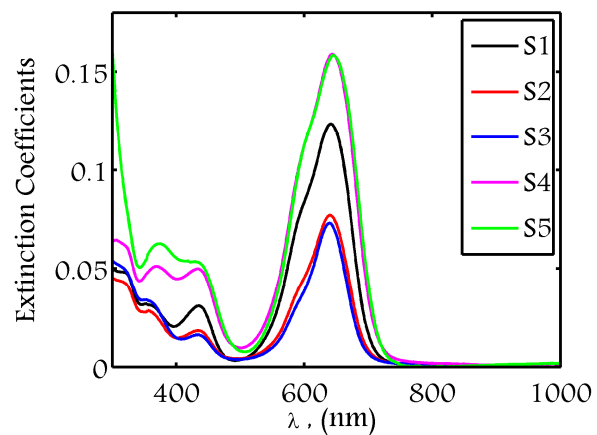**Fig. 6. Dispersion curves of refractive index *n* for different doping materials.**

Fig. 7. Dispersion curves of absorption index *k* for different doping materials.

4. Dielectric characterizations

It is well-known that polarizabiltiy of any solid is proportional to its dielectric constant. The real and imaginary parts of the complex dielectric constant are expressed as [17]:

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$$\varepsilon_1 = n^2 - k^2 \quad \text{and} \quad \varepsilon_2 = 2nk \tag{4}$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric constant, respectively. The dependences of ε_1 and ε_2 on the photon energy are shown in Figs. 8 and 9. The real and imaginary parts follow the same pattern and the values of the real part are higher than the imaginary part. The variation of the dielectric constant with the photon energy indicates that some interactions between photons and electrons in the films are produced in this energy range. These interactions are observed on the shapes of the real and imaginary parts of the dielectric constant and they cause the formation of peaks in the dielectric spectra which depends on the material type.
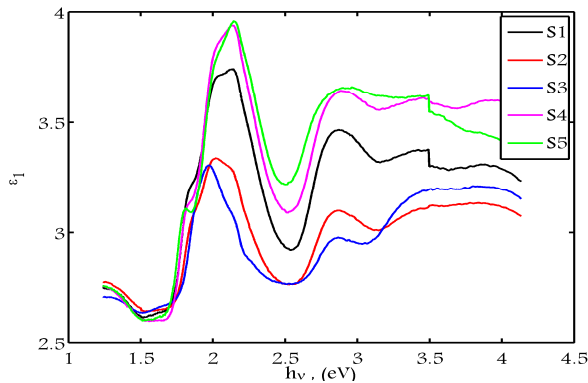

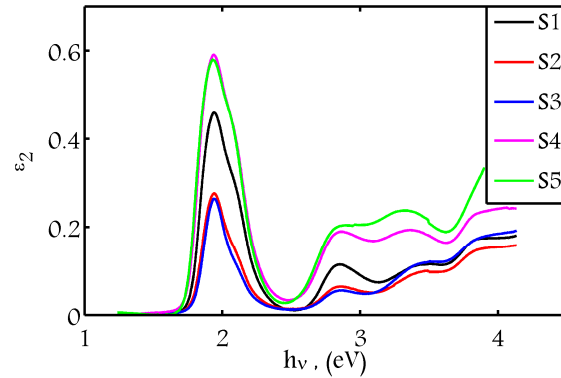Fig. 8. The variation of ε_1 with the photon energy for different doping materials.

Fig. 9. The variation of ε_2 with the photon energy for different doping materials.

5. Optical and electrical conductivity of thin films

The absorption coefficient α can be used to calculate the optical and electrical conductivity σ_{opt} , σ_e as follow [18]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \tag{5}$$

$$\sigma_e = \frac{2\lambda \sigma_{opt}}{\alpha} \tag{6}$$

where c is the velocity of light. Figs.10 and 11 shows the variation of optical conductivity σ_{opt} and electrical conductivity σ_e as a function of photon energy hv, it is worthwhile to note that the metal inclusion has greatly reduced the dielectric constant and increased the optical conductivity. The increased of optical conductivity at high photon energies is due to the high absorbance of sample thin films with different doping and also may be due to the electron excited by photon energy [19].
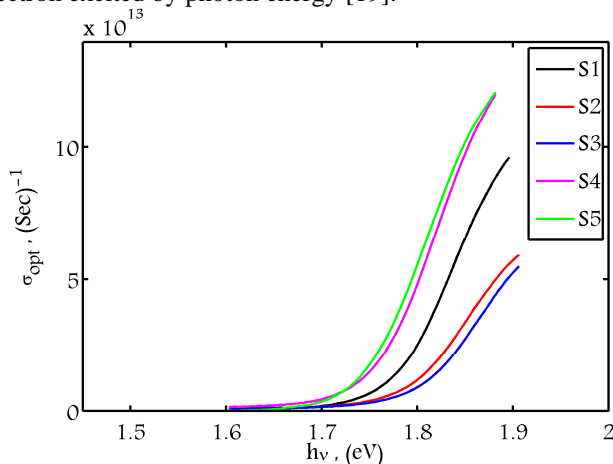

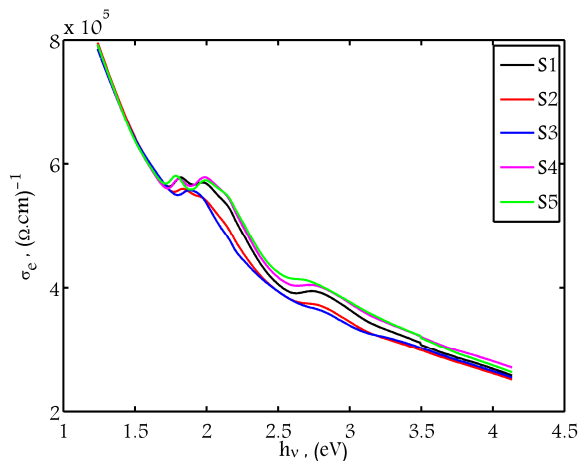Fig.10. Optical conductivity of MG with different doping materials.

Fig.11. Electrical conductivity of MG with different doping materials.

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Simple empirical relation based on generalized Miller's rule can be used for the estimation of the nonlinear refractive index and susceptibility $\chi^{(3)}$. The nonlinear refractive index and susceptibility $\chi^{(3)}$ can be calculated by combining Miller's generalized rule [17, 20] and low-frequency linear refractive index estimated from Wemple–DiDomenico single effective oscillator model. The linear optical susceptibility in the case of chalcogenide glasses is given by the relation:

$$\chi^{(1)} = (n^2 - 1)4\pi \qquad (7)$$

Using generalized Miller's rule we obtain

$$\chi^{(3)} = A(\chi^{(1)})^4 \qquad (8)$$

$$\chi^{(3)} = A \ [E_d E_0 / 4\pi (E_0^2 - (hv)^2]^4 \qquad (9)$$

for $hv \to 0$, one obtains

$$\chi^{(3)} = \frac{A}{(4\pi)^4}\left(\frac{E_d}{E_0}\right)^4 = \frac{A}{(4\pi)^4}(n_0^2 - 1)^4 \qquad (10)$$

where $A = 1.7x10^{-10}$ (for $\chi^{(3)}$ in esu).

From inspection of Equ.10 it can be seen that third-order nonlinear optical properties is sensitive to the wavelength of light and doping materials, as shown in Fig.12. Its value also increases when the wavelength of light is approaches the absorption edge (closer to resonance conditions).
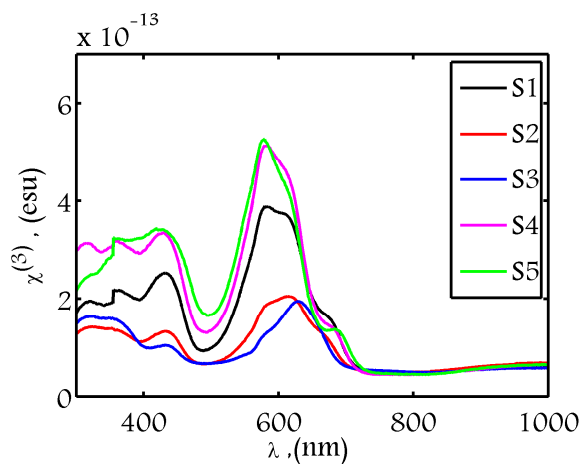
Fig.12 Third order nonlinear optical susceptibility for different doping materials
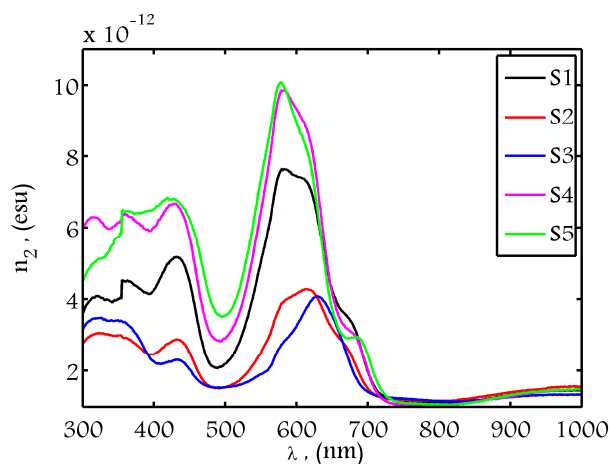
Fig.13: Nonlinear refractive index for different doping materials.

The covalency and ionicity of the chemical bonds strongly influence the magnitude of the nonlinearity. The values of non-linear refractive index, n_2, as shown in Fig.13 are calculated from the semiempirical relation [19]:

$$n_2[esu] = \frac{2.6x10^{-13}(n^2 - 1)^4}{n} \qquad (11)$$

CONCLUSION

Crystalline powder of MG transforms to as-amorphous phase in as-deposited films. Increasing doping concentration at 1um thickness leads to increasing absorbance of MG films without changing peak position. The transmissivity spectra recommends these films as a good band pass or a good band stop optical filter material depending on incident wavelength. The refractive index and absorption index are independent of film thickness. The type of electronic transition responsible for optical absorption is direct allowed transition. The direct energy gap was obtained and equals to 2.667 eV , 2.672 eV, 2.678 eV , 2.638 eV and 2.627 eV for pure , Sodium borohydride (S2

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and S3) and Iodine (S4 and S5) doping thin films, respectively. The third-order nonlinear optical properties and nonlinear refractive index are sensitive to the wavelength of light and doping materials.

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