*Available online at* www.pelagiaresearchlibrary.com

**Pelagia Research Library**

**Advances in Applied Science Research, 2012, 3 (5):2940-2946**

**ISSN: 0976-8610**
**CODEN (USA): AASRFC**

# Determination of the optical constants and optical limiting of doped malachite green thin films by the spray method

**Hussain S. Shaaker, Waleed A. Hussain and *Hussain A. Badran**

*University of Basrah, College of Education, Physics Department, Basrah, Iraq*

## ABSTRACT

*The spray method technique has been successfully used to deposit highly uniform and good adhesion malachite green (MG) thin films. The optical constants of the doping thin films were obtained from the analysis of the experimental recorded transmittance and absorption spectral data over the wavelengths range 300-1000 nm. The values of some important parameters (refractive index n, the dispersion energy $E_d$ the oscillation energy $E_o$ and energy bang gaps $E_g$ ) have been determined by reflection spectra. The third-order nonlinear optical properties, $\chi^{(3)}$ ,of MG thin films film are evaluated from changes of index of refraction using Millers rule. Optical limiting have been observed and studied by means of single beam transmission technique, using a continuous-wave (cw) visible solid state laser beam with a wavelength of 532 nm and 30 mWatt output power.*

**Key words :** Malachite green, Optical constants, Single oscillator, Optical limiting.

## INTRODUCTION

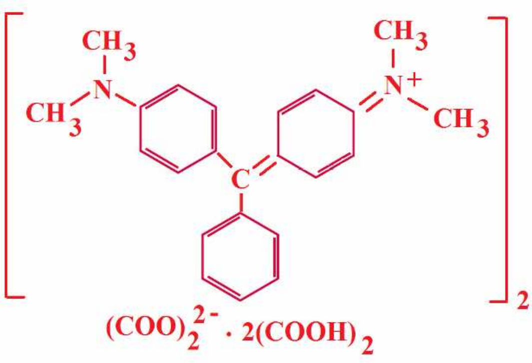
A material is said to be a thin film when it is built up as a thin layer on a substrate by controlled condensation of the individual atomic, molecular or ionic species either directly by a physical process or through a chemical and/or electrochemical reaction. Otherwise, it is a thick film. There are various techniques of producing thin films for scientific application, which include: physical vapour deposition (PVD) technique, chemical vapour deposition (CVD), electrochemical deposition (ECD), hybrid technique, and chemical bath deposition (CBD) technique [1,2].

Thin films occupy a prominent place in basic research and solid state technology. The use of thin film semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their low production cost. Thin film can be made of multi-component, alloy/compound or multi-layers coatings on the substrates of different shapes and sizes [3,4].

In this paper, we present the procedure for preparing different material, undoped (pure MG), $NaBH_4$-doped MG and I-doped MG thin films using spray method technique on glass substrates. The optical constants and band gaps are determined by optical characterization method. Optical limiting have been observed and studied by means of single beam transmission technique, using a continuous-wave (cw) visible solid state laser beam with a wavelength of 532 nm and 30 mWatt output power.

## MATERIALS AND METHODS

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.




$[(C_{23}H_{25}N_2)\cdot(C_2HO_4)]_2\cdot C_2H_2O_4$

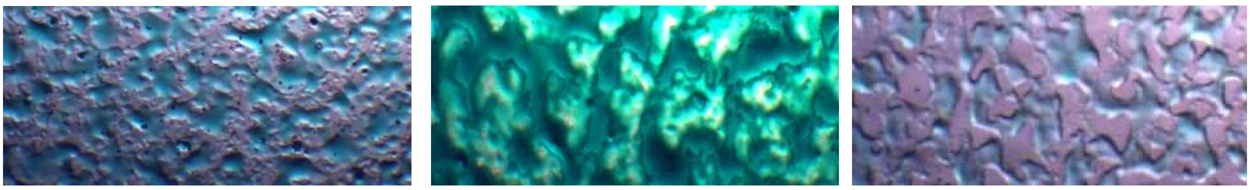
**Fig.1: The chemical structure and formula of MG.**

The deposition of MG thin films is based on the reaction of Iodine (I) and Sodium borohydride ($NaBH_4$) in ethanol solution, respectively. In the present study we use three types of films, a pure MG film, Sodium borohydride ($NaBH_4$) doped MG film and Iodine doped MG film. The 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 solution 0.004M, then the solution was stirred at room temperature for 50 min and then the solution was filtered through a 0.2 mm syringe filter and kept in temperature below $20\,^{0}C$ .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 the films was about 1 μm. The same way have been done to prepare Sodium borohydride ($NaBH_4$) and Iodine doped MG films, respectively and the weights are listed in the Table 1.

**Table 1: The value of the doping ratio**

| Doping type | Doping ratio | Ethanol Solvent (ml) | Weight of MG (gm) | Doping weight (gm) | Film Thickness μm |
|---|---|---|---|---|---|
| Pure | - | 50 | 0.1854 | - | 1 |
| Sodium borohydride | 0.04 | 50 | 0.1854 | 0.0077 | 1 |
| Iodine | 0.18 | 50 | 0.1854 | 0.0407 | 1 |

Electronic microscopy (Novex) was used to describe surface structure of the pure MG thin film, I-doped MG thin film and $NaBH_4$-doped MG film. Images of the both samples are represented in Fig. 2. Relatively homogenous , smooth surface and uniform without cracks or voids. Optical quality of these films was checked by passing 5 mW laser beam. No distortions in the output beam confirm the optical quality of the films.



**(a)** **(b)** **(c)**

**Fig.2: Electronic microscopy images of the (a) Pure film (b) I-doped MG film and (c) $NaBH_4$-doped MG film.**

## RESULTS AND DISCUSSION

### 1. OPTICAL STUDIES

Fig 2 and Fig 3 show UV-VIS absorbance and transmittance spectra of thin films from three different chemical materials (preparatory conditions of chemical materials are presented in Table1). The transmittance/absorbance spectra of MG thin films decreases/increases with film for different materials. Fig. 2 shows the spectral distribution of absorbance sample in the spectral range (300–1000 nm) and the peaks of absorption spectra of thin films from three different chemical materials ( MG, Sodium borohydride and Iodine) are located at 670 nm.

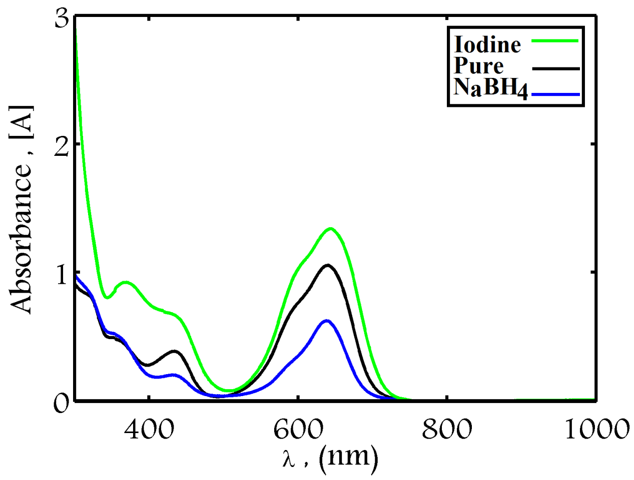



**Fig. 3.Absorbance spectra of the MG thin films deposited at different doping materials.**

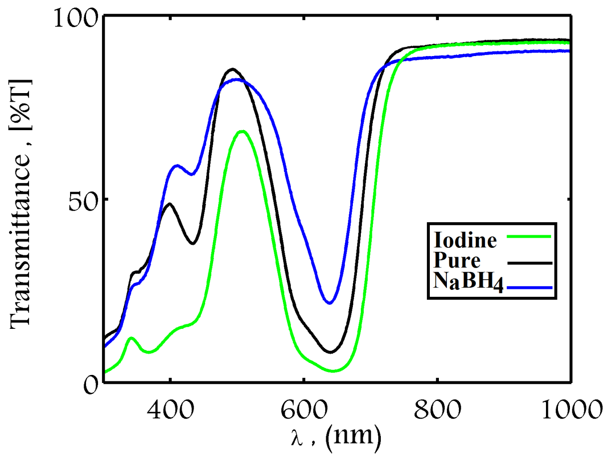



**Fig. 4.Transmittance spectra of the MG thin films deposited at different doping materials.**

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 91% at 780 nm. At shorter 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 two samples.

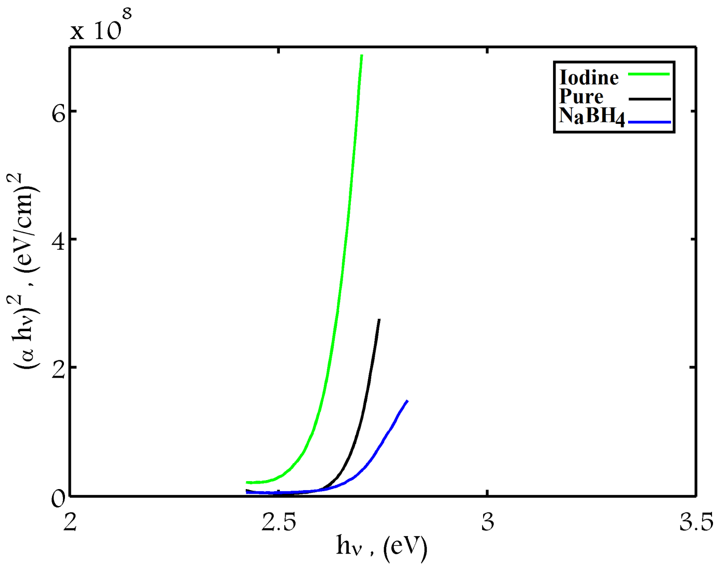



**Fig.5. The plots of** $(\alpha h\nu)^2$ **versus photon energy of MG thin films deposited at different doping materials.**

The theory of optical absorption gives the relation between the absorption coefficient ($\alpha$) and the photon energy ($h\nu$) as [5-8]:

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (1)$$

where is the absorption coefficient ($\alpha$), hν is the photon energy, $E_g$ is the optical band gap and $A$ is the constant which is related to the effective masses associated with the valance band and the conduction band. The n assumes values of 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. For allowed direct type of transitions

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \qquad (2)$$

The plot of $(\alpha h\nu)^2$ versus ($h\nu$)is a straight line whose intercept on energy axis at $\alpha$ = 0 gives the band gap energy, $E_g$ of the MG thin films. The plot of $(\alpha h\nu)^2$ versus $h\nu$ were plotted and are shown in Fig. 3. The band gap energies were estimated by extrapolating straight line portion of the plots to the energy axis. The optical band gap of pure MG is found to be 2.66 eV and decreases continuously down to 2.62 eV for I-doped MG thin film and increase continuously up to 2.67 eV with $NaBH_4$-doped MG thin film. The broad and fine tunable band gap properties of pure MG, I-doped MG and NaBH4-doped MG thin films are suitable for many scientific studies and technological applications such as gas sensors, transparent electrodes, solar cells, piezoelectric and opto-electronic devices.

## 2. REFRACTIVE INDEX AND DISPERSION PARAMETERS

The data of the spectral dependence of the refractive index *n* at low optical frequencies were analyzed in terms of a single oscillator model, following the parameterization suggested by Wemple and DiDomenico (WDD). They introduced an energy parameter, $E_d$, to describe the dispersion of the refractive index. In terms of this dispersion energy, $E_d$, and single oscillator energy, $E_0$, the refractive index can be expressed in the form[9,10]

$$(n^2-1)^{-1} = \frac{E_0}{E_d} - \frac{E^2}{E_0 E_d} \qquad (3)$$

Where $E = h\nu$ is the photon energy. Blotting $(n^2-1)^{-1}$ against $(h\nu)^2$ as shown in Figure 6 for the investigated film allows to determine the values of the dispersion parameters $E_d$ and $E_0$.The calculated values of $E_d$ , $E_0$ and the high-frequency dielectric constant, $\varepsilon_\infty$ for thin films are given in Table 2.

The dispersion energy $E_d$ measures the average strength of interband optical transitions and is associated with the changes in the structural order of the material i.e, it is related to the ionicity, anion valency and coordination number of the material and $E_0$ is the effective oscillator energy. The advantage of using the single oscillator equation for the fit of the experimental data is that it provides an intuitive physical interpretation of the measured quantities. In particular, the average gap, $E_0$, gives quantitative information on the overall band structure of the material. This is quite different from the information coming from the value of optical gap $E_g$, which probes the optical properties near the band edges of the material. In particular, localized states near the conduction or the valence band “tail states” might have a strong effect on the optical absorption and thus decrease the optical gap, whereas if they have a small polarizability, they will result in a small effect on the refractive index: such tail states increase the “Urbach tail”, but have little effect on the average gap $E_0$ [11].

The static refractive index, $n_0$, has been calculated from WDD dispersion parameters , $E_0$ , and , $E_d$, using the formula [9]:

$$n_0 = \left(1 + \frac{E_d}{E_0}\right)^{0.5} \qquad (4)$$

The $M_{-1}$ and $M_{-3}$ moments of the optical spectra can be obtained from the relationships [12]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad \text{and} \quad E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad (5)$$

The obtained values are given in Table 2. The $M_{-1}$ and $M_{-3}$ moments changed due to the formation coordination of complex.

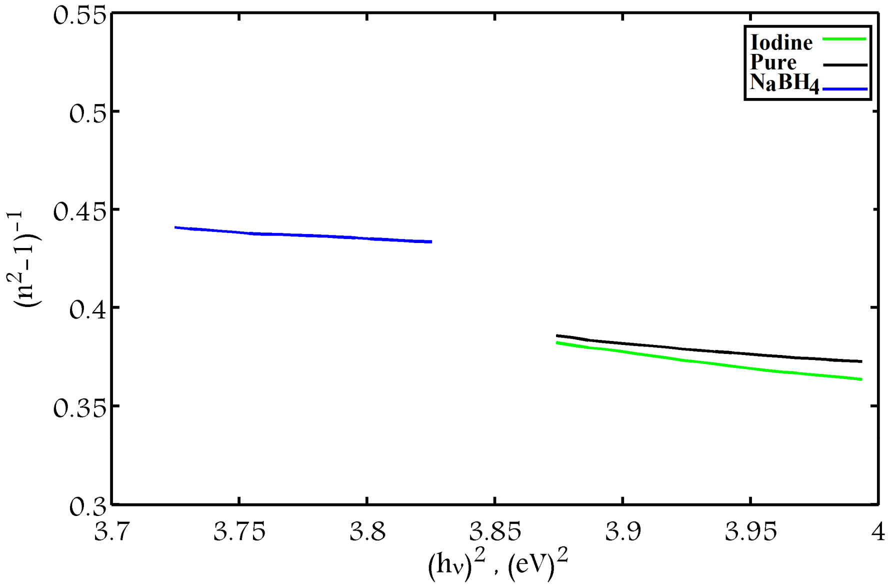



**Fig. 6 Plot of $(n^2-1)^{-1}$ versus $(h\nu)^2$ of MG thin films deposited at different doping materials.**

**Table 2. Optical parameters of the MG thin films**

| Sample | $E_d$ $(eV)$ | $E_\circ$ $(eV)$ | $n_\circ$ | $\varepsilon_\infty$ | $M_{-1}$ | $M_{-3}$ $(eV)^2$ |
|---|---|---|---|---|---|---|
| Pure MG | 6.695 | 4.66 | 1.56 | 2.43 | 1.43 | 0.0661 |
| I-doped MG | 7.58 | 5.086 | 1.57 | 2.46 | 1.49 | 0.057 |
| NaBH4-doped MG | 4.775 | 3.68 | 1.515 | 2.29 | 1.29 | 0.095 |

## 3. NONLINEAR OPTICAL PROPERTIES

The Wemple and Di Domenico expression (1) could also be useful for estimating non-linear effects in chalcogenide glasses from the linear optical index of refraction, *n*. According to Frumar [13] the Miller rule is very convenient for visible and near-infrared frequencies, which equalize the third order non-linear polarizability parameter,($\chi^{(3)}$), the so-called non-linear optical susceptibility, and the linear optical susceptibility, ($\chi^{(1)}$), through the equation:

$$\chi^{(3)} = A(\chi^{(1)})^4 = A\ \ [E_d E_0 / 4\pi(E_0^2 - (h\nu)^2]^4 = \frac{A}{(4\pi)^4}(n_\circ^2 - 1)^4 \qquad (7)$$

where $A = 1.7x10^{-10}$ (for $\chi^{(3)}$ in esu). The covalency and ionicity of the chemical bonds strongly influence the magnitude of the non-linearity.

From inspection of Equ.7 it can be seen that third-order nonlinear optical properties is sensitive to the wavelength of light and doping materials, as shown in Fig.7. Its value also increases when the wavelength of light is approaches the absorption edge (closer to resonance conditions).

To a reasonable approximation, the linear index of refraction is connected to the non-linear one by

$\bar{\chi}^{(3)}$ [14]:

$$n_2 = \frac{12\pi\chi^{(3)}}{n_\circ} \qquad (8)$$

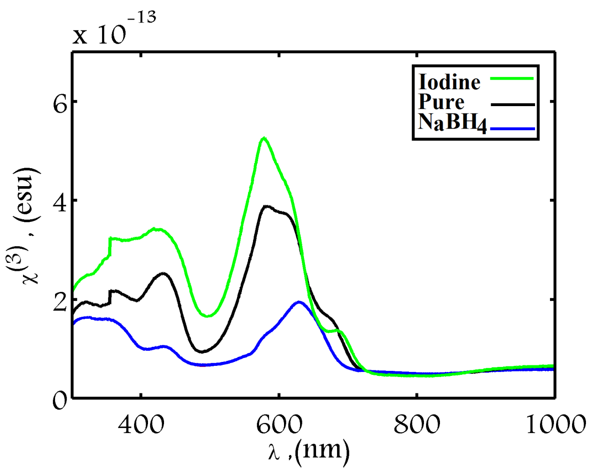



**Fig.7: $\chi^{(3)}$ versus wavelength of MG thin films deposited at different doping materials.**

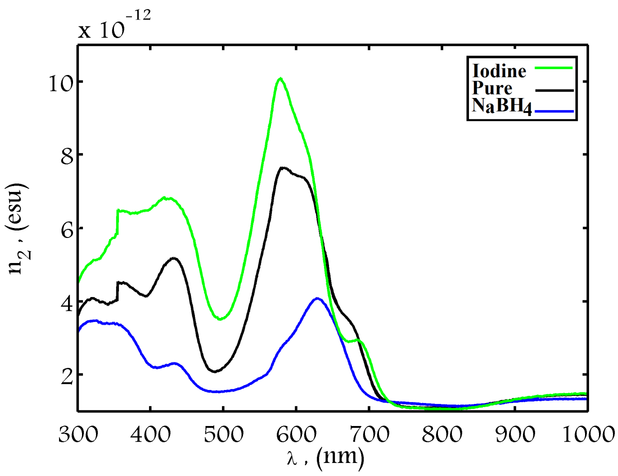



**Fig.8: $n_2$ versus wavelength of MG thin films deposited at different doping materials.**

**4. OPTICAL LIMITING**

For optical limiting experiments the sample thin film in 1µm was placed just after the focus of lens (focal length of 10 cm) where the defocusing occurred. At very high peak intensities (closer to the focus) we could observe diffraction type pattern with concentric ring structures probably due to self-phase modulation. However, for limiting experiments we ensured that there was no ring pattern formation by placing the sample away from focus, yet in the nonlinear regime.

Fig. 9 depicts the optical limiting curve in pure MG thin film and MG thin films recorded for doping ratio of 0.18 and 0.04 for iodine and Sodium borohydride respectively. We could reproduce this behaviour several times within some experimental errors [15,16]. The optical limiting curves obtained with an diode laser of wavelength 532 nm for different materials doped MG film are shown in Fig.9. All the samples show a similar optical limiting behavior. The output power rises initially with increase in input power, but after a certain threshold value the samples start defocusing the beam, resulting in a greater part of the beam cross section being cut off by the aperture. Thus the transmittance recorded by the photo detector remained reasonably constant showing a plateau region. The optical limiting effect shows an increase with Sodium borohydride ($NaBH_4$) doped Malachite green film and decrees with Iodine doped Malachite green film.

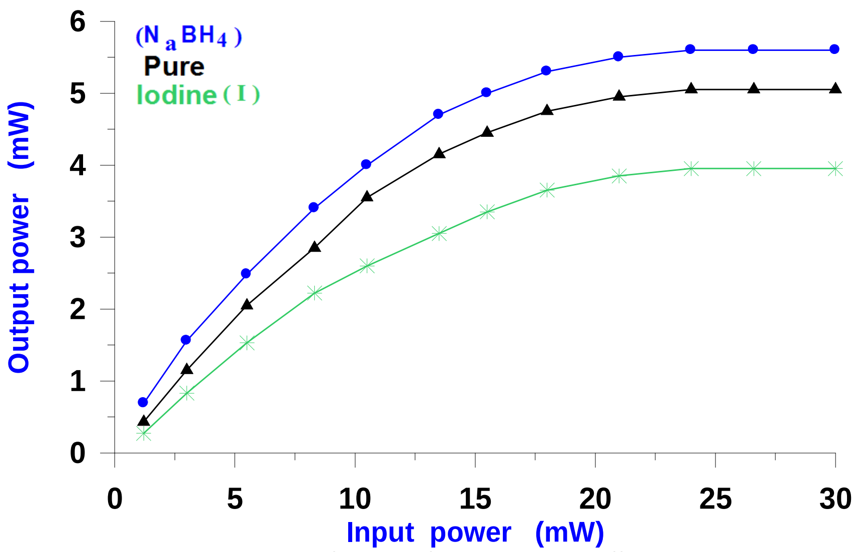



**Fig. 9 optical limiting properties of MG thin films deposited at different doping materials.**

**CONCLUSION**

Malachite green thin films have been deposited on glass substrate by the spray method technique. The MG thin films deposited at different doping materials. Images of the both samples are homogenous, smooth surface and uniform without cracks or voids. The effect of doped material on optical properties of MG thin films deposited onto glass substrates by the spray method technique has been investigated. The direct optical band gaps of the films were found between 2.62 and 2.67 eV. The value of the oscillator strength Ed increased with I-doped MG thin film. The values of $M_{-1}$ and $M_{-3}$ are high which indicates that the studied sample have high polarization. Simple semiempirical relation based on generalized Miller´s rule allows an estimation of nonlinear susceptibility ($\chi^{(3)}$) and non-linear refractive index ($n_2$) from linear refractive index and/or from the dispersion energy and the energy of effective oscillator of the Wemple-Di Domenico model.

## REFERENCES

[1] Ezema F I, *Turkish Journal of Physics* , **2005** , 29, 105 .
[2] Ezema F I, *J. of Res. Sci*, **2004** ,15, 343 .
[3] Ezugwu S C, Ezema F I ,Osuji RU , Asogwa P U,Ekwealor A B, Ezekoye B A,*Optoelectronics and Advanced Materials-Rapid Communication*, **2009**, 3(2), 141.
[4] Mattrox DM , *Deposition Technologies for Thin Films and Coatings*, Noyes Publications, NY. **1982** ,pp 255.
[5] Yadav AA, Barote M A, Masumdar EU, *Materials Chemistry and Physics* **2010,** 121,53.
[6] Okereke NA, Ekpunobi AJ, *Advances in Applied Science Research*, **2012**, 3 (3),1244.
[7] Meshram RS,Thombre RM,Suryavanshi BM, *Advances in Applied Science Research*, **2012**,3,1271.
[8] Meshram RS,Suryavanshi BM,Thombre RM, *Advances in Applied Science Research*, **2012,**3,1563.
[9] Wemple S H , DiDomenico M , *Physical Review* , **1971**, B3, 1338.
[10] Wemple S H , *Physical Review* **,** **1973**, B7, 3767.
[11] Solomen I , Schmidt M P , Senemaud C , Khodja M D , *Physical Review* , **1988**, B38, 13263.
[12] Yakuphanoglua F, Cukurovalib A and Yilmazb I , *Physica* , **2004**, B351, 53.
[13] Frumar M ,Jedelsky J, Frumarova B, Wagner T ,Hrdlicka M **,** *Journal of Non- Crystalline Solids*, **2003**, 326-327, 399.
[14] Tichá H, Tichý L , *Journal of Optoelectronics and Advanced Materials* , **2002** ,4, 381.
[15] Chidiebere U,Suleiman FA, Surakat LY, Oluwole IL, Angela JU, *Advances in Applied Science Research*, **2011**, 2, 297.
[16] AlaaYA,Hussain AB,Qusay MA,Chassib AE, *Advances in Applied Science Research*,**2012**,3,706.