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Optical properties of vanadyl phthalocyanine thin films and nonlinear refractive index of vanadyl phthalocyanine doped PMMA by using thermal lens spectrometry technique

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Abstract

The optical properties of vanadyl phthalocyanine (VOPc) thin films have been studied in the spectral range 300-900 nm. Variations in the optical constants with wavelength are found to be thickness dependent of the films. The optical band gap E_g and optical conductivity σ_{opt} were determined. The analysis of the optical absorption data indicates that the optical band gap Eg was indirect transitions. The optical band gap of the VOPc thin films was found to increase with thickness of the film. According to Wemple and DiDomenico method, the optical dispersion parameters E_o and E_d were determined. Thermal lens spectrometry is applied to measure the thermo-optic coefficient *dn/dT* and nonlinear refractive index for VOPc doped Poly methylmeth acrylate (PMMA) film. The measurements were carried out using the SDL laser at wavelength 635 nm, as both probe and excite source.

Keywords: Thin film, Optical constants, Nonlinear refractive index, Thermal lens spectrometry

1. Introduction

In recent years, organic materials are intensively investigated due to their wide range of applications in electronics (Yakuphanoglu et al.2006). Phthalocyanines (Pcs) are a common class of organic compounds available in high purity due to the ease of crystallization and sublimation; extraordinary thermal and chemical stability. It has received much attention due to their wide application fields, such as organic solar cells (Peumans et al.2002; Pfeiffer et al. 2002), in organic field effect transistors (Bao et al.1996), in organic light emitting diodes in which Pcs can be used as a hole transport layers (Blochwitz et al.1998 ; Zhou et al. 2001)or emitting layers (Fujii et al.19978)and in gas sensors (Nagasawa et al.1998 ; Newton et al.200). These materials are also promising organic electrophotographic materials, nonlinear optical materials and optical recording materials (Mckeown 1998; Dogo et al. 1992 ; Chen et al. 1994).

The refractive index is one of the fundamental properties of a material, since it is closely related to the electronic polarizability of ions and the local field inside the material (Yakuphanoglu et al.2004). The evaluation of refractive indices of optical materials is of considerable importance for applications in integrated optic devices such as switches, filters and modulators, etc., where the refractive index of a material is the key parameter for device design (Neumann et al.1979).

Optical properties of a functional organic material with a π conjugated such as Pcs system depend strongly on the as-prepared molecular orientation, either stacking or packing, film thickness, rate of deposition, substrate temperature, crystallinity and annealing temperature (Senthilarasu & Sathyamoorthy 2006). Optical constants have been calculated in various MPcs thin films, such as MgPc (El-Nahass et al. 2008; Kamath et al. 2002; Rajesh & Menon 2001)CuPc (Karan & Mallik 2007; Jungyoon et al.2003), NiPc (El-Nahass et al.2005), ZnPc (El-Nahass et al.2004), $SnPcCl_2$ (El-Nahass et al. 2004), CoPc (El-Nahass et al.2003), SnPc (El-Nahass & Yaghmour 2008). The aim of the present study is to investigate the optical constants of vanadyl phthalocyanine (VOPc) thin films such as refractive index, n, optical band gap, E_g , optical dispersion parameters, E_o and E_d, and optical conductivity, σ_{opt}. The effect of film thickness on these quantities was studied. We also discuss the use of thermal lens spectrometry TLS technique to measure the thermo-optic coefficient, dn/dT, and nonlinear refractive index,n_2, of VOPc doped Poly(methylmethacrylate) (PMMA) film as a function of film thickness.

2. Experimental

2.1 *Preparation of the films*

The preparation of vanadyl phthalocyanine is done according to the procedure given in reference (Achar et al. 1987). In the present study we use two types of films, first one is VOPc, second one is VOPc doped PMMA**.** The VOPc film was prepared as follows: 0.5 g of the VOPc powder was dissolved in 20 ml of nitrobenzene, the solution was stirred at room temperature for 50 min then the solution was filtered through a 0.2 mm syringe filter. The film was prepared by the spray method on a clean glass slide substrate of 25mm x 25 mm x 1mm in a size. The thickness of the film was about 2 μm. In order to prepare the second sample, a known quantity of PMMA and VOPc was dissolved in nitrobenzene separately, later both solutions were mixed and stirred for 2 hr using a magnetic stirrer. The ratio of PMMA solution and VOPc solution is 1:1. The film was

prepared on a clean glass slide by the casting method and dried at 20 ^{o}C for 24 hrs. The thickness of the film was about 72 μm. The other films for VOPc with 3,6 and 8 μm thickness and for VOPc doped PMMA with 74,76 and 78 μm thickness were also prepared in a similar manner. The film samples have good purity and uniform thickness. The code of VOPc film with 2,3,6 and 8 μm thickness are C1,C2,C3 and C4, respectively, while the code of VOPc doped PMMA with 72,74,76 and 78 μm are B1,B2,B3 and B4, respectively.

2.2 Electronic microscopy study

Electronic microscopy (Novex) was used to describe the surface structure of the VOPC film and VOPc doped PMMA film. Images of both samples are represented in Fig. 1. This figure shows homogenous and smooth surfaces 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.

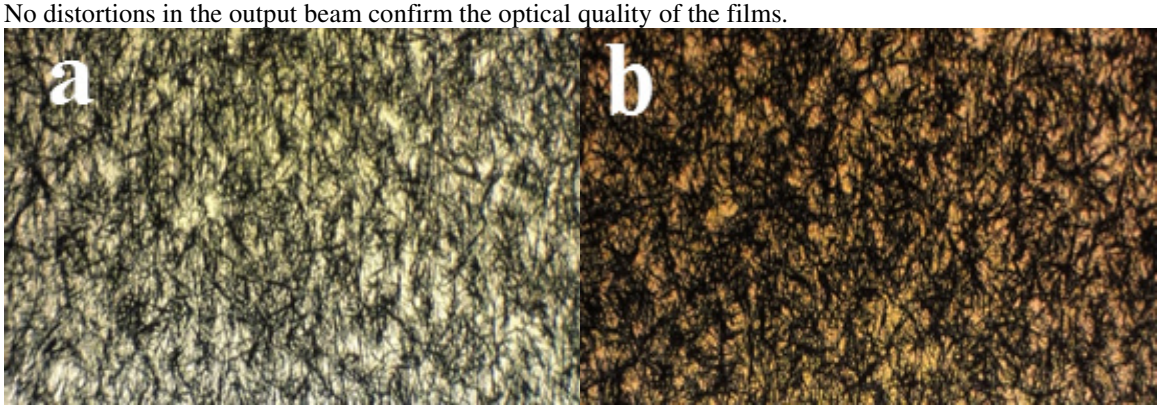

Fig. 1 Electronic microscopy images of (a) VOPC film and (b) VOPc doped PMMA film.

2.3 UV-Visible spectroscopic studies

The UV-Visible spectra of the VOPc thin films were recorded using Cecil Reflected-Scan (CE 3055) reflectance spectrometer at room temperature. The optical absorption, transmittance and reflectance spectra were analyzed to determine the optical constants such as refractive index, n, and absorption coefficient, α. The analysis of the absorption coefficient was also carried out to determine optical band gap and the nature of transitions.

2.4 Thermal lens spectrometry

Thermal lens spectrometry (TLS) was first reported by (Gordan et al.1965). Since then the technique has proved to be a valuable method to study transparent materials. It is based on the indirect measurement of absorbance via the so-called thermal lens effect. This phenomenon is a result of the heat generated in an irradiated sample by the non-radiative relaxation of absorbed energy (Fang & Swofford 1983; Georges 1999 ; Šikovec et al. 2001). When a laser beam with a Gaussian profile is used as an excitation source, the energy deposited in the sample results in a characteristic Gaussian radial temperature distribution and in the corresponding refractive index gradient. A lens-like optical element is consequently formed within the irradiated sample and the initial intensity profile of the laser beam changes. The relative change in the laser intensity at the beam axis is a direct measure of the thermal lens strength, that itself is proportional to the amount of heat generated in the irradiated sample, and is consequently dependent on the power, P, of the excitation light, absorbance, A, of the sample, beam divergence and sample concentration. Furthermore, the magnitude of the thermal lens signal and the sensitivity of the technique depend on the thermo optical properties of the sample (such as dn/dT, the temperature coefficient of refractive index and k_1, the thermal conductivity).

The TLS experiments were performed in VOPc doped PMMA film. The experimental set-up for observation of a single thermal lens spectrometer is shown in Fig. 2. In order to obtain thermal lens signal, a solid state laser (635 nm) was used as pump/probe source. The laser beam was allowed to irradiate the sample or blocked using a signal generator (EM - 1634) which modulates the laser beam at100 Hz frequency. The laser beam was focused by an +5 cm focal length lens and passed through the sample located at the confocal distance. The beam intensity change was measured through 3 mm aperture which was mounted in front of the photo detector placed at 30 cm distance from the sample which was connected to an oscilloscope (LODESTAR MOS-620CH).

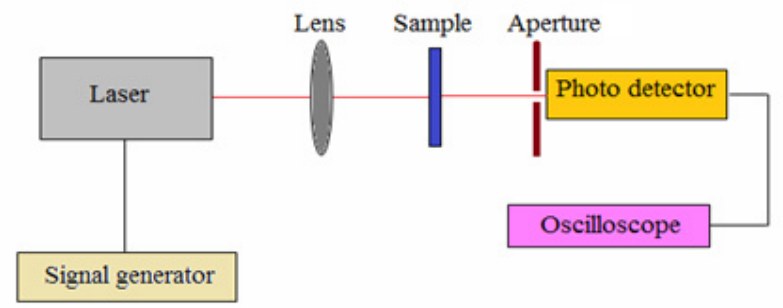

Fig. 2. Schematic diagram of thermal lens spectrometer**.**

3. Results and discussion

3.1 Linear optical properties

3.1.1 Transmittance measurements

In order to study the effect of film thickness on optical properties the absorbance (A), transmission (T) and reflectance (R) spectra of thin films with different thickness are shown in Figs.(3-5) respectively. We can see from the Fig.3 that the absorbance of the sample increases with increasing the thickness of the film this due to increase number of molecular per unit volume, so the absorbance will be increased. In case of VOPc film with 2μm thickness, transmittance (T) is as low as 75% at longer wavelength (900 nm) and gradually rises towards shorter wavelength until it reaches its maximum value of 92% at 537 nm. At shorter wavelengths, transmittance decreases rapidly, and approaches near zero at around 300 nm. 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 to the conduction band of VOPc thin film. Similar type of behaviour is observed for the other three samples. From these spectra it is seen that the average transmittance of the films decreases with increasing the thickness of the film.

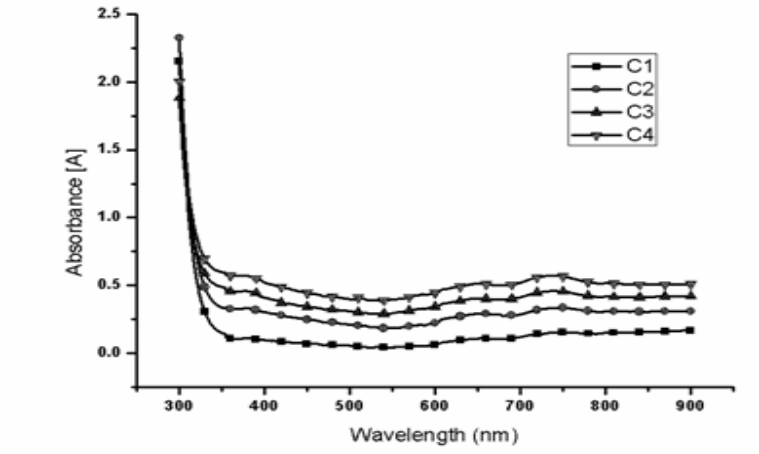

Fig. 3 Optical absorption spectra of VOPc films with different thicknesses.

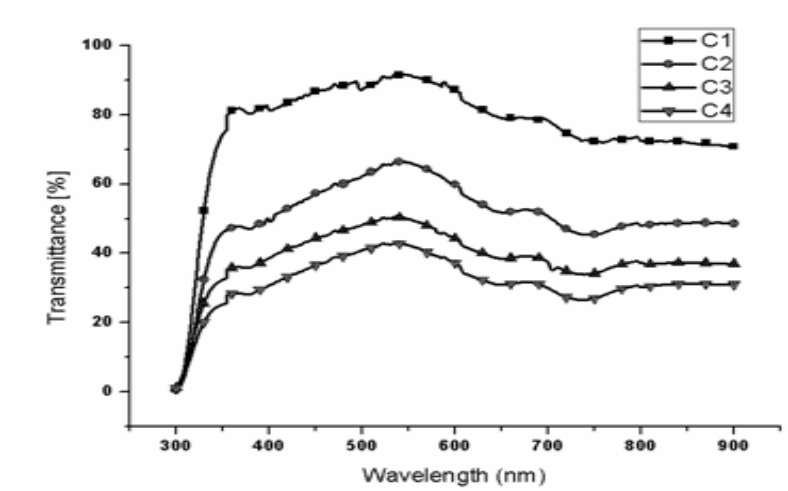

Fig. 4 Optical transmittance spectra of VOPc films with different thicknesses.

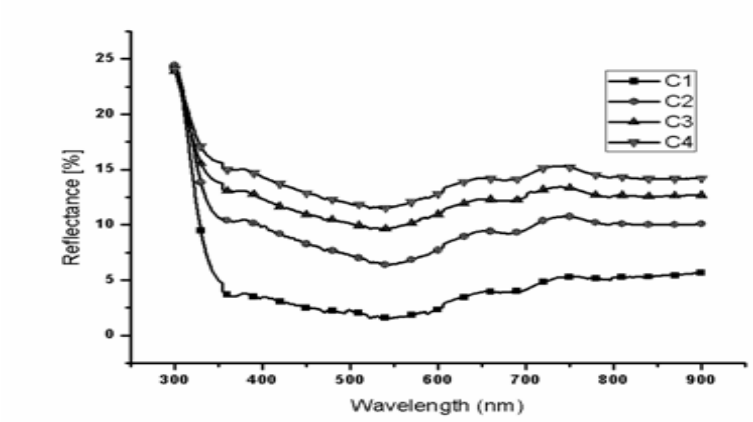

Fig. 5 Optical reflectance spectra of VOPc films with different thicknesses.

3.1.2 Determination of the absorption coefficient

The absorption coefficient α has been obtained directly from the absorbance against wavelength curves using the relation (Yakuphanoglu et al. 2007)

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

Where A and d are the absorbance and thickness of the film respectively. The variation of absorption coefficient (α) as a function of incident photon energy (hv) for VOPc thin films at different thickness is shown in Fig.6. It has been observed that the value of the absorption coefficient increases with the increase in photon energy hv. Near the absorption edge, α increases more rapidly with hv.

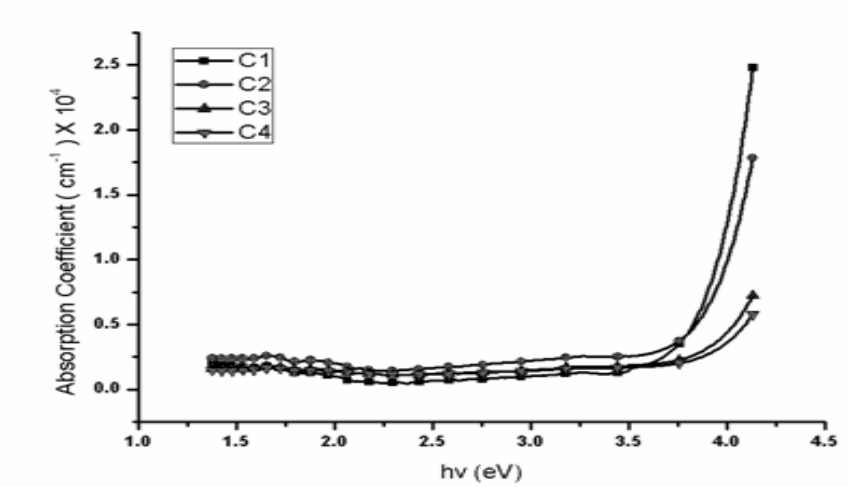

Fig. 6. Variation of α vs. hv of the VOPc film for different thickness film.

3.1.3 Determination of the optical band gap

The analysis of the optical absorption spectra can reveal the optical energy gap E_g between the conduction band and the valence band due to the 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 (Mott & Davis 1979):

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

where hv is the energy of 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 the direct and indirect allowed transition, respectively(Tauc 1974).The energy gaps were determined by the intercept of the extrapolations to zero absorption with the photon energy axis which taken as the values of the indirect energy gaps E_g. Fig 7 shows the variations of $(\alpha h\nu)^{1/2}$ vs. hv. The values of indirect band gaps calculated from the graphs and they are listed in the Table 1.

The increase in film thickness can produce an increase or decrease in the band gap (Al-Ghamdi et al. 2010; Yakuphanoglu et al.2005). In the present study it is clear from the Fig. 7 that indirect band gaps increase with increasing film thickness. The indirect band gaps increased from 3.72 to 3.81 eV when the film thickness increased from 2 to 8 μm. This can be interpreted in terms of the elimination of defects in the amorphous structure (Chaudhuri et al.1988; El-Wahabb 2000). 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. Thicker films are characterized by a homogenous network, which minimizes the number of defects and the localized states, and thus the optical gap increases.

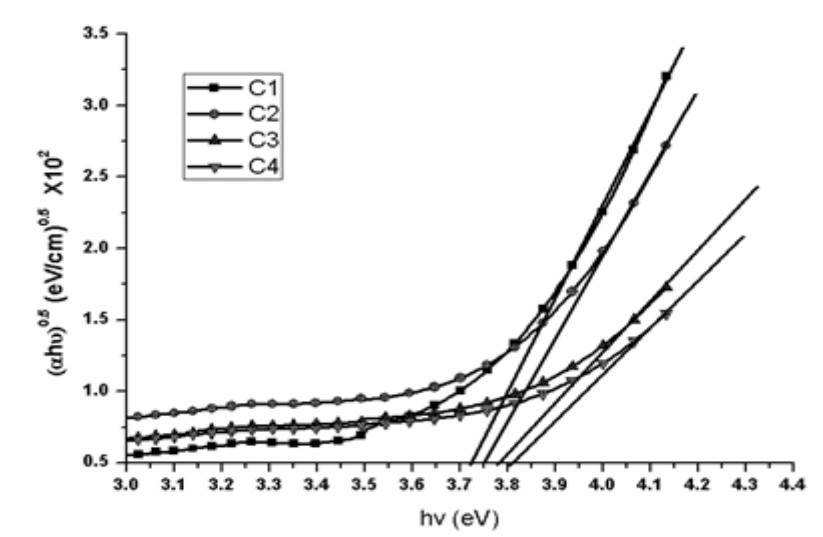

Fig.7. Variation of $(\alpha h\upsilon)^{1/2}$ versus hv for VOPc film with different thickness.

3.1.4 Calculation of the refractive index

The refractive index, n, can be determined from the following relation (Ilican et al. 2009)

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

where k is the extinction coefficient (=αλ/4π). The variation of refractive index with wavelength for various film thickness is shown in Fig. 8. The value of n was found to decrease with increasing wavelength up to 550 nm. For λ> 550 nm it increases slightly. Also we observed that the refractive index increases with the increasing of the thickness of the film.

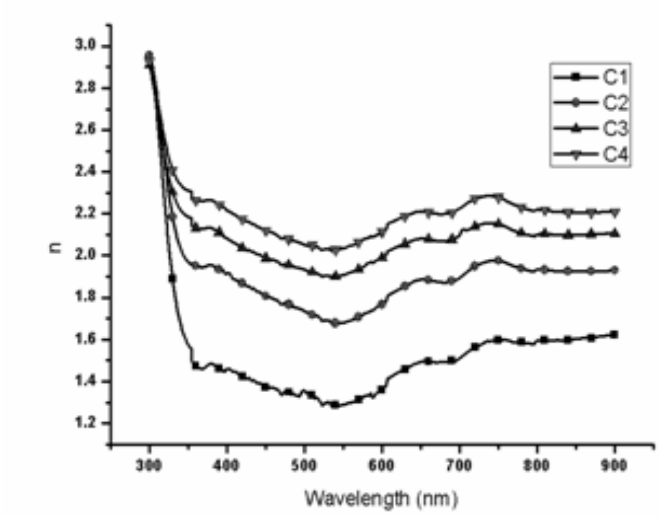

Fig.8. Variation of refractive index with wavelength for VOPc film.

3.1.5 Dispersion energy parameters

In the normal dispersion region, the refractive index dispersion is analyzed using the Wemple and DiDomenico single oscillator model (DiDomenico &Wemple1969 ; Wemple & DiDomenico 1971). In terms of this model, the refractive index can be expressed as a function of photon energy.

$$(n^2 - 1) = \frac{E_\circ E_d}{E_\circ^2 - (h\upsilon)^2} \qquad (4)$$

Where E_d and E_o are single-oscillator constant, E_o is the oscillator energy and E_d is the dispersion energy, which is a measure of the average strength of the interband optical transition or the oscillator strength. The single oscillator energy, E_o and the dispersion energy ,E_d, can be obtained from Eq. (4) by plotting $(n^2\text{-}1)^{-1}$ against $(hv)^2$ as shown in Fig.9. E_o and E_d can be determined from the plot, using the linear fit parameters. The values of E_d and E_o are obtained from intercepts and the slope of the curve. Using the curve shown in Fig. 9 the estimated values of oscillator parameters E_o and E_d for VOPc thin films are given in Table 1. Also we noticed that values of E_o and E_d increase with increasing film thickness.

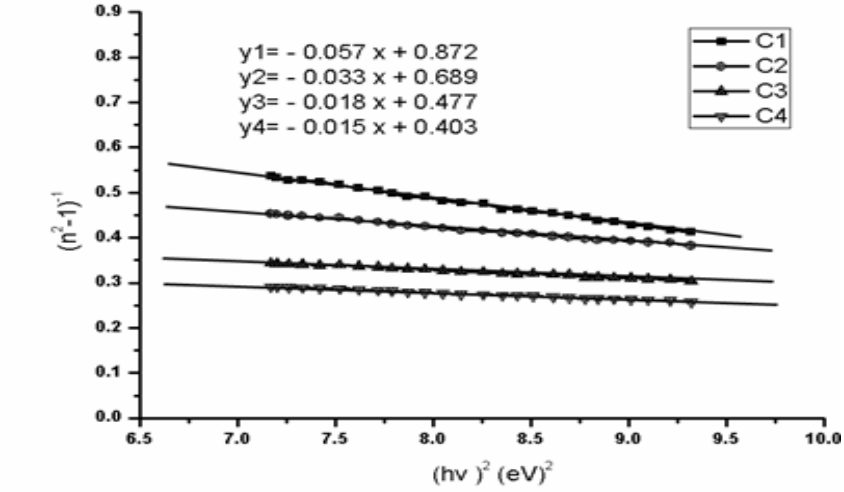

Fig.9. Plots of $(n^2\text{-}1)^{-1}$ against $(hv)^2$ for VOPc film.

Table1: Optical parameters of VOPc thin films. The standard error of all estimated optical properties was 0.81%.

Thickness (μm)	E_g (eV)	E_o (eV)	E_d (eV)	n at 750 nm
2	3.72	3.91	4.48	1.59
3	3.75	4.56	6.63	1.97
6	3.78	5.14	10.79	2.15
8	3.81	5.18	12.86	2.27

3.1.6 Optical conductivity

The optical conductivity σ_{opt} can be estimated from the absorption coefficient α using the following relation (Pankove 1975).

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \qquad (5)$$

where c is the velocity of the light. Fig.10 shows the variation of optical conductivity σ_{opt} with photon energy hv. The increase of optical conductivity at high photon energies is due to the electron excitation by photon energy (Assim 2008).

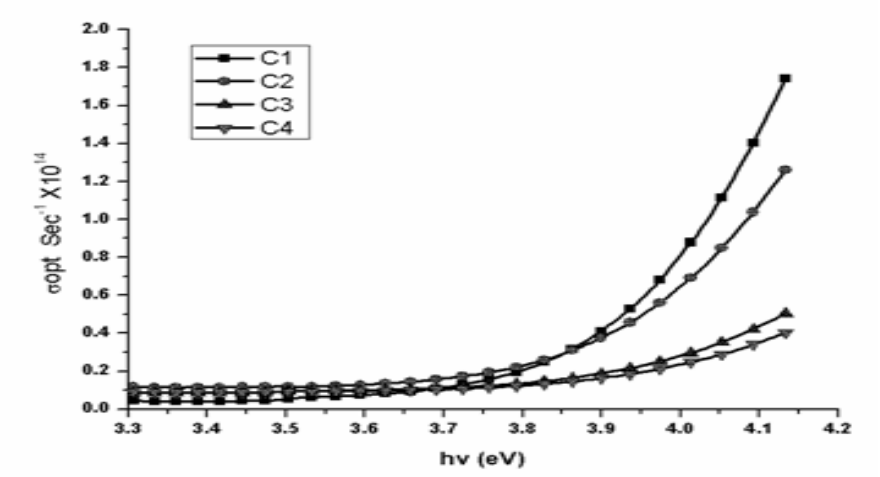

Fig.10. Dependence of optical conductivity σ_{opt} on the photon energy hv for VOPc film.

3.2 Nonlinear optical properties

3.2.1 Absorption coefficient

The absorption spectra for VOPc doped PMMA film is shown in Fig. 11. The optical absorption increases with increasing thickness of the film as can be seen in Fig. 11. The values of absorption coefficient ,α,at wavelength 635 nm for VOPc doped PMMA film with different thickness are calculated using Eq.1 ,see Table 2.

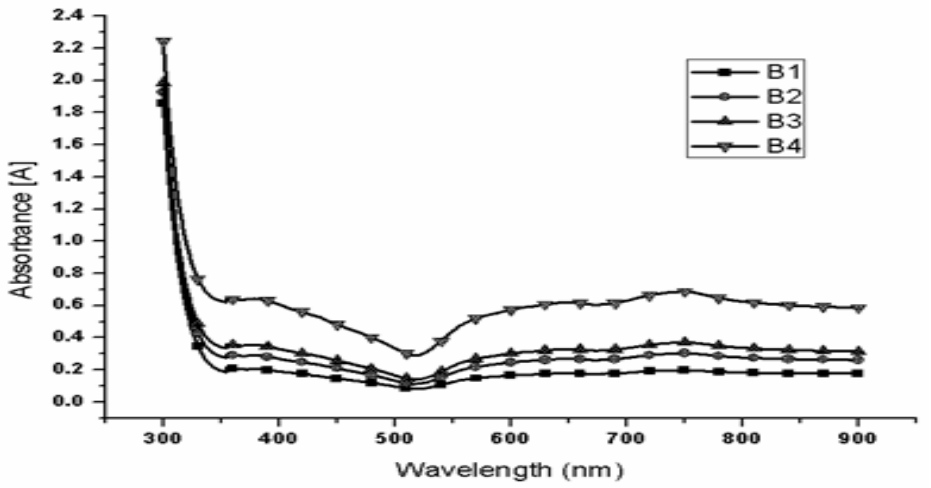

Fig.11.Optical absorption spectra of VOPc doped PMMA films with different thicknesses.

3.2.2 Nonlinear refractive index

The thermal lens signal is expressed as the relative change in power (Shemirani & Shokoufi 2006).

$$\frac{I(0)-I(\infty)}{I(\infty)} = -\frac{2.303(dn/dT)}{\lambda k_1} \qquad PA = 3.303EA \qquad (6)$$

$$E = -\frac{dn/dT}{\lambda k} P \qquad (7)$$

where $I(0)$ and $I(\infty)$ are the transmitted power before and after the formation of the thermal lens respectively, P is the laser power, λ is the pump laser wavelength and E represents the so-called enhancement factor. The enhancement factor is a function of the thermodynamic and optical properties of the medium and on the power used to excite the sample. This expression assumes that all of the absorbed light is converted into heat.

Fig. 12 shows the image of the transmission of the laser beam when thermal lens is induced in VOPc doped PMMA film monitored on the oscilloscope screen. In Fig.13 we see a typical transient TL signal for the VOPc doped PMMA film with different thickness for a pumping power of 26 mW at room temperature. From the study of the thickness effect on thermal lens measurements, it was found that the magnitude of the thermal lens signal intensity is strongly dependent on the thickness of the film.

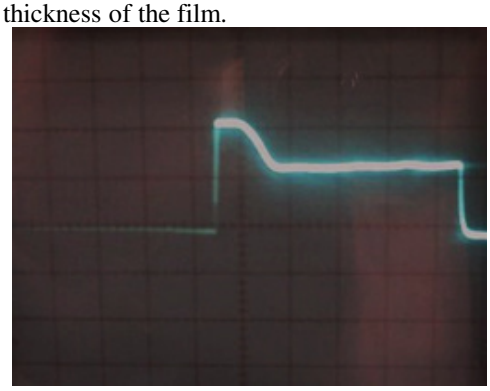

Fig.12.Image of the transmission of the laser beam when thermal lens is induced in VOPc doped PMMA film.

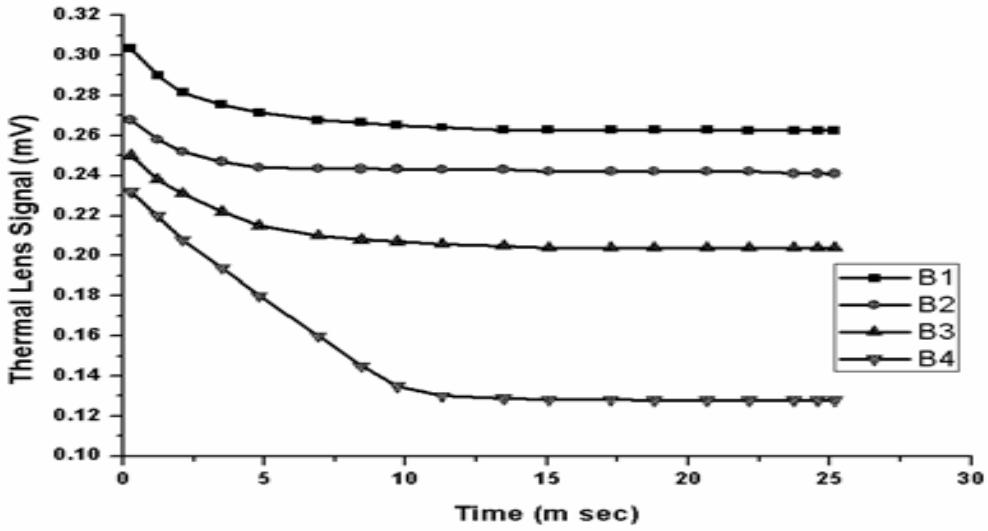

Fig.13. Typical transient TL signal for VOPc doped PMMA film.

Nonlinear refraction resulting in thermal lensing essentially arises from the phenomenon of non-radiative energy transfer from dye molecules to the solid host and is therefore, strongly governed by the thermo–optic properties of the solid host . In order to reduce the effects of thermal nonlinearity, the use of solid hosts having high specific heat and low d*n*/d*T* would be preferable (Peterson 1979). In addition, thermal conductivity of the host material also plays a critical role when the dye doped solid based optical device is operated in the pulsed mode at a high repetition rate or in the continuous wave mode. For a PMMA host, the value for thermal conductivity is 0.19 $Wm^{-1}K^{-1}$. From the Fig. 13 we can find the values of I(0) and I(∞), and by using Eq. 6 we found the values of dn/dT for the samples and they are given in Table 2.

The thermal-induced third-order nonlinear refractive index, n_2, can be estimated by the thermal nonlinear optical theory (Boyd 2003)as

$$n_2 = \frac{dn}{dT}\frac{\alpha\omega_\circ^2}{k_1} \qquad (8)$$

Based on the absorption coefficients and thermo-optical coefficient measured in experiment, the theoretical values of n_2 In Eq. (8) are calculated and they are given in Table 2. We can see from the Table 2 when the thickness increases the absorbance will increase, this may be due to the increasing number of the molecules per unit volume and this will cause increase amount of heat generated in the irradiated sample, therefore the variation of the refractive index with temperature will increase as seen in the Table 2, so the nonlinear refractive index increases with increasing the thickness of the film.

Table 2. Thermo-optical and nonlinear refractive index for VOPc doped PMMA film.

Thickness μm	Absorbance at 635 nm	α cm^{-1} at 635 nm	dn/dT x10^{-6} K^{-1}	n_2 x10^{-7} cm^2/W
42	0.17	93.2	- 0.91	-0.43
44	0.23	120.3	- 0.98	-0.58
46	0.32	160.2	- 1.39	-1.11
48	0.61	292.6	- 2.67	-3.87

The high nonlinear refractive index (-3.87 x 10^{-7} cm^2/W at wavelength 635 m) compares favorably with the nonlinearities of other representative third-order nonlinear optical materials, such as the oxazine 720 and oxazine 750 in polyacrylamide hydrogel (PAA) host has n_2 = - 9.11 x 10^{-8} cm^2/W and n_2 = -1.1x10^{-7} cm^2/W, respectively (Milanchian et al.2009); the averaged n_2 values for methylene blue doped PMMA film -1.2x10^{-7} cm^2/W (Sukumaran et al. 2011), for tris thiourea zinc sulphate single crystals, n_2 = -5.36x10^{-12} cm^2/W (Girisum & Dhanuskodi 2009), for amido black dye doped polyvinyl alcohol (PVA), n_2 = -1.57 x 10^{-7} cm^2/W (Kumar et al.2007). This predicts that the VOPc doped PMMA film has potential applications for nonlinear optics.

Conclusions

The optical constant and optical band gaps of the VOPc thin films of different thickness have been investigated by optical characterization method. The film thickness changes the indirect optical band gaps, optical constants (refractive index and absorption coefficient) values of the films. The dispersion parameters of the VOPc films were determined and these values increase with increasing film thickness. The type of optical transition responsible for optical absorption was indirect transitions. The optical conductivity σ_{opt} increased with the increasing of the photon energy. The high magnitude of optical conductivity (10^{14} s^1) confirms the presence of very high photo response nature of the material (ILenikhena 2008). This makes the material more prominent for device applications in information processing and computing.

We discuss the use of the TLS technique for investigating the thermo-optic coefficient dn/dT of VOPC doped PMMA film as a function of thickness. It also discussed how the experimentally determined TLS parameters can be used to calculate nonlinear refractive index for the samples.

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