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Dispersion Parameters of Copper Sulphate Doped PMMA

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Abstract

Films of PMMA and copper sulphate doped PMMA have been prepared by casting method.

Absorbance and transmittance spectra were recorded in the wavelength range (300-900) nm in order to calculate, single oscillator energy, dispersion energy, average oscillator strength, the refractive index at infinite wavelength, M_{-1} and M_{-3} moments of the optical spectra, it was found that all these parameters were effected by doping.

Keywords: PMMA, Optical Properties, Casting Method, Doping Effect

Introduction

Poly (methyl methacrylate) PMMA has received great attention due its unique properties such as, excellent mechanical properties [1], thermal capability and electrical performance [2], low optical absorption, simple synthesis and low cost [3], high transparency in the visible region, low refractive index [4], possible to use in nonlinear optics [5].

These characteristics create many potentially commercial applications, like, photonic of nanotechnology [6], as an optical diffuser in a liquid crystal display backlighting unit (BLU) [7], humidity sensing after surface modification of PMMA by argon/ oxygen plasma processing [8], as a gas sensors [9], optical device such as optical lenses and polymer optical fiber [10], PMMA is also widely used in consumer products [11].

Many attempts have been carried out using different materials as an additive in PMMA matrix such as methylene blue and methyl red [12], Al_2O_3 [13], $MnCl_2$ [14].

In this paper we repot the effect of copper sulphate as a doping agent on the dispersion parameters of PMMA in order to use in the optical devices.

Material and Methods:

Films of PMMA and copper sulphate ($CuSO_4$) as a filer agent on the matrix of PMMA with different weight concentration have been prepared by the dispersed polymer dissolve 100 ml chloroform. Different polymer solution (volumetric solution) was casted as a layer, dried at room temperature for 24 hours.

layer thickness were measured using (indicating micrometer 0.25 μm) with an error not exceeding ± 5%, all the layer found to be in the rang of 20 ± 1 μm, these layers were clear, transparent, free from any noticeable defect and showing light bluish color.

The absorbance and transmittance spectra were recorded in the wavelength range (300-900) nm, using double beam SCHIMADZU UV/VIS-

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$160\,\mathring{A}$, all measurements were carried out at room temperature.

Results and discussions

The nature of the optical transition could be determined using the following procedure.

The absorption coefficient (α) was calculated from the transmittance spectra using the relation [15]:

$$\alpha = \frac{\ln(1/T)}{d} \qquad \text{------------- (1)}$$

Where (T) is the transmittance and (d) is the film thickness, the optical absorption dependence of the photon energy is expressed using the relation [16]:

$$\alpha h\nu = A(h\upsilon - E_g)^m \qquad \text{-------- (2)}$$

Where (A) is a constant, E_g is the optical band gap and (m) is a constant which determines the type of optical transition, m= 1/2 and 3/2 for direct allowed and forbidden transition, m=2 and 3 for indirect allowed and forbidden transition respectively.

The type of transition could be obtained by finding the value of m, equation (2) can be written as:

$$\ln(\alpha) = \ln(A) - \ln(h\upsilon) - m\ln(h\upsilon - E_g) \qquad \text{--- (3)}$$

If E_g = 3.7 eV [17], the value of m can be determined from the slope of ln ($\alpha h\upsilon$) versus ln($h\upsilon$ - E_g) Fig. (1) the value of m found to be about 1/2 for all the samples under investigation, which indicate a direct electronic transition.

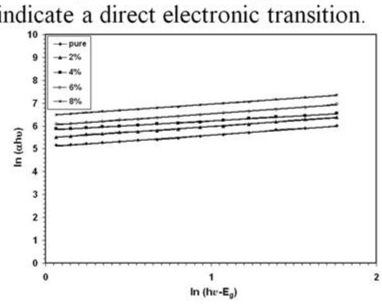

Fig. (1) ln($\alpha h\upsilon$) as a function ln($h\upsilon$-E_g).

The width of the localized states available in the optical band gap affects the optical band gap structure and optical transitions and it is called as Urbach tail, which could be determined by the following relation [18]:

$$\alpha = \alpha_o \exp\left(\frac{E}{E_U}\right) \qquad \text{------------- (4)}$$

Where E is the photon energy, (α_o) is constant and E_U is the Urbach energy which refers the width of the exponential absorption edge.

Fig. (2) shows the variation of ln(α) versus photo energy for PMMA and copper sulphate doped PMMA with different concentration, the value of E_U were calculated from the slope and the obtained value are given in Table (1), which indicates that Urbach energy values increase with the increasing of copper sulfate content. This increase leads to a redistribution of stated from band to tail, thus allows for a greater number of possible band to tail and tail transitions [19].

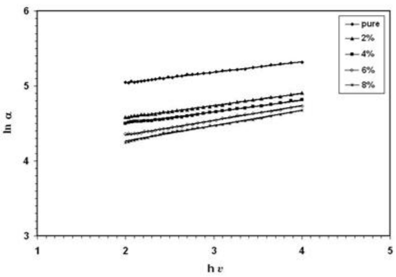

Fig. (2) ln α as a function of h υ .

Table (1) the optical parameters of PMMA and copper sulfate doped PMMA.

Sample	E_U (meV)	E_g (eV)	E_o (eV)	E_d (eV)	n(o)	ε_∞	λ_o nm	S_o x10^{13} m^{-2}	M_{-1}	M_{-3}
Pure PMMA	141	3.36	6.720	16.4	1.85	3.42	187.81	6.75	2.44	0.054
2%Copper sulfate doped PMMA	156	3.32	6.630	17.0	1.88	3.53	184.62	7.67	2.56	0.058
4%	161	3.30	6.612	17.4	1.90	3.61	193.60	7.72	2.36	0.060
6%	195	3.16	6.320	19.0	2.00	4.00	198.76	8.60	3.00	0.075
8%	204	2.89	5.770	20.6	2.14	4.58	214.27	9.9	3.57	0.110

The dispersion in refractive index can be filled the single oscillator model proposed by Wimple and Didomenico, the spectral dependence of refractive index (n) according to this model is then defined by the equation [20]:

$$n^2 - 1 = \frac{E_o E_d}{E_o^2 - (h\upsilon)^2} \qquad \text{---- (5)}$$

Where E_o is the single oscillator energy parameter and E_d is the dispersion energy which is a measure of the strength of the interband transitions.

A plot of $(n^2-1)^{-1}$ versus $h^2\nu^2$ would be linear and give the values of E_o and E_d from the slope $(1/E_oE_d)$ and the intercept of y-axis (E_o/E_d). typical curves for PMMA and copper sulphate doped PMMA are plotted in Fig. (3). The static refractive index n(o) may be evaluated from equation (5)(i.e $n^2=(1+E_d/E_o)$ and then value of static dielectric constant $\varepsilon_\infty = n^2(0)$ was calculated. The oscillator energy E_o is an average energy gap and be related to optical band gap, E_g in close approximate $E_o \approx 2E_g$ [21], the obtained values of E_o, E_d, E_g, n(o), ε_∞ is listed on Table (1).

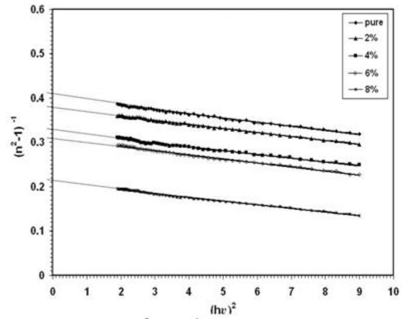

Fig. (3) $(n^2 -1)^{-1}$ as a function of $(h\upsilon)^2$.

It can be seen that the optical band gap values change inversely with E_U values. The dispersion data of refractive index was also fitted by the following relation [22]:

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1 - (\lambda_o / \lambda)^2} \qquad \text{--------- (5)}$$

Where λ is the wavelength of the incident light, So is the average oscillator strength and λ_o is an average oscillator wavelength, the S_o and λ_o values were obtained from the Fig. (4) the S_o^{-1} can be obtained from the slope while $(S_o\lambda_o)^{-1}$ could be obtained from the intercept of y-axis , the values λ_o and S_o were tabulated in table (1).

The interband transition strength could be provided from M_{-1} and M_{-3} moments of the optical spectrum which were expresses as [19]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \qquad \text{------------- (6)}$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad \text{------------- (7)}$$

The obtained values were given in table which shows that M_{-1} and M_{-3} moments change with copper sulfate concentration.

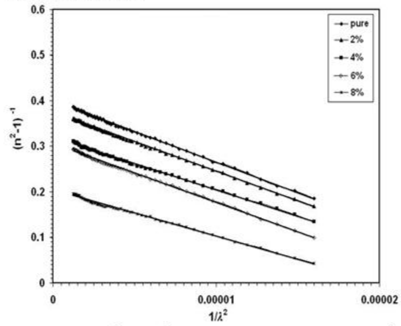

Fig. (4) $(n^2 -1)^{-1}$ as a function of $(1/\lambda^2)$.

Conclusions

The inclusion of dopants into films, expands the width localized state, as the dopant increases the width of the localized state increase.

The refractive index dispersion curves obey the single oscillator model, the dispersion parameters were determined; these parameters were affected by copper sulfate concentration by decreasing E_g, E_o and increasing E_U, E_d, n(o), ε_∞, λ_o, S_o, M_{-3}

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معلمات التفريق للبولي مثيل ميثاكريلات المشوب بكبريتات النحاس

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الخلاصة

حضرت أغشية PMMA و PMMA المشوب بكبريتات النحاس ($CuSO_4$) بطريقة الصب.
سجل طيفي النفاذية والامتصاصية لمدى الطول الموجي nm (300-900). وذلك لغرض حساب طاقة المتذبذب المفردة، طاقة التفريق، معدل قوة المتذبذب، ومعامل الانكسار عند الطول الموجي (مالانهاية) وكذلك العزوم M_{-1} و M_{-3} .لقد وجد بان كافة المعلمات قد تاثرت بالتشويب.