Determination the dispersion parameters and urbach tail of iron chromate doped PMMA films

Sami Salman Chiad [1], Nadir Fadhil Habubi [1], Muhammad Hameed Abdul-Allah [2]

[1] Physics Department, College of Education, Al_Mustasiriyah University

[2]Physics Department, College of Science, Diyala University

E-mails samichiad2003@yahoo.com, nadirfadhil@yahoo.com

Abstract

Films of pure Poly (methyl methacrylate) PMMA and Iron chromate doped PMMA have been prepared using casting method. Transmission and absorptance spectra have been recorded in the wavelength range (300-900) nm, in order to calculate, single oscillator energy, dispersion energy proposed by Wemple - DiDomenico model, average oscillator strength, average oscillator wavelength. The refractive index data at infinite wavelength which was found to obey single oscillator model which was found to increase from 2.27-2.56 as the doping percentage increase. The decreasing in the optical energy gap which was found according to Tauc model were (3.74-3.63) eV , is in good agreement with that obtained by wimple-DiDomenico model. The inverse behavior compared with the value of the energy gap were obtained for Urbach energies by increasing from (266-308) meV upon doping.

Key words
PMMA,
Optical Properties,
Casting Method,
Doping Effect.

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تحديد معلمات التفريق وذيل اورباخ لاغشية بولي مثيل ميثا اكريلات المشوبة بكرومات الحديد

سامي سلمان جياد[1] ، نادر فاضل حبوبي[1] ، محمد حميد عبدالله[2]

[1] قسم الفيزياء ، كلية التربية، الجامعة المستنصرية

[2] قسم الفيزياء، كلية العلوم، جامعة ديالى

الخلاصة

حضرت اغشية من البولي مثيل ميثا اكيلات النقي والمشوب بكرومات الحديد بطريقة الصب. سجل طيفي النفاذية والامتصاصية في مدى الاطوال الموجية (300-900) nm لغرض حساب طاقة المتذبذب المفردة ، طاقة التفريق المقترحة من قبل انموذج Wemple – DiDomenico ، متوسط القوة للمتذبذب .
لقد وجد بان بيانات معامل الانكسار للطول الموجي اللانهائي تخضع لانموذج المتذبذب المفرد والتي وجد بان قيمها تزداد من 2.27 الى 2.56 بازدياد نسبة التشويب . تبين ان النقصان الحاصل في فجوة الطاقة (3.63-3.74) eV وفقا لانموذج Tauc ، قد اتفقت مع النتائج المستحصلة من انموذج Wemple – DiDomenico. تم الحصول على سلوك معاكس لتغير قييم فجوة الطاقة عند حساب طاقة اورباخ والتي ازدادت نتيجة التشويب (308-266) meV .

Introduction

Poly (methyl methacrylate) PMMA has received a considerable attention in recent years owing to its low cost, good tensile strength, and hardness, high rigidity, transparency, low optical loss in the visible spectrum, low glass temperature, good insulation properties and thermal stability dependent on tactility [1-5], it can be considered as a good host for inorganic nanoparticle due to their high surface to bulk ratio which can significantly affect the properties of PMMA matrix [6]. As a result of the above properties, PMMA has been extensively used in various industrial sectors such as, PMMA is frequently used as a substrate material for precision optics components [7], in memory materials [8], gas sensing [9], and PMMA can be tailored chemically to fit wide range of photonics and optoelectronics applications [10], liquid crystal display[11].

In this work an attempt was done to graft iron chromate molecules into PMMA matrix, the same guest molecule may be covalently bonded to the polymer chain and the other ones are only embedded into polymeric matrix, in order to determine optical constants such as refractive index and optical energy gap which consider to be the fundamental parameters of an optical material due to their relation with electronic properties of material.

Experimental Details

Poly (methyl methacrylate) from (sigma Aldrich GMBH Germany) was dissolved in chloroform solution of 99.8% purity, iron chromate eas also dissolved in chloroform.

The solution of iron chromate was added to the dissolved polymer with a suitable volumetric concentration (2%, 4%, 6%). The mixture was cast on a glass dishes and kept in dry atmosphere at 313 K for 24 hours to ensure removal of solvent traces.

The films thickness were measured with the help of thickness gauge (indicating micrometer) and was found to be in the range of 20 ± 1 μm.

The absorbance and transmittance spectra were recorded utilizing double beam UV/VIS-160 a SCHIMADZU (Japan) in wavelength range (300-900) nm, all the measurements were carried out at room temperature.

Results and discussions

The analysis of determined of absorption coefficient (α) on photon energy in the high absorption region is carried out to obtain the detailed information about the energy band gaps.

The optical energy gap of the films is determined by the following relation[12]:

$$\alpha h\nu = B(h\upsilon - E_g^{opt})^m ----(1)$$

where (B) is an energy independent constant, E_g^{opt} is the optical band gap and (m) is an index that characterizes the optical absorption process (m = ½, 3/2, 2,3) depending on the kind of transition . Since PMMA films are direct transition type, the optical energy gap can be estimated by plotting $(\alpha h\upsilon)^2$ versus hυ (hυ is the photon energy), then extrapolating the straight line part of the plot to the photon energy axis Figures (1), (2) and (3) show the variation of the optical energy gap for pure and iron chromate doped PMMA with different amount of iron chromate content. As the iron chromate increased from (0 to 6%), we obtained optical energy gap of 3.74, 3.69, 3.63 eV, respectively. The reduction in the optical band gap might be due to cross – linking [13].

The width of the localized states available in the optical band gap of the as deposited films affects the optical band gap structure and optical transitions and is called the Urbach tail, which is related directly to a similar exponential tail for the density of states. The Urbach tail of the films can be determined from the following relation [14]:

$$\alpha = \alpha_o \exp\left(\frac{h\upsilon}{E_U}\right) ------(2)$$

where (α_o) is constant, (hυ) is the photon energy, and E_U is the Urbach energy which corresponds to the width of the band tail and can be evaluated as the width of the localized state.

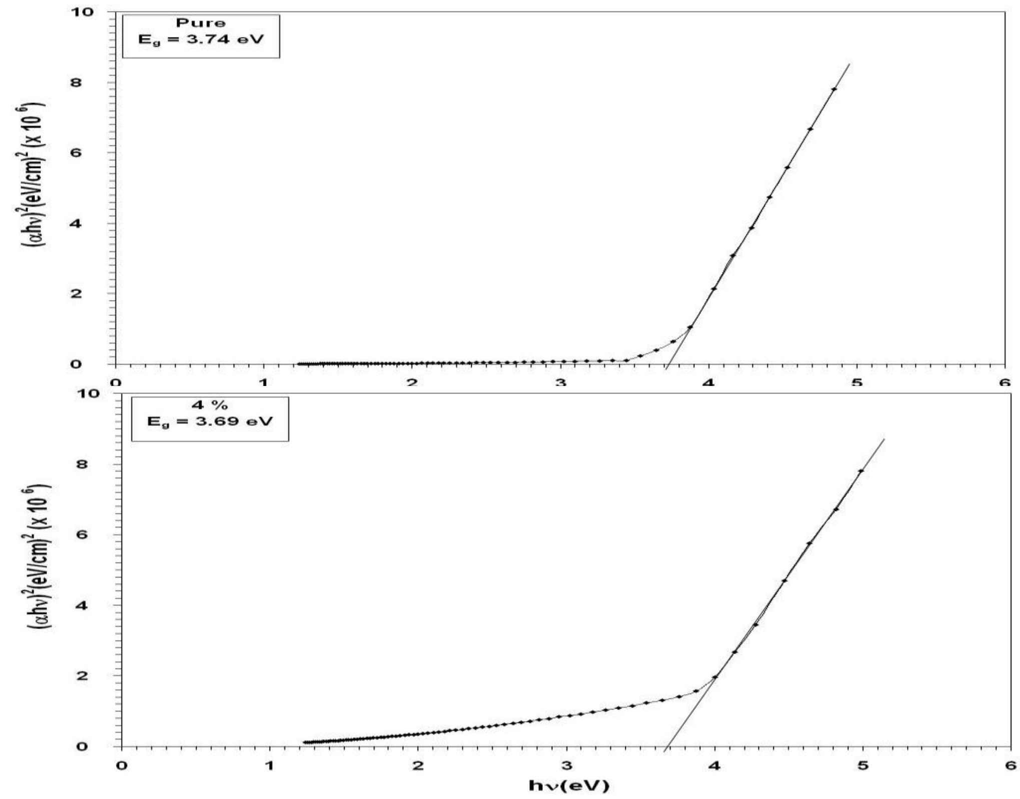

Fig. (2) (αhv)2 versus photon energy for Iron chromate doped PMMA thin films.

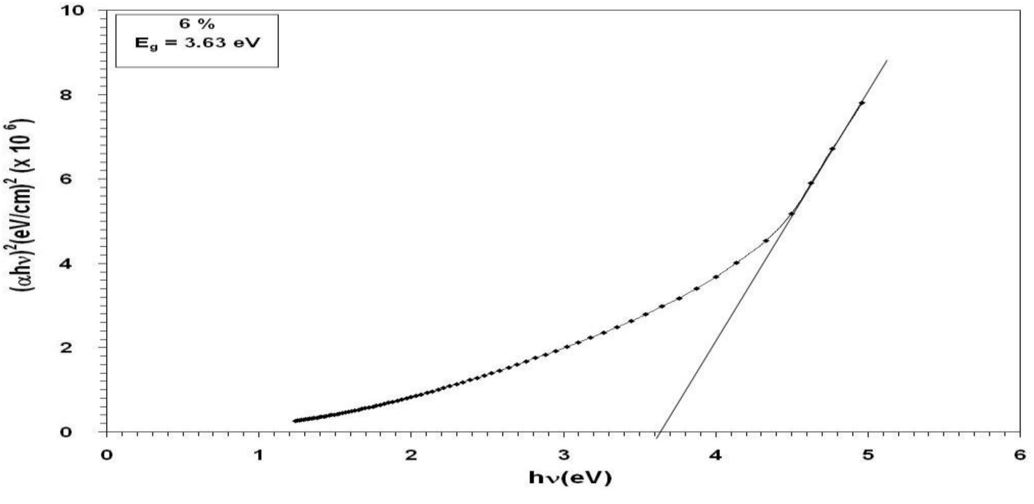

Fig. (3) (αhv)2 versus photon energy for Iron chromate doped PMMA thin films.

Thus the plot of ln (α) versus photon energy should be linear. Urbach energy can be obtained from the inverse of the slope of Fig. (4).

The obtained E_U value are shown in Table (1) Urbach energy values of the films increase with increasing Iron chromate content the decrease in E_g^{opt} is attributed to the increase of disorder of the PMMA occurred by doping [15].

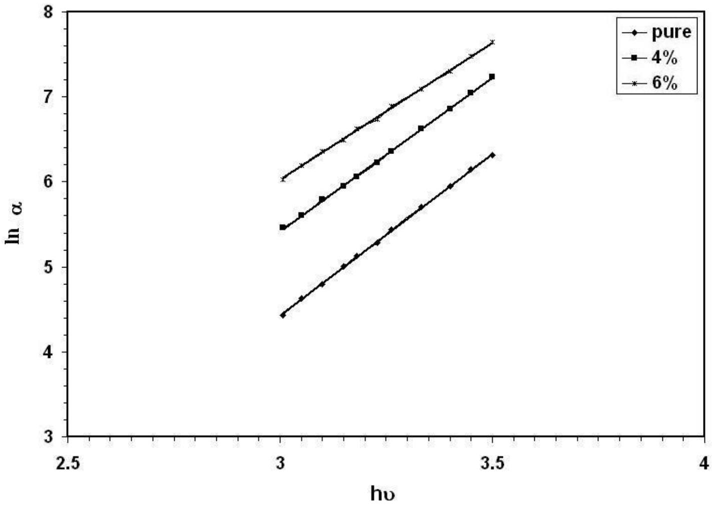

Fig. (4) ln α as a function of h υ.

Table (1): The optical parameters of Iron Chromate doped PMMA.

Sample	E_g^{opt} **(eV)**	**E$_U$ (meV)**	**E$_o$ (eV)**	**E$_d$ (eV)**	**E$_g$ (eV)**	ε_∞	**n(o)**	**λ$_o$ nm**	**S$_o$ x10^{13} m^{-2}**
Pure PMMA	3.74	266	7.745	32	3.87	5.16	2.27	218	11.30
Iron Chromate doped PMMA 4%	3.69	277	7.302	30	3.57	5.34	2.31	214	10.65
Iron Chromate doped PMMA 6%	3.63	309	7.070	38	3.53	6.53	2.56	211	9.30

The data of the dispersion of the refractive index (n) were evaluated according to the single oscillator model proposed by wimple and DiDomenico.

They found that all the data could be described, to an excellent approximation, by the following formula [16]:

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\upsilon)^2} \quad ----(3)$$

where E$_o$ is the oscillator energy and E$_d$ is the oscillator strength or dispersion energy.

Plotting of $(n^2\text{-}1)^{-1}$ against $(h\nu)^2$ as shown in Fig. (5) allows us to determine, the oscillator parameters, by fitting a linear function to the smaller energy data, E$_o$ and E$_d$ can be determined from the intercept, (E$_o$/E$_d$) and the slope (1/E$_o$E$_d$) the dependence of single effective oscillator parameters on iron chromate is shown in Table (1), E$_o$ is considered as an average energy gap to good approximation, it varies in proportion to the Tauc gap E_g^{opt}, that this to say $E_o \approx 2E_g^{opt}$. by comparison with the value of the optical energy gap as been tabulated in Table (1). It seems to be in good agreement with the data obtained from E$_o$. The static refractive index n(o) is evaluated from equation (3) I . e $n^2(o) = 1 + E_o/E_d$, and the value of static constant $\varepsilon_\alpha = n^2$ (o), their values are tabulated in Table (1).

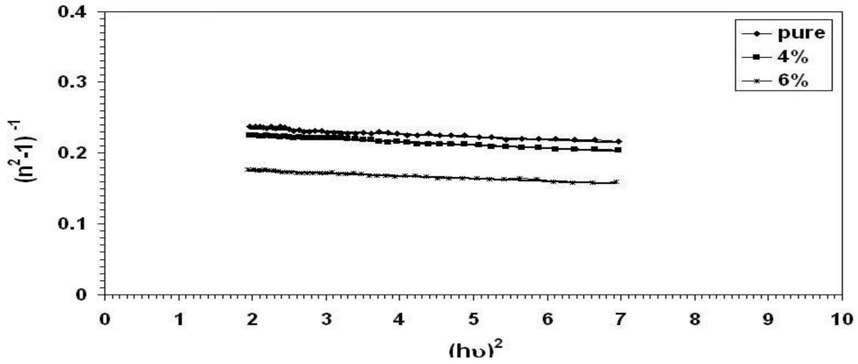

Fig. (5) $(n^2-1)^{-1}$ as a function of $(h\upsilon)^2$ for the prepared samples

The oscillator model can be also written as [17]:

$$n^2-1=\frac{S_0\lambda_0^2}{1-(\frac{\lambda_0}{\lambda})^2}--------(4)$$

where λis the wavelength of the incident light, S_o is the average oscillator strength and λ_o is an average oscillator wavelength.

In order to analyze the above formula for the present case, the curves of $(n^2-1)^{-1}$ against $(1/\lambda^2)$ are plotted in Fig.(6) and the data are fitted into straight lines indicating the sell Meier's dispersion formula is applicable to the film which were obtained in the present work. The value of S_o and (λ_o) could are estimated from the slope $(1/S_o)$ and the infinite wavelength intercept $(1/S_o\lambda_o^2)$, the calculated parameters are summarized in Table (1) indicating S_o and λ_o decrease by increase of iron chromate.

Conclusions

Organic films of PMMA and iron chromate doped PMMA were prepared by casting method. The optical band gap is appropriately fitted to the direct transition model proposed by Tauc.

The results indicate that E_g^{opt} decrease with the increase, the amount of iron chromate ε_∞ and $n(o)$ increase by iron chromate doping while E_o, E_U, S_o and λ_0, decrease as the iron chromate percentage increase.

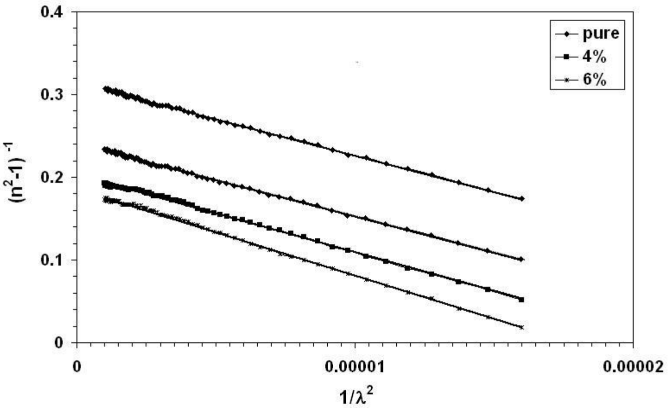

Fig. (6) $(n^2-1)^{-1}$ as a function of $(1/\lambda^2)$ for the prepared samples

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