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Optical energy gap and optical constants of poly (Methyl methacrylate) films doped with $ZnCl_2$

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Abstract
In the present work, we have studied the effect of $ZnCl_2$ dopant on the optical properties of (polymethyl methacrylate) (PMMA) polymer. Pure and $ZnCl_2$ doped PMMA films were prepared using solvent casting method. Optical energy band gap E_g was estimated by using UV-VI-NIR spectra and it was classified as an indirect allowed transition. In general, E_g was found to decrease with the increasing of dopant concentration. The refractive indices of the samples were measured and it was found to increase with the increasing of dopant concentration. Optical transmittance, reflectance and extinction coefficient were also investigated and correlated with the action of doping process.

Keywords: PMMA, Energy gap, optical transmittance, extinction coefficient

1. Introduction
PMMA is a transparent polymeric material that possesses many desirable properties such as light weight, light transmittance, chemical resistance, uncolored, resistance to weathering corrosion and good insulating properties (Yuichi *et al.*, 1997). Figure 1 below shows the structure of PMMA.

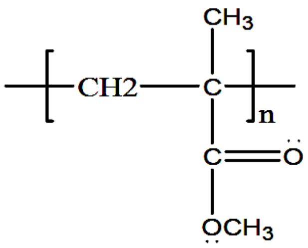

Fig 1: The Structure of PMMA

PMMA is vinyl polymer and is prepared by free radical vinyl polymerization from its monomer methyl methacrylate. PMMA has an amorphous morphology and its Tg is 1200C. It has polar functional group in its polymer chain that exhibit high affinity for lithium ion. It has oxygen atom which contain lone pair electron that is expected to form coordinate bond with the lithium ion from the doping salts [1].

PMMA as a polymeric waveguide has attracted much attention for use as optical components and in optoelectronics devices due to their low cost and volume productivity. Recently, some researchers reported optical components such as an optical switch, a coupler, a splitter and a transceiver [2]. Polymeric composites of PMMA are known, for its importance in technical applications [3]. Studies of doping transition metal halides (TMH) into PMMA are important for determining and controlling the operational characteristic of the different PMMA composites. The addition of TMH to the PMMA network will cause a remarkable change in their properties [4]. Different properties of PMMA have been studied after doping by various dopants. The study of physical properties of polymers, optical absorption spectrum is one of the most important tool for understanding band structure and electronic properties of pure and doped polymers [5].

The aim of this work is to produce PMMA/$ZnCl_2$ thin films by means of solvent casting method at different concentration of $ZnCl_2$ and to investigate some optical parameters.

2. Experimental Procedure
A high purity PMMA with molecular weight (300000 g/mol) from BDH was used as a host polymeric material in this research. Acetone of purity (99.98 %), Ethanol and ($ZnCl_2$ from BDH) were used as a solvents and dopant respectively. PMMA grains of weight (2 g) were dissolved in (10 ml) Acetone, the mixture was then shaken well by stirring for about (30 min), in order to obtain homogenous solution, (10 ml) of the prepared solution was transferred into a clean glass Petri dish with (6 cm) diameter and dried for at least (2 days), and then left to cool slowly at a room temperature. The dried films were then removed easily by using tweezers clamp. Other similar films were casted in order to ensure dried samples without bubbles and thermal damage. The measured thickness of the prepared films was about (0.5 mm) found by using a digital micrometer.

Doped films were fabricated by dissolving at a room temperature in Ethanol of Concentration (4 %) than mixed with PMMA solution. Absorptance and transmittance measurements were carried out by using a double beam UV⁄VIS spectrometer (Shimadzu Japan) in the wavelength range (190-900) nm.

3. Results and Discussion
Fig.2, shows the optical transmission (T%) and reflection (R%) of pure and $ZnCl_2$ doped PMMA films. The reflectance R can calculate from the relationship that correlating the absorptance A, Reflectance R and the Transmittance (T) as below: -

$$R=1-A-T \tag{1}$$

From Fig.2, it is clear the transmission of the PMMA films decreases with dopaing, while the reflection of the films increases with doping. The optical absorption coefficient (α) of PMMA is very important because it provides information on the electronic band structure, the band tail and energy gap. The absorption coefficient (α) can be determined as a function of frequency using the formula [6, 7]:

$$\alpha = \frac{2.303\,A}{d} \qquad (2)$$

Where:
d = the film thickness, A = absorbance.

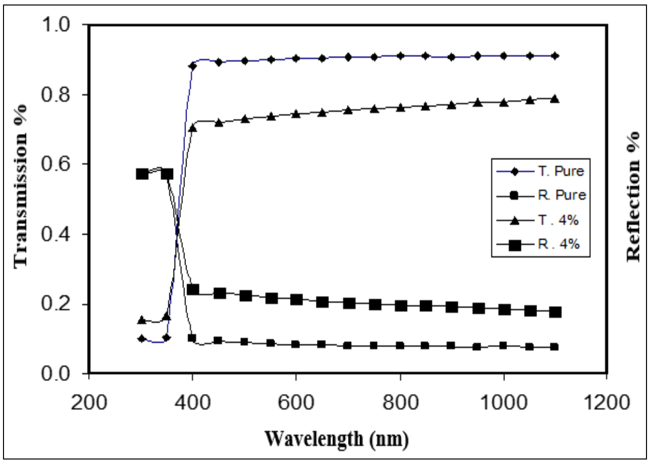

Fig 2: Transmission (%) and Reflection (%) of Pure PMMA, 8 wt% $CuSO_4$ doped PMMA

The absorption coefficient is connected with the nature of electronic transitions. Type of the electron transitions can be known by dependence on the values of the absorption coefficient; if the values of ($\alpha > 10^4$ cm^{-1}), this means the direct transitions takes place in material, while indirect transitions occur for ($\alpha < 10^4$ cm^{-1}) [8]. The optical absorption spectra could reveal the energy gap E_g between the Conduction Band (CB) and the Valence Band (VB) due to direct and indirect transitions of both crystalline and amorphous materials. The results show the value of (α) for pure and 4 wt% $ZnCl_2$ doped PMMA films is less than (10^4 cm^{-1}). In order to confirm the nature of optical transition the optical data was analyzed using the relation:

$$\alpha h\nu = B(h\nu - E_g)^m \qquad (3)$$

Where:
h = Planck constant.
E_g= Optical energy band gap.
B = A constant known as the disorder parameter which is nearly independent of the photon energy. Parameter (m) is the power coefficient with the value that is determined by the type of possible electronic transitions, i.e., m = 1/2, 3/2, 2or 1/3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden respectively [6]. The plot of the product of absorption coefficient and photon energy $(\alpha h\nu)^{1/2}$ versus the photon energy at room temperature shows in Fig. (3). Extrapolation of the linear portion of this curve to a point $(\alpha h\nu)^{1/2}$ =0, gives the optical energy band gap (E_g) for the pure as well as doped PMMA films.

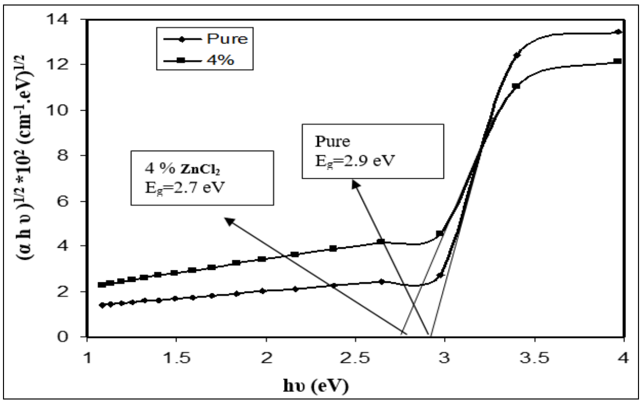

Fig 3: The variation of $(\alpha h\nu)^{1/2}$ with hν for pure films and 4 %wt $ZnCl_2$ doped PMMA.

The extinction coefficient can be calculated by the relation [9]:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (4)$$

Where (λ) is the wavelength, (α) is the absorption coefficient.
The refractive index (n) of the film was calculated by the following equation [10]:

$$n = \left[\left(\frac{1+R}{1-R}\right)^2 - \left(k^2+1\right)\right]^{1/2} + \frac{1+R}{1-R} \qquad (5)$$

Where k is the extinction coefficient and R is the reflectance.
The evaluation of refractive index of an optical material is important for many applications especially in optical devices. Fig.4 and 5 shows the variation of refractive index n and extinction coefficient k with wavelength.
We can see from this figure that the values of n and k in general increased with doping.
All the change in optical parameters of PMMA after doping can attribute to the effect of $ZnCl_2$ doped on the structure of PMMA, which creates a localized energy states in the forbidden band gap acts as a tail to the conduction band which reduced the energy gap.

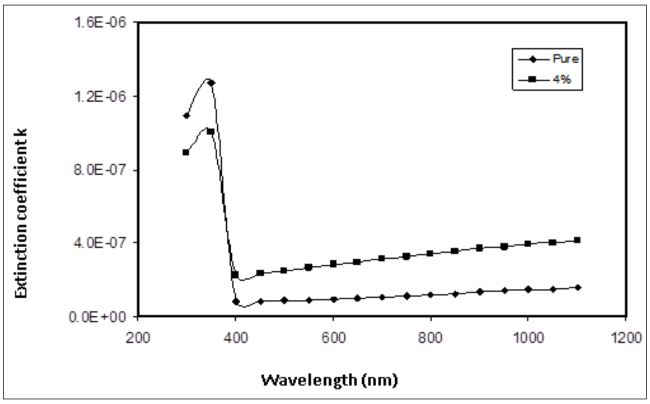

Fig 4: The variation of k with Wavelength of pure and 4% $ZnCl_2$ doped PMMA films.

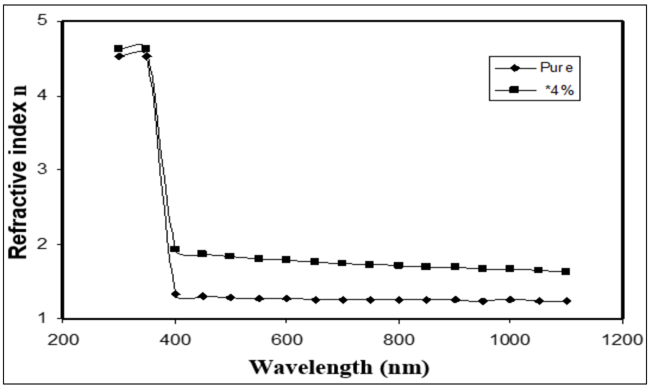

Fig 5: The variation of n with Wavelength of pure and 4% $ZnCl_2$ doped PMMA films.

4. Conclusions

From the present work, the followings can be concluded: -

1. The doping process decreases the transmission, while the reflection increases with doping.
2. The type of electronic transition was found to be an indirect allowed transition.
3. Optical energy band gap decreases with doping.
4. Refractive index and extinction coefficient increases with doping.

5. References

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