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Effect of doping on energy gap of PMMA/ Cr_2O_3 blend Films

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Abstract
PMMA and PMMA doped with Cr_2O_3 films with different concentration (1%, 3%, 5%), were prepared using the casting technique in order to study the effect of doping on energy gap of films. The optical properties of all films were investigated using spectrophotometric measurements of absorbance and transmittance in the wavelength range (250-800) nm, FTIR was carried out of (PMMA and PMMA/Cr_2O_3), with range 400-4000 cm^{-1}. The absorption coefficient (α) was increase with doping of Cr_2O_3.The energy gap of indirect transition were found for all films and the energy gap (Eg) of pure about (4.8eVand 4.6eV)and the magnitude of energy gap of doped films were found to be increased with increasing the concentration of Cr_2O_3.

Keywords: PMMA, thin film, energy gap, Cr2O3

1. Introduction

Films of poly methyl methacrylate (PMMA) as a polymeric waveguide has steadily gained attention for use in optical components and in optoelectronic devices. Newly, some researchers have reported optical components like an optical switch, a coupler, a splitter and a transceiver. Polymeric composites of PMMA are quite popular because of their low cost, volume productivity, high strength to weight ratio, noncorrosive properties and easy fabrication techniques. They are known for their importance in technical applications [1].

Polymeric materials make up the most important type of organic substances, technically and economically. The customary plastics, fibers, elastomers and biological materials that surround us attest to this importance. Such materials, which are consisted of large many identical groups or repeating units, are known as (high polymers). Polymers composed of more than one kind of repeating units are termed copolymers [2]. PMMA is an amorphous thermoplastic; it is produced by the addition polymerization of methyl methacrylate. The polymer has quite good optical properties. It has good dimensional stability because of rigid polymer chains. It has good weather resistance, and is stable to acid and alkalis. It has the better transparency and optical properties of commercially obtainable thermoplastic. PMMA is a transparent plastic, i.e. transmits light about perfectly (92%), which make them favorable to serve as a channel for light [3]. PMMA has been broad used because of its physical and optical properties decisive about its wide applications. This is the thermoplastic substances with a very good tensile, strength, hardness, high rigidity, transparency, and good insulation properties and thermal stability dependent on toxicity [4, 5]. The PMMA now is commercially used in many optical application (lenses, LEDs, light sources covers and optical fibers) [6].

In last years, the doped polymers have been the topic of attention for both theoretical and experimental studies, due to the physical and chemical properties necessary for certain application can be obtained by adding or doping with some dopant. Several studies have indicated that optical properties of PMMA is influenced by using different dopants or by rising the doping concentrations [1, 7].

Chromium (III) oxide is the inorganic compound has the formula Cr2O3. It is one of essential oxides for chromium and is used as a pigment. It is created by the decomposition of chromium salts like chromium nitrate or by the exothermic decomposition of ammonium dichromate.

$$(NH4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4\,H_2O$$

The reaction has a low ignition temperature less than 200°C and is often used in "volcano" Demonstrations. due to its large stability, chromia is a usually used pigment and was originally called viridian. chromia is used in paints, inks, and glasses. It is the colourant in "chrome green" and "institutional green." Chromium(III) oxide is a precursor to the magnetic pigment chromium dioxide, depending to the following reaction [8, 9]:

$$Cr_2O_3 + 3CrO_3 \rightarrow 5CrO_2 + O_2 \qquad \text{……… (1)}$$

The aim of the this work is to prepare Poly-methyl Methacrylate (PMMA) doped with different concentrations of chrome oxide (Cr2O3) films by using a simple and low cost method. Moreover, investigate the effect of doping on the energy gap of films.

Table 1: Properties of Cr_2O_3 [10-12]

Chemical formula	Cr_2O_3
Molar mass	151.9904 g/mol
Appearance	light to dark green, fine crystals
Density	5.22 g/cm^3
Melting point	2,435 °C (4,415 °F; 2,708 K)
Boiling point	4,000 °C (7,230 °F; 4,270 K)
Solubility in water	Insoluble
Solubility in alcohol	insoluble in alcohol, acetone, acids
Refractive index (n_D)	2.551
Crystal structure	Hexagonal

2. Experimental Work

Casting method was used to prepare pure and doped Poly (Methyl Methacrylate) films by Cr_2O_3 at different concentrations (1%, 3%, %5). PMMA solution was prepared by dissolving PMMA in Chloroform ($ChCl_3$), the Cr_2O_3 used as a dopant. The solution was stirred, using a magnetic stirrer for (3h) until the polymer completely dissolved. The solution was poured into flat glass plate dishes. Homogeneous films were obtained after drying in air for 48 h at room temperature. The thicknesses of the produced films (88 +10) µm were measured using a digital micrometer.

The optical properties of the samples were Measured by using a double beam UV/VIS spectrometer Shimadzu Japan UV-160A in the wavelength range (250-900) nm. The characterization of pure PMMA and PMMA/Cr_2O_3, have been carried out using Shimadzu FTIR-8400S Fourier Transform infrared spectrophotometer with range 400–4000 cm^{-1}.

3. Results and Discussion

The absorption coefficient of (PMMA and PMMA:Cr_2O_3) films can be calculated from the equation [14].

$$\alpha = 2.303\ (A/\ t) \qquad \text{………. (3)}$$

Where, x is sample thickness. The absorption coefficient of (PMMA) films for pure and different concentration doped Cr_2O_3 are illustrated in Figure (1). From this figure the absorption coefficient of films it can be noted that absorption is relatively small at low energy. That's means the possibility of electron transition is low, due to the energy of the incident photon is not sufficient to move the electrons from the valence band to the conduction band ($h\upsilon<Eg$). At high energies, absorption is high, a great transitions consequently were occur, where the energy of incident photon is enough to move the electron from the valence band to conduction band, this means that the energy of the incident photon is greater than the forbidden energy gap [15]. This shows that the absorption coefficient assists in figuring out the nature of electron transition, when the values of the absorption coefficient is high ($\alpha>10^4$) cm^{-1} at high energies, it is expected that direct transition of electron occur, the energy and moment are maintained by the electrons and photons, on the other hand when the values of the absorption coefficient is low ($\alpha<10^4$)cm^{-1} at low energies, it is expected that indirect transition of electron occur, and the electronic momentum is maintained with the assistance of the phonon [16]. Among other results is that the coefficient of absorption for the films was less than 10^4 cm^{-1}, this explains that the electron transition is indirect. The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical band gap, Eg. The relation between the absorption coefficient, α, and the incident photon energy, hν, is Tauc's relation [17]:

$$(\alpha h\nu)^n = B(h\nu - Eg) \qquad \text{……………(2)}$$

where B is an constant depending on the transition probability and n is an index that characterizes the optical absorption process and is theoretically equal to 1/2,2, 1/3 or 2/3 for indirect allowed, direct allowed, indirect forbidden and direct forbidden transition, respectively. figure (2) for allowed indirect and forbidden indirect transition of pure (PMMA) and energy gap was (4.8eV) and (4.6eV) the creation of the site levels in forbidden indirect energy gap lead to facilitate the crossing of electron from the valence band to the local levels to conduction band. In other meaning, the electronic conduction depends on added impurities [15].

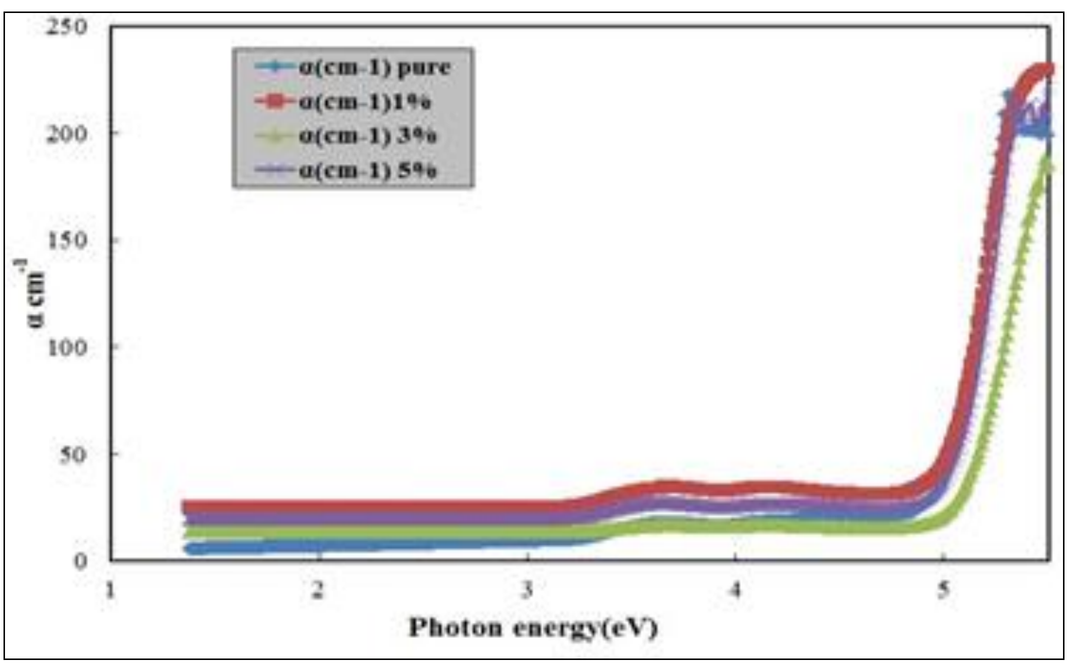

Fig 1: The absorption coefficient of (PMMA-Cr_2O_3) as a function of photon energy

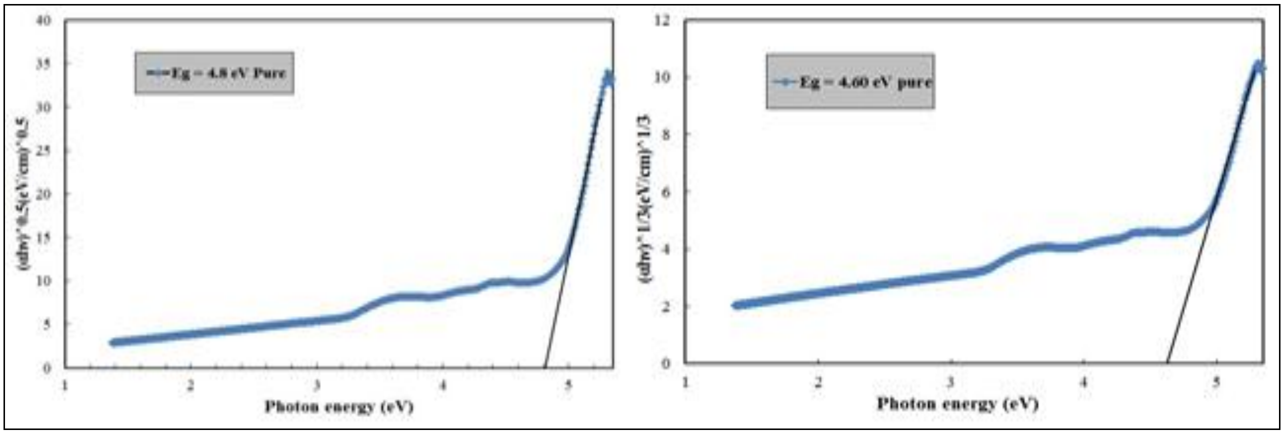

Fig 2: The relationship between [(αhυ) $^{1/2}$, (αhυ) $^{1/3}$] with photon energy of pure PMMA

Figure (3) illustrated the energy gap for different concentration of (PMMA:Cr_2O_3) the energy gap of doped films were more than pure films which attributed to the doping of Cr_2O_3 was executed shifting in absorption edge to the high energy or named (Burstein-Moss Shift) which is the near level from condition band were full with electrons then the electrons needs electrons to transition that seemed the energy gap was increased [18, 19].

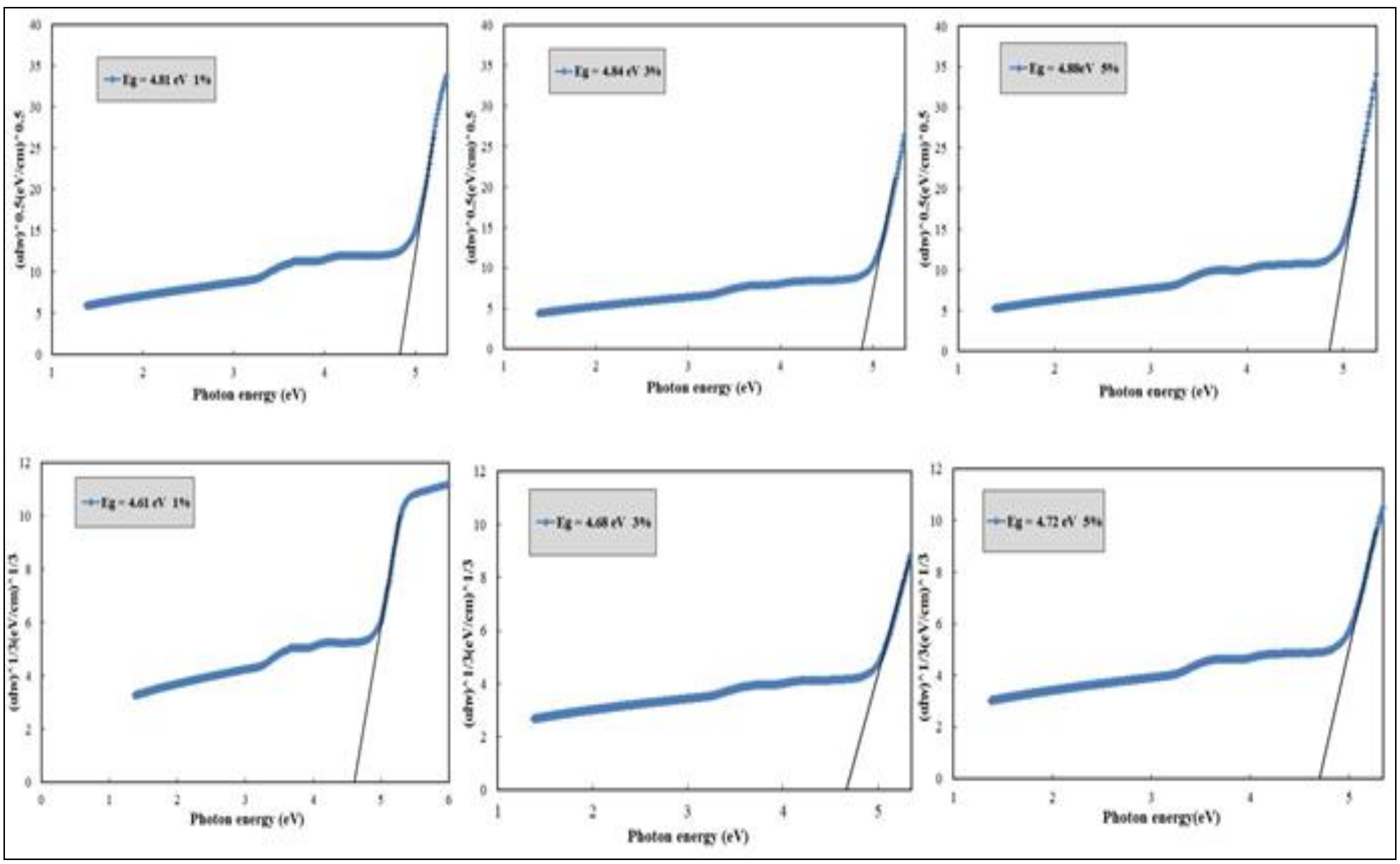

Fig 3: The relationship between [(αhυ) $^{1/2}$, (αhυ) $^{1/3}$] with photon energy of doped PMMA

The FTIR spectrum of PMMA in Figure (4a) which indicates the details of functional groups present in the PMMA. A intense peak appeared at 2999 and 2954 cm^{-1} due to the presence the CH stretching vibration. The peak ranging from 1737-1710 cm^{-1} can be refer to the C-O double bond stretching vibration. The peak ranging at 1433-1483 cm^{-1} is attributed to the presence of CH_3 and CH_2 deformation vibration. The peak ranging at 1134-1272 cm^{-1} and the paek at 966 cm^{-1} are assigned to C-O-C cm^{-1} single bond stretching vibrations [20, 21]. Figure (4b) shows the FTIR spectra of PMMA/Cr_2O_3 films. The new peak at 441may be refer to Cr_2O3.

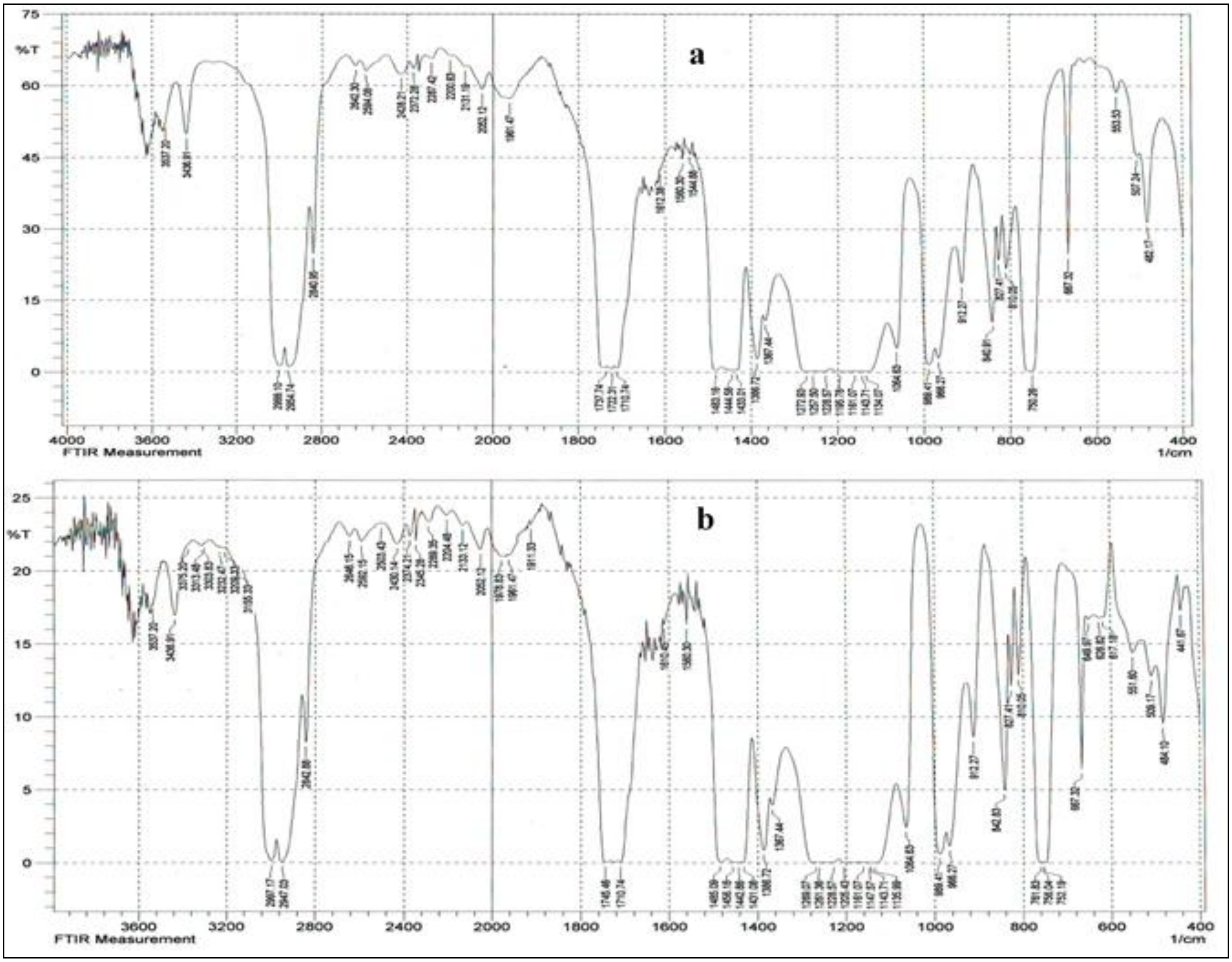

Fig 4: The FTIR spectra for a) pure PMMA and b) PMMA/Cr2O3 at 3% films

4. Conclusion

1. Pure PMMA and PMMA/ Cr_2O_3 with the different concentration have been prepared successfully by casting method.
2. The optical absorption coefficient (α) were calculated and were found to increase progressively after doping with increasing concentrations. The type of optical transition responsible for optical absorption was found to be indirect allowed transitions.
3. That there was an increase in the energy gap (Eg) as the doping concentration increased which indicate that there was shifting to the higher energy in the optical absorption edge.

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