

Optical properties of some metal complexes of poly(vinyl chloride)-2-mercapto-5-phenyl 1,3,4-oxadiazole

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Abstract: The present study focused on modification of the optical properties of Poly(vinyl chloride) (PVC) films 2-mercapto-5-phenyl 1,3,4-oxadiazole complexes, The polymers films were cast from THF solvent with the thickness of 30 micrometer. The optical data were analyzed and interpreted in term of electronic transition. According to energy gap data the conductivity of polymers.

Key words: Optical properties, metal complexes polyvinyl chloride, oxadiazole, mercapto-5-phenyl 1,3,4-oxadiazole.

Introduction

Optical properties of polymers constitute an important aspects in study of electronic transition and possibility of their application as optical filters, cover in solar collection, selection surfaces and green house⁽¹⁾.

The information about the electronic structure of crystalline and amorphous semiconductors has been mostly accumulated from the studies of optical properties in wide frequency range. The significance of amorphous semiconductors is in its energy gap⁽¹⁾.

The simplest definition of the optical gap is the minimum energy difference between lowest minimum of conduction band and the highest maximum of valance band⁽²⁾.

The main two types of optical transitions are direct and indirect transition, both involve the interaction of an electromagnetic wave with the electron in the valance band with may cross the forbidden gap to the conduction band⁽³⁾.

Indirect transition is possible only by phonon-assisted transition. The value and shape of the mobility gap in the amorphous semiconductors depend on the proportion conditions such as

substrate temperature, annealing temperature, degree of impurity and defect of the material. Any variation in such parameters lead to a shift in the absorption edge towards higher or lower energy⁽⁴⁾.

The absorption coefficient is defined by⁽⁵⁾. This can be determined from the normal incidence transmission through plane-parallel plate of thickness (d). Interference and multiple reflections are neglected. The reflectance (R) and transmittance (T) are related by equation (1):-

$$T = B(1 - R)^2 \exp(-\alpha d) \quad \dots\dots\dots (1)$$

Where B is a constant. This equation can be rewritten in equation (2):-

$$\alpha d = 2.303A + \ln[B(1-R)^2] \quad \dots\dots\dots (2)$$

A is the optical absorbance, (A = - log T).

The long wavelength tail of absorbance spectrum is attributed to background absorption which in turn refers to the term $\ln[B(1-R)^2]$ in equation (1). So the absorption coefficient $\alpha(\omega)$ in term of absorbance become :-

$$\alpha(\omega) = 2.303 \frac{A}{d} \quad \dots\dots\dots (3)$$

For direct band- to - band transition, the energy dependence of absorption coefficient is of the form:-

$$\alpha = \frac{\alpha_0 (h\nu - E_g)^r}{h\nu} \quad \dots\dots\dots (4)$$

Where (hν) is the photon energy and (E_g) is the energy gap, (r) is constant depending on the type of the electronic transition. It takes the value (1/2) for allowed direct transition and (3/2) for forbidden direct transition and the absorption coefficient ($\alpha \geq 10^4 \text{ cm}^{-1}$). The energy dependence absorption coefficient is of the form:-

$$\alpha = \frac{\alpha_0 (h\nu - E_g \pm E_p)^r}{h\nu} \quad \dots\dots\dots (5)$$

where (E_g) is the minimum energy gap, (E_p) is the phonon energy, (+) absorbed (-) Emitted, (r) take the value of 2 for allowed indirect transition and 3 for forbidden indirect transition, indirect transition occurs for ($\alpha < 10^4$).

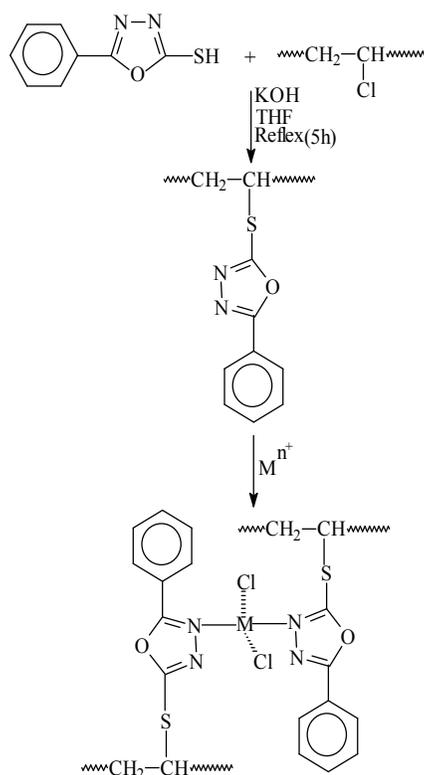
Polymers, in general, are transparent and colorless the existence of conductive additive

raising the transition wavelength into visible region and the optioned lighter structure is very useful in some specific advanced technology such as electrochromic displays [5]. Optical switching and rechargeable batteries⁽⁶⁾.

Experimental

Synthesis of PVC complex

Metal complexes of poly (vinyl chloride)-2-mercapto-5-phenyl 1,3,4-oxadiazole were prepared by method described by Aliwi et al(7). Scheme (1) shows reactions for the synthesis of PVC-L-MII polymer.



Where M = Ni, Cu, Zn and Sn

Scheme (1) Reaction for synthesis of PVC-L-MII.

Purification of Poly (vinyl chloride)⁽⁸⁾

Commercial Poly (vinyl chloride) (PVC) supplied from Pet Kim company (Turkey) was freed from additives by re-precipitation from tetrahydrofuran (THF) solution in ethanol. The purified polymer was dried under reduced pressure at room temperature for 24 hours.

Techniques

Films Preparation

A certain concentration of PVC and PVC-L-M^{II} solution (5 g/100ml) in tetrahydrofuran (THF) was used to prepare 30 micrometer thickness of polymer films, (measured by a micrometer type 2610 A, Germany) of the complexes prepared. The films were prepared by evaporation technique at room temperature for 24 hours. To remove the possible residual tetrahydrofuran solvent, film samples were further dried at room temperature for three hours under reduced pressure. The films were fixed on stand specially used for irradiation

which is made of aluminum plate (0.6 mm) in thickness supplied from (Q-panel) company USA.

The optical absorbances (A) of the sample were measured as a function of wavelength (λ) ranged from 200 to 900 nm by using Shimadzu Uv-vis 160A-Ultraviolet-spectrophotometer and all measurements were performed at room temperature.

Results and Discussion

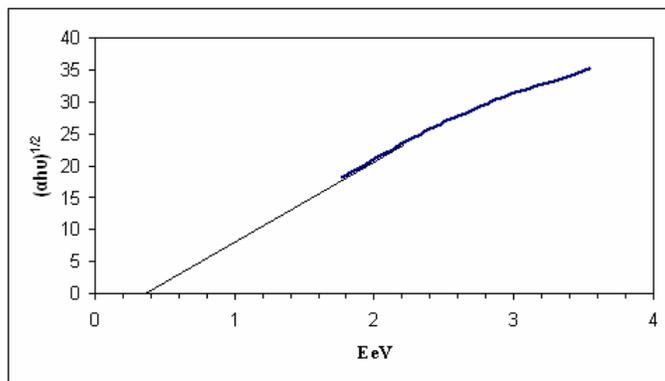
The relation between $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{2/3}$ versus photon energy for the doped and undoped PVC sample (Control) is shown in Figures (1 and 8) for allowed and forbidden transition. The difference in the values of energy gab (Table 1 and 2) could be attributed to the type of metal complexes⁽¹⁰⁾. The effect of the metal complexes addition on the values of activation energies is investigated and the result are shown in Table (1,2).

Table (1). Allowed indirect transition and assisting phonons energies

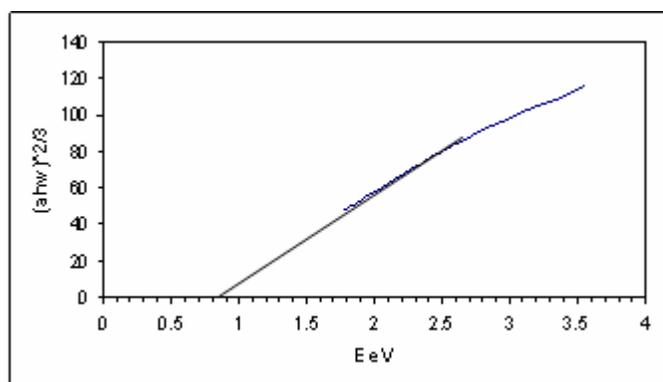
Samples	Eg (eV)
PVC-L-Ni	0.39
PVC-L-Cu	0.40
PVC-L-Zn	0.41
PVC-L-Sn	0.41
PVC	0.42

Table (2). Forbidden indirect transition and assisting phonons energies

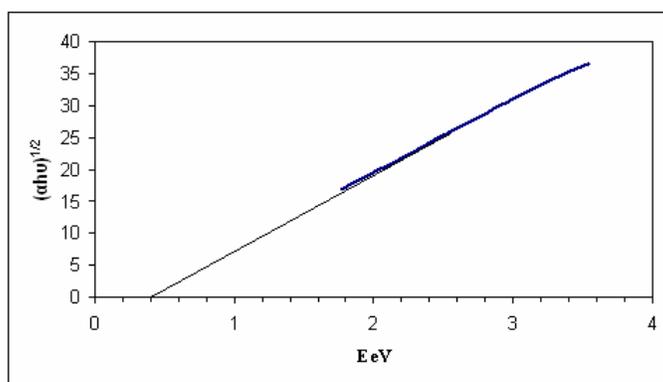
Samples	Eg (eV)
PVC-L-Ni	0.75
PVC-L-Cu	0.8
PVC-L-Zn	0.85
PVC-L-Sn	0.91
PVC	1.05



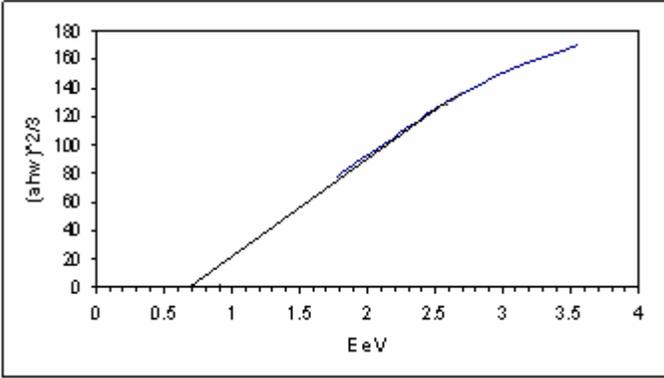
Figure(1) Allowed indirect transition $(\alpha h\nu)^{1/2}$ Vs. Energy for PVC-L-Ni^{II}



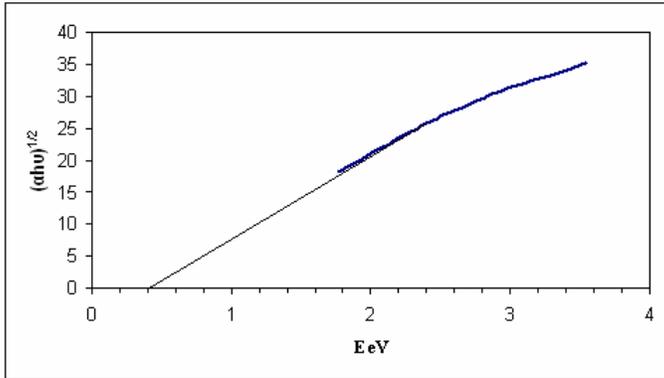
Figure(2) Forbidden indirect transition $(\alpha h\nu)^{2/3}$ Vs. Energy for PVC-L-Ni^{II}



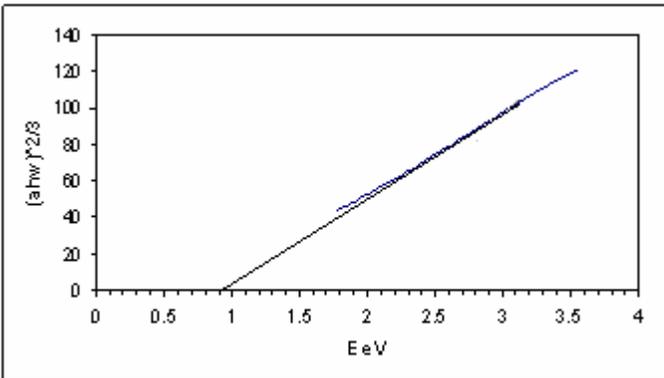
Figure(3) Allowed indirect transition $(\alpha h\nu)^{1/2}$ Vs. Energy for PVC-L-Cu^{II}



Figure(4) Forbidden indirect transition $(\alpha h\nu)^{2/3}$ Vs. Energy for PVC-L-Cu^{II}



Figure(5) Allowed indirect transition $(\alpha h\nu)^{1/2}$ Vs. Energy for PVC-L-Sn^{II}



Figure(6) Forbidden indirect transition $(\alpha h\nu)^{2/3}$ Vs. Energy for PVC-L-Sn^{II}

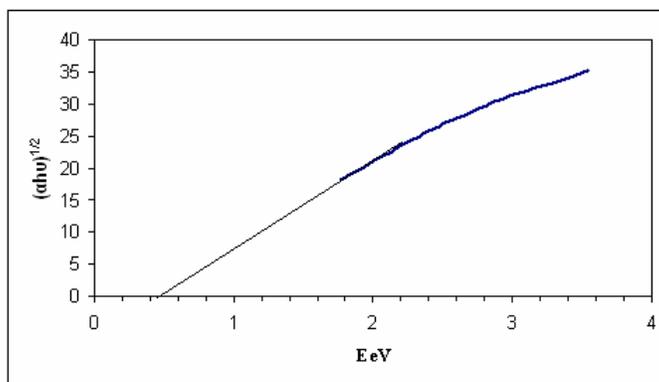
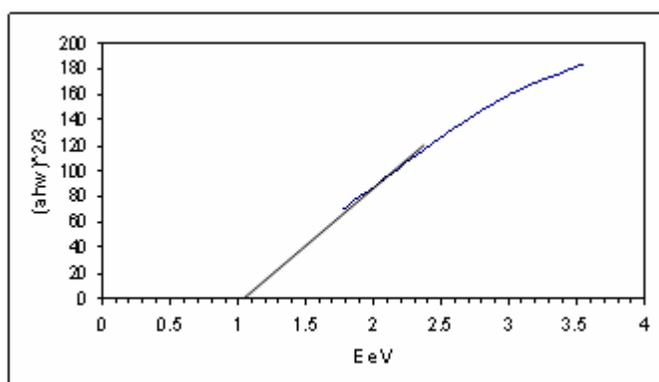


Figure (7) Allowed indirect transition $(\alpha h\nu)^{1/2}$ Vs. Energy for PVC



Figure(8) Forbidden indirect transition $(\alpha h\nu)^{2/3}$ Vs. Energy for PVC

Conductivity measurement ⁽¹¹⁾ of PVC with and without additive can obtained by adopting the data of energy gap, (see Table 1 and 2) and Figures from (1 to 8). The conductivity measurement for PS in the presence of additive increase in the following order:

PVC, PVC-L-Sn^{II}, PVC-L-Zn^{II}, PVC-L-Cu^{II} and PVC-L-Ni^{II}

The trend obtained might be attributed to the nature of the complexes and the electron configuration of the metal ion in the complexes⁽¹⁰⁾ as shown below:

$_{28}\text{Ni}^{2+}$	$[\text{Ar}]_{18}$	$3d^6$	$4s^2$
$_{29}\text{Cu}^{2+}$	$[\text{Ar}]_{18}$	$3d^7$	$4s^2$
$_{30}\text{Zn}^{2+}$	$[\text{Ar}]_{18}$	$3d^8$	$4s^2$

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