

## Effect of CuI concentration on structural and optical properties of PVA: CuI nanocomposites

Mustafa Al-Hamdany<sup>1</sup>, Mohamed Ghazi<sup>1</sup>, Mahdi Hasan Suhail<sup>2</sup>

<sup>1</sup>Department of Physics, College of Science, University of Al Anbar

<sup>2</sup>Department of Physics, College of Science, University of Baghdad

E-mail: mhsuhail@yahoo.com

### Abstract

The nanocomposite on the base of synthesis Copper iodide nanoparticles and polyvinyl alcohol (PVA/CuI) with different concentration of CuI were obtained using casting technique. PVA/CuI polymer composite samples have been prepared and subjected to characterizations using FTIR spectroscopy, The FTIR spectral analysis shows remarkable variation of the absorption peak positions with increasing CuI concentration. The obtained results by X-ray diffraction indicated the formation of cubic CuI particles. The effects of CuI concentrations on the optical properties of the PVA films were studied in the region of wavelength, (190-1100) nm. From the derivation of Tauc's relation it was found that the direct allowed transitions was more probable in PVA/ CuI nanocomposite. The results indicate that the obtained values of optical absorption edge, and energies band gap decreases from 4.05 to 3.89 eV for direct transitions with the increasing salt contents.

### Key words

Nanocomposite, CuI nanoparticle, optical band gaps, particle size, PVA.

### Article info.

Received: Mar. 2016

Accepted: Apr. 2016

Published: Sep. 2016

### تأثير التركيز على الخصائص التركيبية و البصرية للمركب (PVA: CuI)

مصطفى فواز الحمداني<sup>1</sup>، محمد غازي محمد<sup>1</sup>، مهدي حسن سهيل<sup>2</sup>

<sup>1</sup>قسم الفيزياء، كلية العلوم، جامعة الانبار

<sup>2</sup>قسم الفيزياء، كلية العلوم، جامعة بغداد

### الخلاصة

تم الحصول على مركب نانوي (متناهي في الصغر) على قاعدة نانوية من تركيب يوديد النحاس و البولي فينيل الكحول (PVA: CuI) مع تراكيز مختلفة من يوديد النحاس (CuI) باستخدام تقنية الصب. تم اعداد عينات من مركب البوليمر (PVA: CuI) و معرفة الاوصاف باستخدام FTIR الطيفي. ويظهر التحليل الطيفي FTIR التغير الملحوظ في مواقع قمم الامتصاص مع زيادة تركيز CuI. و اشارت النتائج التي تم الحصول عليها بواسطة حيود الاشعة السينية بتكوين جسيمات CuI مكعبة. تم دراسة تأثير تركيزات CuI على الخصائص البصرية لاجشية بولي فينيل الكحول (PVA) في المنطقة من الطول الموجي، (190-1100) nm. من اشتقاق علاقة Tauc و تبين ان الانتقالات المباشرة المسموحة كانت اكثر احتمالاً في المركب النانوي (متناهي في الصغر) (PVA: CuI). و تشير النتائج الى ان القيم التي تم الحصول عليها من حافة الامتصاص البصرية، و فجوة الطاقة الفرة تتناقص مع زيادة محتويات الملح.

### Introduction

Among the various polymers, PVA has been used extensively due to some associated unique properties such as: good film forming, non-toxicity, high performance hydrophilic, process

ability, having high dielectric strength, good charge storage capacity and dopant-dependent structural and optical properties and it is also resistant to grease, oil and solvents; moreover PVA have a carbon

chain backbone with hydroxyl groups (OH) attached to methane carbon, which can be a source of hydrogen bonding and trap the ions and nanoparticles to form complexes [1,2]. The different fillers or dopants like various transition metal salts, metal sulphides, metal oxides, and different types of carbon nanotubes in the nanoscale, have been used in the preparation of nanocomposites as reported in the literatures [3-6]. The nanocomposites materials find a wide number of applications in many diverse fields such as UV shields, microwave absorbents, optoelectronics, gas sensors, in batteries and fuel cells, etc. The properties of composites films can be adjusted by varying the composition. Their fabrication shares the same advantages of organic device technology, such as low cost production and the possibility of device fabrication on large area and flexible substrates [7].

The characteristics of these composite films can be manipulated by controlling the type, size and shape of the particles [8-10], and the method used to prepare the composite [9]. The optical properties of polymers can be suitably modified by the addition of material particles and type material depending on their reactivity with the host matrix [10].

Cuprous iodide (CuI) has attracted a great attention, as it is a versatile candidate in band gap materials (CuI, CuSCN and CuAlO<sub>2</sub>) were identified in the preparation of optical properties of the film [11-13]. CuI belongs to the I-VII semiconductors with zinc blende structure. Conducting and optically transparent films aroused much interest in the capability of application in electronic devices such as liquid crystal displays,

photovoltaic devices, photothermal collectors and so on [14].

The complex dielectric constant is a fundamental intrinsic property of a material. The real part of the dielectric constant shows how much it can slow down the speed of light in a polymeric material. The imaginary part shows how a dielectric in the polymer absorbs energy from an electric field caused by dipole motion [15].

In this study, a trail will be carried out to produce and characterize the PVA/CuI nanocomposite using casting technique. The analysis will focus on the influence of concentration of CuI nanoparticle on the structure and optical properties of the PVA films, using UV/Vis analysis, which gives an evidence for understanding the effect of nanoparticle on the optical parameters and energy band diagram on the host polymer.

## Experimental

Microscope glass slides were used as the substrate during the deposition process. The substrates were first cleaned in ethanol solution, subsequently ultrasonically washed with distilled water. The polymer matrix is Poly vinyl alcohol (PVA), [(C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>, where n = 1,60,000], chemicals used in the present study were provided by HIMEDA Chemical Company, India. Polymer layers were prepared by the solution cast technique. PVA solution was prepared by adding first distilled water to solid PVA [1g of PVA in 30ml of distilled water] and using magnetic stirrer [at 90<sup>o</sup> C for 2 h ] for the mixing process to obtain more homogeneous solution. CuI particles were added with concentrations (0, 1, 3, 5, 7, 9 and 20) wt%. By using casting method, we get the films from this mixture in the template in Petri-glass dishes and left for two weeks

at room temperature to dry. In order to investigate the structure of the polymer layers, X-ray diffraction studies were carried out using SHIMADZU diffractometer type XRD 6000 using Cu  $k_{\alpha}$  radiation operating at 30 kV and 15 mA, taken for the  $2\theta$  range of (10-90) degree. The various peaks obtained in the diffraction pattern gave the information about the size and interplanar spacing of the compound. Fourier transform infrared spectrophotometer [FTIR] spectra of the samples were obtained in the spectral range of (4000–400)  $\text{cm}^{-1}$ . films of PVA–CuI was measured in the wavelength range 190–1100 nm using Metertech SP 80001 UV–visible spectrophotometer at room temperature. The Optical Interference Method was used to measure the thickness of PVA/CuI films and was about 0.5  $\mu\text{m}$

The average crystallite size ( $D$ ) is calculated by using Scherer's formula [1]

$$D = \frac{0.9 \times \lambda}{\beta \times \cos \theta} \quad (1)$$

where  $D$  is the average crystallite size,  $\lambda$  is the X-ray wavelength,  $\theta$  is the diffraction angle of the peak and  $\beta$  is the value of the full width at half maximum (FWHM).

The absorption coefficient ( $\alpha$ ) is related to the optical absorbance  $A$  and thickness of the film  $d$ , based on the Lambert Beer's law [16, 17] that is:

$$\alpha = 2.303A/d \quad (2)$$

The optical energy gap ( $E_g$ ) of the films has been determined from absorption coefficient data as a function of photon energy ( $h\nu$  in eV). According to the generally accepted model proposed by Tauc for higher values of absorption coefficient, the optical absorption of materials are

given by the Tauc [18] and Mott-Davis model [19]:

$$(\alpha h\nu) = \beta(h\nu - E_g)^n \quad (3)$$

where  $\beta$  is a constant called the band tail parameter and  $n$  is the exponential constant index which determine the type of electronic transition responsible for the absorption mechanism of electron transition. There are four types of transition in materials that can be represented with  $n$ . The values of  $n$  are commonly 1/2, 3/2 for indirect allowed, indirect forbidden respectively, and  $n$  equal to 2, 3 for direct allowed, and direct forbidden transitions respectively, depending on the nature of the electronic transition responsible for absorption mechanism of electron transition [20]. The optical dispersion of a polymer can be determined by transmission measurements or interferometry. Each measurement is used to obtain a complex optical dielectric constant and refractive index given by Eqs.

$$N = n + i k \quad (4)$$

$$E = \epsilon_r + i \epsilon_i \quad (5)$$

$$N = E^2 \quad (6)$$

where  $E$  complex dielectric constant and  $N$  the complex refractive index

The real and imaginary parts of the dielectric constant are related to the refractive index by Eqs.

$$\epsilon_r = n^2 - k^2 \quad (7)$$

$$\epsilon_i = 2nk \quad (8)$$

The refractive index  $n$  of the films was calculated using the following

$$n = (1 + R)/(1 - R) + \sqrt{4R/(1 - R)^2 - k^2} \quad (9)$$

in which  $k = \lambda\alpha/4\pi$ .

## Results and discussion

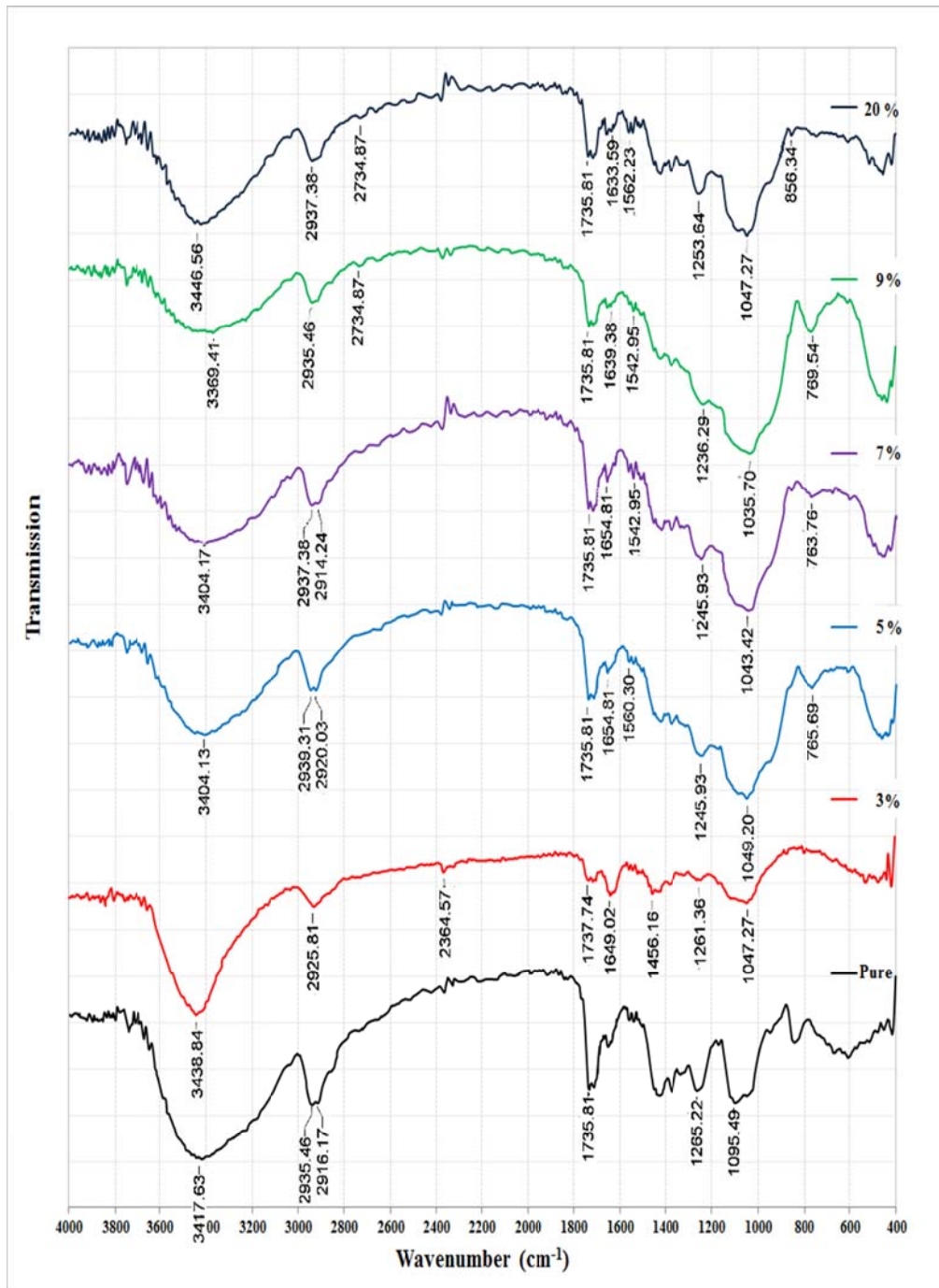
### 1. FTIR spectroscopy

FTIR spectroscopy has been used to analyse the interactions among atoms

or ions in PVA polymer and PVA\CuI polymer composites. These interactions may induce changes in the vibrational modes of the polymer and PVA/CuI polymer composites under investigation.

The FTIR spectrum exhibits some bands characteristic of stretching and bending vibrations of O -H, C-H, C =C

and C -O groups, The FTIR spectrum of pure PVA and PVA/ CuI polymer composite with different concentration of CuI were shown in the Fig.1 after addition (CuI) nanoparticles some polymer chains have been broken and some other chains have been formed instead this agreement with Urbach[20].



**Fig. 1: FTIR spectra for PVA/ CuI polymer composites with different concentrations of CuI 0 wt%, 3wt%, 5 wt%, 7 wt).% 9 wt% and 20 wt. %.**

We notice through FTIR, if CuI particles are present in films PVA/ CuI composites, it leads to restriction of molecular vibrational motion, and special vibrational motion at three dimensions for PVA/CuI composite and will most probably be affected by IR energy. This restricted of molecular polymers move reason occurrence apparent distortion for some the parts functional for polymers (functional groups); therefore, that films nanocomposite has characteristic nano approximately being restricted. The new bands may be correlated likewise with defects induced by the charge transfer reaction between the polymer chain and the dopant.

Increasing the FTIR spectrum in the range of (1400 to 1600)  $\text{cm}^{-1}$  corresponds to C–H bond of  $\text{CH}_2$  and shows the broken chains. CuI nanoparticles have generated new bonds in this range. Decreasing the FTIR spectrum in the range of 2500 to 3700  $\text{cm}^{-1}$  shows the produced polymer chains corresponds to O–H stretching and C–H stretching bonds. FTIR spectra of pure PVA and doped CuI films are in agreement with Makled and Sheha [10].

The absorption peaks of pure PVA at 3417  $\text{cm}^{-1}$  was assigned to O-H

stretching vibration of hydroxyl groups. The band corresponding to C–H asymmetric stretching vibration occurs at 2935  $\text{cm}^{-1}$  and C–H symmetric stretching vibration at 2916  $\text{cm}^{-1}$ . The bands at 1735  $\text{cm}^{-1}$  corresponds to C=C stretching vibration and 1654  $\text{cm}^{-1}$  corresponds to an acetyl C=O group and can be explained on the basis of intra/inter molecular hydrogen bonding with the adjacent OH group. Two strong bands observed at 1562 and 844  $\text{cm}^{-1}$  has been attributed to bending and stretching modes of  $\text{CH}_2$  group, The strong band at 1265  $\text{cm}^{-1}$  and sharp band at 1095  $\text{cm}^{-1}$  could be attributed to the stretching mode of C–O and C=C groups, respectively.

The IR band positions and their assignments are presented in Table 1, which reflects the effect of CuI on the chemical structure of the PVA membrane. FTIR spectra show shift in some bands and change in the intensities of other bands comparing with pure PVA. As shown from Table 1, the strength of hydrogen bond on O–H, C–H, and  $\text{CH}_2$  groups differs according to the CuI.

**Table 1: FTIR absorption bands positions and their assignments for pure PVA and PVA/CuI polymer composites.**

Band assignments Pure	0%	3%	5%	7%	9%	20%
O-H stretching vibration	3417	3438	3404	3450	3369	3446
C-H asymmetric stretching vibration	2935	2925	2939	2937	2935	2937
C-H symmetric stretching vibration	2916	2860	2920	2914	2734	2734
C=C stretching vibration	1735	1737	1735	1735	1735	1735
Acetyl C=O group	1654	1649	1654	1654	1639	1633
Bending modes of $\text{CH}_2$ group	1562	1456	1560	1542	1542	1562
Stretching mode of CO group	1265	1261	1245	1245	1236	1253
Stretching mode of CC group	1095	1047	1049	1043	1035	1047
Stretching modes of $\text{CH}_2$ group	844	796	765	763	769	856

On the other hand, the intensity of band (C=C) stretching vibration at  $1735\text{ cm}^{-1}$  shifts to lower wave numbers, which indicates a decrease in the force constant by adding CuI according to hook's law [21]. The increase in the force constant gives an insight into specific interactions between the dopant and the polar groups of pure polymer. Such changes in O-H, C-H, and C=O vibrations have been observed in other report [22]. After doping CuI, some polymer chains have been broken and some other chains have been formed instead.

## 2. X-Ray diffraction

Fig.2 represents the X-ray diffraction of film for the as deposited PVA films pure and doped with CuI (1, 3, 5, 7, 9 and 20) wt% on glass at substrate at room temperature with

thickness equal to about 500 nm. This figure reveals polycrystalline structure for as deposited and doping samples, which indicates that these films have cubic structure according to American standard of testing materials (ASTM) card.

The first broad peak appears at  $2\theta \approx 19.44^\circ$  correspond to the PVA semi-crystalline phase. The semi-crystalline nature of PVA results from the strong intermolecular interaction between PVA chains through the intermolecular hydrogen bonding this agreement with Sheng-Jian Huang [23]. The observed small intensity diffraction peaks at scattering angle  $2\theta = 25.5^\circ, 29.45^\circ$  are corresponding to reflections from (111) and (020) crystal planes, confirmed the formation of the CuI particles in a PVA matrix.

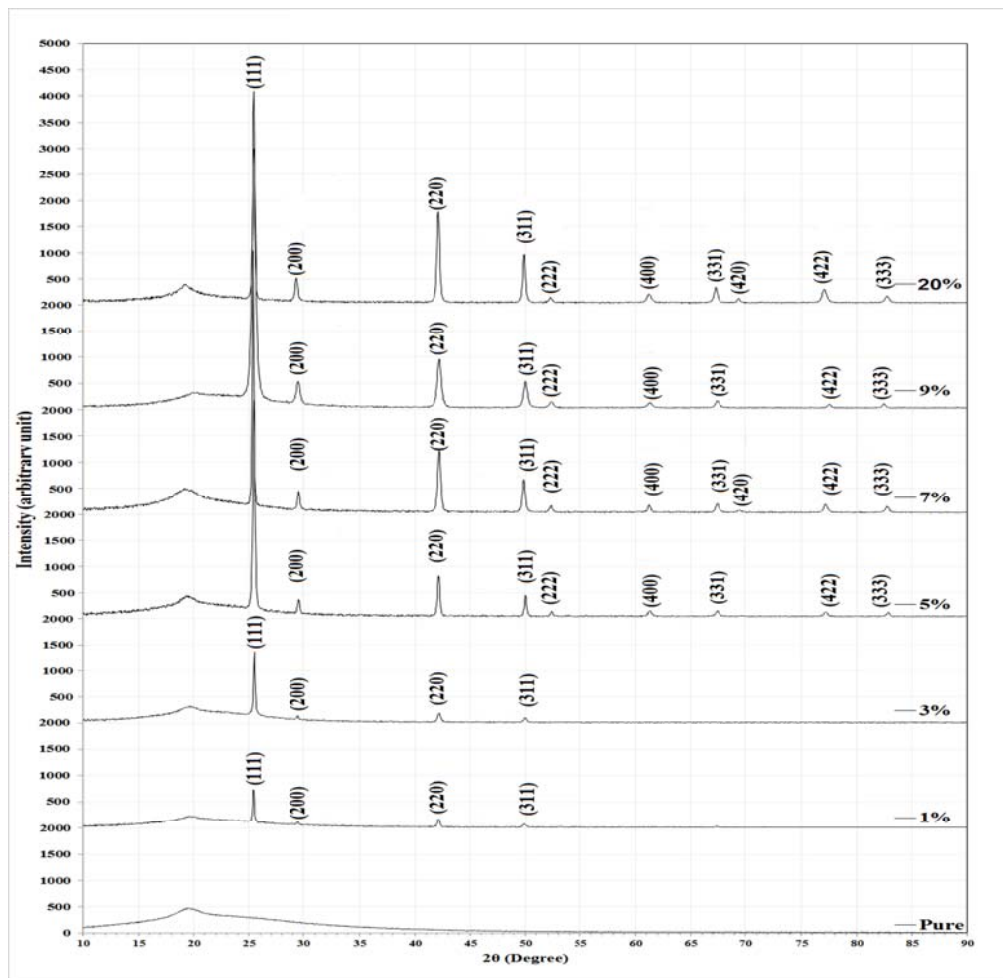


Fig. 2: X-ray diffraction pattern of pure PVA and PVA/CuI film composites.

By increasing the concentration ratio, the number of peaks increases and becomes more intense, indicating an improvement in the crystallinity. This improvement may be attributed to the recrystallization of the films, by the enhancement of the rearrangement atoms in the film structure. Furthermore, it can be observed that the average particle size decreases with increasing the concentration on increasing significance of crystallization or agglutination-grained, and as shown in the Table 2 and that all Bragg peaks shifted slightly toward lower values of the diffraction angle for the films, indicating the changes in the lattice parameters. As the CuI concentration ratio increase up to 5, new Sharp peaks raised at  $25.5^\circ$ ,  $42.24^\circ$  and  $49.99^\circ$  corresponding to the (111), (020) and (202) planes of CuI crystals which could be indexed to cubic structure This is due to the increase in the density of matter and thus an increase in the crystallization of the films due to the structure is full of gaps in the film and stacking atoms This is in agreement with Hodge et al. [23] and Cooper et al. [29]. Above such concentration a broadness and reduction of height of the essential peak of PVA was observed. This is in agreement with Hodge et al. [23]. The variation of x-ray diffraction parameters with doping is listed in Table 2.

It can be seen that the crystallite size of the films decreases with increasing

concentration of CuI and found that Grained size (GS) is inversely proportional to the the full width at half maximum (FWHM) for the same level and that's what we're observing Level (111), FWHM increased values while decreasing grain size (GS), and the increase in intensity the higher the concentration ratio, Level (111) summit appear when the  $2\theta = 25.425^\circ$  and using the Barak Law found that the  $d(111) = 3.5004 \text{ \AA}$  and this value is consistent with what was published Sirimanne et al[30].which indicates that the process of grain formation could be explained by considering that the increasing concentration of CuI induces the coalescence of small grains by grain boundary diffusion which results in major grain growth. The grain growth mechanism includes the transfer of atoms at grain boundaries from one grain to another and the final crystallite size depends upon the specific concentration conditions.

### 3. Optical absorption

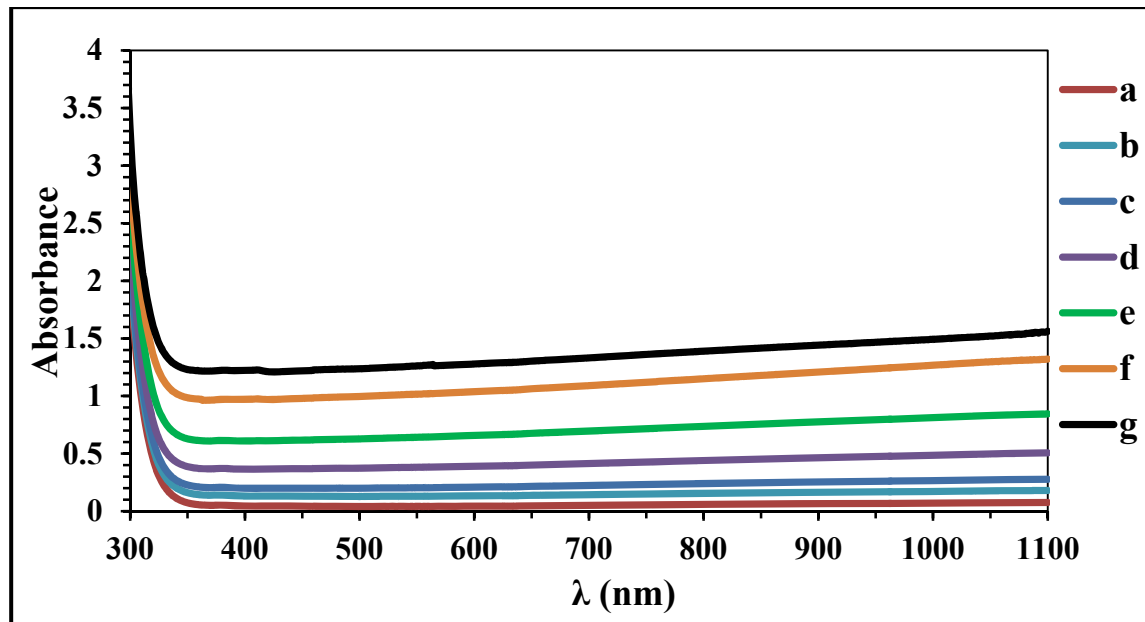
UV-vis absorption is a commonly used analytical tool for studying the interactions between electrons and radiation. which corresponds to the electron excitation from the valance band to the conduction band, can be used to determine the nature and value of the optical band gap.

Fig. 3 illustrates the plot of the absorption against wavelength in the UV-visible range for (PVA\CuI) composites.

Table 2: XRD parameters of (PVA/CuI) polymer composites.

CuI%	2 $\theta$ (Deg.)	FWHM (Deg.)	Intensity (a. u.)	d <sub>hkl</sub> Exp.(Å)	G.S (nm)	d <sub>hkl</sub> Std.(Å)	hkl	card No.
pure								
1	25.425	0.173	679	3.5004	47.1	3.5005	(111)	96-900-4457
	29.456	0.205	44	3.0300	40.1	3.0315	(200)	96-900-4457
	42.158	0.256	158	2.1418	33.2	2.1436	(220)	96-900-4457
	49.903	0.307	57	1.8260	28.6	1.8281	(311)	96-900-4457
3	25.499	0.177	1115	3.4904	46.0	3.5005	(111)	96-900-4457
	29.461	0.155	85	3.0294	53.1	3.0315	(200)	96-900-4457
	42.209	0.309	166	2.1393	27.6	2.1436	(220)	96-900-4457
	49.976	0.309	85	1.8235	28.4	1.8281	(311)	96-900-4457
5	25.456	0.222	3996	3.4962	36.8	3.5005	(111)	96-900-4457
	29.554	0.221	275	3.0201	37.1	3.0315	(200)	96-900-4457
	42.168	0.221	786	2.1413	38.5	2.1436	(220)	96-900-4457
	50.007	0.222	389	1.8224	39.6	1.8281	(311)	96-900-4457
	52.379	0.222	96	1.7454	39.9	1.7502	(222)	96-900-4457
	61.314	0.369	100	1.5107	25.0	1.5158	(400)	96-900-4457
	67.443	0.369	100	1.3875	25.9	1.3909	(331)	96-900-4457
	77.190	0.369	83	1.2348	27.5	1.2376	(422)	96-900-4457
82.876	0.295	79	1.1639	35.9	1.1668	(333)	96-900-4457	
7	25.381	0.178	5000	3.5064	45.8	3.5005	(111)	96-900-4457
	29.547	0.221	373	3.0208	37.1	3.0315	(200)	96-900-4457
	42.220	0.296	1176	2.1388	28.8	2.1436	(220)	96-900-4457
	49.847	0.297	619	1.8279	29.5	1.8281	(311)	96-900-4457
	52.303	0.295	115	1.7477	30.0	1.7502	(222)	96-900-4457
	61.237	0.296	131	1.5124	31.2	1.5158	(400)	96-900-4457
	67.439	0.370	163	1.3876	25.8	1.3909	(331)	96-900-4457
	69.437	0.369	42	1.3525	26.2	1.3557	(420)	96-900-4457
	77.187	0.369	152	1.2349	27.5	1.2376	(422)	96-900-4457
	82.800	0.369	115	1.1648	28.7	1.1668	(333)	96-900-4457
9	25.460	0.400	5050	3.4957	20.4	3.5005	(111)	96-900-4457
	29.500	0.376	434	3.0255	21.8	3.0315	(200)	96-900-4457
	42.220	0.400	918	2.1388	21.3	2.1436	(220)	96-900-4457
	50.000	0.400	498	1.8227	21.9	1.8281	(311)	96-900-4457
	52.360	0.376	120	1.7459	23.5	1.7502	(222)	96-900-4457
	61.300	0.447	100	1.5110	20.7	1.5158	(400)	96-900-4457
	67.460	0.424	130	1.3872	22.5	1.3909	(331)	96-900-4457
	77.500	0.300	70	1.2307	34.0	1.2376	(422)	96-900-4457
	82.500	0.300	80	1.1683	35.2	1.1668	(333)	96-900-4457
20	25.420	0.282	5000	3.5011	28.9	3.5005	(111)	96-900-4457
	29.460	0.282	700	3.0295	29.1	3.0315	(200)	96-900-4457
	42.180	0.306	2400	2.1407	27.8	2.1436	(220)	96-900-4457
	49.940	0.306	1250	1.8247	28.6	1.8281	(311)	96-900-4457
	52.000	0.400	70	1.7572	22.1	1.7502	(222)	96-900-4457
	61.220	0.329	298	1.5128	28.1	1.5158	(400)	96-900-4457
	67.400	0.353	320	1.3883	27.1	1.3909	(331)	96-900-4457
	77.140	0.282	350	1.2355	36.0	1.3557	(420)	96-900-4457
	82.780	0.306	200	1.1650	34.6	1.2376	(422)	96-900-4457
69.500	0.300	60	1.3514	32.2	1.1668	(333)	96-900-4457	





*Fig.3: Optical the absorbance for solid films of (PVA\CuI) polymer composites with different concentrations of CuI .a- 0wt% (b)1wt% (c)3wt% (d)5wt% (e) 7wt% (f)9wt% (g)20wt.*

An absorption spectrum is a fingerprint of a molecule or polymer material. Pure PVA is a colorless polymer without any noticeable absorption in the visible range. It can be seen from this figure that the absorption peak position is affected with varying the concentration of CuI and shows shift for solid films while the absorption peak for composite colloidal appears in narrow wavelength range (300–375 nm). In addition the absorption edge varies also with increasing the concentration of CuI in PVA polymer matrix, consequently, by the increase of the weight percentages of CuI particles. it is directly proportional to the absorbance according to Lambert Beer Law, and the reason for this is due to the increased focus within the same volume of solution which failed later so increasing the number of molecules that were to absorb the incident light, absorbance is increased. These results are in agreement with Caixia Kan et al and Makled and Sheha [10, 24].

Fig. 4 shows the transmittance of (PVA\CuI) polymer composites, as a function of the wavelength. It can be noticed from the figure that the transmittance increases with increasing of wavelength from (300-350) nm then transmittance decreases with increasing of the concentration of CuI composite. This figure clearly indicates that after adding CuI in PVA polymer, a valley at 380 nm has been created, that its intensity continuously decreasing with increasing concentration of the dopant. This new valley is attributed to the formation of charge transfer complexes [25]. The appearance of this valley in the visible region is due to the surface Plasmon resonance (SPR) nature of the CuI nanoparticles embedded in PVA polymer dielectric medium. Increase doping increases the number of positional levels between the valence and conduction bands, and thus decrease the transmittance the result agreement with Aziz and Abdullah[31].

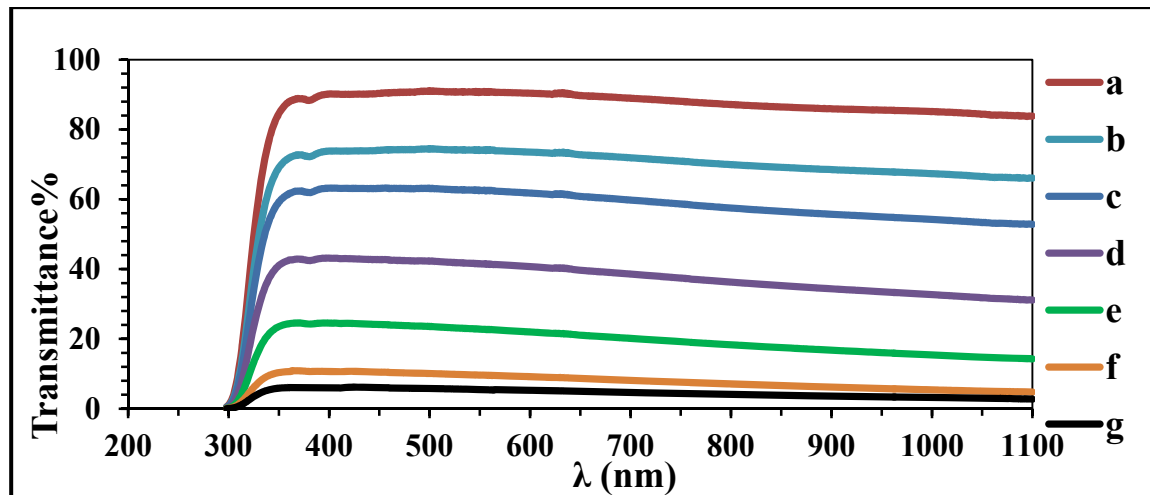


Fig. 4: Optical the transmittance for solid films of PVA\CuI polymer composites with different concentrations of CuI. (a) 0wt% (b) 1wt% (c)3wt% (d)5wt% (e)7wt% (f)9wt% (g)20wt%.

The absorption coefficient  $\alpha$  for films of PVA\CuI polymer composites with different concentrations of CuI

as a function of wavelength is shown in Fig.5.

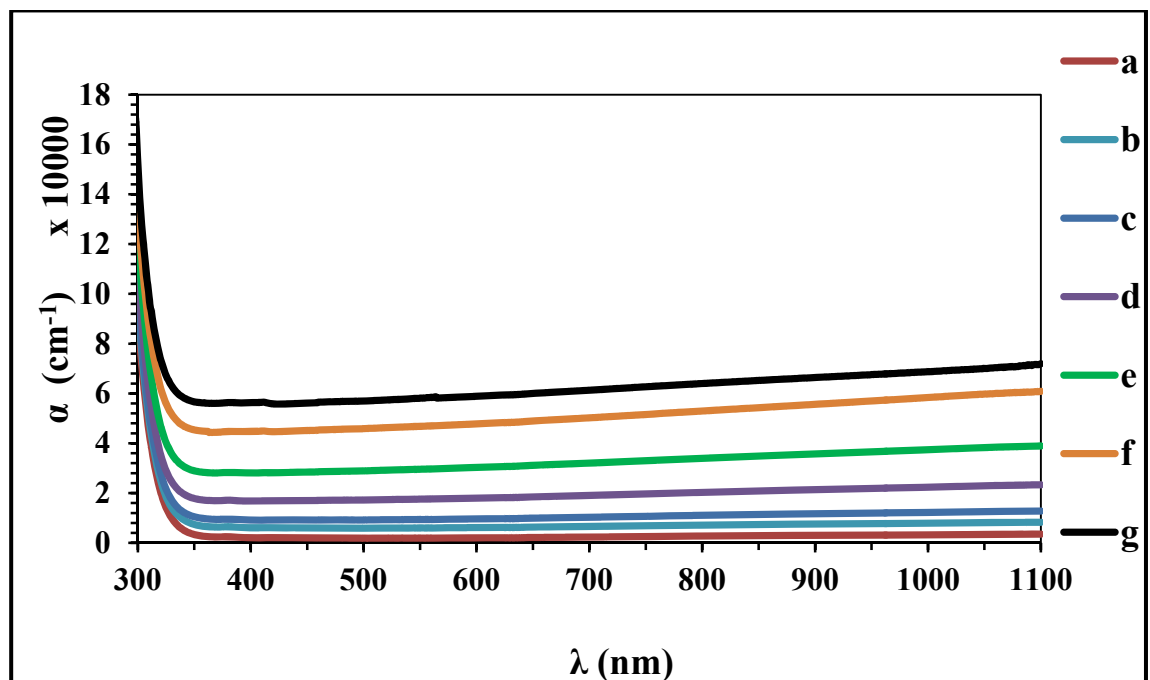


Fig. 5: The absorption coefficient for solid films of PVA\CuI composites with different concentrations of CuI. (a) 0 wt%(b)1wt%(c)3wt%(d)5wt%(e)7wt%(f)9wt%(g)20wt%.

The larger absorption peak appeared in UV range is due to the energy gap of the PVA polymer which decreases owing to increasing the concentration of CuI nanoparticles in the structure of the films. The position of the absorption edge was determined by extrapolating the linear part of  $\alpha$

versus wavelength curves to zero absorption value. The band edge showed a decrease with increasing concentration of CuI nanoparticles in PVA matrix. The absorption edge shifts towards higher wavelength, indicating the decrease in the optical band gap for the doped films. Shift of

the absorption edge in the UV region is due to changes in the electron hole in the conduction and valence bands.

The most used method for estimation of the band gap energy from optical measurement is the one proposed by Tauc and Grigorovici [25]. The optical band gap energy of samples was deduced from the intercept of the extrapolated linear part

of the plot of  $(\alpha h\nu)^{1/2}$  versus the photon energy  $h\nu$ .

Fig. 6 shows the relation between  $(\alpha h\nu)^2$  of PVA/CuI polymer composites as a function of photon energy. The average value of  $E_g$  for PVA/CuI polymer composite form is equal to 4.05 and 3.89 eV for direct transitions.

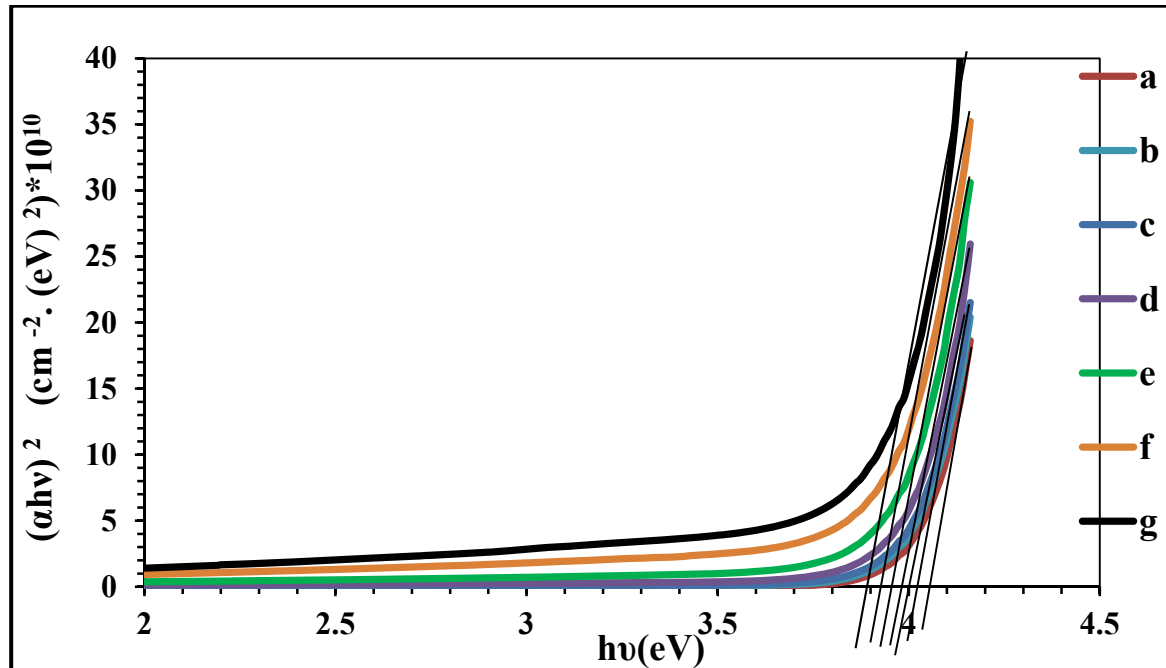


Fig .6: Direct transition band optical energy gap solid films of PVA\CuI composites with different concentrations of CuI. (a) 0wt% (b)1wt% (c)3wt% (d)5wt% (e)7wt% (f)9wt% (g)20wt%.

Fig. 7 shows the relation between  $(\alpha h\nu)^{1/2}$  of PVA/CuI polymer composites as a function of photon energy. The band gap lies in the range 3.75–3.35 eV for indirect transitions.

In an indirect gap, a photon cannot be emitted because the electron must pass through an intermediate state and transfer momentum to the crystal lattice.

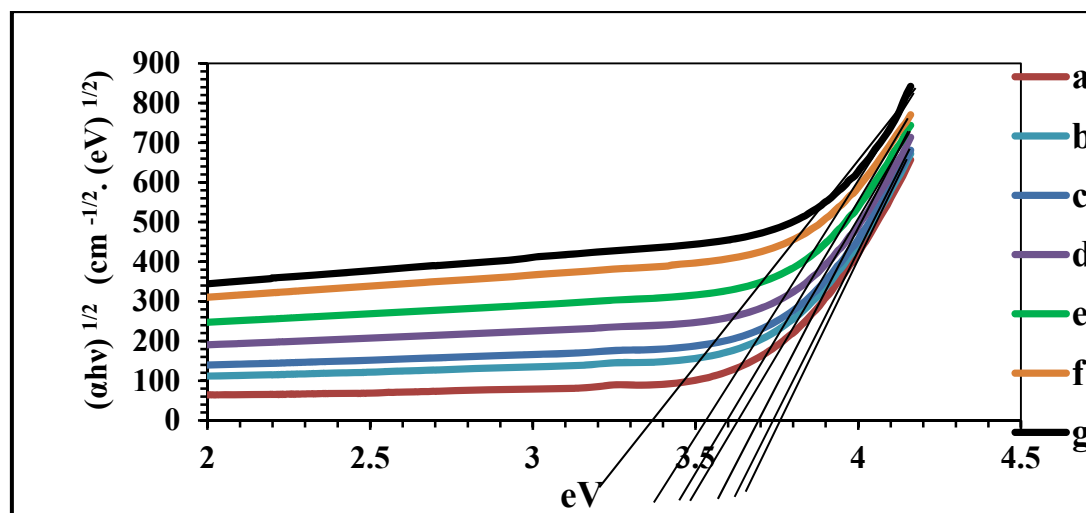


Fig. 7: Indirect transition band optical energy gap solid films of PVA/CuI composites with different concentrations of CuI. (a) 0wt% (b) 1wt% (c) 3wt% (d) 5wt% (e) 7wt% (f) 9wt% (g) 20wt%.

In general, band gap decreases with increasing CuI concentration this can be attributed to the salt complexation with the polymer matrix besides the expected particle aggregation and may be to creation of site levels in the forbidden optical energy gap, the transition in this case is conducted in two stages that involve the transition of electron from the valence band to the local levels to the conduction band as a result of increasing the CuI nanoparticles weight percentage. The variation of the calculated values of optical band gap reflects the role of formation of CuI nanoparticles in modifying the electronic structure of the PVA matrix [26, 27]. These CuI-nanoparticles may be responsible for the formation of localized electronic

states in the Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular Orbital (HOMO-LUMO) gap. These localized electronic states dominate the optical and electrical properties vis-à-vis their role as trapping and recombination centers, thus enhancing the low energy transitions leading to the observed change in optical band gap. The decrease in the optical band gap also reflects the increase in the degree of disorder in the films which arises due to the change in polymer structure [27, 28].

This behaviour is attributed to the fact that nanocomposites are of heterogeneous type. The obtained values are shown in Table 3.

Table 3: Values of optical energy gap for the direct allowed and indirect allowed transition for of PVA/CuI polymer composites.

(CuI) (wt.%)	Eg (eV)	
	allowed direct	allowed indirect
0	4.05	3.75
1	4.01	3.72
3	4.0	3.69
5	3.99	3.61
7	3.95	3.59
9	3.92	3.51
20	3.89	3.35

Optical properties, such as complex refractive index and dielectric constant for a certain range of wavelength between ultraviolet and near infrared, are important criteria for the selection of fabricated films for various applications. The refractive index is one of the fundamental properties of a material, because it is closely related to the electronic polarizability of ions and the local field inside the material, The refractive index (n) and extinction coefficient (k) variations versus wavelengths of the films are calculated at different values of  $\lambda$ , then, the obtained values are shown in Table 4 at different concentration ratio of CuI at wavelength  $\lambda=550$  nm. It is obvious that a remarkable variation is observed in both n and k values with different concentration ratio of CuI,

The real and imaginary part of dielectric constants was calculated by use Eq.(7) and (8) respectively with

different values of  $\lambda$ . Then, the obtained values are shown in Table 4 at different concentration ratio of CuI at wavelength  $\lambda=550$  nm. The real part of dielectric constant is related to the dispersion. In order to explain the dispersion it is necessary to take into account the actual motion of the electrons in the optical medium through which the light is traveling. The imaginary part represents the dissipative rate of electromagnetic wave propagation in the medium. It can be concluded that  $\epsilon_r$  is larger than  $\epsilon_i$  because it mainly depends on N. With increasing the amount of CuI nanoparticles in PVA, the real part of dielectric constant is decreased. It is due to decrease of the dielectric property of films because of CuI nanoparticles metal lattice in the host PVA polymer matrix.

**Table 4: The values of optical Constants for of PVA\CuI polymer composites at  $\lambda=550$  nm.**

CuI %	T%	$\alpha$ (cm <sup>-1</sup> )	K	n	$\epsilon_r$	$\epsilon_i$
0	90.92	1904	0.008	1.720	2.960	0.026
1	74.37	5923	0.024	2.560	6.551	0.121
3	63.06	9223	0.037	3.157	9.964	0.232
5	42.26	17230	0.069	4.329	18.737	0.594
7	23.54	28935	0.115	5.080	25.792	1.170
9	10.08	45901	0.183	4.445	19.720	1.624
20	5.79	56991	0.227	3.622	13.067	1.643

## Conclusions

From the obtained results and discussions one can conclude the following:

1. The FTIR spectrum peaks correspond to molecular vibrations and chemical bonds, indicate the presence of CuI in the PVA polymer structure.
2. characterization using XRD demonstrated that CuI particles grew in PVA polymer matrix whereas the intensity of the peaks increases with increasing CuI.

3. The obtained optical parameters were found to be strongly affected by CuI contents. The absorption spectrum of PVA/ CuI polymer composite is increased by increasing CuI concentration between 0 and 20 wt%, while the transition and optical energy gap decrease whenever the CuI concentration increased. Refractive index and dielectric constant are increased in general with increasing the concentration of CuI nanoparticles.

## References

- [1] O. Gh. Abdullah, S. R. Saeed, Chemistry and Materials Research, 3, 11 (2013) 19-24.
- [2] J. Xu, X. Cui, J. Zhang, H. Liang, H. Wang, j. Li, Bull. Mater. Sci., 31, 2 (2008) 189-192.
- [3] V.L. Colvin, M.C. Schlamp, A.P. Allvisatos, Nature, 370(1994) 354-357.
- [4] B. Ramaraj, S.K. Nayak, K.R. Yoon, Journal of Applied Polymer Science, 116, 3 (2010) 1671-1677.
- [5] S. Gandhi, R.H.H. Subramani, T. Ramakrishnan, A. Sivabalan, V. Dhanalakshmi, M.R.G. Nair, R. Anbarasan, Journal of Materials Science, 45, 6 (2010) 1688-1694.
- [6] R.K. Karimi, A.B. Shamili, A. Aslani, K. Kaviani, Physica B, 405, 15 (2010) 3096-3100.
- [7] B.Z. Tong, Y. Geng, J.W.Y. Lam, B. Li, X. Jing, X. Wang, F. Wang, A.B. Pakhomov, X.X. Zhang, Chem. Mater. 11 (1999) 1581-1589.
- [8] K. Tonooka, K. Shimokawa, O. Nishimura, Thin Solid Films, 411 (2002) 129-133.
- [9] S.L. Dhare, S.S. Latthe, C. Kappenstein, S.K. Mukherjee, A.V. Rao, Appl. Surf. Sci. 256 (2010) 3967-3971.
- [10] M. Makled and E. Sheha, Journal of Advanced Research, 4 (2013) 531-538.
- [11] M.H. Al-Humairi, M.Sc. Thesis, University of Babylon, College of Education for Pure Sciences, (2013).
- [12] K. Tennakone, G.R.R.A. Kumara, I.R.M. Kottegoda, V.P.S. Perera, G.M.L.P. Aponsu, K.G.U. Wijayantha, Sol. Cells, 55 (1998) 283-289.
- [13] G.R.R.A. Kumara, A. Konno, G.K.R. Senadeera, P.V.V. Jayaweere, D.B.R.A. De Silva, T. Tennakone, Sol. Energy Mater. Sol. Cells, 69 (2001) 195-199.
- [14] A. Kiesow, J.E. Morris, C. Radehaus, A. Heilmann, J. Appl. Phys. 94 (2003) 6988-6991.
- [15] J.C. Phillips, Physical Review Letters, 20, 11 (1968) 550-553.
- [16] O.Gh. Abdullah, B.K. Aziz, D.M. Salh, Indian Journal of Applied Research, 3, 11 (2013) 477-480.
- [17] A.N. Alias, Z.M. Zabidi, A.M.M. Ali, M.K. Harun, M.Z.A. Yahya, International Journal of Applied Science and Technology, 3, 5 (2013) 11-38.
- [18] D.L. Wood, J. Tauc, Phys. Rev. B 5, 8 (1972) 3144.
- [19] N.F. Mott, E.A. Davis, "Electronic processes in non-crystalline materials". Clarendon press, Oxford, (1979).
- [20] F. Urbach, Journal of Physical Review, 92 (1953) 627-636.
- [21] A. S. Kutsenko and V. M. Granchak, Theoretical and Experimental Chemistry, 45, 5 (2009) 313-318.
- [22] F. C. Krebs, T. Tromholt, M. Jorgensen, Nanoscale, 2(2010)873-86.
- [23] R.M. Hodge, G.H. Edward, G.P. Imon, Polymer, 37 (1996) 1371-1376.
- [24] Caixia Kan, Chang shun Wang, Jiejun Zhu, Hong Chen Li, J. of Solid State Chemistry, 183 (2010) 858-865.
- [25] J. Tauc and R. Grigorovici, Physics Status Solidi (B), 15, 2 (1966) 627-637.
- [26] C. U. Devi, A. K. Sharma, V. V. R. N. Rao, Materials Letters, 56, 3 (2002) 167-174.
- [27] J. Rozra, I. Saini, A. Sharma, Materials Chemistry and Physics, 134, 2-3 (2013) 339-1024.
- [28] M. Abdelaziz, Physica B, 406, 6-7 (2011) 1300-1307.
- [29] M. A. Cooper, F. C. Hawthorne The Canadian Mineralogist 35, (1997) 785-786.
- [30] P.M. Sirimanne, T. Shirata, Damodarel, Hayashiy, Soga Tand Jimbo T, 77 (2003) 15.
- [31] B. K. Aziz and O. Gh. Abdullah, Asian Transaction on Science and Technology, 1, 4 (2011) 12-15.