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The optical characterization of polyvinyl alcohol: cobalt nitrate solid polymer electrolyte films

Omed Gh. Abdullah[1*], Dlear R. Saber[1], Sherzad A. Taha[2]

[1]Advanced Materials Research Lab., Department of Physics, Faculty of Science and Science Education, School of Science, University of Sulaimani, Kurdistan Regional Government, Iraq
[2]Department of Physics, College of Education, Salahaddin University, Kurdistan Region, Iraq

[*]Corresponding author. Tel: (+964) 7702400288; E-mail: omed.abdullah@univsul.edu

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ABSTRACT

Optical properties of solid polymer electrolyte films based on polyvinyl alcohol (PVA) with different concentration of cobalt nitrate $Co(NO_3)_2$ (3-12) wt% have been studied. The parameters such as refractive index, extinction coefficient, and optical energy gap were investigated by using the absorbance measurement from UV-visible spectrophotometer in the spectral range (190-790) nm. This study reveals that the optical properties of PVA are affected by salt concentration, where the absorption increases and absorption edge decreases as $Co(NO_3)_2$ concentration increases. The refractive index, and extinction coefficient values were found to increase with increasing $Co(NO_3)_2$ percentage. The optical energy gaps have been investigated and showed a clear dependence on the $Co(NO_3)_2$ concentration. The interpreted absorption mechanism is both direct- and indirect- electron transition, and it was found to be decreasing with increasing $Co(NO_3)_2$ concentration. The single oscillator model has been used to analyses the dispersion behavior of the refractive index, and the dispersion parameters are calculated. Copyright © 2015 VBRI press.

Keywords: Polymer electrolyte; optical energy gap; complex refractive index; single-oscillator model.

Omed Gh. Abdullah, is PhD assistant professor in physics department, School of Science, University of Sulaimani, Kurdistan Region-Iraq. His principle research interests have been in the fields of solid state physics, material science, and powder technology. His interests include fabrication and characterization of thin films, simulation of powder compaction, physical properties of polymer electrolyte, and nanocomposite material. He is author or coauthor of 32 publications in refereed journals. He is a member of IACSIT, Iraqi Physics and Mathematics Society, Kurdistan Physicists' Syndicate, Kurdistan Academics Association, and Kurdistan Chemists & Physists Society.

Dlear R. Saber, was born in Sulaimani, Kurdistan Region, on Jun 1966, He received M.Sc. and PhD degrees in Material Science from Baghdad University, in 2000 and 2009 respectively. Now he is a lecturer in physics department, School of Science, University of Sulaimani, Kurdistan Region. His principle research interests have been in the fields of material science, and characterization of ciramic materials. He is a member of Iraqi Physics and Mathematics Society, Kurdistan Academics Association, and Kurdistan Chemists & Physists Society.

Sherzad A. Taha, was born in Erbil, Kurdistan Region-Iraq, on June 1965. He received M.Sc. degree in Semiconductors from Salahaddin University, in 1993, and PhD degree in Atomic Physics from Al-Mustanssrya University (Bagadad- Iraq), in 2007. He was worked as a lecturer in the Salahaddin University. Now he is assistant professor in Physics Department, College of Education, Salahaddin University, Kurdistan Region-Iraq. His principle research interests have been in the fields of Atomic Physics, Molecular Physics, and Solid State Physics. He is author or coauthor of 14 publications in refereed journals.

Introduction

The growing interest in solid polymer electrolytes arises from the possibility of their applications in various solid state electrochemical devices **[1, 2]**. Polymer electrolytes are ion conducting solid solution of inorganic electrolyte salt in ion-coordinating polymers **[3]**. Optical characterizations of polymer electrolytes are of particular importance, as these materials are intended for practical application in various fields **[4]**.

The optical absorption spectrum is one of the most important tools for understanding band structure, electronic properties and optical constants of pure and electrolyte polymers **[5]**. Analysis of the absorption spectra in the lower energy part gives information about atomic vibrations, while the high energy part of the spectrum gives knowledge about the electronic states in the atom **[6]**.

The mechanism of ion interaction with polymer chain has remained a subject of great interest to researchers in many disciplines; the phenomena are difficult to characterize **[7]**. The incomplete understanding of the formation of charge transfer complexes in solid polymer electrolytes is considered to be one of the main hurdles in achieving the required ambient product **[8]**.

One of the main advantages of solid polymer electrolyte samples is that the electrical and optical properties of polymers can be considerably modified by the addition of salts depending on their reactivity with the host matrix **[9]**. Therefore, the main goal of the present work is to investigate the optical characterization of PVA:$Co(NO_3)_2$ solid polymer electrolyte films with different $Co(NO_3)_2$ concentration, over the wavelength range (190-790) nm.

Experimental

Solid polymer electrolyte based on Polyvinyl alcohol (PVA) powder supplied by Sigma-Aldrich, and cobalt nitrate $Co(NO_3)_2$ are prepared by the solution cast technique. The PVA was dissolved in distilled water and heated gently in a water bath up to 90 ^oC to prevent thermal decomposition of the polymer. The solution was stirred well using a magnetic stirrer for 3 hours, until completely dissolved, and then different weight percent of the $Co(NO_3)_2$ material (3, 6, 9, and 12) wt% was added to the polymer solution under stirring until completely dissolved. The homogenous solutions were poured into a clean plastic Petri dish and left to dry slowly in room temperature for two weeks to remove any residual solvent. The thickness of the produced films was between (0.12-0.14) mm. The optical absorbance spectra were recorded at room temperature, in the wavelength range (190-790) nm using computerized double beam UV-VIS-NIR spectrophotometer (Model: Lambda 25) from Perkin Elmer.

Results and discussion

The UV-VIS absorbance spectra in the region (190-790) nm for prepared solid polymer electrolyte films are shown in **Fig. 1**. It is clear from the figure that the absorption spectra for all films decreased with increasing wavelength, while it was increased with increasing $Co(NO_3)_2$ concentration. This is an agreement with the same trend reported by earlier workers for different solid polymer electrolytes **[10-12]**, in accordance with Beer's Law. The absorption is proportional to the number of absorbing molecules **[6]**. The formation of a new peak at 515 nm for the solid electrolyte polymer indicate a considerable interaction between PVA and $Co(NO_3)_2$ **[12]**. It is also clear that the peak intensity continuously increasing with increasing of $Co(NO_3)_2$ concentration.

The optical absorption coefficient (α) which is a function of wavelength, has been obtained directly from the optical absorbance (A), and the thickness of the film (d), based on the Lambert-Beer using the relation **[13, 14]**.

$$\alpha = \frac{2.303}{d}\log\left(\frac{I_o}{I}\right) = \frac{2.303}{d}A \quad (1)$$

where I_o and I are the intensities of incident and transmitted radiation beams respectively.

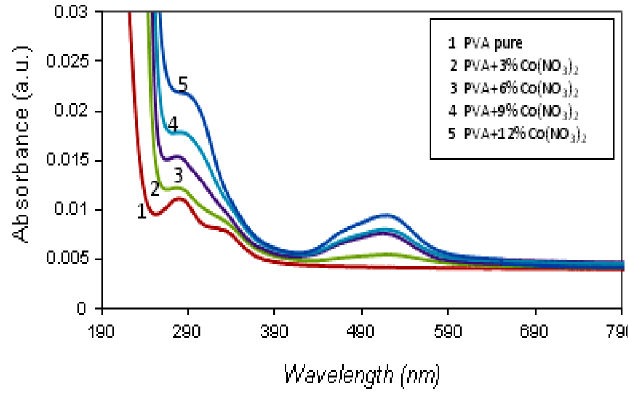

Fig. 1. Absorption spectra of PVA:$Co(NO_3)_2$ solid polymer electrolyte films with different $Co(NO_3)_2$ concentration.

The optical absorption coefficient as a function of photon energy ($h\nu$) for PVA: $Co(NO_3)_2$ solid polymer electrolyte films is shown in **Fig. 2**. The optical absorption coefficient can be divided into three regions, namely, high level absorption, exponential region, and weak absorption. High level absorption is basic optical transition. Whereas, the weak absorption region is lower than the exponential region which depend on the sample preparation, impurity and thermal annealing history **[15]**. The exponential region was first observed by Urbach in an agbrabsorption experiment, this region is called the Urbach edge, which depends on the photon energy **[16]**.

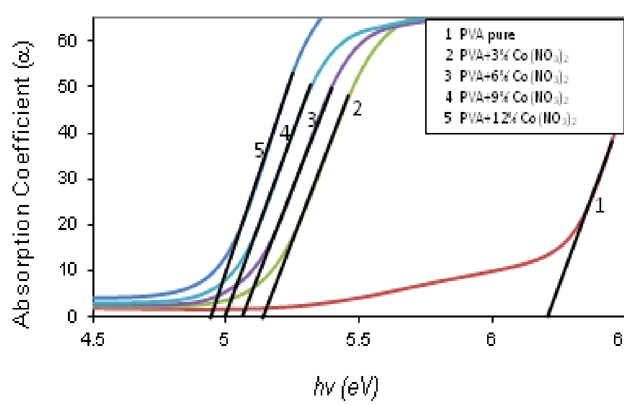

Fig. 2. Absorption coefficient (α) of PVA:$Co(NO_3)_2$ solid polymer electrolyte films with different $Co(NO_3)_2$ concentration.

It is interesting to observe that the absorption coefficient (α) increases with increasing the photon energy ($h\nu$) as well as $Co(NO_3)_2$ concentration. Extrapolation of the linear portion of the curves has been used to calculate the values of absorption edge which are listed in **Table 1**.

This absorption edge decreases with the increasing of the increases of $Co(NO_3)_2$ concentration. The reason for this behavior is that the increases of $Co(NO_3)_2$ concentration lead to increasing the localized state density which reduces the absorption edge values.

Table 1. The values of optical parameters for PVA:$Co(NO_3)_2$ solid polymer electrolyte films.

$Co(NO_3)_2$ wt%	*d* (mm)	*α* Edge (eV)	E_{gd} (eV)	E_{di} (eV)
0	0.14	6.185	6.285	5.985
3	0.12	5.140	5.330	4.958
6	0.13	5.065	5.215	4.884
9	0.13	5.005	5.128	4.818
12	0.12	4.948	5.072	4.770

The dependence of the extinction coefficient (k) on the photon energy for PVA:$Co(NO_3)_2$ solid polymer electrolyte films is shown in **Fig. 3**. It is clear that the extinction coefficient for solid polymer electrolyte shows an increase in values in the energy range from (5-6.5) eV. The increasing of the extinction coefficient for solid polymer electrolyte films with increasing $Co(NO_3)_2$ concentration is due to the increase in absorption coefficient, where the extinction coefficient depends on the absorption coefficient by the following equation **[17, 18]**:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (2)$$

Where λ is the wavelength of the incident photon.

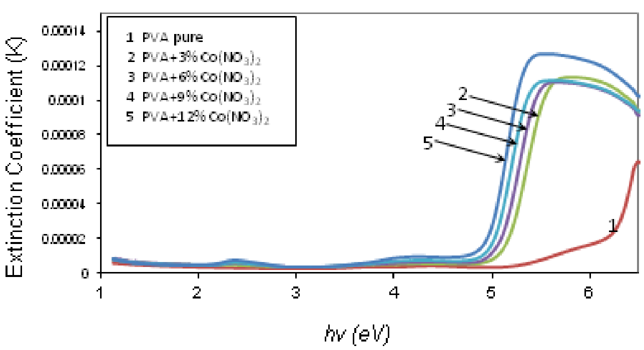

Fig. 3. Variation of the extinction coefficient as a function of wavelength for PVA:$Co(NO_3)_2$ solid polymer electrolyte films.

The refractive index (n) is a fundamental optical property of materials that is directly related to the other optical, electrical, and magnetic properties, and also of interest to those studying the physical, chemical, and molecular properties by optical techniques [19]. Refractive index was determined from the optical reflectance (R) and extinction coefficient of the investigated films using the following formula:

$$n = \left(\frac{1+R}{1-R}\right) + \left(\frac{4R}{(1-R)^2} - k^2\right)^{1/2} \qquad (3)$$

Plots in **Fig. 4** represent the dispersion in the refractive index for the polymer electrolyte films in the investigated range of wavelengths. Inspection of **Fig. 4** indicates for all compositions that the refractive index increases with increasing incident photon energy. The figure shows that the refractive index increases as a result of an increase in the percentage of $Co(NO_3)_2$, this behavior can be attributed to the increasing of the packing density as a result of salt content.

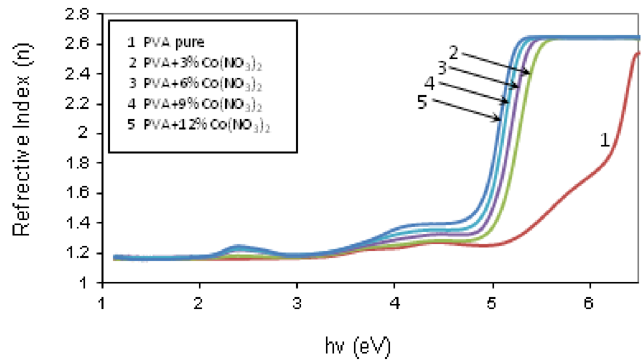

Fig. 4. Refractive index as a function of wavelength for PVA:$Co(NO_3)_2$ solid polymer electrolyte films.

Formation of new peaks for all solid polymer electrolytes is an indication of the change in the molecular structure of PVA **[12]**.

The optical absorption for non-crystalline materials is given by the Tauc and Davis-Mott model **[20, 21]**.

$$(\alpha h\nu)^{\gamma} = \beta\left(h\nu - E_g\right) \qquad (4)$$

Where β is a constant and γ is the exponential constant index. The exponential constant index is an important parameter that describes the type of electronic transition. There are four types of transition in amorphous materials that can be represented with γ. The values of γ are commonly 1/3,1/2, 2/3, and 2 for indirect forbidden, indirect allowed, direct forbidden, and direct allowed transitions, respectively **[22]**.

In order to determine the precise value of the optical direct-energy gap E_{gd} and indirect-energy gap E_{gi} of the investigated films, graphs of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ were plotted as shown in **Fig. 5** and **Fig. 6** respectively. The optical band gap energy was calculated from the intercept of the extrapolated linear part of the plot with abscissa. The values of direct- (E_{gd}) and indirect-energy band gap (E_{gi}) are tabulated in **Table 1**.

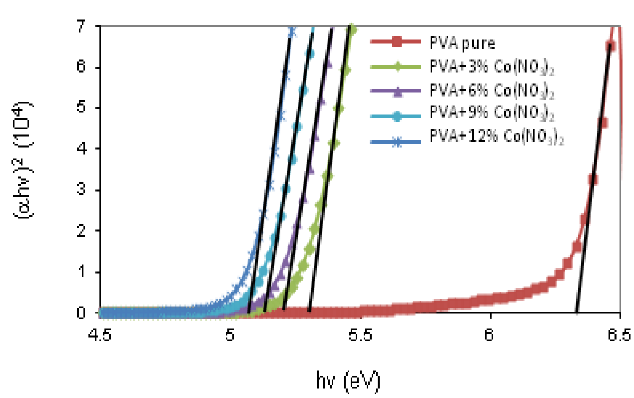

Fig. 5. Relation between the $(\alpha h\nu)^2$ versus $(h\nu)$ for PVA:$Co(NO_3)_2$ solid polymer electrolyte films.

The decrease in optical band gap energy of polymer electrolytes may be explained on the basis of the fact that the incorporation of small amounts of salt forms charge transfer complexes in the host polymer matrix, which provide additional charges in the mixture, causing the decrease of optical band gap energy **[14, 23]**. Also, the decrease in the optical band gap can be attributed to the increase in the degree of disorder in the electrolyte films which arises due to the change in polymer structure **[24, 25]**.

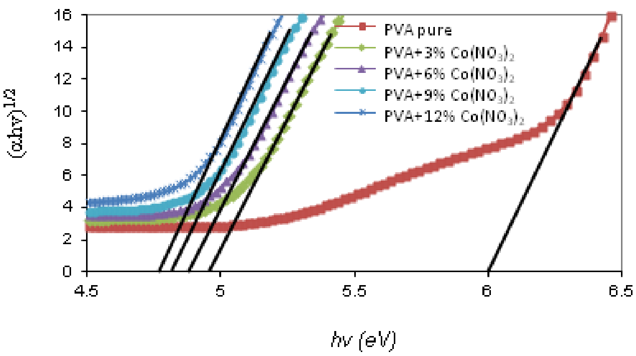

Fig. 6. Relation between the $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ for PVA:$Co(NO_3)_2$ solid polymer electrolyte films.

The dispersion behavior of the refractive index which is a significant factor in optical communication, and designing devices, has been analyzed using the single oscillator theory developed by Wemple-DiDomenico **[26]**. In terms of the dispersion energy parameter E_d which is a measure the average strength of inter band optical transitions, and single oscillator energy E_o is which usually considered as an average energy gap, the refractive index n at frequency can be written as **[27]**:

$$\frac{1}{n^2-1} = \frac{E_o}{E_d} - \frac{1}{E_d E_o}(h\nu)^2 \quad (5)$$

The values of oscillating parameters E_o and E_d can be determined from the intercept and slope of the linear part of $1/(n^2-1)$ plot versus $(h\nu)^2$ near the absorption edge, as shown in **Fig. 7**, the slope of the line represented $(-1/(E_o E_d))$, and (E_o/E_d) determined from intercept on the vertical axis. The obtained values of the dispersion parameters (E_o and E_d) are listed in **Table 2**.

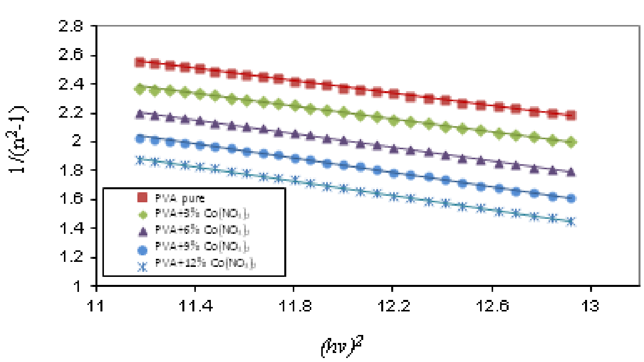

Fig. 7. Plots of $1/(n^2-1)$ verse $(h\nu)^2$ for different $Co(NO_3)_2$ concentration.

With the increase of salt content, the single-oscillator energy E_o decreases, while the dispersion energy E_d increased. Since the dispersion energy E_d, measures the average strength of inter-band optical transitions, we expect the increase of bound strength, i.e. formation of charge transfer complex between PVA molecules and the $Co(NO_3)_2$ salt, which lead to increases in degree of disorder.

Table 2. The oscillating parameters for PVA:$Co(NO_3)_2$ solid polymer electrolyte films.

$Co(NO_3)_2$ wt%	E_d (eV)	E_0 (eV)	M_{-1} $(eV)^2$	M_{-3} $(eV)^2$
0	0.9760	4.7880	0.2038	0.0089
3	0.9672	4.7210	0.2049	0.0092
6	0.9349	4.5130	0.2072	0.0102
9	0.9267	4.4224	0.2096	0.0107
12	0.9224	4.3194	0.2135	0.0114

Based on single-oscillator model the moment of optical spectra (M_{-1}) and (M_{-3}) can be determined from the following relations [**4, 28**]:

$$E_o = \sqrt{\frac{M_{-1}}{M_{-3}}} \quad ; \quad E_d = \sqrt{\frac{(M_{-1})^3}{M_{-3}}} \quad (6)$$

The obtained (M_{-1}) and (M_{-3}) are both increases as the $Co(NO_3)_2$ concentration increased as shown in **Table 2**. The optical moments are related to the macroscopic quantities like dielectric constants, effective number of valence electrons in the investigated material **[28, 29]**.

Conclusion

The results indicate that the concentration of cobalt nitrate $Co(NO_3)_2$ can effectively enhance the PVA optical properties. The presence of $Co(NO_3)_2$ leads to an increase in the absorption and to a decrease in the absorption edge as $Co(NO_3)_2$ concentration increases. The extinction coefficient, and refractive index values show dependence on $Co(NO_3)_2$ concentration where they increase with increase of $Co(NO_3)_2$ concentration. The optical energy band gaps of the solid polymer electrolytes decreased with increasing the Cobalt salt concentration. Finally the refractive index and consequently the related dispersion parameters of PVA:$Co(NO_3)_2$ solid polymer electrolyte films have been determined and explained using single oscillator model.

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