INFLUENCE OF BARIUM SALT ON OPTICAL BEHAVIOR OF PVA BASED SOLID POLYMER ELECTROLYTES

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Abstract

Solid polymer electrolyte films based on polyvinyl alcohol complexed with Barium nitrate salt at different weight percent were prepared using solution cast technique. The optical absorption coefficient was used to study the nature of electronic transitions between the valence and conduction bands. From the derivation of Tauc's relation it was found that the optical absorption is due to direct- and indirect allowed transitions. The reduction of energy band gap and increase of tail localized states was observed with increasing Barium nitrate content. The values of refractive index, extinction coefficient, the optical complex dielectric constant have been also calculated. The higher refractive index of solid polymer electrolytes was attributed to the higher molecular packing density compared to that of pure polymer. The increase of optical dielectric constant with increasing salt concentration indicates the presence of a higher density of states and increase in the amount of charge carrier concentration within the polymer electrolyte films.

Keywords: Polymer electrolyte, optical properties, energy band gap, dielectric constant

1. Introduction:

The ever-growing interest in polymer electrolytes arises from the possibility of their applications in various solid state electrochemical devices (Ramya, 2008), (Dias, 2000). A polymer electrolyte is defined as a solvent–free system whereby the ionically conducting pathway is prepared by dissolving metal salts in high molecular weight polymer matrix (Marzantowicz, 2007). Polyvinyl alcohol PVA is a polymer with a carbon chain backbone with hydroxyl groups attached to methane carbons, these hydroxyl groups are sources of hydrogen bonding and hence assist the formation of polymer composite (Saroj, 2012), (Abdullah, 2012). PVA is a polymer that has been studied intensively because of its excellent film forming ability and these films have high tensile strength, tear and chemical resistance, and good insulating material (Ravi, 2011), (Gautam , 2010), (Yang , 2009).

Solid polymer electrolyte have recently been the subject of extreme interest, currently intensive investigation has been reported on electrical and optical properties of PVA electrolytes (Huang , 1993), (Gimenez, 1996), (Krumova, 2000), (Rozra, 2012), because of their potential specific applications in variety of solid state electrochemical device such as super capacitor, solid-state batteries, sensors, photo-electrochemical solar cells, optical switching, and single electron transistors (Saroj, 2012), (Kumar, 2013).

The study of the optical absorption spectra in solid polymer electrolyte provides essential information about the band structure and the energy gap in the crystalline and non-crystalline materials. Analysis of the absorption spectra in the lower energy part gives information about atomic vibrations while the higher energy part of the spectrum gives knowledge about the electronic states in the atom (Deshmukh, 2008). Therefore an accurate measurement of optical constants is extremely important. Thus the main objective of present work is to achieve a deeper insight into optical characterizations of Polyvinyl alcohol PVA films incorporation with different concentration of Barium nitrate $Ba(NO_3)_2$ over a UV/VIS wavelength region.

2. Experimental detail:

Pure Polyvinyl alcohol PVA supplied by Sigma-Aldrich, and Barium nitrate $Ba(NO_3)_2$ with molecular weight 261.33 g/mol have been used as the raw materials in this study without further purification. The solid polymer electrolyte (SPE) films were prepared by the solution cast technique with distilled water as a solvent at 90 ^oC, and the solution is stirred well using magnetic stirrer for 3 hours to get a homogenous solution, and then different amount of $Ba(NO_3)_2$ (5, 10,15, and 20 wt%) was added under stirring. The homogenous solutions were caste in a plastic Petri dish and allowed to evaporate the solvent slowly in room temperature for two weeks. The films were transferred into a desiccators for continuous drying with blue silica gel. The prepared films were free from air bubbles and uniform thickness of the range from (0.17-0.21) mm. Table 1 shows the concentration of the prepared samples.

Table 1. Composition of PVA-$Ba(NO_3)_2$ solid polymer electrolytes films.

Sample designation	PVA (g)	$Ba(NO_3)_2$ (wt. %)	$Ba(NO_3)_2$ (g)	Thickness (cm)
SPE1	2	0	0	0.021
SPE2	2	5	0.105	0.016
SPE3	2	10	0.222	0.017
SPE4	2	15	0.353	0.017
SPE5	2	20	0.500	0.017

3. Optical absorption and energy gap:

The optical absorption spectra of prepared films are measured at room temperature, in the wavelength range (190-1100) nm, by double beam UV-vis spectrophotometer (Model: Lambda 25). The absorption coefficient is an important macroscopic quantity of the medium, which describes the relative decrease in the wave intensity with unit distance.

The optical absorption coefficient (α) which is a function of wavelength, has been obtained directly from the optical absorbance (A) against wavelength using the relation (Ballato, 2003), (Raja, 2003).

$$I = I_o \exp(-\alpha d) \qquad (1)$$

Hence;

$$\alpha = \frac{2.303}{d}\log\left(\frac{I_o}{I}\right) = \frac{2.303A}{d} \qquad (2)$$

where I_o and I are the intensities of incident and transmitted radiation beams respectively, and d is the film thickness.

Fig.1 shows the absorption spectra as a function of wavelength for prepared solid polymer electrolyte (SPE) films. It can be seen that in the visible region the absorbance is decreases exponentially, however at high wave length it is almost constant. The responsible change in the absorbance profile, and red shift in the exponential region of the spectrum, reveals the effect of the Barium nitrate content on the band structure of pure PVA.

Fig.2 shows the absorption coefficient as a function of photon energy ($h\nu$) for all SPE films. It is interesting to observe that the absorption coefficient (α) increases with increasing the photon energy ($h\nu$) as well as $Ba(NO_3)_2$ concentration. Extrapolation of linear portion of the curves has been used to determine the values of absorption edge which are listed in Table 2.

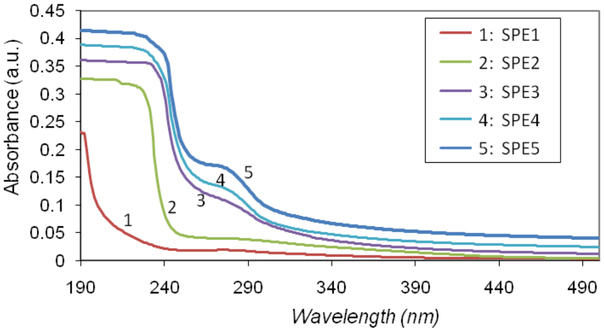

Fig.1. Optical absorption as a function of wavelength for PVA-Ba$(NO_3)_2$ solid polymer electrolyte films.

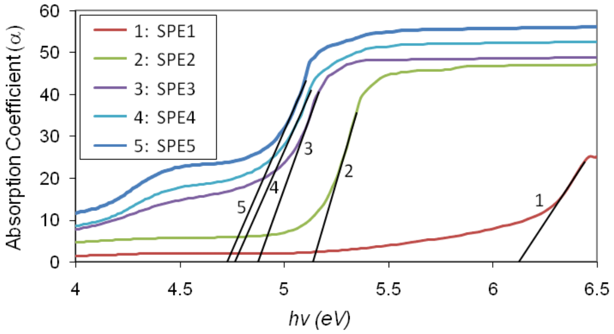

Fig.2. Variation of absorption coefficient (α) with photon energy (hv) in PVA-Ba$(NO_3)_2$ solid polymer electrolyte films.

The analysis of the absorption coefficient has been carried out to obtain the optical band gap (E_g), which is the most important parameter of organic and inorganic materials. The direct and non-direct optical energy gap of the films was measured by applying Tauc's relationship (Tauc, 1970), (Souri, 2011):

$$\alpha hv = C_o \left(hv - E_g\right)^{\gamma} \qquad (3)$$

where C_o is a constant related to the properties of the valance and conduction bands (Reicha, 2003), hv is the photon energy, and the value of γ determines the type of the absorption transition. For direct transitions γ=1/2, or 3/2, while for indirect ones γ=2, or 3, depending on whether they are allowed or forbidden, respectively (Khare, 2000). By taking the natural logarithm and the derivation, we can rearrange the Tauc's equation as (Muhammad, 2011):

$$\frac{d \ln(\alpha hv)}{d(hv)} = \frac{\gamma}{\left(hv - E_g\right)} \qquad (4)$$

According to equation (4), a peak in the curve of $\left(d\ln(\alpha h\nu)/d(h\nu)\right)$ versus $(h\nu)$ should be observed at about a point where $h\nu = E_g$. Fig.3 shows the plot of $\left(d\ln(\alpha h\nu)/d(h\nu)\right)$ versus $(h\nu)$ for all samples. The appeared peak at a particular energy value provides the approximate value of E_g. By utilizing this initial value of E_g, a graph of $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ was plotted to determine the value of γ. From the slope of the curves in Fig.4, γ was determined to be equal to (0.8). Interestingly, this estimation provides evidence for the presence of a direct gap (γ=0.5), and also indirect gap (γ=2), between the energy bands in these electrolyte films.

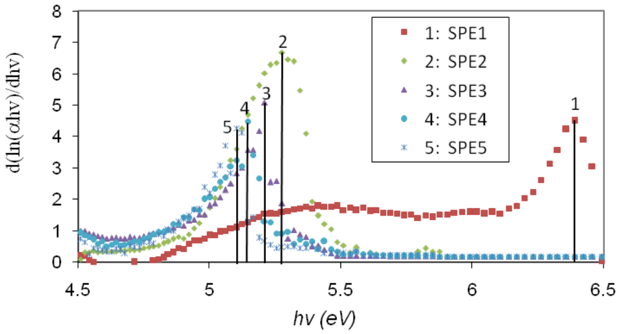

Fig.3. Plot of $\left(d\ln(\alpha h\nu)/d(h\nu)\right)$ versus $(h\nu)$, to estimate the value of E_g, for PVA-$Ba(NO_3)_2$ solid polymer electrolyte films.

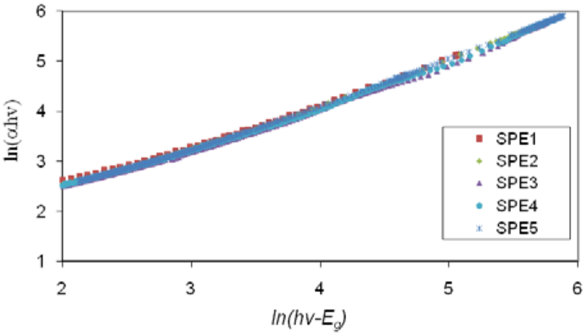

Fig.4. Plot of $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ to determine the value of γ.

In order to determine the precise value of the optical direct- and indirect energy gaps of the investigated films, graphs of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ were plotted for all films as shown in Fig.5. It is to be noticed that the curves are characterized by the presence of an exponentially decaying tail at low photon energy. The values of allowed direct- and indirect- optical band gap E_g have been calculated from the extrapolation of the linear portion of the graph to the photon energy axis. The plot shows straight lines with some deviations from linearity at the lower photon energy which possibly due to imperfections in the material (Redfield, 1967), but this region of the curve is still not fully understood.

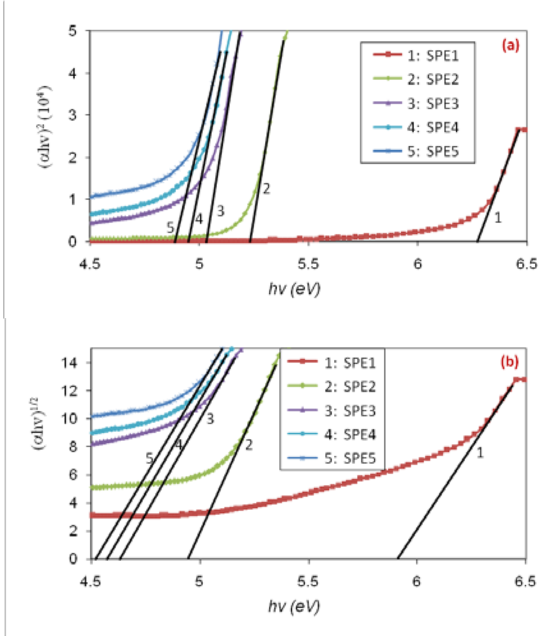

Fig.5. Relation between the a: $(\alpha h\nu)^2$ and b: $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ for PVA-Ba$(NO_3)_2$ solid polymer electrolyte films.

The calculated values of E_g for all SPE samples are given in Table 2. It is evident that the values of the optical band gap E_g decreases upon the addition of Barium nitrate salt. These results indicate the fact that multiple states was introduced between the valence and conduction bands, i.e. an increase in the density of defect states. Therefore the variation of optical band gap could be discussed on the basis of density of state model proposed by Mott and Davis (Mott, 1979). Polymers films always contain a high concentration of unsaturated bonds or defects, these defects are responsible for the presence of localized states in the amorphous band gap. Also the decrease in optical energy gap E_g on adding salt, may be explained on the basis of the fact that the incorporation of small amounts of Ba$(NO_3)_2$ forms charge transfer complexes in the host polymer matrix (Raja, 2003), (Devi, 2002). These charge transfer complexes increase the optical conductivity by providing additional charges, this results in a decrease of the optical energy gap.

The transition occurs between extended states of band and localized states of tail of other band and absorption coefficient (α) is given by Urbach relation (Urbach, 1953):

$$\alpha(v) = \alpha_o \exp\left(\frac{hv}{E_e}\right) \qquad (5)$$

where α_o is a constant and E_e is width of tail of localized states in band gap that associated with amorphous nature of materials. In general largest value of E_e, related to greater in structural disorder.

Urbach plot is used to calculate the width tail of localized states in the band gape E_e, and are listed in Table 2. It is clear that values of band tail increase with increasing the $Ba(NO_3)_2$ concentration in solid polymer electrolyte.

Table 2. Absorption Edge, Optical band gap, and Tail width, for PVA-$Ba(NO_3)_2$ films.

Samples	Absorption edge (eV)	Direct energy gap (eV)	Indirect energy gap (eV)	Tail width (eV)
SPE1	6.125	6.273	5.915	0.1726
SPE2	5.140	5.223	4.943	0.1801
SPE3	4.875	5.029	4.638	0.3731
SPE4	4.760	4.948	4.573	0.3850
SPE5	4.725	4.880	4.521	0.3924

4. The optical constants:

The most important optical properties are the refractive index *n* and the extinction coefficient *k*, which are generally called optical constants, are calculated using the fundamental relations of photon transmittance *T* and absorbance *A*. The complex refractive index define as (Ezema, 2007):

$$N^* = n - ik \qquad (6)$$

The optical behavior of the material has been utilized to determine its extinction coefficient (*k*), which measures the attenuation of the wave amplitude with the propagation distance inside the medium. The extinction coefficient was calculated for the studied films by its correlation with the absorption coefficient α and wavelength λ using:

$$k = \alpha\lambda / 4\pi \qquad (7)$$

The refractive index as a function of wavelength can be determined from the reflection coefficient data *R* and the extinction coefficient *k* using equation:

$$n = \left(\frac{4R}{(1-R)^2} - k^2\right)^{(1/2)} - \frac{(R+1)}{(R-1)} \qquad (8)$$

The extinction coefficient *k* over the exponential absorption region for all solid polymer electrolyte samples are shown in Fig.6. The low value of *k* at long wavelengths, indicating that the films are highly transparent, while at low wavelength (high photon energy) the extinction coefficient increases to a maximum value, due to the predominance of the absorption behavior. It is also evident from Fig.6 that *k* increases with $Ba(NO_3)_2$ concentration in PVA films. The higher *k* value for solid polymer electrolyte indicates that the films dissipate more photonic energy than those of pure PVA when exposed to electromagnetic radiation (Muhammad, 2011).

For the same region, the refractive index values have been calculated from a combination of reflectance and absorbance measurements at normal incidence. The variations of refractive index *n* with wavelength are shown in Fig.7. It is clear from this figure, that the refractive index *n* is decrease with increasing wavelength; while the increase with salt concentration can be seen. At higher wavelength, the films showed non-dispersive behavior and *n* tended to be constant. The higher refraction coefficient of the polymer electrolyte films compared to that of the pure PVA may be attributed to the differences in their molecular packing density. A high refractive index is preferred for some specific optoelectronic devices, such as organic solar cell (Muhammad, 2011).

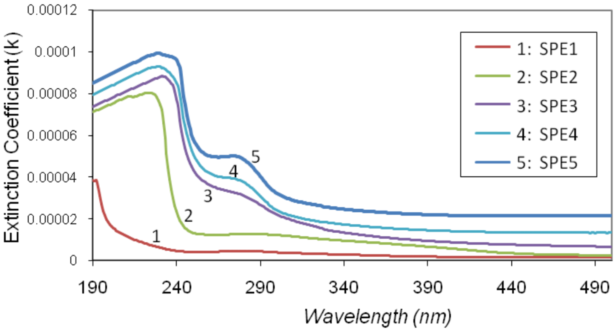

Fig.6. Extinction coefficient *k* as a function of wavelength for PVA-$Ba(NO_3)_2$ solid polymer electrolyte films.

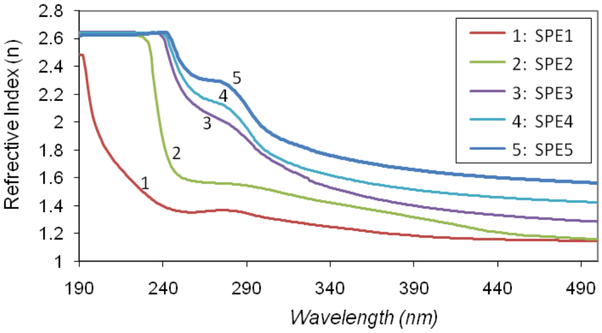

Fig.7. Refractive index as a function of wavelength for PVA-$Ba(NO_3)_2$ solid polymer electrolyte films.

5. Complex optical dielectric constant:

The complex dielectric constant for a wavelength range between ultraviolet and near infrared, is important criteria for the selection of fabricated films for various application (Ghanipour, 2013). The real part of dielectric constant is one of the fundamental properties of a material, because it is related to the polarizability inside the material.

The complex dielectric constant is a materials property depending on wavelength, temperature, conductivity, size, shape, and spatial arrangement of the constituents (the filler in the matrix), (Chandrakala, 2013), (Brosseau, 2000). The complex dielectric constant is described in the form;

$$\varepsilon^* = \varepsilon_r - i\varepsilon_i \qquad (9)$$

where, the real part ε_r is the dielectric constant which is related to the energy stored in the material, and imaginary part ε_i is dielectric loss which is proportional to the energy dissipate in material (Aziz, 2014). For practical purposes, the dielectric constant plays an important role in designing optical devices, especially in the field of optical communication (Muhammad, 2011).

The imaginary part of dielectric constant ε_i is always greater than zero and is usually much smaller than ε_r. The real and imaginary parts of dielectric constant (ε_r and ε_i respectively) were calculated from the obtained values of *n* and *k* using the following relations (Ezema, 2007):

$$\varepsilon_r = n^2 - k^2 \qquad (10)$$

$$\varepsilon_i = 2nk \qquad (11)$$

The behavior of both dielectric constant ε_r, and the dielectric loss factor ε_i versus wavelength are shown in Figs(8, 9). The general trend for all composition is decreases the dielectric loss factor in the investigated wavelength region, while there are a significant increase in dielectric constant with increasing the Barium nitrate content, and finally reaches nearly a constant value in the higher wavelength.

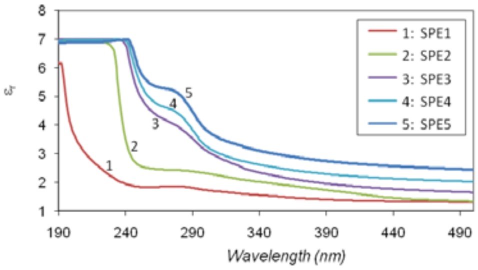

Fig.8. Real part of dielectric constant ε_r as a function of wavelength for PVA-Ba$(NO_3)_2$ solid polymer electrolyte films.

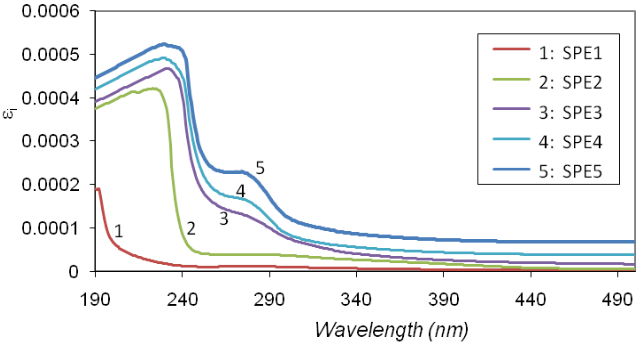

Fig.9. Imaginary part of dielectric constant ε_i as a function of wavelength for PVA-$Ba(NO_3)_2$ solid polymer electrolyte films.

It can be seen from Figures 8 & 9, that (ε_r) and (ε_i) increases with increasing salt concentration. The increase in the value of dielectric constant (ε_r) can be ascribed to the increase of electrical polarization due to contribution of salt concentration in the sample i.e., the increase in the dielectric constant represents a fractional increase in charges within the polymer electrolyte, and hence an increase in polarization as well as optical conductivity (Abdullah, 2013), as shown in Fig.10.

The observed effect of Barium nitrate on the optical conductivity and conduction behavior of PVA films can be explained on the basis of charge transfer complex formation.

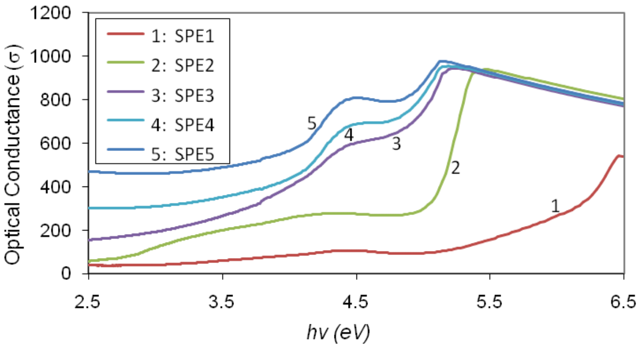

Fig.10. Optical conductivity σ as a function of photon energy ($h\nu$), for PVA-$Ba(NO_3)_2$ solid polymer electrolyte films.

6. Conclusions:

PVA/$Ba(NO_3)_2$ solid electrolyte films were prepared by casting of aqueous solutions with varying $Ba(NO_3)_2$ content. The influence of Barium Nitrate $Ba(NO_3)_2$ salt, on the optical properties of Polyvinyl Alcohol (PVA) films were investigated at room temperature. The derivation of Tauc's relation shows that the optical absorption is due to direct- and indirect-allowed transition. The decrease trend of the optical band gap with increase in $Ba(NO_3)_2$ concentration was explained in terms of electronegativity difference between the elements involved in making the polymer electrolyte, and the increase in the amount of disorder in the polymer matrix. The value of refractive indices, and dielectric constant were tended to be more stability at high values by increasing the Barium nitrate content in PVA matrix, through the investigated range. Due to the large absorption coefficient and compositional dependence of absorption these materials may be suitable for optical memory devices.

Acknowledgement:

The author gratefully acknowledge University of Sulaimani, for financial support for this research work.

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