STUDIES ON OPTICAL PROPERTIES OF PVA BASED COMPLEX POLYMER ELECTROLYTE

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ABSTRACT
Solid Polymer Electrolytes (SPE) based on polymer (PVA) Polyvinyl Alcohol is doped with Sodium Nitrate (NaNO₃), a membrane is prepared by solution casting method. Here outcomes of the optical transmission, optical absorption, optical absorption coefficient, optical refractive index, optical extinction coefficient, direct energy band gaps, indirect energy bandgap, absorption edge, estimated band gap, optical conductance studies are given. Optical properties are taken by UV-visible (Ultraviolet-visible) Absorption spectroscopy wavelength within the range of 200 nm to 800 nm. optical transmittance wavelength is 200 nm. Energy band gap changes from 5.6eV to 4.9eV. Indirect, direct and absorption edge is high for polymer pure PVA. By increasing the salt concentration to the polymer the above-mentioned parameters are decreasing gradually. For the concentration of 70% PVA: 30% NaNO₃ has a low value of direct and indirect energy bandgap.

Keywords: Solid Polymer electrolyte film, absorption, transmittance, refractive index, absorption coefficient, energy band gap, optical conductance.

INTRODUCTION
Material research aims to prepare new material properties with an application to identify the chemical, physical processes that establish the properties. In this process, the material is combining with the polymers in different concentrations.¹ The given Polymer electrolytes (PE) properties are generally analyzed for fundamental purposes and useful applications. Polymer-based electrolytes are not only combining the useful properties of polymers and dopant, but it also shows various new-found properties.² The polymer properties can be enhanced and regulated substantially by combining a proper dopant.³ Polyvinyl Alcohol, which is prepared from polyvinyl acetate. It is very simply degradable in biological organisms and completely soluble in inorganic liquids such as water and ammonia, etc.⁴ PVA is a semi-synthetic polymer that is used worldwide during the 20th century. When PVA is doped with an inorganic salt, the dopant interacts with the O-H group of PVA either in the crystalline phase or the amorphous phase after that changes its properties.¹ It is used in the medical, industrial, commercial, and food packing sectors. It is utilized to generate a lot of products, like resins, surgical threads, and food-related packing materials.⁵,⁶ PVA is one of the biodegradable type materials and is used in textile sizing and paper coating.⁷ This type of polymer is usually used by mixing other polymers then it is used for several drug and chemical industries.⁸,⁹

EXPERIMENTAL
PVA (polyvinyl alcohol) is bought from Sigma Aldrich chemicals. Based on biopolymer electrolytes films are doped with pure sodium nitrate (NaNO₃) are prepared in various ratios (90:10) (80:20), (70:30) and (60:40) by solution casting method. Various concentrations of PVA and NaNO₃ are combined with double distilled water as a solvent. The blend of the solution is stirred for 12 hours by keeping the temperature
60°C. Then the homogeneous solution is formed, and it is poured into polypropylene dishes and kept in a vacuum chamber at 60°C. Water in this homogeneous solution is evaporated slowly under the vacuum drying process. After 24 hours the partial transparent films are formed. These films are taken from polypropylene dishes and positioned in a vacuum desiccator up to the next test. The dried polymer films are characterized by the JASCO (V-670) UV-VIS-NIR Photo Spectrometer. The effect of solvent in the solid polymer electrolyte, optical parameters, and optical characterizations are studied from the UV-Visible spectrometer at normal temperature.

**RESULTS AND DISCUSSION**

**Absorption and Absorption Coefficient Studies**

UV absorption spectra are obtained under room temperature. UV Spectrometer is used to determine the absorption spectra of the sample wavelength range of 200 nm -900 nm. The absorption optical studies are applied to examine the optic transition and structure of the film sample. Here in this spectrum, the absorption shows between 260 nm-340 nm. The pure and different doped concentrations of NaNO₃ are represented in given Fig.-1. In polymers, several electron transitions may occur. The absorption spectra show a strong growth absorption at a wavelength near to absorption edge. Band structure, absorption edge and optical energy band gaps are determined by absorption studies. No absorption is seen for pure polymer but by increasing doping concentration the absorption is increasing gradually. The absorption increases up to PVA 70%: NaNO₃ 30% arrived at 280 nm. In this research at this concentration, the change in the band structure and coefficient of absorption is high. Again this absorption is decreased for PVA 60%: NaNO₃ 40% concentration. The optical absorption can be measured by a coefficient of absorption (α.), which is also named as a power fraction of material absorption.

**Fig.-1: PVA and NaNO₃ Various wt.% Ratios of Optical Absorption Spectra**

**Fig.-2: PVA and NaNO₃ Various wt.% Ratios of Optical Absorption Coefficient Spectra**
The coefficient of optical absorption can be analyzed by using the given formula.

$$\alpha = \frac{2.303}{t} \times A$$

Where ‘A’ is data from optical absorption, ‘d’ is the thickness of a given sample. Here Fig.-2 signifies the coefficient absorption vs. the energy of photon for pure and doped concentrations. It is cleared that lower photon energy is absorbed for PVA 70%: NaNO$_3$ 30% concentration and the photon energy is shifted towards lower energy. Photon energy range from 5.25 eV- 4.45 eV represents a reduction of band energy gaps of doped samples.

**Transmittance**

Transmission spectra for PVA pure composites with several ratios of NaNO$_3$ are calculated in the wavelength range (200 nm–800 nm) is indicated in Fig.-3. It is detected that pure PVA is a high transmission and decreases by rising the dopant concentration of NaNO$_3$. The transmission decreases in PVA samples by increasing NaNO$_3$ concentration leads to reduction. A small transmission is noticed at about 293 nm. If optical absorption is more and the optical transmission is at a low level. Due to this, its occurred low optical transmission for PVA 70%: 30% NaNO$_3$ concentration. The photon energy is perfectly observed by the films then it transmits a very low amount of energy.

**Refractive Index**

Optical properties of optical extinction coefficient and optical refractive index can produce an optical constant of the material. Specific optoelectronics applications relate to this refractive index, atomic structure, electrical properties, and electronic bond structure. The given figure 4 indicates the material refractive index for pure polymer PVA and various salt concentrations of NaNO$_3$. The optical refractive
index is calculated from optical reflectance ‘R’. This is the very basic property of the material and it can show dispersion at all wavelengths of light.

The refractive index of an optical material indicates electronic and molecular polarization of the electromagnetic field of light. These plots showing the change in the refractive index. The refractive index nearly minor and constant for all samples up to 4 eV, it can increase by increasing photon energy. Then after again they become constant. Normally by increasing doping concentration, the refractive index is also changed by changing the dopant concentration to the polymer. Finally, the optical refractive index is high for 70%PVA: 30% NaNO\textsubscript{3}. Then subsequently, electronic and molecular polarization and dispersion are very high and wavelength is the lower value.

The reflectance in terms of optical refractive index is given by

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2}$$

And

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$$

Here optical reflectance is ‘R’, ‘K’ is a coefficient of extinction, ‘n’ is the refractive index of the sample.
value. The optical absorption and transmission take place due to the orientation and polarization of the particles. The refractive index is changed by changing the orientation of the particles. Finally, these parameters affect the material conductivity. 70% PVA: 30% NaNO\textsubscript{3} concentration achieved the maximum conductivity due to optical absorption and refractive index. The optical conductance value is obtained from coefficient absorption, optical refractive index, and speed (velocity) of the light passing through the pure and doped concentration sample material. The expression for optical conductance is represented by.

$$\sigma = \frac{\text{a} \cdot \text{n} \cdot \text{c}}{4\pi}$$

Here ‘a’ is the coefficient of absorption, ‘n’ is the refractive index value for the sample, ‘c’ is the speed of light.

**Extinction Coefficient (K)**

The extinction coefficient is represented as an imaginary component of the optical refractive index. In the given figure 6 extinction coefficient spectra versus wavelength behaviour are shown for different doped concentrations polymer PVA and salt NaNO\textsubscript{3}. The variation of the extinction coefficient with wavelength shows such interaction between medium and photon energy. The small fraction of electromagnetic energy loss is known as coefficient extinction. Optical absorption is an effect on the extinction coefficient. Due to this reason only the extinction coefficient value is maximum for 70%PVA: 30% NaNO\textsubscript{3} concentration. In the given graph extinction coefficient is increased by raising the wavelength and doping concentration. Then its value is improved up to 70%PVA: 30% NaNO\textsubscript{3}. Again by increasing salt doping concentration, it starts to decrease.

We can calculate the optical excitation coefficient from the formula:

$$K = \frac{\alpha \lambda}{4\pi}$$

Here ‘\lambda’ represents wavelength, ‘\alpha’ is coefficient absorption. With the help of this excitation, the coefficient can calculate real, imaginary, and complex parts.

**Energy Band Gap**

Data from the graph can be achieved from the study of optical absorption. Mostly, the bandgap is dividing semiconductors and insulators into two major parts, they are direct energy bandgap and indirect energy bandgap materials. Valence and conduction bands both are exhibited a very less (zero) crystal momentum indirect bandgap. But in the indirect bandgap, the conduction band doesn’t agree to crystal zero momentum and shift of the phonon energy. Shalliday and Davis had explained both the direct and indirect bandgap that occur near the basic edge of the band can be described from the plots (\(\alpha h\upsilon\))\textsuperscript{2} & (\(\alpha h\upsilon\))\textsuperscript{1/2} Vs. photon energy (\(h\upsilon\)). Optical absorption edge, absorption, transmission, and electron shift from valency to the conduction band is determined by wavelength or photon energy (\(h\upsilon\)).

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The energy bandgap is determined from the graph of \((\alpha h\nu)^2\) vs. \((h\nu)\) photon energy.\(^{23}\) The acquired values of energy band gaps are represented in Table-1. The energy bandgap values attained from Fig.-7 and Fig.-8, are the plot representing forbidden indirect transition \((x = \frac{1}{2})\) and allowed indirect transition \((x = \frac{2}{3})\) respectively. The results of the energy bandgap for direct electronic transition \((x = 2)\) are representing in Fig.-9. Here \((\alpha h\nu)^2\) vs. photon energy \(\nu\) generates the direct bandgap value. In this present research work, a bandgap of 5.6 eV is obtained for pure PVA. In this UV-visible spectrum. The absorbance is decreased by increasing the wavelength.

A decrease in absorption shows the identification of an optical bandgap of the material.\(^{24}\) The absorption edge, direct bandgap, indirect allowed and forbidden gap are decreased by increasing the doping concentrations are given in Table-1. For all the above-mentioned parameters band gaps are minimum for the concentration 70\% PVA: 30\% NaNO3 and from here again band gaps are increased by increasing the doping concentrations. Here in the given data, \(E_g\) decreases by increasing the dopant salt percentage.\(^{22}\)

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**Fig.-7:** PVA and NaNO3 Various wt.% Ratios of Forbidden Indirect Energy Bandgap Spectra

**Fig.-8:** PVA and NaNO3 Various wt.% Ratios of allowed Indirect Energy Bandgap Spectra

**Fig.-9:** PVA and NaNO3 Various wt.% Ratios of Direct Energy Bandgap Spectra
Table-1: Optical Parameters for Pure PVA and PVA: NaNO₃ Doped Concentrations

| Composition     | Absorption edge (eV) | Refractive index | Forbidden indirect band gap (eV) | allowed indirect band gap (eV) | Direct band gap (eV) |
|-----------------|----------------------|-----------------|---------------------------------|-------------------------------|---------------------|
| 100% PVA: 0% NaNO₃ | 5.25                 | 0.52            | 5.03                            | 5.51                          | 5.6                 |
| 90% PVA: 10% NaNO₃ | 4.93                 | 1.06            | 4.84                            | 5.07                          | 5.11                |
| 80% PVA: 20% NaNO₃ | 4.74                 | 1.33            | 4.67                            | 5.02                          | 5.05                |
| 70% PVA: 30% NaNO₃ | 4.4                  | 2.23            | 4.24                            | 4.79                          | 4.93                |
| 60% PVA: 40% NaNO₃ | 4.6                  | 1.5             | 4.52                            | 4.96                          | 4.98                |

CONCLUSION

In this present research, Solid Polymer Electrolyte membranes (SPE) are made by different concentrations (PVA: NaNO₃) (pure PVA, 90:10, 80:20, 70:30, 60:40 wt%) using solution casting technique. The study and evaluation of optical parameters for doped NaNO₃ with PVA are observed and the optical studies of the film are explained and identified that the material optical refractive index is increased by increasing of doping content of NaNO₃ into the PVA. An optical refractive index is changing by optical conductance of material and parallely the density of the electrolyte is enhanced by an increase in the concentration of NaNO₃. By comparing the films, it is clarified that electrical energy disappears in highly doped composition than less doped composition materials. The optical conductivity is reduced gradually by decreasing photon energy \( h\nu \) and finally it becomes constant value gradually. The result suggested that the drop in optical sample conductivity is caused by reducing the energy of photon \( h\nu \). The reduction in energy band gap by doping PVA with wt% NaNO₃ is observed. Finally, it is observed that by raising the dopant content NaNO₃ to polymer PVA then optical conductivity, optical edge of absorption, a direct band of energy indirect band gaps decrease as well as the refractive index increased up to certain concentration levels.

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