

Effect of Doping Fe³⁺ Ions on Optical Studies of PVP Polymer Electrolytes

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Abstract: Films of polymer electrolytes based on Polyvinyl Pyrrolidone (PVP) embedded with different concentrations (1, 2, 3, 4 and 5 mol%) of Fe³⁺ ions were prepared by a solution casting technique. Fourier transform infrared spectroscopy (FTIR) and UV - Vis spectroscopy confirm the complexation between Fe³⁺ ions and pure PVP polymer electrolyte. UV - Visible spectral absorption in the 200 - 800 nm wavelength range were used to calculate the direct and indirect optical energy band gaps and optical absorption edge. Both the optical band gaps showed decreasing trend with the increase in Fe³⁺ ion concentration. FTIR studies on pure and Fe³⁺ doped PVP polymer films resulted in the vibrational changes that occur due to the effect of dopant Fe³⁺ ions in the polymer. On the whole, Fe³⁺ as a dopant, is suggested as a good choice to improve the electrical conductivity of PVP polymer electrolytes.

Keywords: Polymer electrolytes, PVP, FTIR, UV - Visible spectroscopy.

1. Introduction

Solid polymer electrolyte research has focused on improving electrical and optical applications for their commercial use in the field of solid state electrochemical devices. Polymeric electrolytes now play a key role in technical applications such as computers, communication devices, industrial controls, electric vehicles, spacecraft, laboratory equipment, etc. [1 - 3]. Further, they have a straight need in the portable electronic market like solar cells, pacemakers, remote controls and toys. Solid polymer electrolytes have advantages in terms of shape, geometry, strength and electrode - electrode contact capability.

Among the polymers, Polyvinyl Pyrrolidone (PVP) attracts the most attention because it has good electronic properties and the low cost for its infinite abundance. Further, it can be synthesized by chemical or electrochemical methods, to produce a powder or thin film. Compared to other semi - crystalline polymers, PVP is an amorphous polymer with low scattering loss, making it an ideal polymer for ion doping materials for optical applications [4]. The chemical structure of PVP is shown in Figure 1. The carbonyl group (C=O) present in the PVP side chain plays an important role in the formation of the variety of complexes with various inorganic salts. It interacts well with several types of ions and enhances the number of free ions in the system. Another advantage of PVP is that it can be thermally cross - linked [5], which results in exceptional thermal stability and mechanical strength. Furthermore, PVP is highly soluble in polar solvent like water [6].

The combination of polymers with transition metal ions is very popular with excellent performance. Polymers with the incorporation of Mn, Ni, Fe, Co, Cr exhibit the enhanced magnetic spin order, high conductivity, controllable morphologies and high dispersive ability to present the agglomeration of the active catalyst. The optical behavior and band gap values also change the partially filled d - electron shells of the magnetic elements. Ferric chloride, FeCl₃, with trivalent iron ions of 3d⁵ has been selected as a

filler because of its magnificent optical and electrical properties. Among the transition metal oxides, Fe³⁺ ion is of great interest to modern emerging technology, i. e. applications in micro electronics, solid state ionics and optoelectronics [7, 8]. However, to the best of our knowledge, there has been no study on Fe³⁺ ions doped PVP films. Hence, the authors have aimed at investigating the effect of doping Fe³⁺ ions on optical properties of PVP polymer electrolyte films.

2. Experimental details

The films of Polyvinyl Pyrrolidone (S. D. Fine – chemical Ltd., India) based polymer solution doped with FeCl₃ (MOLY CHEM Ltd, India) were prepared by using solution casting technique, in which double distilled water used as a solvent. For this purpose, a stock solution of 5% of PVP and solutions of various FeCl₃ concentrations (1, 2, 3, 4 and 5 mol %) were prepared separately. Both solutions were separately stirred at room temperature using a magnetic stirrer for an hour to obtain transparent solutions. The aqueous solutions of pure PVP and one of the various concentrations of FeCl₃ were then mixed and continuously stirred magnetically for 10 - 12 hours to get a homogeneous mixture and then poured on to cleaned Petri - dishes. The resultant solution was slowly evaporated at room temperature to obtain the polymer film and the resulting film was kept in a vacuum desiccator. The absorption spectra of pure and Fe³⁺ doped PVP polymer electrolytes were measured on a JASCO UV – VIS – NIR spectrophotometer (model – V.700, Japan Spectroscopic Co., Japan) in the range of 200 - 800 nm. The fundamental vibrations of the polymer electrolytes were studied with an FTIR spectrometer (Perkin - Elmer Co., USA, model - 1605) in the wave number range of 500 - 4000 cm⁻¹. The electrical properties of the as prepared polymer electrolyte films at room temperature were studied by using Hioki 3532 - 50 LCR Hi - Tester (Hioki USA corp., New Jersey, USA) over frequency range 42 Hz - 5 MHz.

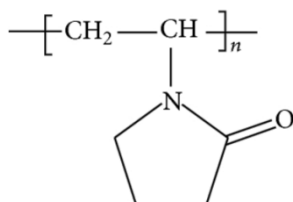


Figure 1: The Chemical structure of PVP

3. Results and Discussion

3.1 FTIR analysis

FTIR is a dominant technique used to distinguish the nature of bonding and the presence of different functional groups in a sample by monitoring the vibrational bands, which are basically an identification for different molecules [9]. The FTIR spectra of the pure and the Fe^{3+} (1, 2, 3, 4 and 5 mol %) doped PVP polymer films were recorded in the transmittance mode which are shown in Figure 2. The observed FTIR band positions and their peak assignments of pure and different concentrations of (1, 2, 3, 4 and 5 mol %) Fe^{3+} ions doped PVP polymer electrolyte films are given in Table 1. From the Figure, it is observed that a broad and very strong band observed at $2857 - 3652 \text{ cm}^{-1}$ which is resulting from the O–H stretching vibrations, is an indicator of the presence of the OH hydroxyl groups in the pure PVP. The broadness of O–H stretching band reflects the existence of non - bonded OH. For doped films, this band position has changed to $2887 - 3666$, $2841 - 3666$, $2863 - 3643$, $2899 - 3631$ and $2899 - 3643$ in the 1, 2, 3, 4 and 5 mol% Fe^{3+} -complexed PVP films respectively. The peaks appearing at 2566 , 2317 and 2140 cm^{-1} indicates the C–H stretching, CH_2 bending and C=O stretching. With increasing dopant concentration, the band positions are changed and the intensity of these bands in PVP is found to decrease. The spectral region $1012 - 896 \text{ cm}^{-1}$ consists of a mixture of CH_2 rocking and C–O stretching vibrational modes. The vibrational band observed at 1012 cm^{-1} and 931 cm^{-1} are attributed to C–O stretching vibrations of PVP. In addition to that, one small absorption peak was observed at 896 cm^{-1} which is assigned to CH_2 rocking in PVP. The intensity of the three bands at 1012 , 931 and 896 cm^{-1} decrease and their positions shifted to lower wavenumbers with increasing salt concentration. It leads the distorted helical conformation or stretched with the increase in salt concentration [10].

With the increase in Fe^{3+} ion concentration, the intensity of most of the bands showed a decreasing trend. These observations indicate the Fe^{3+} ion has same interactions with the polymer electrolyte. The interactions of the oxygen atom with the Fe^{3+} might assist the cations to transfer through the polymer chain [11]. These interactions play an important role in ion conduction behavior in the complex polymer electrolytes.

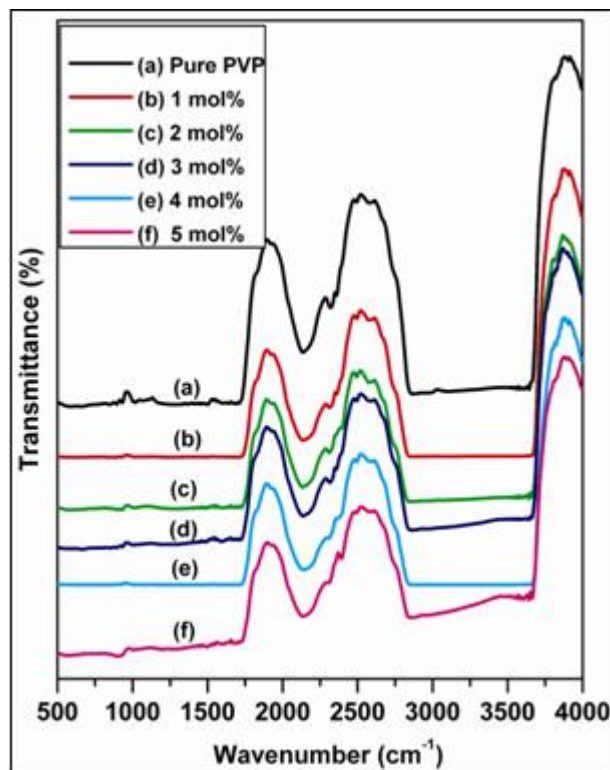


Figure 2: FTIR spectra of the Pure and the Fe^{3+} (1, 2, 3, 4, and 5 mol %) doped PVP polymer electrolyte films.

Table 1: FTIR Peak assignment of the pure and the Fe^{3+} doped PVP polymer electrolytes

Wave number (cm^{-1})	Band assignment
3631 - 2857	O–H stretching.
2566	C–C stretching.
2317	CH_2 bending
2140	C=O stretching
1012	C–O stretching.
931	C–O stretching
896	CH_2 rocking in PVP.

3.2 Optical absorption studies

The optical absorption spectra of the pure and the Fe^{3+} (1, 2, 3, 4 and 5 mol %) doped PVP polymer films were studied at room temperature in the wavelength range $200 - 800 \text{ nm}$, which are depicted in Figure 3. Optical band gap (E_g) and the position of the fundamental band edge were calculated from the optical absorption studies. The absorption coefficient (α) can be obtained from the spectra by using equation (1).

$$\alpha = 2.303 \times A/d \quad (1)$$

Where A is the absorption coefficient and d is the thickness of the film. Figure 4 shows the variation in the absorption coefficient with incident photon energy for undoped as well as Fe^{3+} (1, 2, 3, 4 and 5 mol %) doped PVP polymer electrolytes. In the present work, the absorption edge determined for the pure PVP polymer electrolyte is around 3.94 eV , where as for doped films it was found that the absorption edge shifted from 3.84 to 3.52 eV and are given in Table 2. When a direct band gap exists the absorption coefficient has the following dependence on the energy of the incident photon ($h\nu$) [12, 13].

$$\alpha h\nu = c (h\nu - E_g)^{1/2} \quad (2)$$

Where E_g is the band gap energy, C is a constant dependent on specimen structure, ν is the frequency of incident light, and h is the Planck's constant.

A plot of $(\alpha h\nu)^2$ vs $h\nu$ for pure and Fe^{3+} (1, 2, 3, 4 and 5 mol %) doped PVP polymer electrolytes are shown in Figure 5. The intercept on the energy axis by extrapolating the linear portion of the curve to the $h\nu$ axis (the x - axis) gives the the direct band gap value. For the pure PVP polymer electrolyte, the direct band gap determined is 3.76 eV where as for doped films the value varies from 3.72 eV to 3.03 eV, which are given in Table 2.

For an indirect transitions, an interaction with the lattice vibrations takes place; thus the wave vector of the momentum change will be taken or given by phonons. In other words, if the minimum of the conduction band is from the maximum of the valence band in the K - Space, a direct optical transition from the upper end of the valence band to the lower end of the conduction band is forbidden. For indirect transitions that require a phonon assistance, the absorption coefficient depends on the energy of the phonon,

$$\alpha h\nu = A (h\nu - E_g + E_p)^2 + B (h\nu - E_g - E_p)^2 \quad (3)$$

Where E_p is the phonon energy associated with the transition and A, B are constants depending on the structure of the band.

The indirect band gaps were obtained from the plots of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ (Figure6). For the pure PVP polymer film the indirect band gap is 3.48 eV, while for the doped films the value varies from 3.35 to 2.41 eV. From Table 2, it is clear that the edge of the band, the direct band gap and indirect band gap values show a decrease with the increase of the dopant. Similar behavior was observed [for the PEO/PVP blended with gold nano particles and the PVA/PVP blended with methylene blue [12, 13]]. The decreasing trend in optical band gaps is due to the fact that the charge - transfer complexes (CTCS) are present in the host lattice [14], Which are due to the formation of coordination bonds between Fe^{3+} and PVP polymer molecules, which leads to increase in ionic conductivity [15, 16].

Table 2: Optical energy band gap values of the Pure and the Fe^{3+} ions doped PVP Polymer electrolyte films

Concentration (mol%) Fe^{3+} : PVP	Direct band gap (eV)	Indirect band gap (eV)	Absorption edge (eV)
Pure PVP	3.76	3.48	3.94
1	3.72	3.35	3.84
2	3.64	3.21	3.74
3	3.52	2.84	3.65
4	3.41	2.65	3.57
5	3.03	2.41	3.52

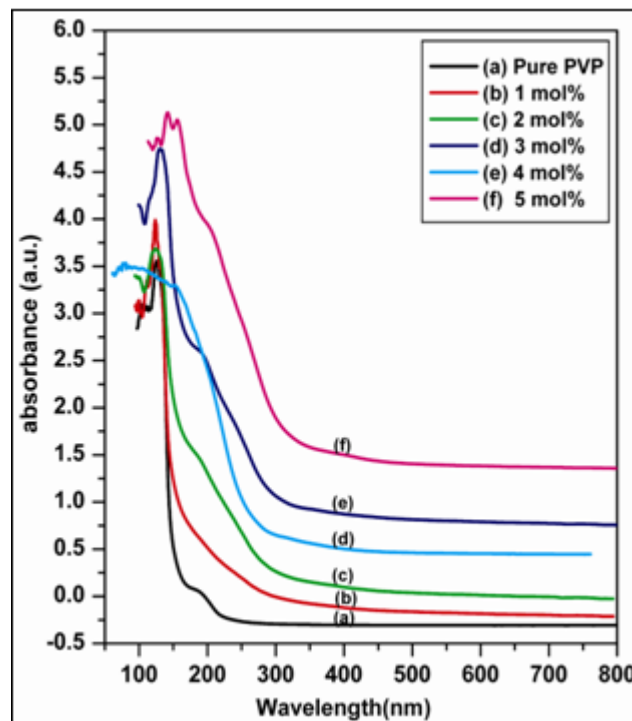


Figure 3: Absorption spectra of the Pure and the Fe^{3+} (1, 2, 3, 4, and 5 mol%) doped PVP Polymer electrolyte films.

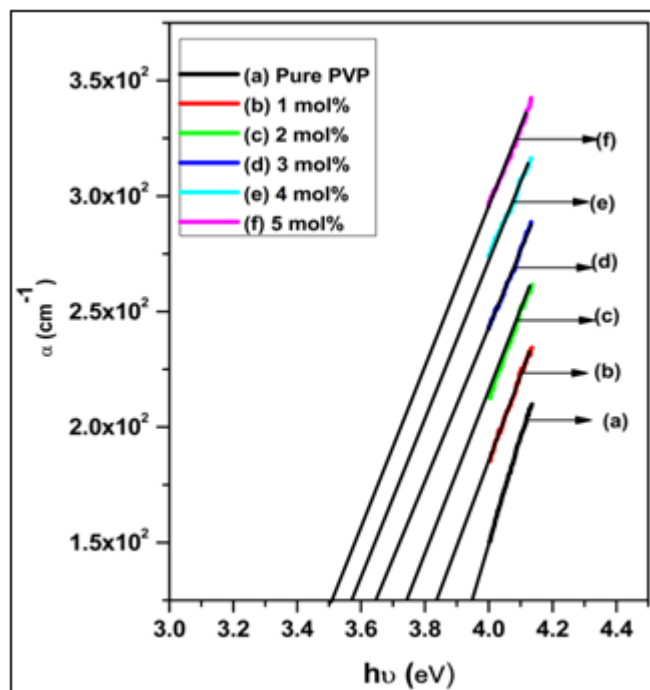


Figure 4: α vs $h\nu$ plots of the Pure and the Fe^{3+} (1, 2, 3, 4, and 5 mol %) doped PVP polymer electrolyte films.

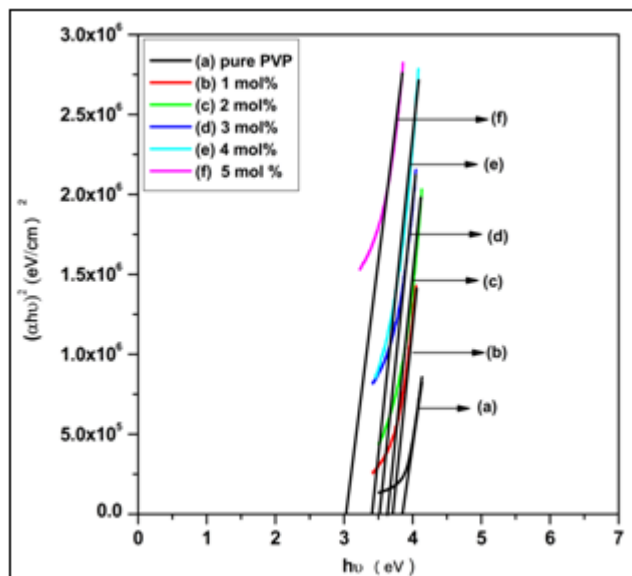


Figure 5: $(\alpha h\nu)^2$ vs $h\nu$ plots of the Pure and the Fe^{3+} (1, 2, 3, 4, and 5 mol%) doped PVP polymer electrolyte films.

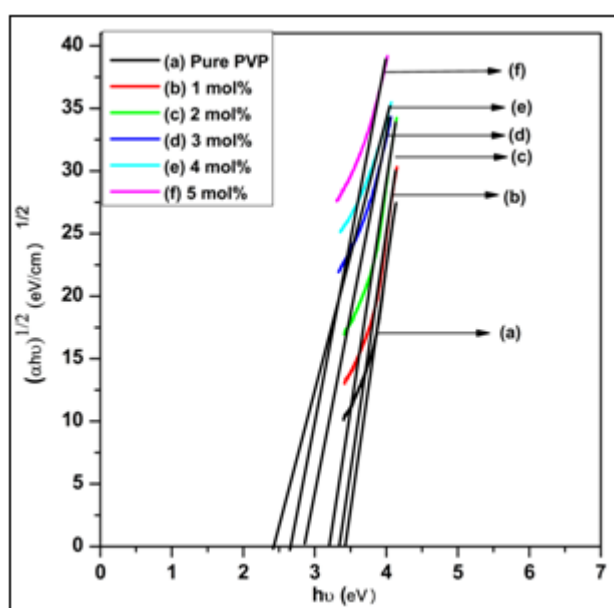


Figure 6: $(\alpha h\nu)^{1/2}$ vs $h\nu$ plots of the Pure and the Fe^{3+} (1, 2, 3, 4, and 5 mol%) doped PVP polymer electrolyte films

4. Conclusions

Solution casting technique is employed to prepare PVP polymer electrolytes with different concentrations of Fe^{3+} ions as the dopants. From FTIR spectra of prepared samples, it was observed that complexation between the Fe^{3+} ions and the host polymer was confirmed in terms of changes in intensity and certain bands position. The optical band gaps (both direct and indirect) showed the decreasing trend with increasing dopant concentration. Hence, the observed properties of pure and Fe^{3+} ions doped PVP polymer electrolytes look very desirable and promising for battery applications.

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