

Optical Behaviour of PEO-LiClO₄-ZnO Nanocomposite Polymer Electrolyte Films

S. U. Patil¹, S. S. Yawale², S. P. Yawale³

Department of Applied Physics¹, Director², Department of Physics³,

Government College of Engineering, Chandrapur¹

Pre Indian Administrative Services Training Institute, Nagpur²

Government Vidarbha Institute of Science and Humanities, Amravati³

Email: s19_patil@yahoo.co.in¹, ssyawale@rediffmail.com², spyawale@rediffmail.com³

Abstract- Nanocomposite solid polymer electrolyte films based on Poly (ethylene oxide), (PEO) complexed with lithium perchlorate (LiClO₄) and ZnO nanoparticles were prepared for optimized high conducting concentrations of ZnO nanoparticles by sol gel technique. Scanning electron microscopy has been used to study surface morphology. The optical transmission and absorption spectra were recorded in the wavelength range 200-800 nm for optimized high conducting concentrations of ZnO nanoparticles in the polymer matrix. Values of absorption coefficient, direct band gap energy, measure of extent of band trailing or Urbach energy, absorption edge and constant, B, have been investigated by optical characterization method. Effect of concentration of ZnO nanoparticles in the polymer matrix on these parameters has been discussed. It was found that addition of ZnO nanoparticles increases structural disorder and fluctuations of the internal fields associated with it. Small change in the concentration of ZnO nanoparticles changes optical properties of nanocomposite polymer matrix.

Index Terms- Absorption coefficient; optical energy gap; optical properties; absorption edge; Urbach energy; bang trailing; nanocomposite polymer matrix.

1. INTRODUCTION

Inorganic nanocomposites are extremely promising for applications in light-emitting diodes, photodiodes, photovoltaic cells, smart microelectronic device, and gas sensors among others [1]. The optical properties of nanocomposites films can be adjusted by varying the composition. For understanding the basic mechanism of optically-induced transitions in crystalline and non-crystalline materials and to provide information about band structure the optical absorption, particularly, studying the shape and shift of absorption edge is a very useful technique. The basic principal behind the technique depends on the absorption of photons with energies greater than the band gap energy of carrier which undergoes transitions from occupied states in valance band to unoccupied states in conduction band [1-2]. In these materials two types of optical transitions may occur, direct and indirect [3]. In a direct transition as there is no phonon interaction electron's wave vector remains same, whereas in an indirect transition cooperation of a phonon is necessary for conserving momentum and the electron's wave vector changes.

There exists strong interest in transparent conducting film to be used in solar cells, photo detectors, sensor devices, optoelectronic devices, etc. The measurement of optical properties of polymers has been vigorously pursued due to their wide application in optical devices. The optical properties

can be customized by the addition of some filler, which depends upon its reactivity with the host polymer matrix. Since the discovery of high electrical conductivity from blending poly (ethylene) oxide (PEO) with salts, polymer electrolytes have attracted a lot of interest because of their potential use in thin film batteries [4]. PEO is a unique polymer because it is soluble both in aqueous and organic solvents and is available in a variety of molecular weight. Many studies on PEO-salt composites, based on electrical and thermal properties, have been reported [5]. Investigation of optical properties of these systems is limited.

Thin films can be deposited by different techniques including, sputtering [6], metal organic chemical vapor deposition [7], sol gel [8] and spray pyrolysis [9]. Sol-gel technique is widely adopted due to its comparatively simple procedure and it has a wide range of advantage of large area deposition and uniformity of film thickness. Sol-gel process also offers other advantages like outstanding control of the stoichiometry and easy doping in film compositions. In the present work films of PEO-LiClO₄- m wt% ZnO nanocomposite polymer matrix were prepared for optimized high conducting concentrations [10] of ZnO nanoparticles by sol-gel method. Scanning electron microscope was used to study surface morphology and optical properties are investigated by using the UV1800 UV-Vis spectrophotometer.

2. EXPERIMENTAL

2.1 Materials

Poly (ethylene oxide) (PEO) (MW: 300000) was obtained from Alfa Aesar, Ward Hill, MA 01835, USA. Zinc oxide (ZnO) nanopowder (Purity: 99%, APS: 20 nm) was purchased from Nanoshell, Wilmington, DE 19808, USA. Lithium perchlorate (LiClO₄) was analytically pure and dried at 353 K for one day before use. Acetonitrile was used as the solvent in the film casting process.

2.2 Preparation of nano-composite polymer electrolyte films

Poly (ethylene oxide) (PEO)/LiClO₄ weight ratio was fixed to 90:10 and the mixture was blended with various weight percentages of ZnO nanopowder. To prepare composite samples first predetermined amount of LiClO₄ and m wt% ZnO nanopowder was dissolved in acetonitrile. The solution was stirred for 1 hour and then calculated amount of PEO was added to the solution. The mixture was stirred vigorously for 5 to 6 hrs to obtain homogeneous mixture. Films were obtained by transferring the mixture on the plane Teflon plate. Films were first dried in the open atmosphere to allow the solvents to evaporate and then dried in vacuum for 24 hrs to completely remove the residual traces.

2.3 Optical properties measurement

The optical absorption is an important tool to find the optical band gap energy of crystalline and amorphous materials. The fundamental absorption corresponding 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. The optical data, resulting from photons of energy $h\nu > E_g$, can be investigated using the near edge optical absorption. On the other hand, for optical transitions caused by photons of energy $h\nu < E_g$, the absorption of photons will be related to the presence of localized tail states in the forbidden gap. The width of this tail is an indicator of the defect levels in the forbidden band gap. The optical absorption coefficient, α (ν), at the given frequency (ν) is given by

$$\alpha = B(h\nu - E_{opt})^n/h\nu \quad (1)$$

Where, $h\nu$ is the photon energy, E_{opt} is the optical energy gap and n is the number which characterizes the optical absorption processes. The value of n for different kind of transitions [11-12] are as follows, $n=1/2$: direct allowed transition; $n = 1$: non-metallic material; $n = 3/2$: direct forbidden transition; $n = 2$: indirect allowed transition; $n = 3$: indirect forbidden transition.

The constant B in equation (1) is constant and is given by

$$B = (4\pi\sigma_{min})/(Cn_D\Delta E) \quad (2)$$

Where, σ_{min} is extrapolated d.c. conductivity at $T = \infty$, C is the velocity of light, n_D is the refractive index and ΔE measures the width of the tails of localized states, associated with the amorphous state in the forbidden gap, also called as Urbach energy (E_u). It is observed that the absorption coefficient near the band edge shows an exponential dependence on photon energy and this dependence is given as

$$\alpha = \alpha_0 \exp(h\nu/E_u) \quad (3)$$

Where, α_0 is a constant. It is believed that the exponential dependence of photon energy may arise

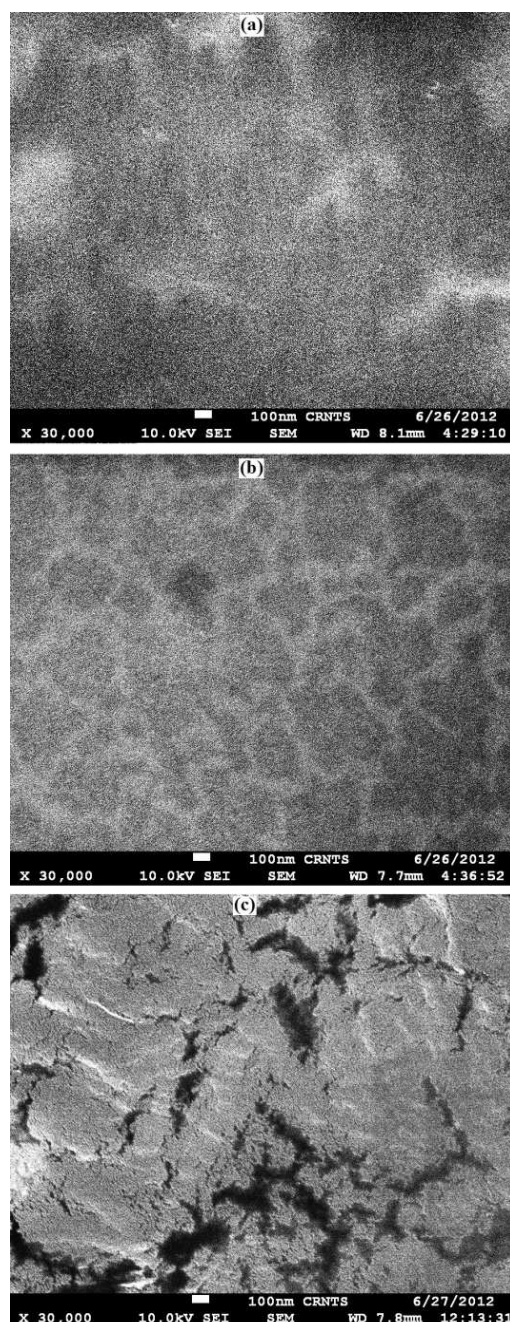


Fig. 1 SEM photographs of PEO-LiClO₄-m wt% ZnO electrolyte (a) m = 9, (b) m = 10 and (c) m = 11

from random fluctuations of the internal fields associated with the structural disorder in many amorphous materials. The structural disorder occurs due to introduction of defects in a material.

3. RESULT AND DISCUSSION

3.1 SEM analysis

Scanning electron microscopy has been used to study the compatibility between various components of the nanocomposite polymer electrolytes through the detection of phase separations and interfaces. Fig. 1 shows the surface morphology of optimized high conducting samples of the PEO-LiClO₄-m wt% ZnO nanocomposite polymer electrolyte films. The samples are completely amorphous and homogeneous. No crystals were developed in the samples containing 9 and 10 wt% of ZnO. Fig. 1(a) and 1(b) shows the smooth surface morphology, which is related to the reduction of PEO crystallization with lithium salt. As the concentration of ZnO nanoparticles increases streak development increases on the smooth surface and severe phase separated domains also increases with the concentration of ZnO nanoparticles (Fig. 1b & 1c). Changes in the texture and morphology of electrolytes indicate the slight interaction of ZnO nanoparticles with the polymer system.

3.2 Optical studies

The absorbance 'A' and transmittance 'T' of PEO-LiClO₄-m wt% ZnO nanocomposite polymer films were measured at room temperature by UV1800 UV-Vis spectrophotometer in the spectral range 200-800 nm at normal incidence. We used this spectral range to find the position of optical absorption edge, optical energy gap and the effect of concentration of ZnO on the absorption edge and the value of optical energy gap. Fig. 2 illustrates absorption and transmittance spectra of PEO-LiClO₄ polymer films, doped with 9, 10 and 11 wt% ZnO nanoparticles at normal incidence. The spectra show that with increase in the concentration of ZnO nanoparticles the absorbance

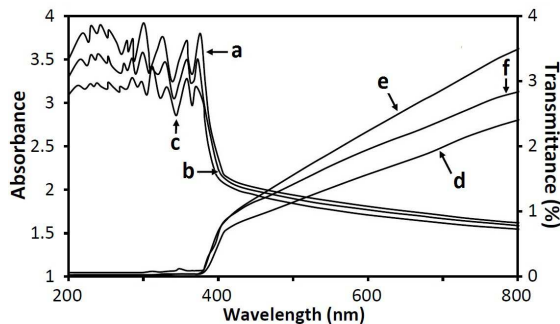


Fig. 2 Spectral dependence of absorption for (a) 9, b) 10, c) 11, and transmittance for d) 9, e) 10, f) 11 wt% ZnO on wavelength

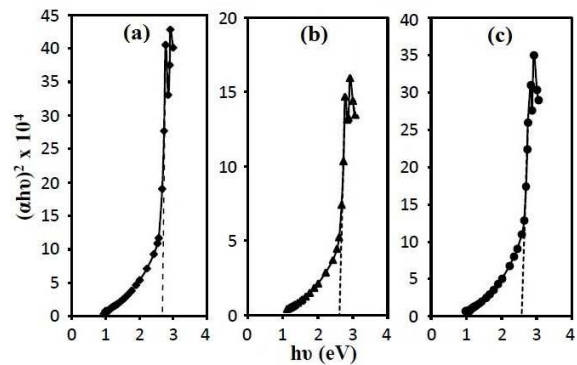


Fig. 3 Variation of $(\alpha hv)^2$ vs photon energy a) 9, b) 10 and c) 11 wt% ZnO

decreases. The spectra also show that with decrease in frequency the absorbance decreases and transmittance increases.

Fig. 3 shows the plots of $(\alpha hv)^2$ vs photon energy for different wt% of ZnO nanoparticles. Similar behavior was observed by other workers [13-14]. The presence of linear region in the plots of $(\alpha hv)^2$ vs photon energy indicates the direct type of transitions. The direct optical energy gap was measured from extrapolation of linear region on the energy axis. The values of direct optical energy gaps and constant B, from the slopes of the derived curves for 9, 10 and 11 wt% of ZnO nanoparticles are summarized in table 1. With increase in the concentration of ZnO nanoparticles the value of optical energy gap decreases. Fig. 4 shows the plots of $\ln(\alpha)$ vs photon energy for different wt% of ZnO nanoparticles. The values of Urbach energy obtained from fig. 4 by extrapolation of linear region on energy axis are listed in table 1. As the concentration of ZnO increases the structural disorder increases the fluctuations of the internal fields associated with it, hence Urbach energy increases. Fig. 5 shows the changes in the absorption coefficient with respect to photon energy. The values of absorption edge were determined from Fig. 5 by extrapolation of linear region to energy axis. The absorption edge was found decreasing with

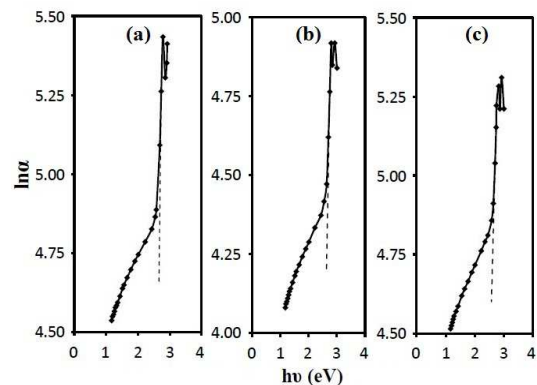
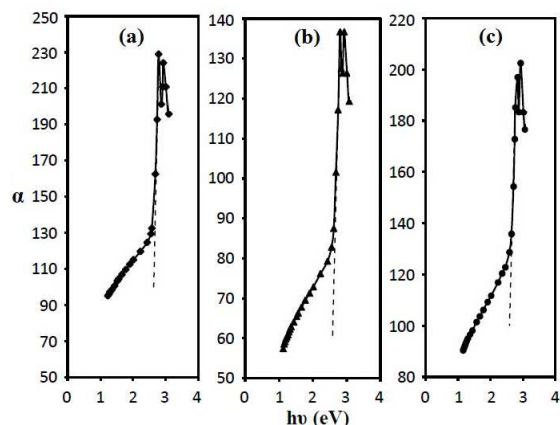


Fig. 4 Variation of $\ln(\alpha)$ vs photon energy a) 9, b) 10 and c) 11 wt% ZnO

Table1. Calculated parameters absorption edge, direct optical band gap, constant B and Urbach energy of PEO-LiClO₄-m wt% ZnO films

ZnO Concentration	Absorption Edge (eV)	Direct Optical Band Gap (eV)	Constant B (cm ⁻¹ eV ^{-1/2})	Measure of Extent of Band Trailing ΔE or E_u (eV)
9 wt%	2.51	2.66	17.67	0.184
10 wt%	2.41	2.62	9.44	0.206
11 wt%	2.39	2.57	12.04	0.217

Fig. 5 Variation of α vs photon energy a) 9, b) 10 and c) 11 wt% ZnO

increase in the concentration of ZnO nanopowder.

4. CONCLUSION

Nanocomposite films comprising of PEO and LiClO₄ with different concentrations of ZnO nanoparticles were synthesized. SEM images showed smooth surface morphology. The samples were completely amorphous and homogeneous. The optical absorption and transmittance in the UV visible region for ZnO doped PEO-LiClO₄ films were measured as a function of ZnO wt% at room temperature. The direct optical energy gap found to be dependent on the ZnO wt%. It was found that the absorption edge as well as optical energy gap decreases with increase in the ZnO wt%. Direct band gap fits in the energy region of fundamental absorption edge. Also it was found that with increase in the ZnO wt% the structural disorder increases the fluctuations of the internal fields associated with it. The lower values of Urbach energy indicates fewer introductions of tail states at the band edges and the increase in the E_u values confirm further introduction of tail states with increase in the ZnO wt%.

References

- [1] Murri, R., *et al.* (1992): Journal of Non-crystalline Solids, 139, pp. 60-66.
- [2] Urbach, F. (1953): Physical Review, 92, p. 1324.

- [3] Davis, P. W.; Shalliday, T. S. (1960): Physical Review, 118, pp. 1020-1022.
- [4] Fenton, D. E.; Parker J. M.; Wright P. V. (1973): Polymer, 14, p. 589.
- [5] Saqan, S. A.; Ayeshe, A. S.; Zihlif, A. (2004): Optical Materials, 24, pp. 629-636.
- [6] Soon-Jin, So.; Choon-Bae, Park. (2005): Journal of crystal growth, 285, pp. 606-612.
- [7] Tan, S. T. *et al.* (2005): Journal of Crystal Growth, 281, pp. 571-576.
- [8] Young-Sung, K.; Weon-Pil, T.; Su-Jeong, S. (2005): Thin Solid films, 491, pp. 153-160.
- [9] Martins, R. *et al.* (2005): Material Science and Engineering, B118, p. 135.
- [10] Patil, S. U.; Yawale, S. S.; Yawale, S. P. Bulletin of Material Science. In press.
- [11] Hosseini, A. A.; Hogarth, C. A. (1999): Journal of Science I. R. Iran, 10, p. 136.
- [12] Al-Ani, S. K. J.; Hogarth, C. A. (1995) Internal Journal of Electronics, 58, p. 123.
- [13] Mohammad, Elahi.; Dariush, Souri. (2006): Indian Journal of Pure and Applied Physics, 44, p. 468-472.
- [14] Yakuphanoglu, F. *et al.* (2007): Journal of Optoelectronics and advanced Materials, 9/7, p. 2180-2185.