Asian Resonance

Conduction Mechanism in (ZnO/PVC) Polymer Nanocomposite

Abstract

The electrical conductivity of ZnO nanoparticle doped PVC polymer of different concentrations and thickness has been investigated as a function if applied electric field and temperature. The LnJ versus $E^{1/2}$ plot for the pure sample shows transition field but for highly doped sample, the plot shows curvature for both low and high field, i.e. there is no transition field. This nonlinearity of the plot is due to space charge built up in the sample. The value of β is calculated from the slope of LnJ versus $E^{1/2}$ plot and compared with the theoretical value. The result shows the Poole-Frenkel mechanism of conduction is operative.

Keywords: *ZnO, PVC, doping, nanocomposite, Poole-Frenkel*

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Introduction

Conducting polymers are organic polymers that conduct electricity, such compound may have metallic conductivity or can be a semiconductor. The advantage of conducting polymers are their process ability mainly by dispersion. Conducting polymers are generally not plastic but like insulating polymer, these are organic materials. They can offer high electrical conductivity but do not show mechanical properties as other commercially used polymers do. The electrical properties can be fine-tuned using the method of organic synthesis and by advance dispersion techniques[1]. The most recent research in conducting polymers is to develop high conducting with stability and acceptable processing attributes. So for most well studied conducting polymers are (i) nitrogen containing polymers, i.e Poly(pyrrole)s (PPY), polyanilines (PANI). (ii) Sulphur containing polymers, i.e.Poly(thiophene)s (PT), Poly(3,4–ethylenedioxythiophene)(PEDOT),Poly(p-phenylenesulfide) (PPS) and (iii) other polymers i.e. Poly(acetylene)s (PAC), Poly(p-phenylene vinylene) (PPV), Polyethylene terephthalate (PET) etc.

The ZnO material material is a wide band gap 3.3 eV (at room temperature) n-type semiconductor. Advantages associated with a large band gap include higher breakdown voltage ability to sustain large electric field, lower electronic noise, high temperature and higher power operation. The band gap of ZnO can further be tuned to 3-4 eV by its alloying magnesium oxide or cadmium oxide[2].

Nanostructured ZnO materials are current importance in electronic, optic and photonic applications and for the basis of nanotechnology applications in sensors and molecular electronics. The nanostructured exhibit novel electrical, mechanical, chemical and optical properties which are belived to be due to the surface confinement effects or nanostructures in one dimension. These one dimensional objects are of great importance in understanding some basic physics related phenomena in the low dimension system to form the basis of next generation higher performance nanodevices[3].

As ZnO has high electron mobility and wide band gap so, ZnO nanoparticle is doped in PVC film, electrical property of the nanocomposite film will change from the pure PVC film. The present study, an attempt is made to investigate the conduction mechanism in pure PVC,(having excellent electrical insulation property as mentioned above), film and ZnO nanoparticle doped PVC film at different applied voltage, temperature and doping concentrations.

Experimental:

(i)Formation of pure film: PVC granule form supplied by the Reliance industry Surat, Gujarat and Cyclohexanon supplied by S D Fine Chem Ltd Mumbai for the present study form a solution (4 gram of PVC and 20 cc of cyclohexanon). The solution kept at room temperature for one week for complete dissolution. The solution is poured on the glass plate to make a thin film. The glass plate is placed over a pool of mercury for perfect leveling

so as to ensure uniform thickness. The whole system was allowed to evaporate at room temperature in dust free chamber for 6 days and after complete evaporation the film was detached from the glass plate. Thus a pure (PVC+cyclohexanon) film is formed.

(ii) Formation of ZnO nanoparticle doped film

After a solution is form as above, ZnO nanoparticles supplied by Material Science Laboratory, B N College, Patna, is doped with different quantities i.e. 0.00325 gm/cc, 0.00653gm/cc and 0.01303gm/cc. Now, the mixture (PVC + ZnO) is stirred by Magnetic stirrer (Eltect-MS 205) for 8 hrs¸ then the mixture is poured on the glass plate and proceeds as above. Thus the ZnO nanoparticle doped PVC film is formed. The sample preparation is same as that reported earlier[4]. The thickness of the sample was measured by travelling microscope and found to be 0.035 cm, 0.0175 cm, 0.03 cm and 0.019 cm.

(iii) Measurement of conductivity

The sample is cut circularly slightly greater than the surface area of the electrode having area 5.067 x 10^{-4} sq. m to avoid edge effect. The sample is placed between the two electrodes under light constant pressure in the sample holder. The sample holder is placed inside the temperature controlled bath, Ultra-thermostat (*U-10, Germany*)

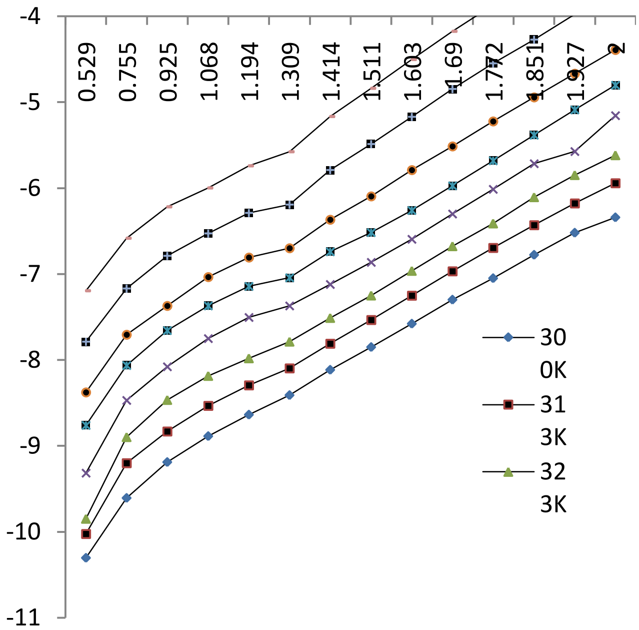
The different potential is applied across the sample by the power supply (EHT-11) supplied by Scientific Equipment, Roorkee. The value of potential across the sample is varied from 0 to 1400 volt by an interval of 100 volt at constant temperature. The potential drop across 1 MΩ resistor is recorded by digital multimeter. The same operation is repeated for different values of temperature from room temperature 300 K to 373 K by an interval of 10 K. In order to make uniform heating the sample is kept at constant temperature for 30 minute for each consecutive reading. The conductivity measurement is same as that reported earlier[5].

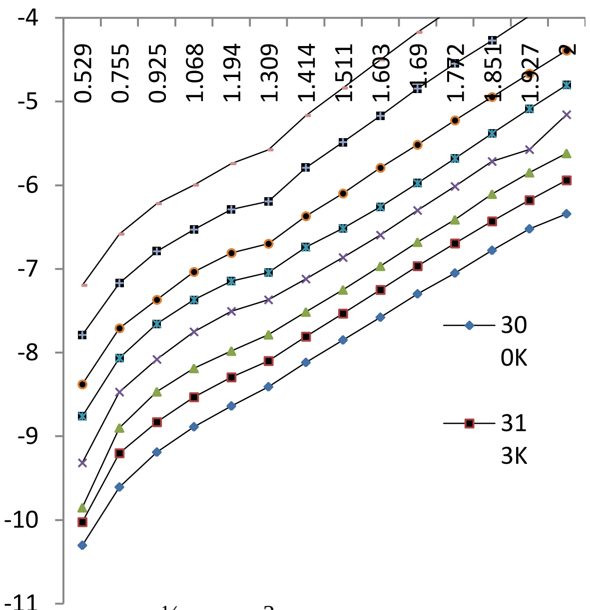
Result and Discussion

The plot of LnJ versus $E^{1/2}$ (figure 1-4) show that mechanism of conduction for different applied field and temperature. For the pure PVC field (sample A), is almost linear upto 1.5x10^3 V/m and this applied field the plot is linear with more stiff then that in the lower field. Similarly for the ZnO nanoparticle doped PVC film at the rate of 0.0065 gm/cc (sample B) and 0.00326 gm/cc(sample D) the plot are almost linear beyond the applied field 1.849 x10^3 V/m and 2.05x10^3 V/m respectively with greater stiff to that lower field. For different rate of ZnO nanoparticle doping the transition field are different also due to the doping on pure PVC film the transition field are shifted from the pure PVC film. The samples are under the action of applied `filed are just to that in vacuum diode-space charge limited current, (Mott & Gurney 1964). If ZnO nanoparticle is doped 0.0130 gm/cc the plot shows the curvature for both low and high field i.e. there is no transition field. The nonlinearity of the plot is due to space charge build up in the sample (Aldert 1957). Generally in polymers the Ln J versus E ^{½} plot for different temperature, show straight line in high electric field region, in which JαE^{½},the case of hot electrode i.e. energy required by the field is greater than the thermal energy. The Schottky and Poole-Frenkel mechanism of conduction are dominant process of conduction in insulator or semiconductor at high field (Lamb D R 1996, Ballan R.V and Winddowson A.E 1972**)**. Heavy reliance has been made on the measured slope of Ln J versus E ^{½} for the interpretation of the experimental data.

It was found experimentally that, emission current increases with increasing field strength at the cathode, which is contradictory to that independence of current in thermionic emission. Schottky showed that a lowering of the work function due to an increase in the applied field was responsible for such a behaviour. Hence due to high field Schottky emission of electron may occur from the metal contact at the negative potential into the conduction band of the insulator. This mechanism corresponds to thermal activation of electron over the metal insulator interface barrier with added effect that the applied field reduce the higher of the barrier. Considering the origin of the surface barrier, Schottky argued that, there are two regions (1) polarization field and (2) an image field. The Schottky effect is associated with the barrier of the surface of the metal and insulating material, whereas the Poole- Frenkel emission associated with the barrier in the bulk of the material. In both effect the restoring force is due to coulomb interaction between the escaping electron and a positive charge, they differ in that, the positive image charge is mobile with Schottky emission and fixed for Poole- Frenkel barrier. Hence lowering of barrier is greater for Poole- Frenkel than that for Schottky effect.The current density for Schottky(S) and Poole- Frenkel (PF) process follows the relation Lamb D R (1967).

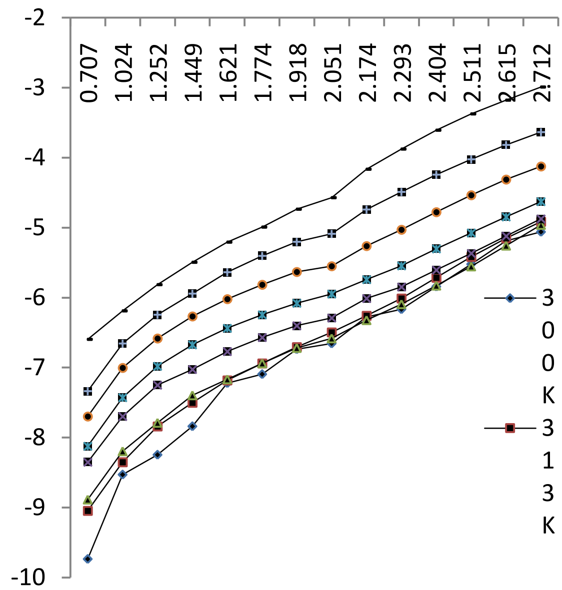
$$J = J_0 \exp\left(\frac{\beta E^{\frac{1}{2}}}{kT}\right) \quad \text{... ... ... (1)}$$





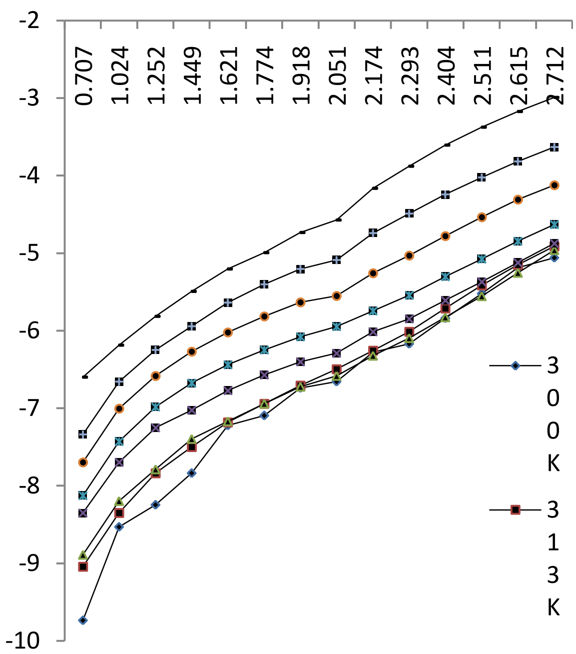
$E^{½}$ X 10^3V/m

Variation of LnJ versus $E^{1/2}$ for the sample (A)



$E^{1/2}$ X 10^3 V/m

Variation of LnJ versus $E^{1/2}$ for the sample (D)



$E^{1/2}$X 10^3 V/m

Variation of LnJ versus $E^{1/2}$ for the sample (C)

Where $\mathbf{J_0} = \mathbf{AT^2}\ \mathbf{exp}\ (-\frac{\varphi}{kT})$ (Schottky mechanism)

$\mathbf{J_0} = \frac{\sigma_0 \mathbf{V}}{\mathbf{d}}$ (Poole- Frenkel mechanism)

T= absolute temperature
k = 1.36x 10^{-23} J/K Boltzmann constant
σ_0 = low field conductivity
V= applied field
d = thickness of the sample

$\boldsymbol{\beta}(\mathbf{s}) = \sqrt{(\frac{e^2}{4\pi\varepsilon_0\varepsilon})}$ (Schottky constant) ... ... (2)

$\boldsymbol{\beta}(\mathbf{pf}) = \sqrt{(\frac{e^2}{\pi\varepsilon_0\varepsilon})}$ (Poole- Frenkel constant) ... (3)

ε_0 = permittivity of free space
ε = permittivity of the material.

From equation (1) it is suggested that the plot of Ln J versus E ^{½} should be linear having slope β/kT. The value of β was calculated from such plot (putting k = 1.36x 10^{-23} J/K**)** for all temperature.

If ZnO nanoparticle is doped to pure PVC film the value of LnJ is increase with E ^{½}. As PVC is partially syndiotactic material, with sufficient irregularity of structure that crystallinity is quite low (Billimeyer 2008) i.e. almost amorphous in nature. The presence of amorphous regions gives rise to localized state. Since there are many localized states, the release or excitation carriers in these states dominants the conduction process. The dopant ZnO present in sufficient quantity and remarkably affect the position of Fermi level. The molecules of dopants enter either in the amorphous regions of the polymer or at the disordered regions chain folds. If they are present in low concentration they will give rise to additional molecular sites for trapping of charges. Such localized site formed by dopant molecules can be defined in molecular terms using the difference in ionization potential as an indication of trap depth. It the dopant concentration is increased, the dopant molecules starts bridging in separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carrier between the two localized states (Sangawar*et.al.*2007). the dopant ZnO has high mobility also n-type semiconductor so if it is doped to pure PVC the energy level lies just below the conduction band, i.e. the width of the band gap is decreased, which result electrons move into the conduction band with increased of applied field.

The theoretical values of β(s)and β(ps) were calculated from equation (2) and (3) using e= 1.6×10^{-19}C, ε=3.0 and ε_0=8.85×10^{-12} F/m. It is clear from the table that the Poole- Frenkel mechanism of conduction is operative.

Conclusion:

The present experimental investigation reveals that the conductivity of ZnO nanoparticle doped PVC film increases more sharply than the undoped PVC film within intermediate range of temperature. In such sample electronic current is operative as its low activation energy. So it is concluded that such polymer nanocomposites could be used as good semiconducting materials for many electronic devices.

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