

SYNTHESIS AND ELECTRICAL PROPERTIES OF DOPED POLYPYRROLE WITH HEXAGONAL FERRITE

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The alternate current (ac) and direct current (dc) electrical conductivity of polypyrrole doped with strontium hexaferrite composite has been investigated at different temperatures in the frequency range of 100 Hz to 1 MHz. A conducting polymer, Polypyrrole was synthesized by chemical polymerization method and doped with dodecylbenzenesulphonic acid (PPy-DBSA). Y-type hexagonal ferrite $Zn_2Sr_2Fe_{12}O_{22}$ was prepared by normal microemulsion route. Composite was prepared by mixing the $Zn_2Sr_2Fe_{12}O_{22}$ with already synthesized conducting polymer PPy-DBSA by 1:1 molar ratio. Phase analysis was performed by using X-ray diffraction (XRD) analysis. The microstructure was examined by scanning electron microscopy (SEM) showing heterogenous distribution of grains. The experimental results showed that the DC electrical conductivity of the composite increased with increasing temperature more rapidly as compared to that of pristine polypyrrole. Activation energy, density of states and hopping length were calculated and found to be influenced by adding ferrites. AC electrical conductivity of the composite are changed with temperature and frequency of applied electric field.

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1. Introduction

Conductive Polypyrrole doped with Dodecylbenzenesulfuric acid (PPY-DBSA) has been studied extensively because of its ease of synthesis in aqueous media, environmental stability and special electrical properties. It is a suitable candidate for a variety of technological applications [1] such as solar cells, electromagnetic shielding, electrodes for rechargeable batteries, sensors, etc. Most recently, as one of the most intensively studied conducting polymers in the last 15 years, doped polypyrrole PPY-DBSA has attracted considerable attention for the preparation of its composites with inorganic particles. In order to fulfill the requirements of polymer industry many researchers usually blend polymers together in order to reach an optimum balance of properties, this approach allows high flexibility in property adjustment and avoids development of new macromolecules which is generally long and expensive compared to polymer alloying. Vigorous developments of polymer composite and extensive utilization of polymer materials in technology have led to the polymer composites. The importance of polymers is mainly because polymers are still regarded as a cheap alternative material that is manufactured easily. The intensive use of polymer in broad use has led to the development of materials for specific applications namely composites. Recently polymer matrix-ceramic filler composites receive increased attention due to their interesting electrical and electronic properties, integrated decoupling capacitors, angular acceleration accelerometers, acoustic emission sensors and electronic packaging some potential

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applications. Ceramic materials are typically brittle, possess low dielectric strength and in many cases are difficult to be processed requiring high temperature. On the other hand, polymers are flexible, can be easily processed at low temperatures and exhibit high dielectric break down fields. Ferrite/polymer composites are of technological interest on account of their unique mechanical, electrical and magnetic properties. Such as sharply reduced dielectric loss as compared to the bulk ferrites, uninfluenced microwave absorption properties owing to the domination of natural ferromagnetic resonance absorption in the loss mechanism of the ferrite absorption materials make them quite attractive for applications of capacitive and also inductive materials. Polymer-based composites have attracted much attention due to their flexibility, tunable properties, and easy processibility.

The electronic transport in polymeric materials has become an increasing area of research to understand the general theory of polymer physics [2-9]. Intrinsically, conducting polymers may have poor stability [10], poor mechanical properties [11], low conductivity [12] and insolubility in organic solvents [13]. An effective method to overcome these problems is to prepare blends of conducting polymers with non-conducting polymers as fillers in elastomeric matrices and to prepare conducting polymers doped with sulfuric acids, such as dodecylbenzenesulphonic acid (DBSA), to overcome the problem of solubility [14,15]. Early attempts to get highly conductive, thermally stable and soluble conducting polymer were mainly focused on chemical synthesis of polyaniline by treating with various polar group fuming sulfuric acid [16-20], sulphobenzoic anhydride [21].

In this paper, Temperature dependence of AC and DC electrical conductivity of strontiumhexaferrite and Polypyrrole doped with dedocylbenzenesulfuric acid composite at different temperatures has been studied. The frequency utilized in the study was from 100 Hz to 1 MHz, the results cover direct current (dc) and alternate current (ac) electrical conductivity temperature dependent, Activation energy, and hopping length were calculated. In the present study we also report the morphology, structural and charge transport mechanism of both doped polypyrrole-DBSA and strontiumhexaferrite are discussed.

2. Experimental

Pyrrrole was obtained from the Aldrich chemical and was vacuum-distilled before its use. Ammoniumper sulfate (APS) was obtained from Fluka while hydroquinone and poly (methyl methacrylate) supplied by Aldrich, were used as received.

2.1 Synthesis of PPy-DBSA

The required amount of DBSA (0.15M) was dispersed in 100 ml of distilled water and then 0.3M of pyrrole was added to the mixture. The solution was stirred for 3 h. The required amount of oxidant i.e. ammonium persulphate (0.15) dissolved in 200 mL distilled water and was added drop wise to the above mixture under vigorous stirring. Then after 24 h 1 liter of methanol was added in the solution and the reaction mixture was kept at room temperature for 2 days. After that the suspension was filtered and washed. The black paste of doped polypyrrole was obtained which was dried under vacuum at 90°C for 24 h.

2.2 Synthesis of Ferrite

The chemicals used in the synthesis of Y type strontium zinc hexaferrites were $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Riedel-de Haen, 97%), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck, >99%), $\text{Sr}(\text{NO}_3)_2$ (Merck, 99%), CTAB (Merck, 97%) as a surfactant, NH_3 (Fisher Scientific, 35%) as a precipitating agent and methanol (Merck, 99%) as washing agent. The strontiumhexaferrite sample with nominal composition $\text{Sr}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ were prepared by the normal microemulsion method. The metallic salt solution of the required molarities were prepared in deionized water and mixed in a baker. The aqueous solution of CTAB in metal to surfactant ratio 1:1.5 was also added in the mixture. The solution was stirred on the magnetic hot plate at 60°C until it formed a clear solution. After that the

2M ammonia solution was added to get the precipitates which were washed with de-ionized water several times and finally with methanol. Then the precipitates were dried in an oven at 150°C and finally annealed at 1000 °C for 8 h in a temperature programmed (Heyaius, D – 6450 Hanau, Germany).

2.3 Ferrites-Polymer Composite

The composite was prepared by mixing the doped PPy-DBSA with $\text{Sr}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ by 1:1 molar ratio. The mixture was grinded in an agate mortar and pestle. After grinding, the composite powder was pressed into the disk shaped pellets with diameter of 8 mm and thickness of 3 mm under the load of 25 KN by using the Paulotto Weber hydraulic press.

2.4 Characterization

The X-ray diffraction patterns were recorded using a computer controlled diffractometer model JDX-3532 JEOL Japan which was operated at 40KV and at 30mA. The radiation used was CuK_α ($\lambda = 1.5406\text{\AA}$) with Ni filter. Samples were scanned in 2θ range of 10° to 50° . DC conductivity was measured for the sample which was pressed into pellets of 8 mm diameter and 3 mm thickness at pressure of 10 ton. The samples were connected to a Keithley 117 electrometers and a current source electrometer. The temperature was controlled by cryostat and measured by digital bimetallic thermometer. The conductivity of all the samples and its reproducibility were checked. Scanning electron microscopy was carried out on an EVO50 ZEISS instrument.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction was carried out at room temperature to determine the phase and Crystallinity of investigated samples. All the diffraction peaks in XRD patterns of $\text{Sr}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ were compared with JCPDS 00-019-019-0100. It shows that the $\text{Sr}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ formed well defined Y-type hexagonal phase. There was a co-existence of PPy-DBSA and $\text{Sr}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ phases in the composite sample as indicated in the XRD patterns shown in Fig. (1). The decrease in intensity of the peaks in the composite sample may be attributed to the amorphous nature of PPy-DBSA and few peaks disappeared with addition of PPy-DBSA in the pure ferrite. Pure phase formation of the Zn_2Y ferrite was achieved at the annealing temperature of 1000°C, which is lower than the 1100°C reported in the literature [19-20,]. Peaks of the XRD pattern of composite sample are broad. The broadening of the peaks is due to the nanometer size of the crystallites [21].

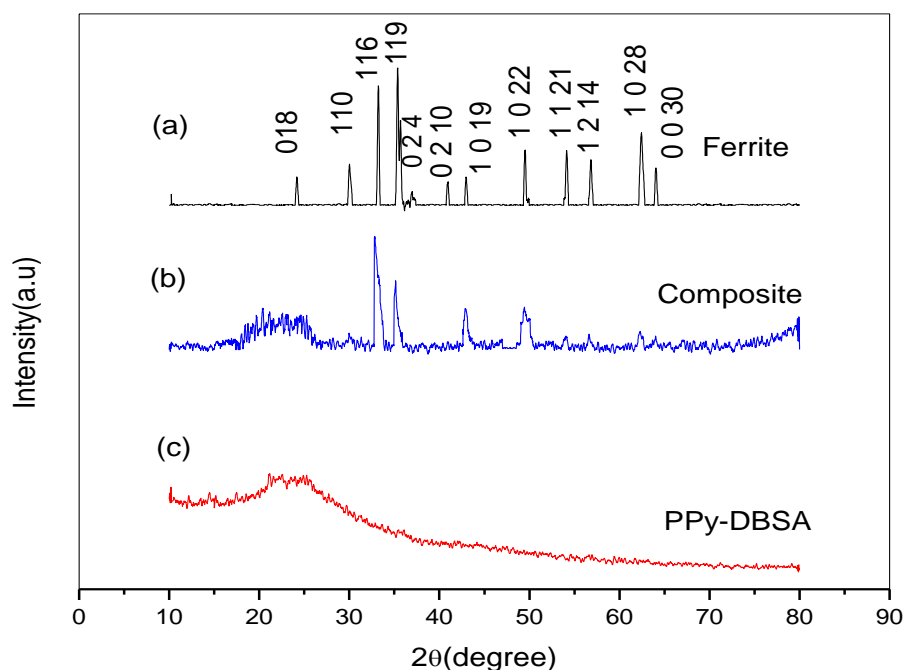


Fig. 1. XRD patterns for (a) ferrite $Sr_2Zn_2Fe_{12}O_{22}$, (b) composite $Sr_2Zn_2Fe_{12}O_{22} + PPy-DBSA$ (c) polymer $PPy-DBSA$

The crystallite size for each sample was calculated from XRD pattern by using Scherer's formula given as $D = k\lambda/\beta\cos\theta$ [22], where k is the shape constant having value 0.89 for hexagonal system, λ is the wavelength of x-rays used having a value of 1.5406 Å, β is the broadening of the diffraction line measured at half width of maximum intensity and θ_B is the Bragg's angle of diffraction. The calculated crystallite size is presented in Table (1). Estimated crystallite size of ferrite, composite and polymer is 34.66, 4.04 and 8.47 nm, respectively. It is an established fact that the grain growth depends upon grain boundary mobility. The mixing of polymer with pure ferrite reduces the grain growth which decreases the grain size. The decreasing of the crystalline size with the addition of polymer may be attributed to the fact that higher the porosity smaller the crystallite size [23].

Table 1. Parameters measured from XRD patterns for ferrite ($Sr_2Zn_2Fe_{12}O_{22}$), composite ($Sr_2Zn_2Fe_{12}O_{22} + PPy-DBSA$) and polymer ($PPy-DBSA$).

Parameters	Ferrite	composite	Polymer
a (Å)	5.88	5.92	
c (Å)	43.37	43.52	
c/a	7.37	7.35	
V (Å) ³	1298.55	1320.83	
D (nm)	34.66	4.04	8.47

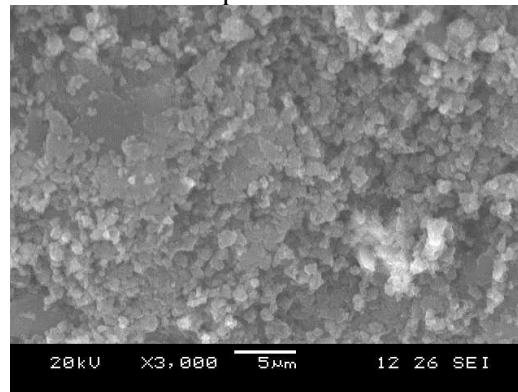
The calculated values of lattice parameters and volume of unit cell are shown in Table (1). All the peaks were indexed and lattice parameters a , c and volume of unit cell for Zn_2Y ferrite and composite was calculated by using the following relations [24-25].

$$\sin^2\theta = \lambda^2/3a^2 (h^2+hk+k^2)+(\lambda^2/4c^2)l^2 \quad (1)$$

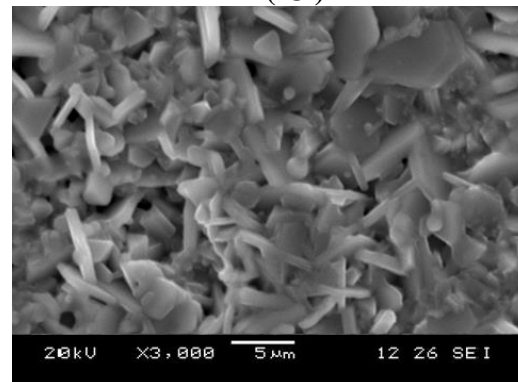
$$V = 0.8666a^2c \quad (2)$$

3.2. Scanning electron microscopy (SEM)

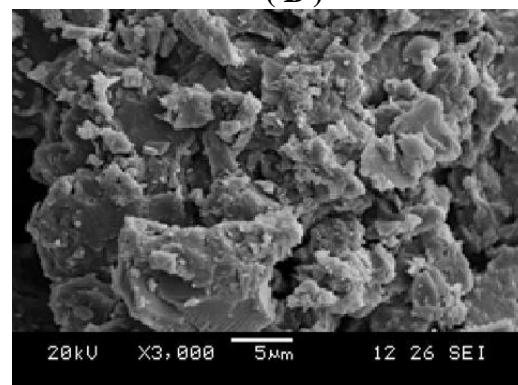
The SEM micrographs for conducting polymer PPy-DBSA, Zn₂Y ferrite sample and (Zn₂Y+ PPy-DBSA) are shown in Fig. 2. The micrographs present a heterogeneous distribution of grain sizes. Some grains agglomerate in different masses. Mixing polymer (PPy-DBSA) in the Zn₂Y ferrite, the grain size as well as the density decreased than that in pure ferrite, a porous microstructure with little densification was observed for composite ferrite. For the ferrite sample more dense and heterogeneous distribution of grain sizes was observed, moreover the grain morphology appears plate-like for ferrite sample.



(C)



(B)



(A)

Fig. 2. Scanning Electron Microscopy (SEM) (a) Pure PPy-DBSA (b) Sr₂Zn₂Fe₁₂O₂₂ (c) Sr₂Zn₂Fe₁₂O₂₂ + PPy-DBSA composites.

3.3. Electrical Conductivity

The dc electrical conductivity (σ_{dc}) of the polymer and its composite with ferrite material was found to be increasing with the increase in temperature. The increment in temperature provides an increase in free volume and segmental mobility. The conductivity increases so as temperature, indicates more ions gained kinetic energy via thermally activated hopping of charge carriers between trapped sites, which is temperature dependence. The sharp increase of dc conductivity between 280 K and 350 K can be attributed to large heat energy absorbed by the samples and thus induce mobility of electrons. It is suggested that in this region, the band gap between valence band and conduction band is reduce significantly and provide easiness for electrons to hop from valence band to conduction band and hence gives higher dc conductivity values as compared to other temperatures. The dc conductivity of PPy-Ferrites composites also increases with the increase of the temperature. The increases in dc conductivity can be attributed to large heat energy absorbed by the samples and thus induce large mobility of electrons. It is suggested that in this region, the band gap between valence band and conduction band is significantly small and large movement of electrons from valence band to conduction band. The dc conductivity increases with the increase of the temperature and indicates that it is fitted to Arrhenius exponential law equation [10] as depicted in Fig.3(a,b) had a semiconducting property. For semiconductors, the higher the temperature is, the higher the electrical conductivity. Moreover 3-D variable range hopping (VRH) was found to be dominant in all the samples. The best fitted Mott's parameters T_0 , $N(E_F)$, R , and W [4, 5] obtained at different temperatures are given in table 2. The density of localized states at the Fermi level increases while the average hopping distance.

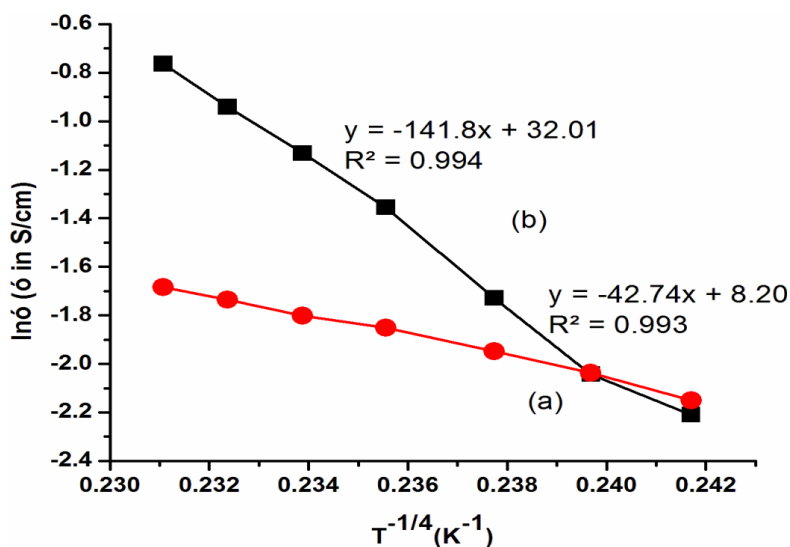


Fig. 3. DC conductivity (σ_{DC}) as a function of $T^{-1/4}$, in a logarithmic scale (a) $Sr_2Zn_2Fe_{12}O_{22}$ + PPy-DBSA composite (b) PPy-DBSA

Table 2. Mott parameters of doped polypyrrole doped with dodecylbenzenesulphonic acid and PPy-DBSA + $Sr_2Zn_2Fe_{12}O_{22}$ composite at 300 K

Sample	T_0 (K)	Density of states $N(E_f)$ ($eV^{-1} cm^{-3}$)	Hopping length R (cm)	Activation energy W (eV)
PPy-DBSA	40.47×10^7	3.67×10^{18}	6.5×10^{-7}	0.237
PPy-DBSA + $Sr_2Zn_2Fe_{12}O_{22}$	33.36×10^5	9.7×10^{17}	1.55×10^{-6}	0.0661

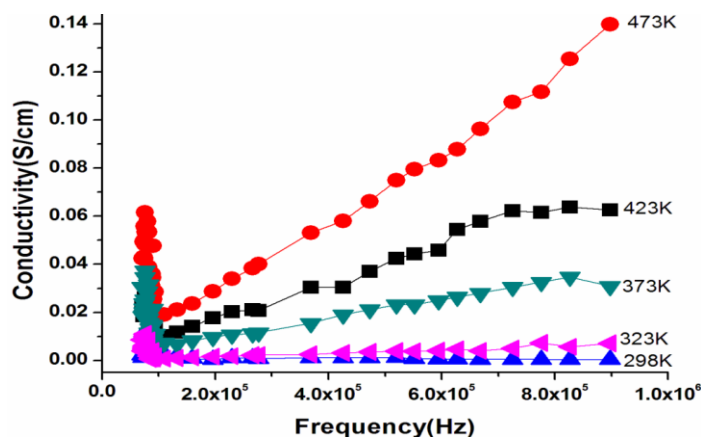


Fig. 4.AC conductivity of PPy-DBSA at different frequencies and temperatures.

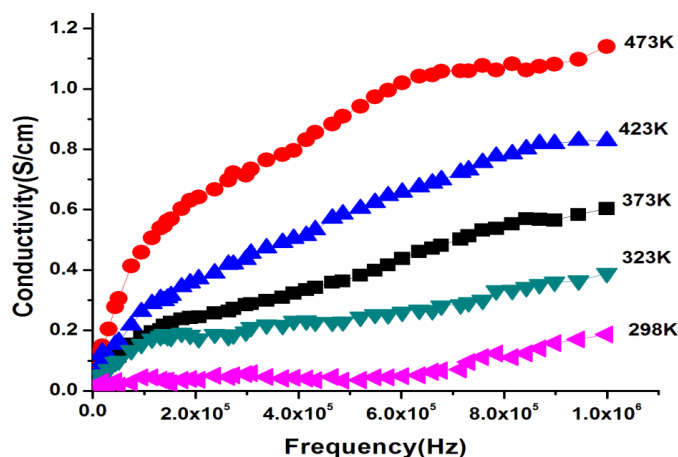


Fig. 5.AC conductivity of $Sr_2Zn_2Fe_{12}O_{22} + PPy-DBSA$ composite at different frequencies and temperatures.

The ac conductivity (σ_{ac}) increases with the increase in frequency and is measured at various temperature. The rise of conductivity upon increasing the frequency and temperature is a common respond for polymeric samples. It is due to the tremendous increase of the mobility of charge carriers in the composite. Frequency dependent conductivity increases with rise in temperature, which may be due to trapped charges in higher frequency region. Temperature dependent AC conductivity of strontiumhexaferrite and Polypyrrole doped with Dedocylbenzenesulfuric acid composite are shown in Figs. 4 and 5. It has been observed that with the increase in frequency the AC conductivity increases due to large jump probability [4]. This large difference in the frequency exponent can be explained, from our point of view, in terms of differences in the number of their inter-chain linkages. In AC conductivity, increasing frequency limits charge transport to shorter segments of the polymer chain. In case of PPy DBSA, which has relatively smaller number of inter-chain links, this progressively limited charge transport to shorter chain segments also decreases inter-chain hopping probability and increases the dominance of intra-chain hopping. As intra-chain hopping is much faster than inter-chain hopping, this leads to strong frequency dependence of AC conductivity in polymer. In the case of composite, on the other hand, the PPy-DBSA provides an additional inter-chain linkage mechanism and hence the inter-chain hopping component remains significant even at higher frequency, which results in hopping model and the dependence of exponents on temperature and n on the frequency allow a comparison of established model of hopping [25].

4. Conclusion

Extensive study on temperature dependence of ac electrical conductivity of strontiumhexaferrite and Polypyrrole doped with Dedocylbenzenesulfuric acid composite had been carried out. The (ac) conductivity increases with the increment of frequency and temperature and it obeys universal power law. An increase of the values of the ac electrical conductivity is driven by mobility of free charges. (i.e. polarons and free ions) as temperature is increased. It confirmed with the gradual increment of values of the (dc) electrical conductivity obtained from different temperatures which is very beneficial in recording media as well as storing devices.

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