Effect of samarium nanoparticles on the electrical transport properties of polyaniline

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Abstract
A comprehensive study of the effect of samarium nanoparticles on electrical transport properties of polyaniline has been reported. Samples are prepared by chemical oxidative polymerization of aniline in the presence of samarium nanoparticles and characterized by XRD, FESEM, EDS, HRTEM and UV-Vis spectrometer. When the samarium content in polyaniline matrix increases, energy band gap decreases and conductivity increases by four orders of magnitude. A transformation of negative to positive magnetoconductivity has been observed by incorporating samarium nanoparticles in polyaniline matrix. Two types of activation behavior have been observed from the dielectric relaxation behavior. AC conductivity strongly depends on magnetic field. Although, at present, no theoretical model is found in literature to explain directly the behavior of ac conductivity in the presence of magnetic field, it may be due to the change of grain and interfacial boundary resistances by magnetic field.

Keywords: polyaniline, samarium, x-ray diffraction, electrical transport, dielectric properties

Classification numbers: 5.10

1. Introduction
Nanomaterials have excellent electrical properties over bulk materials and are thus being used in various electronic devices [1, 2]. Electrical properties of metal nanoparticles embedded in a dielectric medium have been a subject of immense interest. Conductivity of these systems depends on a number of factors, such as the concentration of the conducting fillers, their shape, size, and orientation, and the interfacial interaction between the filler molecules and host matrix; the conductivity also depends on the reaction temperature, time of polymerization, monomer-to-oxidant molar ratio, and oxidizing agent. Polyaniline, polypyrrole etc can be used as dielectric medium. These polymers are semiconductors with low charge carrier mobility. Their conductivity can be increased up to the metallic range by way of doping with different dopants [3, 4] and properties such as electrical, magnetic, optical, and chemical can also be tuned. Hence, these conducting polymers are widely used in different technological applications such as electromagnetic interference shielding, rechargeable batteries, electrodes, light-emitting diodes, sensors, corrosion protection coatings, and microwave absorption [5–8]. Excellent thermal and environmental stability, comparable level of conductivity and most economic synthetic procedure force one to select polyaniline as dielectric medium. It exhibits good electrical, optical, magnetic and chemical properties [9, 10]. Selection of dopant plays a significant role because the dopants can control different properties of the polymers. Structural disorder in the polymer chain may be caused by dopant, and as a result, charge defects can occur in the polymer matrix. Selection of the optimum parameters for synthesis can reduce the disorder and help to promote the conductivity of the polymers. Generally, the carriers in the process of doping in conducting polymers are known to be self-trapped by the conjugated polymeric chains in the form of polarons and bipolarons [11].
Most of the rare earth elements have unique electrical properties and thus we have chosen samarium for this study. There were a few reports in the literature for the composite of polyaniline with samarium. Ameen et al [12] reported synthesis and photoluminescence of this composite. Gupta et al [13] have reported optical and electrical properties of polyaniline samarium nanocomposite. But the detailed mechanism of electrical transport of polyaniline samarium nanocomposite was not investigated earlier. Our main motivation of this investigation is to study the mechanism and effect of samarium nanoparticles on electrical transport of polyaniline below room temperature (77–300 K).

2. Sample preparation and experimental techniques

Synthesis of a material is a vital part of material research, because proper tailoring is necessary to make a material interesting in properties. Of the different methods of preparation, chemical method of preparation of nanomaterials is more advantageous because a good control over stoichiometry of the reactants is obtained. Aniline (Merck), samarium nitrate (Merck), ammonium peroxodisulphate (APS, Merck), nitric acid and acetone (as available) required for this investigation is taken from the local market and purified as required. A simple in situ chemical method of preparation is followed for this investigation. An aqueous 1 mM aniline solution acidified with HNO₃ is mixed with 1 mM samarium nitrate solution and the mixture is stirred slowly with a magnetic stirrer to prepare homogeneous solution. Reaction temperature is maintained at 273 K throughout. Ice-cooled APS solution is added drop wise to this mixture. A green colored solution is obtained which is left in refrigerator at rest for 48 h to complete the polymerization process. A solid mass is obtained on centrifugation at 10 000 rpm for an hour. It is washed with acetone and double-distilled water to get pure nanocomposite. Samples are dried in an oven at 300 K overnight. To compare electrical properties, four samples are prepared using 0, 1, 5 and 10 mM samarium nitrate solution and they are marked as Pani-Sm₀, Pani-Sm₁, Pani-Sm₅ and Pani-Sm₁₀, respectively.

A very small part of the sample is pelletized in a hydraulic press and is coated with gold to take surface morphology by using a field emission scanning electron microscope (FESEM, Carl Zeiss Supra 40 vp). FESEM is conducted at 5 kV and electronic diffraction images are recorded. Elemental analysis is done by EDS x-ray detectors (Thermonoran, model SIX-NS 200). Morphology and the particle size is determined using transmission electron microscope (TEM). The phase identification is performed by Rigaku mini-flex-II desktop x-ray diffractometer (XRD) with nickel filter Cu-kα radiation (λ = 1.54 Å) in 2θ range from 20° to 90°. The UV-Vis spectrum of the samples is taken by a double beam spectrophotometer (U-1700 Shimadzu) using dimethyl sulphoxide (DMSO) as a solvent. Standard four-probe method has been used to measure the dc conductivity and it is measured in the temperature range 77 ≤ T ≤ 300 K in the presence and absence of magnetic field using pellets of individual samples.

3. Results and discussion

Knowledge of the crystal structure XRD analysis (given in figure 1) of polyaniline and its composite with samarium is obtained. The spectrum of Pani-Sm₀ shows no characteristic peak; only a hump near 25° is obtained. Thus, polyaniline is amorphous. The hump at 25° is for regular repetition of aniline monomer. Composite shows characteristic peaks at 2θ = 31, 34, 50 and 60° which are due to Bragg’s reflections from (009), (015), (110), (119) planes of the hexagonal phase of samarium (Joint Committee on Powder Diffraction Standard no-06-0419), respectively. This crystalline behavior of the nanocomposite is for the presence of samarium nanoparticles in polyaniline matrix. Average grain size (D) has been calculated by the Scherer’s formula: $D = \frac{k\lambda}{β\cos θ}$, where $k$ is particle shape factor (generally taken as 0.9), $λ$ is the wave length of Cu kα radiation (λ = 1.5414 Å), $θ$ is the diffraction angle of the most intense peak, and $β$ is defined as $β = \frac{β_m - β_s}{2}$, where $β_m$ and $β_s$ are the experimental full width at half maxima (FWHM) of the investigated sample and FWHM of a standard silicon sample, respectively. Grain size obtained using this formula is ~10 nm.

Inset of figure 2(a) shows FESEM micrograph of Pani-Sm₁₀. Well-resolved and circular-shaped grains are observed. Grains consist of polyaniline and samarium nanoparticles that adsorbed on polyaniline for the strong affinity of samarium nanoparticles to nitrogen atom of polyaniline. Diameter of the grains is ~10 nm. The chemical composition of the grain has been analyzed using EDS analysis. Figure 2(b) shows EDS of Pani-Sm₁₀. Samarium, nitrogen and carbon elements are present in the composite. Nitrogen and carbon are obtained.
from the polyaniline structure. Presence of samarium in the spectrum indicates that the composite must contain samarium element. Presence of gold (Au) is for gold coating used on the sample. Figure 2(c) shows the high resolution transmission electron microscope (HRTEM) image of Pani-Sm_{10}. The image shows particles circular in shape and ~5 nm in size. Particles are not uniform in size. Figure 2(d) shows HRTEM microgram of Pani-Sm_{10} and it shows interplanar d-spacing between the planes which is ~0.3 nm. Figure 2(e) shows selected area electron diffraction pattern of Pani-Sm_{10} indicating polycrystalline nature of the nanocomposite. It shows different circular rings which indicates the plane (009), (015), (110) and (119) of hexagonal phase of samarium. Thus, the nanocomposite is polycrystalline in nature.
To calculate the trend of changes in band gap and conductivity, optical absorption (given in figure 3) of Pani-Sm0 and Pani-Sm10 are taken for the same concentration (0.01% W V$^{-1}$) of each sample in DMSO at room temperature. Two absorption bands are observed at 320 nm (for $\pi-\pi^*$ transition in benzenoid rings of polyaniline) and 600 nm (for $n-\pi^*$ transition in quinoid rings of polyaniline). A similar type of observation was found in the literature [14, 15]. This observation indicates the formation of polyaniline. A red shift of both bands to 330 and 610 nm is obtained in nanocomposite. The red shift of the composite also indicates that the energy required for $\pi-\pi^*$ and $n-\pi^*$ transition in nanocomposite requires a lower amount of energy than in the case of polyaniline due to the interaction of samarium nanoparticles with amine and imine units of polyaniline. An extra peak is observed from optical absorption study. Temperature variation indicates the formation of polyaniline. A red shift of both bands to 330 and 610 nm is obtained in nanocomposite. The red shift of the composite also indicates that the energy required for $\pi-\pi^*$ and $n-\pi^*$ transition in nanocomposite requires a lower amount of energy than in the case of polyaniline due to the interaction of samarium nanoparticles with amine and imine units of polyaniline. An extra peak is obtained at 420 nm which is for the nanocomposites in the composite. Optical absorption is calculated using the equation $\alpha h\nu = A(h\nu - E_g)^n$, where $E_g$, $\alpha$, $h\nu$, $A$ are the band gap, absorption coefficient, frequency, constant, respectively and $n$ can take values of 0.5, 1.5, 2 and 3 depending on the mode of transition [16]. Here $n = 0.5$ offers the best fit for the optical absorption data of the samples and it indicates the allowed direct band transition of the materials. To calculate the band gap, a plot (given in the inset of figure 3) of $(\alpha h\nu)^2$ versus $h\nu$ has been done and then the value of band gap has been extracted by extrapolating the straight portion of the graph on $h\nu$ axis at $\alpha = 0$. Band gap values are 2.7, 2.4, 2.2, 2.1 eV for Pani-Sm0 and Pani-Sm1, Pani-Sm5 and Pani-Sm10, respectively. Conductivity of polyaniline increases in presence of samarium nanoparticles due to the decrease in band gap. Electrical conductivity measurements reflect similar type of result.

DC conductivity of polyaniline is measured to interpret the influence of samarium nanoparticles on it in the temperature range $77 \text{ K} \leq T \leq 300 \text{ K}$. Room temperature conductivity for different samples varies from $10^{-8}$ to $10^{-4} \Omega^{-1} \text{ m}^{-1}$ with increasing the Sm nanoparticles in polyaniline matrix. This is due to the decrease of band gap of the composites in presence of Sm nanoparticles, which has already been observed from optical absorption study. Temperature variation of conductivity for all the samples is shown in figure 4. According to the figure, conductivity increases with increasing temperature i.e. semiconducting nature. With increasing temperature, the charge transfer between Sm nanoparticles and polyaniline may increase and, as a result, conductivity increases with increasing temperature. Generally Mott’s variable range hopping (VRH) theory [17] is responsible for explaining the conduction mechanism in such disordered semiconductor and the conductivity is given by the relation

$$\sigma(T) = \sigma_0 \left(\frac{T_{\text{Mott}}}{T}\right)^{1/2} \exp\left[-\left(\frac{T_{\text{Mott}}}{T}\right)^\gamma\right]$$

(1)

$$T_{\text{Mott}} = \frac{16}{k_B N\langle E_F\rangle L_{\text{loc}}^3}$$

(2)

where $\sigma_0$ is a constant which represents the conductivity at infinite temperature, $T_{\text{Mott}}$ denotes the Mott characteristic temperature, $k_B$ is the Boltzmann constant, $N\langle E_F\rangle$ is the density of states at Fermi level, $L_{\text{loc}}$ is the localization length and $\gamma$ is the VRH exponent, the value of which determines the dimensionality of the charge conduction mechanism i.e. for three dimensions $\gamma = 1/4$, two dimensions $\gamma = 1/3$ and one dimension $\gamma = 1/2$. In order to obtain the actual dimensionality of the charge transport, graphs of $\ln[T^{1/2}\sigma(T)]$ with $T^{1/2}$, $T^{-1/2}$ and $T^{-1/4}$ have been plotted, but a linear variation is obtained in the plot of $\ln[T^{1/2}\sigma(T)]$ with $T^{-1/4}$ (given in figure 4). Hence the linear variation for $\gamma = 1/4$ indicates that the three-dimensional conduction mechanism is responsible for our investigated samples. From the slopes of the linear curve, the values of $T_{\text{Mott}}$ have been calculated, which lies between 3830–6320 K and listed for different samples in table 1.
In order to understand the effect of magnetic field on dc conductivity of the different samples, dc magnetoconductivity at $T = 300$ K has been measured and the variation of magnetoconductivity ratio $\sigma(B, T)/\sigma(0, T)$ with magnetic field ($B < 1$ T) is shown in figure 5. In the figure a transformation of negative to positive magnetoconductivity has been observed due to incorporation of samarium nanoparticles in polyaniline matrix. Generally two types of hopping processes (i) wave function shrinkage model [18, 19] and (ii) forward interference model [20–22] are used to analyze the dc magnetoconductivity. In the wave function shrinkage model, the wave function of electrons is contracted by application of magnetic field and due to which the average hopping length $(R_{\text{hop}})$ reduces. Under this condition, the conductivity of the samples decreases with increasing magnetic field (negative magnetoconductivity) and the magnetoconductivity ratio can be given as [18]

$$\frac{\sigma(B, T)}{\sigma(0, T)} = \exp\left[-t_1 \frac{e^2 L_{\text{loc}}^2}{h^2} \left(\frac{T_{\text{Mott}}}{T}\right)^{3/4} B^2\right]$$  \hspace{1cm} (3)$$

where $t_1$ is a constant ($t_1 = 5/2016$). On the other hand, in forward interference model, the forward interference is occurred among the random paths between two sites spaced at a distance equal to optimum hopping distance and the effect is more prominent for the systems having large value of $R_{\text{hop}}$. In such system magnetoconductivity increases with increasing magnetic field (positive magnetoconductivity) and given by the relation as

$$\frac{\sigma(B, T)}{\sigma(0, T)} = 1 + \frac{C_{\text{sat}} B / B_{\text{sat}}}{1 + B / B_{\text{sat}}}.$$  \hspace{1cm} (4)$$

where $C_{\text{sat}}$ is a temperature independent parameter and $B_{\text{sat}} = 0.7(h/e)(8/3)^{3/2}(1/L_{\text{loc}}^2)(T/T_{\text{Mott}})^{3/8}$. Therefore, due to competition of these two effects, the sign and magnitude of magnetoconductivity of the Pani and Pani-Sm nanocomposites are changed. Different points in figure 5 are the experimental data for different samples and the solid lines are the theoretical best fit obtained from equation (3) for polyaniline and equation (4) for polyaniline-samarium nanocomposites. The localization length $L_{\text{loc}}$ can be obtained from this analysis for different samples and given in table 1. By using the values of $L_{\text{loc}}$ and $T_{\text{Mott}}$ in equation (2) the values of $N(E_F)$ have been calculated and are listed in table 1. Similar results have been obtained in some previous works [23, 24]. In the inset of figure 5, it is observed that the magnitude of the magnetoconductivity ratio of Pani-Sm$_{10}$ increases with increasing temperature. This would be explained by observing the variation of average hopping length with temperature. The average hopping length $(R_{\text{hop}})$ can be expressed by the relation

$$R_{\text{hop}} = \left(3/8\right)(T_{\text{Mott}}/T)^{3/4} L_{\text{loc}}$$  \hspace{1cm} (5)$$

The average hopping length has been calculated for different samples by using the equation (5) and its value increases from 1.82–12 nm with increase of samarium nanoparticle in polymer matrix (listed in table 1). It is observed from the table the value of $R_{\text{hop}}$ for Pani-Sm$_0$ is much less than the values for Pani-Sm$_1$, Pani-Sm$_5$ and Pani-Sm$_{10}$. So the observed negative magnetoconductivity for Pani-Sm$_0$ may be due to lower value of $R_{\text{hop}}$. The temperature variation of average hopping length is shown in figure 6, which is increasing with increasing temperature. Therefore, the enhancement of magnitude of magnetoconductivity ratio with increasing temperature may be due to the increase in average hopping length with temperature.

The frequency dependent dielectric permittivity of a solid arises due to different mechanisms such as (i) displacement of ionic charge w.r.t their nuclei and this contribution is important at high frequency, (ii) displacement of ions from their equilibrium positions and (iii) dipolar contribution. Out of these three contributions only the dipolar contribution

| Parameters | Pani-Sm$_0$ | Pani-Sm$_1$ | Pani-Sm$_5$ | Pani-Sm$_{10}$ |
|------------|-------------|-------------|-------------|---------------|
| $\sigma_{\text{dc}}$ (300 K) ($\Omega^{-1} \text{m}^{-1}$) | $1.2 \times 10^{-8}$ | $7.3 \times 10^{-8}$ | $4.2 \times 10^{-6}$ | $2.3 \times 10^{-4}$ |
| $T_{\text{Mott}}$ (K) | 6320.46 | 6070.17 | 4931.57 | 3830.15 |
| $L_{\text{loc}}$ (nm) | 10.38 | 27.71 | 50.24 | 60.43 |
| $N(E_F)$ (states/J m$^{-3}$) | $7.84 \times 10^{43}$ | $4.28 \times 10^{42}$ | $8.86 \times 10^{41}$ | $6.55 \times 10^{41}$ |
| $R_{\text{hop}}$(nm) | 1.82 | 4.90 | 9.35 | 12.00 |
shows the frequency and temperature dependence at low temperature. In this case the frequency dependent dipolar conductivity obeys the power law. Including the dc contribution, the total frequency dependent conductivity for a semiconductor or a disordered system is found to follow the universal dielectric response (UDR) behavior, which is given by \[17, 25, 26\]

\[
\sigma(f, T) = \sigma_{dc}(T) + \sigma_{ac}(f, T) = \sigma_{dc}(T) + \alpha(T)f^s, \quad (6)
\]

\[
\sigma_{ac}(f, T) = \sigma(f, T) - \sigma_{dc}(T) = \alpha(T)f^s, \quad (7)
\]

where \(\sigma_{dc}(T)\) is the dc conductivity, \(\alpha(T)\) is a constant for a particular temperature, \(f\) is the frequency and \(s\) is the frequency exponent, \(0 \leq s \leq 1\). The magnitude and temperature variation of \(s\) represent the microscopic hopping process and the nature of charge carriers. Figure 7 shows the linear variation of \(\ln\sigma_{ac}(f)\) with \(\ln f\) at 300 K for different samples and the inset of figure 7 shows the same variation for Pani-Sm10 sample at different yet constant temperatures. From the slope of the linear variation of \(\ln\sigma_{ac}(f)\) with \(\ln f\) for each temperature, the value of \(s\) has been calculated at that temperature. The variation of \(s\) with temperature is shown in figure 8 for different samples, which decreases gradually with increasing temperature. In literature it was established that different conduction mechanisms provide the different functional dependency of \(s\) with temperature, which are given below:

1. Quantum mechanical electron tunneling, in which \(s\) is independent of temperature but depends on frequency [25].
2. Small polaron quantum mechanical tunneling, where \(s\) increases with increasing temperature [26]. But in large polaron quantum mechanical tunneling the value of \(s\) first decreases and then increases with further increasing of temperature [25].
3. In classical hopping over barrier (HOB) model, the value of \(s\) is unity [25].
4. For correlated barrier hopping (CBH) model, the value of \(s\) gradually decreases with increasing temperature [26].

Therefore, the actual charge transport mechanism may be obtained from the analysis of the temperature variation of \(s\). Experimental result shows that \(s\) gradually decreases with increasing temperature for different samples. Hence only the CBH model matches with our observed behavior. According to CBH model, the charge carrier hops between the sites (charged defect states) over the potential barrier separating them and the frequency exponent \(s\) can be written as [26]

\[
s = 1 - \frac{6k_BT}{W_H - k_BT\ln(1/\omega\tau_0)}, \quad (8)
\]

where, \(k_B\), \(W_H\), \(\omega\) and \(\tau_0\) are the Boltzmann constant, effective
barrier height, angular frequency and characteristic relaxation time respectively. Variation of $\varepsilon$ with temperature are given in figure 8, where the points are experimental data and solid lines are the best fitted values from equation (8). It is observed that the equation (8) is well fitted with the experimental data. The values of the fitting parameters such as $W_D$ vary from 0.1 to 0.2 eV and $\tau_0$ at 1 MHz varies from $6 \times 10^{-10}$ to $4 \times 10^{-3}$ sec for different samples, respectively.

Capacitance ($C_p$) and dissipation factor ($D$) are measured within a frequency range 20 Hz to 1 MHz and temperature 77 K $\leq T \leq$ 300 K. Real $\varepsilon'$ and imaginary $\varepsilon''$ part of dielectric permittivity can be calculated from the relations

$$\varepsilon' = \frac{C_p d}{\varepsilon_0 A}, \quad (9)$$

$$\varepsilon'' = \varepsilon' D, \quad (10)$$

where $\varepsilon_0$ is the permittivity of free space ($\varepsilon_0 = 8.85 \times 10^{-12}$ F m$^{-1}$), $A$ is the area of the electrodes and $d$ is the thickness of the sample. The variation of the real part of dielectric permittivity with frequency at constant yet different temperatures for Pani-Sm$_{10}$ has been shown in figure 9. It is observed from the fact that the dielectric permittivity is strongly dependent on frequency at lower frequency region, where $\varepsilon'(f)$ decreases with increasing frequency and the variation is enhanced at higher temperature than lower temperature. However, a nearly frequency independent behaviour has been observed at higher frequency $f > 10$ kHz. This is because, the dipoles at lower temperature are freeze and polarization is decayed, due to which a sharp decrease in $\varepsilon'(f)$ has been observed at lower frequency. Such behaviour has been observed in the samples containing different permittivity and conductivity region. The dielectric permittivity of such an inhomogeneous system can be analysed by Maxwell—Wagner-Capacitor model [27–29] by considering the equivalent circuit consisting of resistance and capacitance due to grain and interfacial boundaries. According to this theory, the real part of complex impedance $Z'$ can be expressed as

$$Z' = \frac{R_g}{1 + (\omega R_g C_g)^2} + \frac{R_{gb}}{1 + (\omega R_{gb} C_{gb})^2} \quad (11)$$

where $R_g$, $R_{gb}$, $C_g$ and $C_{gb}$ are the grain resistance, interfacial boundary resistance, grain capacitance and interfacial boundary capacitance, respectively. The experimental value of real part of impedance $Z'(f)$ has been calculated by using the relation

$$Z'(f) = \frac{\varepsilon''(f)}{\varepsilon_0 \varepsilon'[\varepsilon'(f)^2 + \varepsilon''(f)^2]}, \quad (12)$$

Contribution of grain and interfacial boundary resistances and capacitances may give information about the transport process in the composites. The grain and grain boundary resistance and capacitance have been evaluated from the fitting of experimental data with theoretical expression of $Z'$ (equation (11)) at 300 K (not shown in the manuscript) and values lie in the range 0.02 to 1.20 M$\Omega$ for $R_g$, 0.40 to 1.40 nF for $C_g$, 0.35 to 75 M$\Omega$ for $R_{gb}$, 0.06 to 1.50 nF for $C_{gb}$ for different samples. From the values it is observed that interfacial boundary resistance is much greater than that of grain resistance. Thus, interfacial boundary contribution dominated over the grain contribution in the samples. The conduction process can be explained by the hopping mechanism, where the carrier mobility is dominated by a factor that increases with temperature exponentially. This temperature dependent factor is determined by thermal activation in order to overcome the potential barrier between the sites by hopping. Both grain and interfacial boundary resistances follow this mechanism and the total resistance $R = R_g + R_{gb}$ variation can be expressed as follows: $R \sim \exp(E_a/k_B T)$, where $E_a$ is the activation energy. The plots of $\ln R$ versus $1/T$ in figure 10 support the above explanation. According the figure, the
composites exhibit two different activations, one with \( E_a = 7 \)–10 meV for low temperature region and the other with 10–80 meV for high temperature region. This discrepancy probably arises due to the anomalous conduction mechanism in the investigated samples.

The hopping of the charge carriers to a new site can be successful only if it is followed by the polarization cloud around the charge carriers [30]. An electric relaxation time \( \tau \) is required for the mutual movement of the charge and the associated polarization cloud. The relaxation time can be obtained from the peaks of the \( \varepsilon'' - f \) plot [31]. \( \varepsilon'' \) decreases with increasing frequency for these samples (given in the inset of figure 9). The magnitude of \( \varepsilon'' \) may be regarded as the contribution of three distinct effects, dc conductance, interfacial polarization and the usual dipole orientation or Debye loss [32]. It appears that \( \varepsilon'' \) increases with decrease in frequency revealing that there is interfacial polarization in the composite. In general, the conduction due to the conductive part of the disordered systems masks the interfacial polarization [31]. In such cases, the dielectric properties of the samples can be described by the complex electric modulus \( M^* \) [33], which can be defined as

\[
M^* = \frac{1}{\varepsilon''} = M' + iM'' = \frac{1}{\varepsilon' - i\varepsilon''} = \frac{\varepsilon' + i\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \tag{13}
\]

The imaginary part of the complex electric modulus \( M'' \) has been calculated using equation (13) and the frequency dependence of \( M''(f) \) at 300 K is indicated in figure 11(a) for different samples. A loss peak is found in all the curves which may be due to the interfacial polarization at a particular frequency range for each composite. At a fixed temperature, by application of electric field, the charge carriers move freely, however they are blocked at the interface and produce

\[\text{Figure 11.} \quad \text{(a) Frequency dependence of imaginary part of the electric modulus } M'' \text{ at } 300 \text{ K. (b) Frequency dependence of } M' \text{ at different temperature. (c) Normalized plots of } M'/M'_{\text{max}} \text{ with } f/f_{\text{max}} \text{ at different temperatures.}\]
interfacial polarization. The relaxation peaks shifts towards the higher frequency side with an increase of the Sm nanoparticles. By increasing Sm nanoparticles more charges may accumulate at the interface resulting in a decrease of relaxation time, so interfacial polarization increases and relaxation peak shifted to higher frequencies [34]. The frequency dependence of $\varepsilon'(f)$ at different temperature is indicated in figure 11(b) for Pani-Sm$_{10}$ sample. The relaxation peaks shifts towards the higher frequency side with increasing temperature. Due to increase in temperature, motion of the charge carrier increases and accumulation of the free charges occurs at the interface within the sample and also there is an increase of the charge carrier mobility. As a result, the relaxation time decreases and a shift of the loss peak towards the higher frequency side have been observed with increase in temperature.

The normalized plots of $\frac{M^*}{M^+_{\text{max}}}$ with $f/f_{\text{max}}$ have been scaled in figure 11(c) at different temperatures. Spectra for $M^* (f)$ for different temperatures merge on a single curve. This means that all dynamic processes occurring at different temperatures exhibit similar activation energy. Activation energy $E_a$ for hopping which contributes to the relaxation behavior can be obtained by an analysis of the temperature variation of the relaxation time $\tau_m$ given by Arrhenius equation

$$\tau_m = \tau_0 \exp \left( \frac{E_a}{k_B T} \right)$$

where $\tau_0$ is the pre-exponential factor, $E_a$ is the activation energy. The values of $\tau_m$ corresponding to the maxima can be evaluated by an analysis of the temperature variation of the relaxation time $\tau_m$ given by Arrhenius equation

$$\tau_m = \tau_0 \exp \left( \frac{E_a}{k_B T} \right)$$

where $\tau_0$ is the pre-exponential factor, $E_a$ is the activation energy. The values of $\tau_m$ corresponding to the maxima can be evaluated by the relation

$$f_{\text{max}} = \frac{1}{2\pi\tau_m}$$

where $f_{\text{max}}$ is the frequency at which the maximum $M^* (f)$ occurs and $\tau_m$ is the corresponding relaxation time. A plot of $\ln \tau_m$ as a function of inverse temperature (given in figure 12) shows two slopes which indicate the presence of two activation energies. The value of the slopes at lower temperature region (77–150 K) is small (activation energy below 15 meV), whereas the value of the slopes becomes higher (activation energy above 30 meV) at the higher temperature region (150–300 K). The low values of the activation energy may indicate a strong charge transfer due to delocalization of charge carriers along the polyaniline chain [35–38].

Figure 13 shows the magnetic field dependence of the real part of complex conductivity $\sigma' (f)$ for different samples at room temperature and $f = 1$ MHz. It is observed from the figure that the value of the complex conductivity for all the investigated samples increases monotonically with increasing magnetic field. Generally this type of behavior has been observed in multiferroic materials. Although, no theoretical model is available in the literature to explain such behavior in polyaniline–samarium nanocomposite, we try to explain this as follows. It is already established that for heterogeneous samples, the real and imaginary part of dielectric permittivity and impedance strongly depend on the grain and interfacial boundary resistances and capacitances. On the other hand the real part of complex conductivity has been determined from the imaginary part of the dielectric permittivity by the relation

$$\sigma' (B, f) = \frac{d}{A(R_g + R_{\phi})} \times \frac{1 + \alpha^2 R_{\phi} (C_g^2 R_g + C_{\phi}^2 R_{\phi}) / (R_g + R_{\phi})}{1 + \left[ \alpha R_{\phi} (C_g + C_{\phi}) / (R_g + R_{\phi}) \right]^2}$$

where the symbols have their usual meaning. It is observed from equation (16) that the value of real part of complex conductivity strongly depends on the grain and interfacial
boundary resistances and capacitances. Therefore, due to the change of the value of these resistances by application of magnetic field may affect the value of the complex conductivity. In order to compare the result, we have calculated the values of $R_g$, $R_{gb}$, $C_g$ and $C_{gb}$ from the analysis of experimental data for real part of complex impedance with equation (11) in absence and in presence of constant magnetic field $B = 0.8$ T (not shown in the manuscript). From the best fitted values of $R_g$, $R_{gb}$, $C_g$ and $C_{gb}$, we have calculated $\sigma'(0,f)$ and $\sigma'(B,f)$ using equation (16) for the sample Pani-Sm$_{10}$. Hence the calculated value of $\sigma'(B,f)/\sigma'(0,f)$ is 1.018 which is in good agreement with the experimental value 1.0177. From this analysis, it may be presumed that the values of these resistances by application of magnetic field is due to the change of grain and interfacial boundary resistances and capacitances by the applied magnetic field. However, due to unavailability of the mathematical expression for grain and interfacial boundary resistance and capacitance with magnetic field, the measured data cannot be analyzed directly with theory. So, to formulate the actual mechanism, more theoretical and experimental studies are essential.

4. Conclusions

In conclusion Polyaniline–samarium nanocomposite has been prepared by in situ chemical oxidative polymerization of aniline. Samples were characterized by XRD, FESEM, EDS, HRTEM and UV-Vis spectrometer. An enhancement of conductivity is obtained with increase of samarium nanoparticles in polyaniline matrix. Energy band gap of different samples has also decreased from 2.7 to 2.1 eV. A transformation of negative to positive magnetoconductivity has been observed by incorporating samarium nanoparticles in polyaniline matrix and can be explained in terms of orbital magneto conductivity theory. The real part ac conductivity follows the power law $\sigma(f) \propto f^\alpha$. The temperature dependence of universal dielectric response parameter $s$ was found to follow correlated barrier hopping charge transfer mechanism. The frequency dependent real part of complex permittivity can be interpreted by Maxwell–Wegner capacitor model. The grain contribution was found to be smaller than the interfacial boundary contribution. Two types of activation behavior have been observed from the dielectric relaxation behavior. AC conductivity strongly depends on magnetic field; it may be due to the variation of grain and interfacial grain boundary resistances by the application of magnetic field. However, due to the inability of the analytical expression, the measured data can not be compared with the theory. Thus, a more explicit theoretical and experimental study is required to reveal the true mechanism of magnetic field dependent ac conductivity.

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