Structural and Dielectric Properties of Strontium Ferrite Doped Polyaniline Composite

Satish Jogad[1], Rakesh Vishwarup[1], Latha M S[2], V S Betageri[3,*], G H Pujar[1,4*]

[1] Department of Physics, GM Institute of Technology, (Affiliated to VTU, Belagavi), Davanagere-577006, Karnataka, India

[2] Department of PG Studies in Chemistry, Adikavi Sri Maharshi University, Raichur -584104, Karnataka, India

[3] Department of Chemistry, GM Institute of Technology, (Affiliated to VTU, Belagavi), Davanagere-577006, Karnataka, India

[4] Department of Physics, Government First Grade College, Harapanahalli-583131, Karnataka, India

***Abstract*:**

Polyaniline (PANI)/Strontium Ferrite (SrFe) composite samples with various dopant percentages of SrFe were synthesized at a temperature of about 0 – 5^0 C in a freezing mixture to prevent the warming in situ chemical oxidative polymerization method. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were used to characterise the structure of prepared samples and to assess the doping effect of SrFe. The creation polyaniline is confirmed by the X-ray pattern, and the composites were more strongly orientated and their amorphous character vanished as the SrFe percentage grew and SEM study shows that SrFe particles have a significant impact on the morphology of composites with average grain size of 2-5 µm. The dielectric properties of the prepared samples were done by plotting graph of dielectric constant (ϵ) vs logf which shown fall of ϵ with logf indicating semiconductor like behavior of the prepared Polyaniline (PANI)/Strontium Ferrite (SrFe) composite samples.

Keywords: PANI/ SrFe, Hexagonal, granular structure, Strontium Ferrite, Dielectric constant & tan **δ**.

Introduction:

Due to unique as electrical, optical and magnetic properties, conducting polymers have increasing scientific and technical interest and offering the opportunity to prepare new polymer materials [1]. Conducting polymers are characterized by a conjugated structure of alternating single and double bonds. The feature shared by all them originates from the common nature of their π - electron system, an enhanced conductivity in oxidized or in reduced state and reversible redox activation in a suitable environment [2]. Among all the conducting polymers, polyaniline has a unique and wide range electrical, dielectric properties and good stability. Hence polyaniline have been considered as prominent new materials for the fabrication of the devices. Polyaniline (PANI) is an important conducting polymer because of its high conductivity in doped state. PANI has wide range of application due to its flexible properties in different area. Such some applications are solar cell, LED, sensors, radiation absorbers and electromagnetic shields. It is possible to alter the properties of the PANI by the process of doping metal oxide or various types of particles with polyaniline. It is one of so called polyaniline composite, in which conductivity results from a process of partial oxidation or reduction. When the metal oxide or various types of particles are doped with polyaniline, the charge-transfer reaction takes place between polyaniline and doping agent [3-5]. The bond length and angles changes when charges are removed from the polyaniline upon chemical doping. The charge is localized over the region of several repeating units. Since the localized charges can move along the polymer chain, they are regarded as charge carriers in conducting polymer. Ammonium persulfate was used as an oxidant to minimize the presence of residual aniline and to obtain the best yield of PANI [4-6].

Strontium ferrite is a highly magnetic material, has a high packing density, and is a metal oxide and it has found applications in magnetic card strips, speakers, and magnetic tapes. One area in particular it has found success in is long-term data storage; material is magnetic and resistant to temperature, corrosion, and oxidization. Strontium ferrite has been considered for long term data storage [5, 6]. The material has proven to be resistant to a number of different environmental stresses, including humidity and corrosion. Because ferrites are already oxidized it cannot be oxidized any further. This is one reason ferrites are so resistant to corrosion. Strontium ferrite also proved to be resistant to thermal demagnetization, another issue common with long term storage [7]. When strontium ferrite magnets increase in temperature, their high intrinsic coercivity improves, this is what makes it more resistant to thermal demagnetization. Strontium ferrites are robust ceramics that are generally stable to moisture and corrosion-resistant. SrFe is also an oxide so it does not break down due to oxidation as much as a metal alloy might; giving a much greater life expectancy.

The category of permanent magnets known as hexagonal ferrites has a general formula $MFe_{12}O_{19}$, where M is the divalent ion. The oxygen ions in a unit cell with a close-packed hexagonal arrangement and two molecules of $MFe_{12}O_{19}$ create the crystal structure of hexagonal ferrites. The unit cell has a total of 24 Fe^{3+} ions, 38 O^{2-} ions, and 2 M^{2+} ions. Strontium ferrites ($SrFe_{12}O_{19}$) are a class of hard magnetic materials with hexagonal structure used in magnetic tapes, speakers, and card strips. It also has a high packing density [8]. Because of its high resistivity, wide permeability, high magnetization value, and favorable dielectric characteristics at microwave frequencies, hexagonal barium ferrite is employed as a good microwave absorber [5-9].

In the present work, we have studied detailed structural and dielectric properties of SrFe/PANI composites.

Materials and Methods: The first and foremost process of synthesising polyaniline involves dissolution of 5 millilitres of aniline in 200 millilitres of 1M HCl, strontium ferrite sample is added to the mixture in weight percentages of 10, 20, 30, and 40. The mixture is then continually agitated to ensure that the strontium ferrite is suspended in the solution.11.4 gm of Ammonium persulphate ($(NH_4)_2S_2O_8$) is dissolved in 300 ml of 1M HCl, and is added very gradually, drop by drop, to the mixture of aniline, HCl, and strontium ferrite solution while being continuously stirred for two to four hours using a magnetic stirrer. In a freezing mixture, the polymerisation was performed by keeping the reaction mixture between 0 to 5 ^{0}C to avoid warming. The recovered precipitated powder was vacuum-filtered and cleaned using acetone and deionised water. Ultimately, the precipitate was dried in an oven for 24 hours in order to maintain a consistent weight. Thus, four distinct polyaniline-strontium ferrite composites have been created, each containing a varying weight percentage of barium ferrite (10, 20, 30, and 40) in polyaniline [11-14]. The details of process involved in samples's preparation is depicted in **Figure-1**. With acetone present, all of the aforementioned composites are ground into a fine powder in an agate mortar.

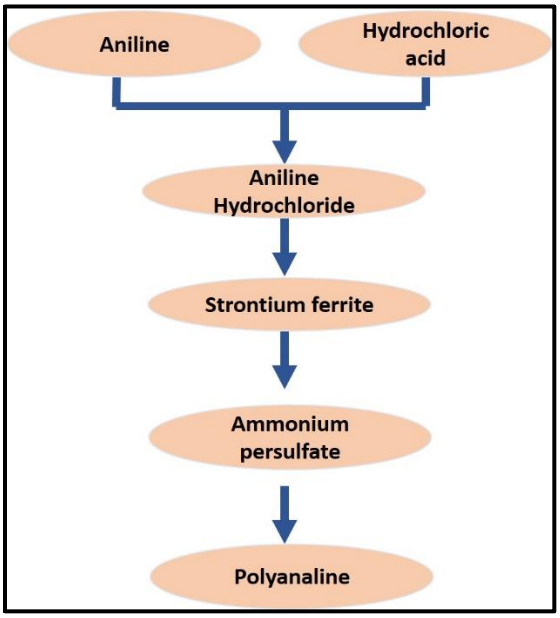

Figure 1. Synthesis route of SrFe/PANI composites.

Results and Discussions:

X-ray diffraction

Material's physical features are highly connected to their crystal structure, which describes their atomic arrangement. The structural analysis of the sample was studies by X-ray diffraction technique. **Figure 2** shows the XRD pattern of the SrFe/PANI for different additive weight percentage (10%, 20%, 30%, & 40%) respectively. Generally polyaniline is the amorphous in nature. From pattern it reveals that, the synthesized pure polyaniline is semi-crystalline [9-15]. The semi-crystalline nature of polyaniline obtained may be due to ammonium persulfate used in the synthesis as oxidant and it is crystalline as doping percentage increases due to the presence of SrFe in the polyaniline[14,16].

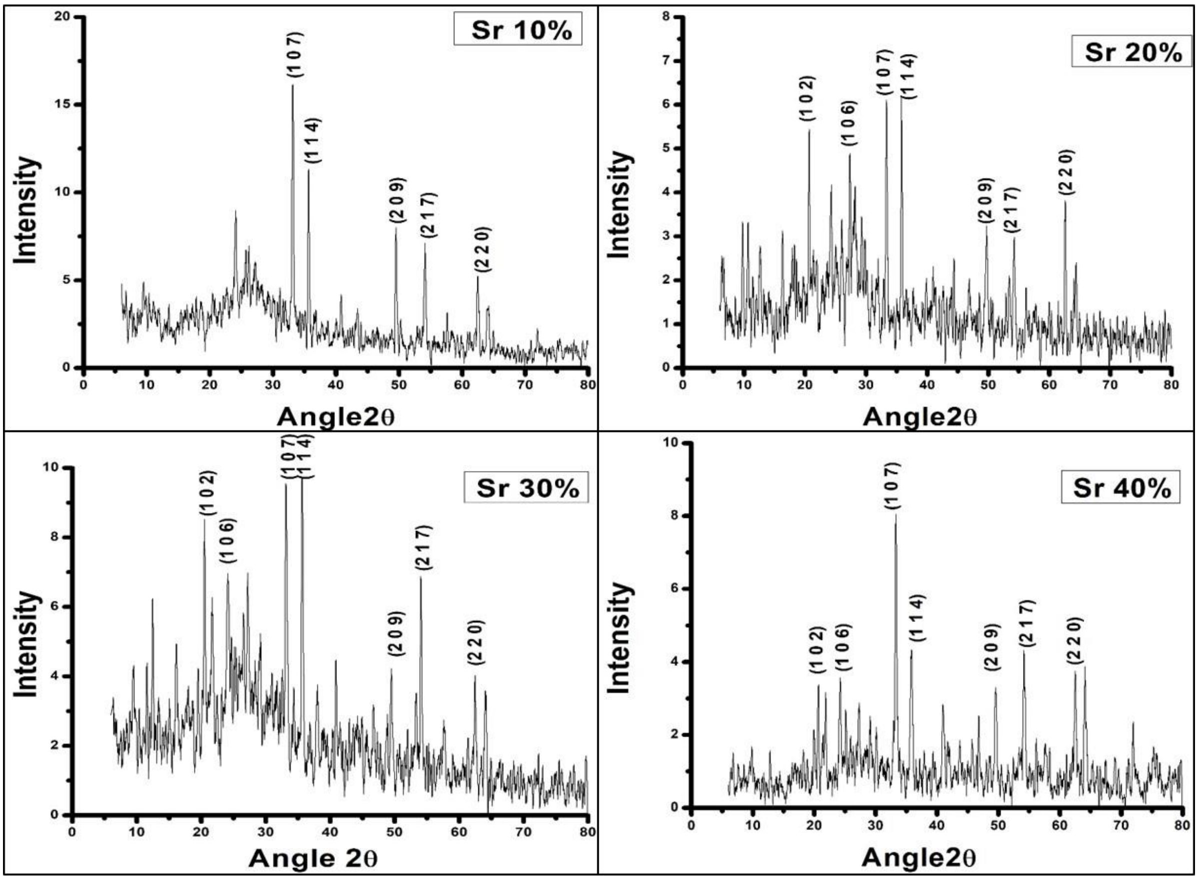

Figure 2. XRD pattern of SrFe /PANI composites.

According to the XRD pattern. Diffraction angles ranged from 0^0 to 80^0 with a 0.01^0 step and a 2^0/min scan rate. The predicted inter-planar spacing and observed inter-planar spacing have been found to be in strong agreement, and the data are well aligned and match the $SrFe_{12}O_{19}$ literature data. The diffraction peaks (107), (114), (209), (217), and (220) correlate to the distinctive crystallographic planes of ferrites [15, 17]. The significant broadening of the observed peaks suggests that the produced ferrites have nano-scale properties. It shows the prominent peaks 2θ near the values 33^0, 35^0, 40^0, 49^0, 54^0, and 62^0.

The average crystalline size of the SrFe/PANI are calculated by using Debye -Scherrer formula,

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \ldots (1)$$

Where D is average crystalline size, λ is wavelength of the X-ray, K is crystallite shape factor a good approximation is 0.9, β is the full width at half the maximum (FWHM) of the X-ray diffraction peak and 2θ is the Braggs' angle (deg.).

The quantity of dislocations in a unit volume of a crystalline material is known as the dislocation density. A crystal lattice will distort due to edge and screw dislocations, creating elastic tension around the dislocation line and resulting in micro strain.

Micro strain (ε) and dislocation density(ρ_D) can be computed using the formula

$$\rho_D = \frac{1}{D^2} \quad \text{... (2)}$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad \text{... (3)}$$

The calculated values of average crystallite size (D), dislocation density(ρ_D), and microstrain(ε) for different weight percentage of Sr ferrites as given in **Table. 1**.

Table. 1 The Average Crystallite size, Dislocation Density Micro Strain and Average Grain size of SrFe /PANI composites.

Percentage of Sr Ferrite in PANI	**10%**	**20%**	**30%**	**40%**
Average Crystallite size D (nm)	53.8	84.9	59.0	85.6
Dislocation Density ρ_D ($X10^{14}\ m^{-2}$)	3.49140	1.4	2.9	1.41
Micro Strain ε ($X10^{-3}$)	0.647	0.409	0.589	0.411
Average Grain size (µm)	5.45	3.15	4.24	6.55

We observe that for highest weight percentage of Sr ferrite, average crystallite size is greater indicating that enhancement of unit cell due to Sr ferrite composition. And we can also observe that dislocation density(ρ_D), and microstrain(ε) values being reduced due increase of weight percentage of Sr ferrite indicating more ordered arrangement of atoms in the unit cell.

Morphological Study:

SrFe /PANI composites were subjected to morphological and microstructural investigation using JEOL Model JSM - 6390LV. The SEM micro images show that by altering the weight percentage of Sr ferrite, morphology changes continually. **Figure. 3** illustrates the surface morphology of pure polyaniline Sr Fe /PANI with the weight percentage of Sr ferrite 10%, 20%, 30%, & 40% respectively. The SEM images of SrFe /PANI composites shows uniform morphology with semi-crystalline like structure in the PANI image.

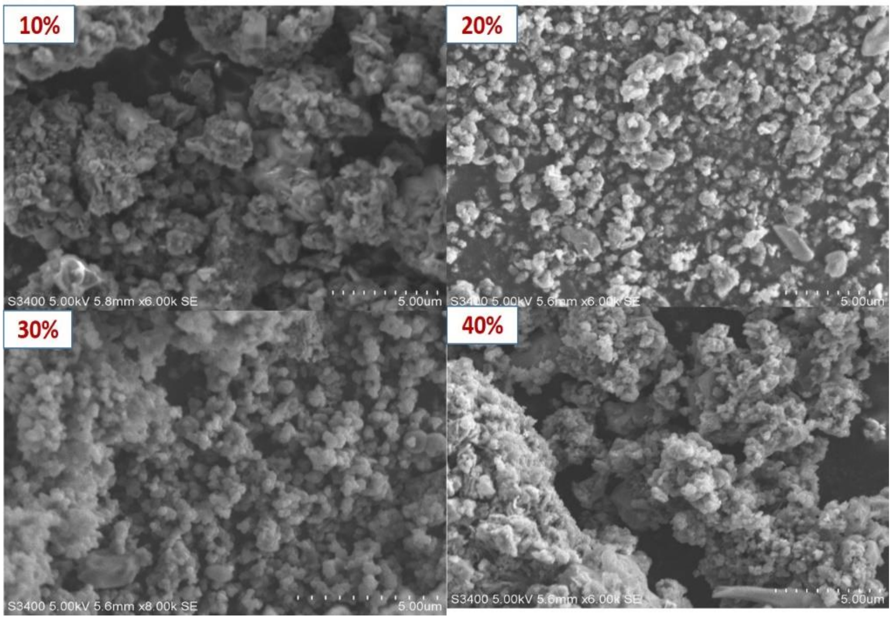

Figure 3. SEM image of SrFe /PANI composites

SEM pictures demonstrate that the weight proportion of Sr Ferrite causes morphology to change continually and that the particles have aggregated into sizable clusters [16-19]. Dopant metal oxide particles are scattered throughout PANI in the SEM picture of SrFe/PANI. PANI is mostly made up of granular, nonporous, aggregated grains of various sizes that are organised irregularly. It has also been noted that the fraction of composites has little effect on the morphological appearance. The natural interplay between magnetic nanoparticles and the heating process prompted the creation of some agglomerated zones in the SEM pictures [18]. The average grain size was calculated as 3-7µm and tabulated in the **Table. 1.** We can observe that highest grain size is obtained for highest weight percentage of Sr ferrite indicating more amount of nucleation process at the highest weight percentage of Sr ferrite and also we observe that the grain size exceeds the crystallite size estimated by Scherer's equation.

Dielectric Properties:

Ferrites are materials that are dielectric, whether the magnetic field is present or not, the dielectric properties are always crucial. As much as 10^{14} times more resistivity exists in ferrites than in metals. This makes it possible for the material to store a lot of electrical charge or to store it for a long time. Greater dielectric constant materials are highly helpful for making high value capacitors. The formula for a parallel plate capacitor's capacitance is

$$C = \left[\frac{\varepsilon_0 \varepsilon_r A}{d}\right] \quad \ldots (4)$$

Where A is area of cross-section and d is pellet's thickness, ε_0 is free space's permittivity and ε_r is the ferrite sample's relative permittivity. Using the relationship given below the samples' dielectric permittivity has been computed.

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \quad \ldots (5)$$

The loss tangent, which is used to express the dielectric loss, is defined as

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'} \quad \ldots (6)$$

Where ε_r' and ε_r'' are real and imaginary parts of the dielectric constant.

The grain size, grain boundary, density, porosity and chemical content of the samples all affect the AC conductivity in general [20-22]. The steps involved in determining AC conductivity from values of the dielectric constant are as follows. Any capacitor will experience some current loss when charged under a voltage because of ohmic resistance or impedance caused by heat diffusion. The AC conductivity for a parallel plate capacitor with a cross-sectional area of A and a plate spacing of d is described by

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon_r \tan\delta \quad \ldots (7)$$

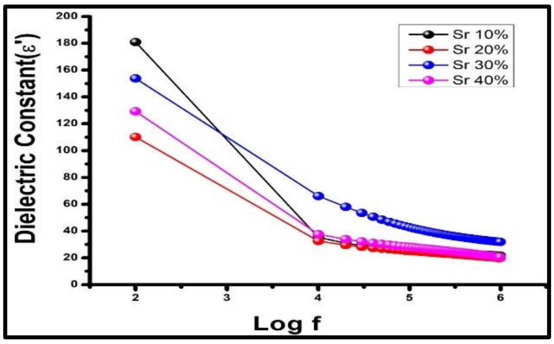

Figure 4. Variation of Dielectric constant (ε') with Log f for SrFe /PANI composites

The Dielectric constant of the material is due Combination of dipolar, interfacial (space charge), ionic, and electronic polarizations [21]. Owing to electric dipole's inability to follow the fast fluctuations of the applied ac electric field at higher frequencies, which led to a reduction in the dielectric constant, polarisation falls exponentially with frequency as shown in **Figure.** 4. At lower frequencies, the dispersion owing to interfacial polarisation, whereas at higher frequencies, electronic polarisation dominates and other types' contributions are negligible [22]. The electrons have no chance to jump at all when the frequency of the applied AC electric field is significantly higher than the hopping frequency of the electrons, and at that point, energy loss is likewise minimal, which results in a dropping of Dielectric constant.

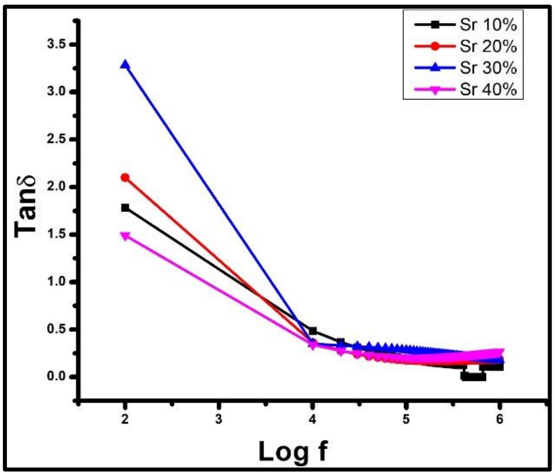

Figure 5. Variation of Tan δ with Log f for SrFe /PANI composites

The ratio of the energy radiated to the energy contained in a component is known as the dissipation factor, or tan δ. The imaginary portion of the dielectric constant **(ε')** determines the value of the dielectric loss (ε"), which is thought to be produced via domain wall resonance [23, 24]. **Figure 5.** is a graph showing the tan δ as a function of applied frequency for SrFe /PANI composite at ambient temperature. It was found that tan δ reduced with an enhancement in frequency, which is consistent with the behaviour of any dielectric material and is explained by Koop's phenomenological model. When polarisation lags behind the applied ac field, the dielectric loss is created. This loss is brought on by the existence of impurities, crystal imperfections and structural inhomogeneities [25, 26].

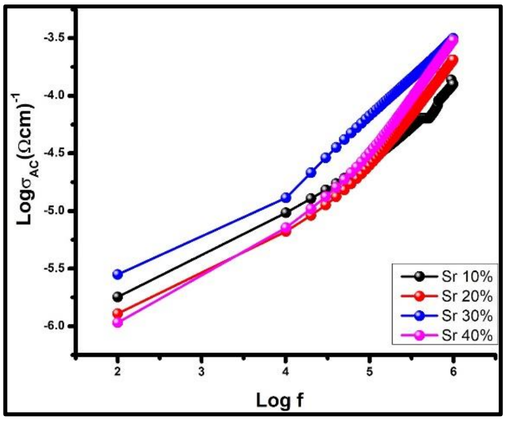

Figure 6. Variation of Log σ_{AC} with Log f for SrFe /PANI composites.

The conductivity of ferrites is often influenced by the density, porosity, grain size, grain boundary, and chemical composition of the samples. The variation of Log σ_{AC} with log f is given **Figure 6**. The plots are essentially linear in the lower frequency range, which supports the theory that charge carriers hopping at the atomic sites to produce conduction in ferrites. The Maxwell-Wagner model also explains how Log σ_{AC} is constant at low frequencies and improves with frequency at higher frequencies. Less conductivity results from low conductive grain boundaries being more active in the lower frequency area, which decreases the frequency of electron hopping [26]. AC conductivity enhances as the frequency of the applied field rises due to large hopping of charge carriers, which improves the conduction mechanism in ferrite sample.

Conclusions: SrFe/PANI composite samples with various dopant percentages of SrFe were synthesized using in situ chemical oxidative polymerization method at 0–5 ^{0}C temperature. The structural and morphology studies of SrFe/PANI composite Support the efficient interaction of PANI and SrFe particles. XRD can be attributed to the substantive internalization between PANI/SrFe particles. The average crystallite size of SrFe /PANI are in the range 53 nm to 86 nm. The addition of Sr ferrite to pure PANI has caused a slight expansion of the unit cell, which has led to enhancement in the crystallite size. The SEM images helped to draw the conclusion that the doping of SrFe had an effect on PANI morphology, and with increased Sr Ferrite content, The SEM images showing granular, nonporous and agglomerated nano-particles which are nearly spherical in shape and remaining are irregular polygons with grain size vary from 3µm to 7µm. The Dielectric constant values are reduced rapidly at low frequencies and slowly and become constant at high frequencies. Conduction in the mixed spinel ferrite is confirmed to occur through the hopping of charge by the variation of AC Conductivity with frequency. Because applied field enhances charge carrier hopping, AC conductivity improves substantially at higher frequencies as applied field frequency increases.

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