Section A-Research paper
ISSN 2063-5346

Study of effect of cobalt ferrite doped polyaniline

Abhishek, Pooja Mallinath, Sharanabasava, Gurunath L N, Nagbasavanna Sharanappa*

Department of PG studies in Physics, Faculty of science and technology, Sharnbasva University, Kalaburagi-585103, Karnataka, India.

Author for correspondence,* nsguragol@sharnbasvauniversity.edu.in

ABSTRACT

In-situ chemical oxidative method was adopted to synthesize cobalt ferrite doped polyaniline (PANI/$CoFe_2O_4$) with different weight percentage of $CoFe_2O_4$. These synthesized samples were characterized by using different techniques to understand their thermal, structural, morphological, electrical and dielectric properties by Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetric (DSC), Scanning Electron Microscope (SEM), AC and DC
and dielectric properties respectively. Synthesized sample are having low conductivity and it indicates towards good dielectric property of the samples. Due to this behavior, these samples may find applications in the area of electronics.

Key words: PANI/$CoFe_2O_4$, SEM, TGA, Dielectric behavior, synthesis method.

1. Introduction

Recently, conducting polymers have experienced a great increase in popularity due to their versatile functions. Not only do they possess the mechanical properties of polymers, but theyalso offer a variety of promising technological uses. Polymers come in two forms: natural and synthetic. Natural polymers include proteins, DNA, and cellulose while manmade polymers, like rubber, plastic, and synthetic fibers are classified as synthetic. Synthetic polymers offer a variety of advantages over their natural counterparts. Polymers have become an integral part of industries across sectors like packaging, automotive, medical devices, electronics, and textiles. They've enabled a revolution in the modern day, and their application is only growing with time. Polyaniline (PANI) has been identified as a notable conducting polymer due to its remarkable environmental durability, appropriate conductivity, corrosion resistance, and lightweight properties. [1-2]. As we enter a new era of lifestyle, organic polymers are playing an essential role in providing insulation and increasing energy efficiency. Plastics have the ability to effectively conduct electricity, which further helps with this purpose. Polymer nanocomposites have been gaining traction recently due to their impressive physical attributes such as low weight, advanced mechanical strength, stiffness, and relatively easy fabrication [3].

Extensive research on Polyaniline/metal oxide Nanocomposite has revealed its unique physiochemical properties which can be further utilized for various academic and technological purposes [4-6]. The Polyaniline/$CoFe_2O_4$ nanocomposite has demonstrated unique characteristics due to its dual components, making it a promising material in numerous applications such as electronics, photonics and catalysis. This has been well documented in existing research [7-10]. Magnetic materials have been at the forefront of modern technology growth in the last half- century. Ferrites, ceramics and other ferromagnetic substances are considered essential electronic components for today's technological advancements. In recent times, physicists and electronic engineers have been fascinated by magnetism and the growing applications of ferrites for high-frequency purposes. The special physical and mechanical qualities of Cobalt Ferrites make themin valuable in nanomedicine.

Cobalt ferrite is unique in the world of spinel ferrites due to its inverted spinal structure. This occurs when Co^{+2} ions are located at an octahedral (B) site. Nanocrystalline cobalt ferrite stands out for its prominent features like high saturation magnetization high Curie temperature [11, 12]. Spinel ferrite $CoFe_2O_4$ has several uses that range from magnetic cards, solar cells, and recording devices to even magnetic drug delivery. It is becoming increasingly popular due to its versatility and benefits [13, 14].
In the present research work, we have attempted to synthesize PANI/$CoFe_2O_4$ by *in-situ* chemical oxidative polymerization method. The effect of $CoFe_2O_4$ on polyaniline was studied at different weight percentage and characterized by various techniques. Main focuses towardselectric and dielectric properties the synthesized sample.

2. Experimental.

2.1 Materials

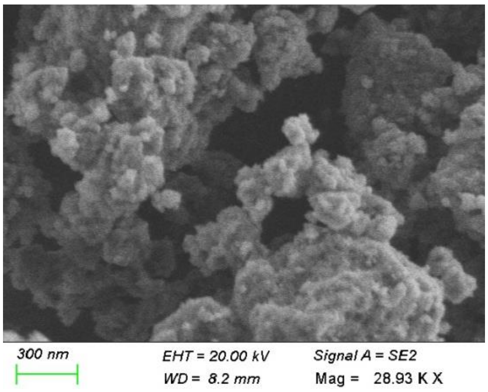
All chemicals and substances utilized are of analytical grade (AR). Distilled water was used throughout the process. $CoFe_2O_4$ were synthesized by Co-precipitation method. Aniline, ammonium dichromate and hydrochloric acid were used to synthesize pure polyan1iline.Polyaniline (PANI) composites of different weight percentage (PANI/$CoFe_2O_4$) were synthesized by in-situ chemical oxidative polymerization process.

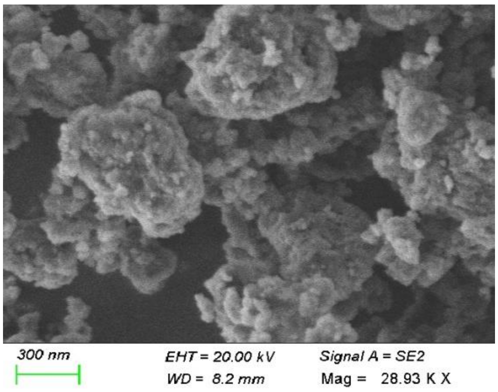
2.2 Preparation of PANI/$CoFe_2O_4$ Nanocomposite.

The in-situ chemical oxidative method was adopted to synthesize cobalt ferrite doped polyaniline nanoparticles. Aniline (0.25M) and hydrochloric acid (1N) was disintegrated in 100ml of water. The solution was allowed to react for 3 hours to form the anilinehydrochloride. The ferrite powder was added to the above arrangement under steady mixing to keep the ferrite powder consistently suspended in the combination. To, blend the oxidizing agent ammonium dichromate $(NH_4)_2Cr_2O_7$ (0.25M) was gradually added drop wise with vigorous stirring at room temperature for 10 hours to finish reaction. The PANI/$CoFe_2O_4$ solution is collected by vacuum filtration.The gathered sample was dried using oven at a temperature of 85^{o}C for 4 hours to get the steady mass and final powder product was in powder form [15].

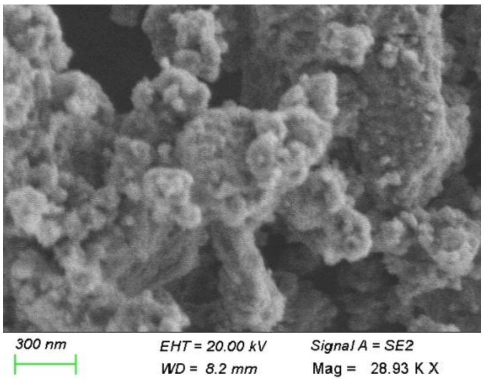
3. Result and Discussion

3.1. Scanning electron microscope





(a) (b)



(c)

Figure.1 (a-c): SEM micrographs of the prepared PANI/$CoFe_2O_4$ nanoparticles for 5%, 10% & 15% respectively.

The SEM images of PANI/$CoFe_2O_4$ nanoparticles for 5, 10 and 15 weight percentage is shown in Figure 1. SEM images suggest that the morphology is porous in nature at the surface. It is because of the notable degree of agglomeration of the PANI/$CoFe_2O_4$ nanoparticles. From the SEM images shown above for all weight percentage, we can conclude that the particles are irregular in shape and aggregated to form larger particles. It was also observed that the percentage of complexes had no significant effect on the morphological image. The PANI layers are wrapped on the surface of Cobalt ferrite nano particles, which appears as small aggregated globules. The average grain size is calculated by the line intersect method was found to be in the range of 70-85 nm [16-18].

3.2. Thermal Analysis (TGA/DSC)

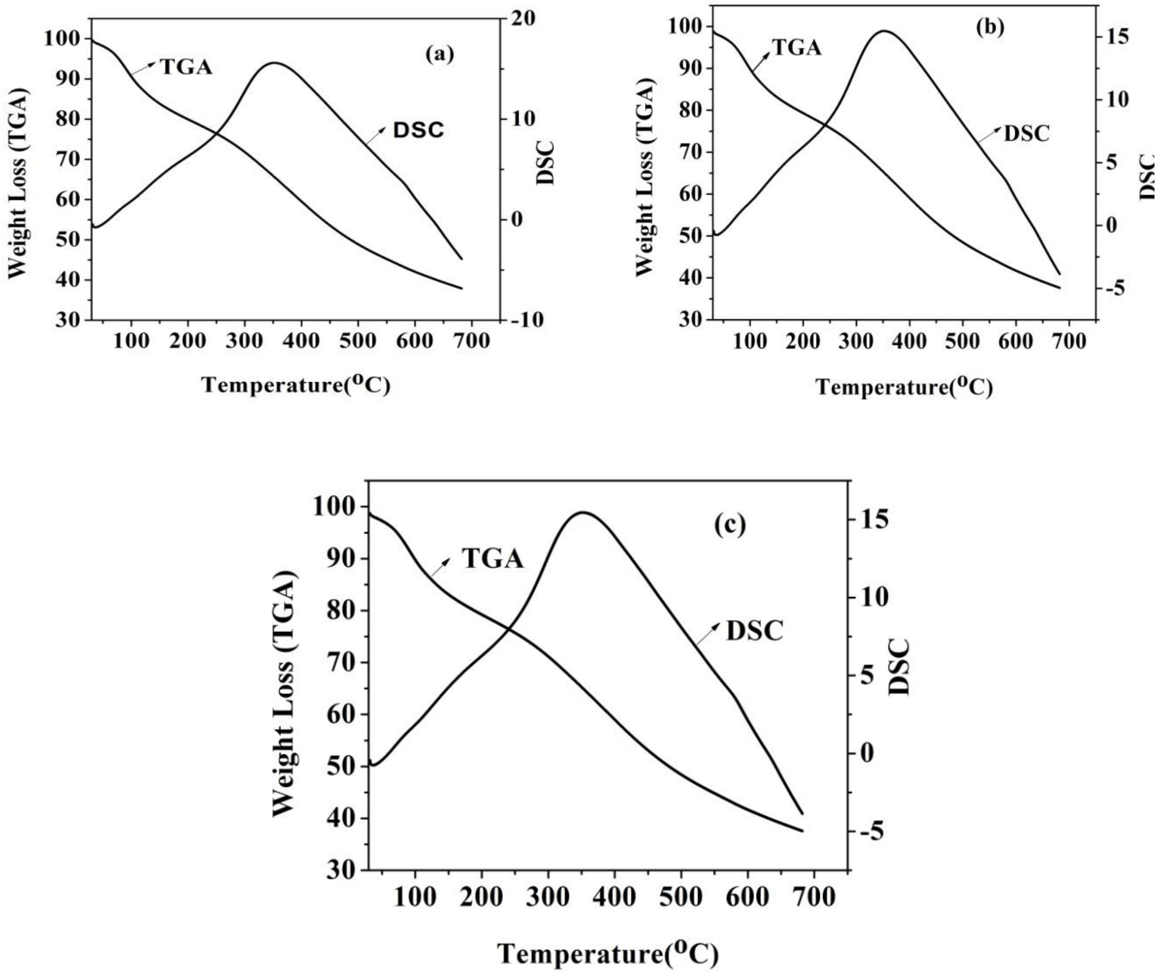


Figure.2 (a-c) TGA and DSC stability of PANI/$CoFe_2O_4$ nanoparticles for 5%, 10% & 15% respectively.

DSC curves of PANI/ $CoFe_2O_4$ powder for different weight percentage are shown in Figure 2. (a-c) Some exothermic peaks are observed in DSC curve over RT to 700°C temperature. The Exothermic broad peak is obtained at 360° C, 370°C and 375°C for 5, 10 and 15% composites. The thermal transitions associated with the weight loss are analyzed by TGA as a function of temperature. Figure 2 (a-c) shows the curves correspond to PANI /$CoFe_2O_4$ (5%, 10% and 15%) respectively. The decomposition temperature of PANI/$CoFe_2O_4$ composites was found to depend on the amount of $CoFe_2O_4$ nanoparticles present in the composite. The trends of degradation for all the weight percentage (5, 10 and 15%) are similar and they present two steps weight loss process. The first decomposition temperature was observed from 90°C to 200°C due to moisture and next may be other constituent's degradation from 200°C to 420°C.

3.3 Electrical Conductivity Analysis:

DC Conductivity

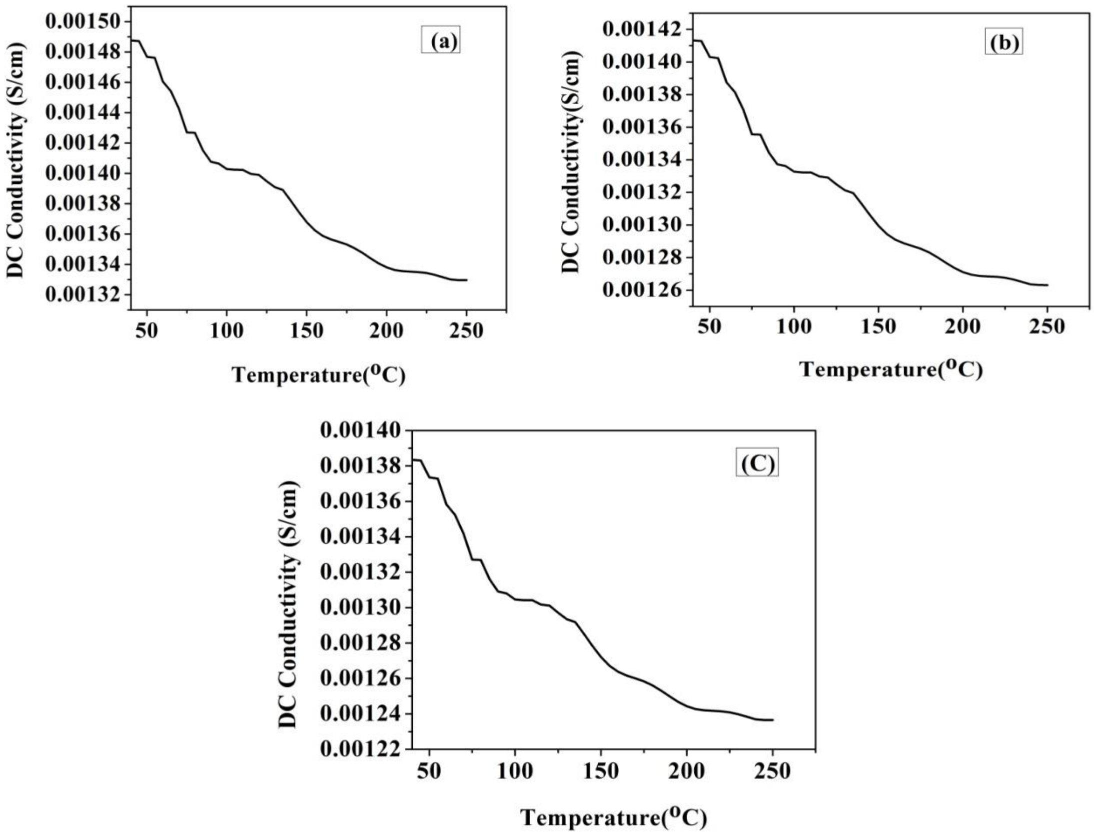


Figure 3(a-c): DC conductivity of PANI/$CoFe_2O_4$ composites for 5%, 10% and 15%.

The temperature dependence of DC-Conductivity for PANI/ $CoFe_2O_4$ composites of 5%, 10% and 15% in a temperature range of 30°C to 250°C is illustrated in Figure 3. It is observed that in all the cases, DC conductivity of PANI/$CoFe_2O_4$ decreases with increase in the temperature. Figure 3 (a-c) also reveals that conductivity of the PANI/$CoFe_2O_4$ is high at low temperature. The maximum conductivity 0.00149 S/cm, 0.00141S/cm and 0.0138 S/cm was observed for PANI/$CoFe_2O_4$ composite of 5, 10 and 15% respectively. Similar behavior was observed for all doping concentration. The electrical DC resistance decreases with increasing temperature, which ensures the semiconductor behavior of the sample.

AC Conductivity

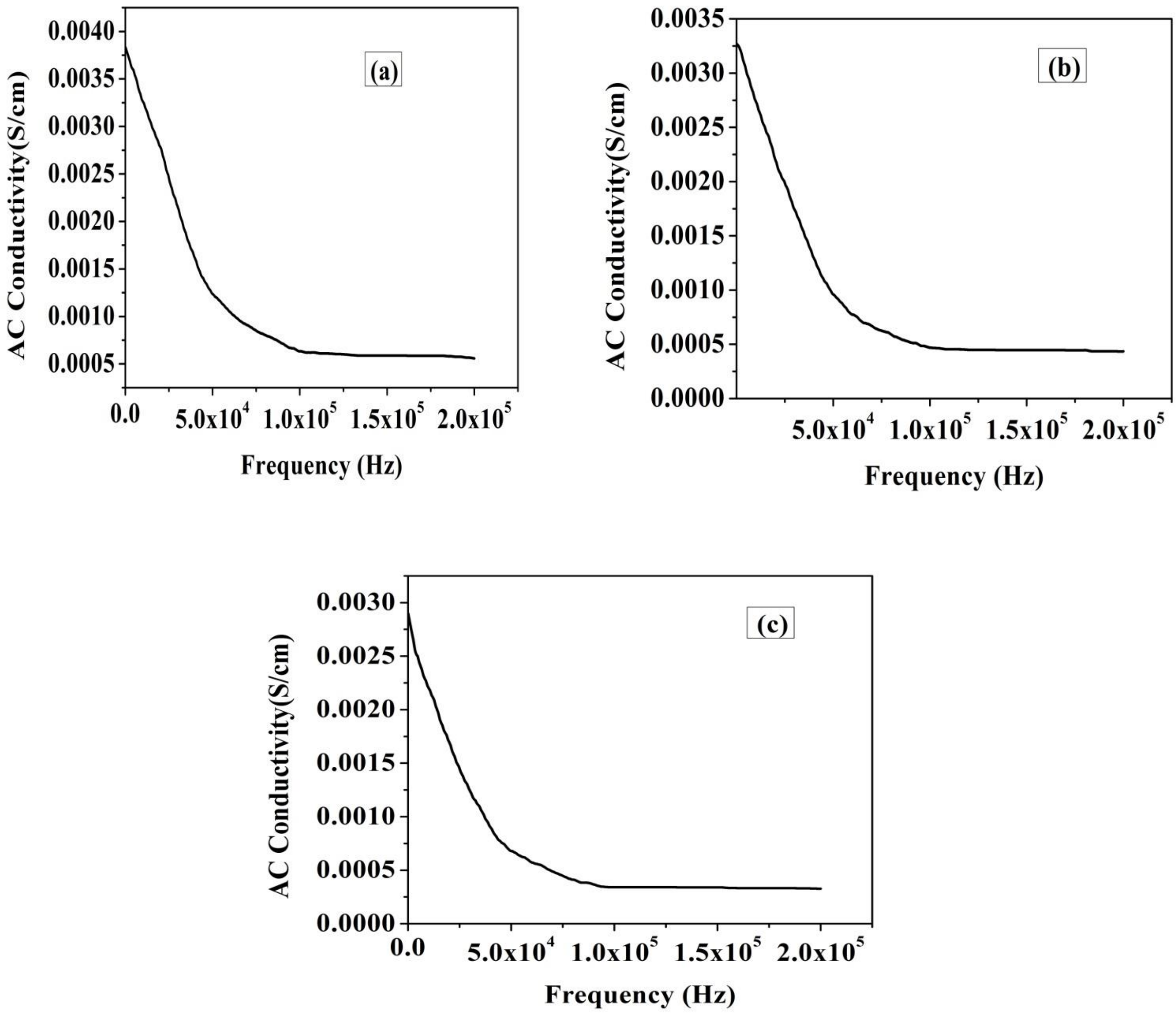


Figure.4 (a-c): AC conductivity of PANI/$CoFe_2O_4$ composites for 5%, 10% and 15%.

The AC conductivity of PANI/$CoFe_2O_4$ composites was carried out at the frequency range from RT to 2.0×10^5 Hz. Figure 4 shows the variation of AC conductivity as a function of frequency for PANI/$CoFe_2O_4$ for 5%, 10% and 15%. Figure 4 shows that conductivity of all PANI/CoFe2O4 nanocomposites decreases gradually with the increase in the frequency. The conductivity is high at lower frequency. At higher frequency i.e. from 1.0×10^5 Hz to 2.0×10^5 Hz. AC conductivity among all the composites were recorded high value as 0.0036 S/cm and low as 0.005 S/cm.

3.4 Dielectric Constant and Dielectric Loss

Dielectric constant

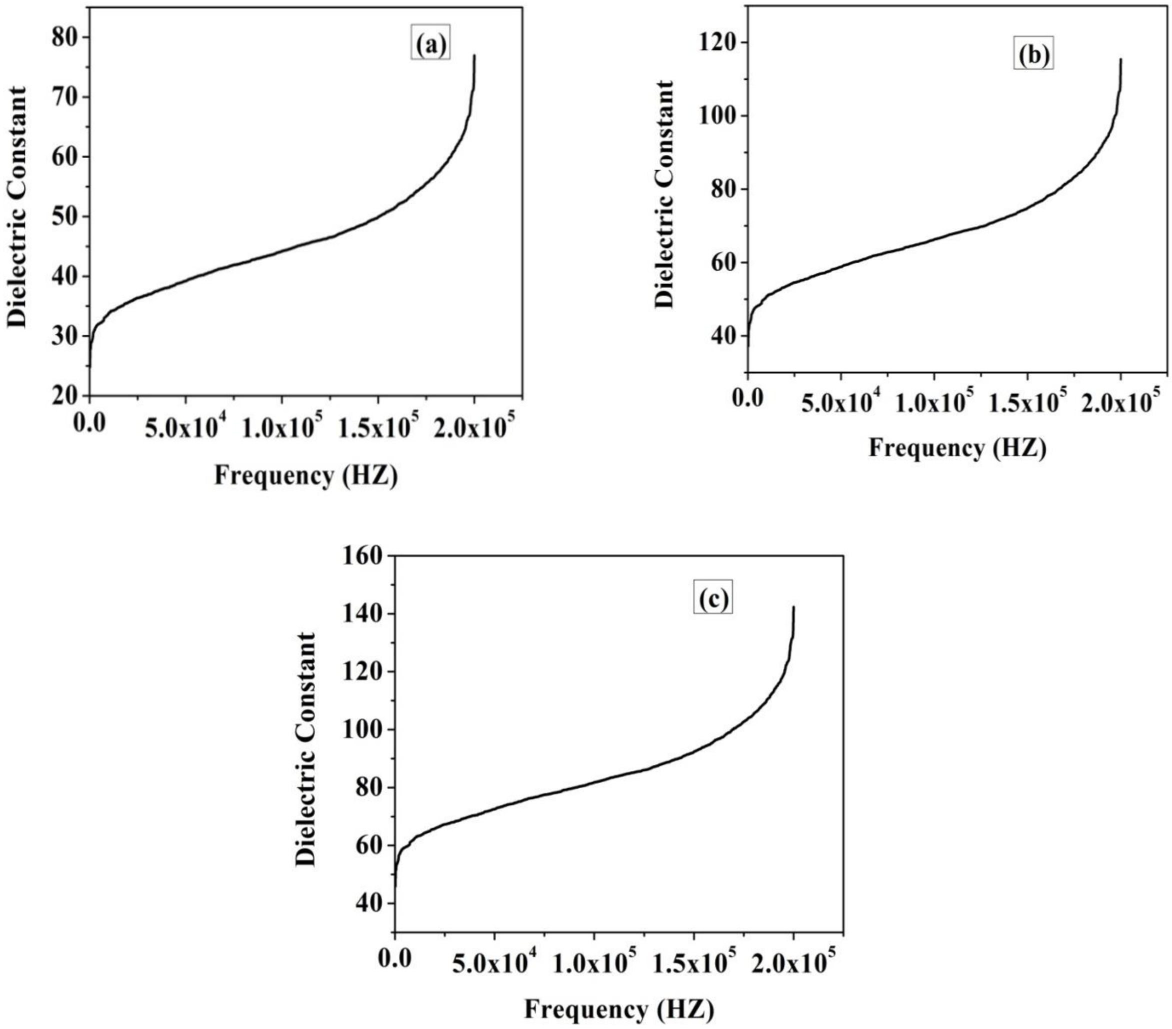


Figure.5 (a-c): Dielectric constant cures of PANI/$CoFe_2O_4$ nanoparticles obtained using 5, 10 & 15 weight percentage of Cobalt ferrite.

The dielectric constant of PANI/CoFe2O4 was measured as a function of frequency and shown in Figure 5. The dielectric constant is studied for the frequency range of zero to $2.0x10^5$ Hz. For all the weight percentage the value of the dielectric constant is low at low frequency then the dielectric constant value increases as frequency increases. The graph reveals that as the concentration of doping increases in the dielectric there is a increase in dielectric constant value. Increases as frequencies From initial frequency to $1.55x10^5$Hz frequency the dielectric constant increases gradually but it can be seen that above 1.55x105 Hz frequency there is dramatically increase in the dielectric constant. The friction against dipole motion decrease with frequency as the dielectric constant frequency increases.

Dielectric loss

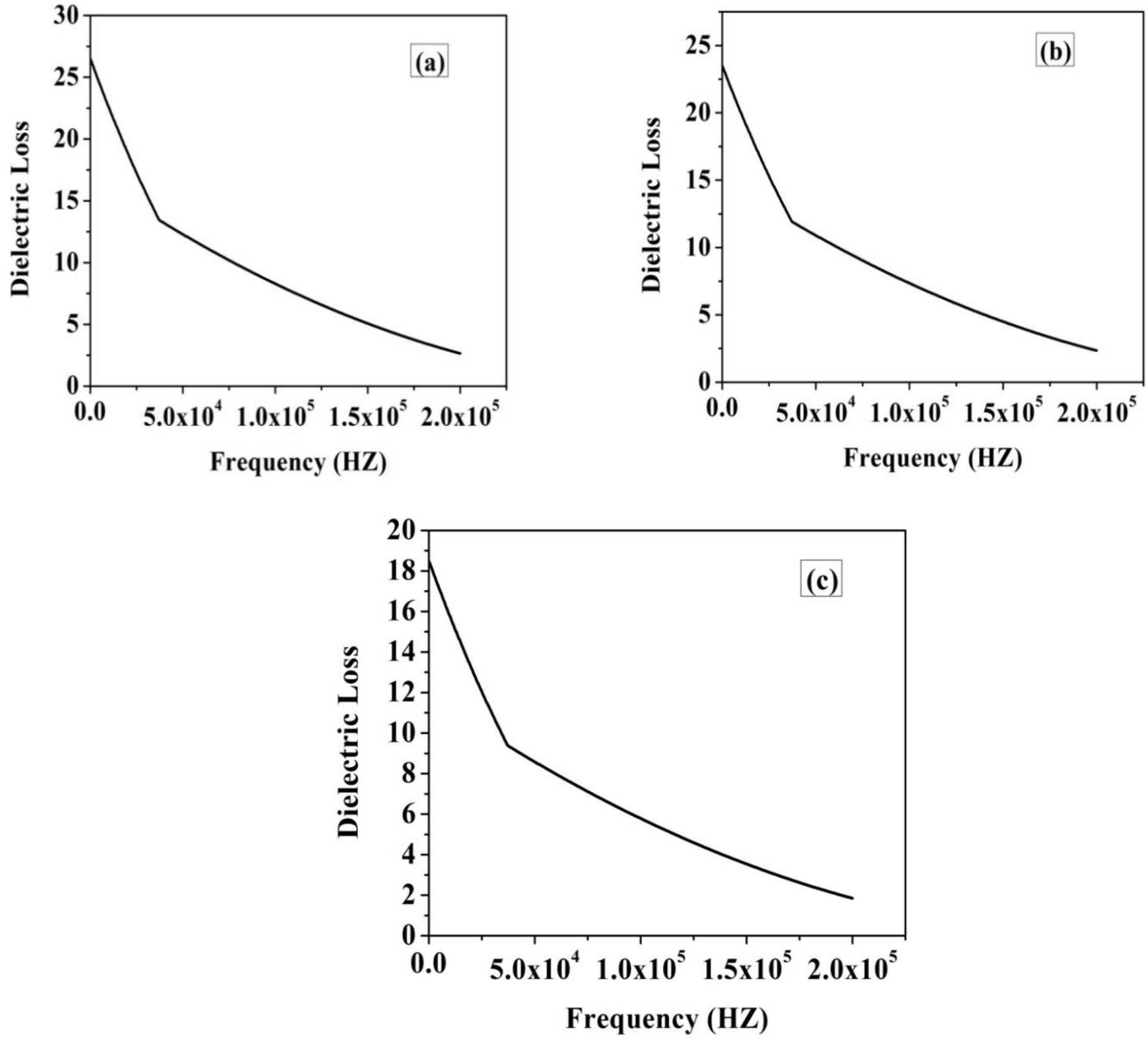


Figure.6 (a-c): Dielectric loss cures of PANI/$CoFe_2O_4$ nanoparticles obtained using 5, 10 & 15 weight percentage of Cobalt ferrite.

The frequency dependent dielectric loss of samples was shown in Figure 6. The dielectric loss on the frequency for the range of zero to $2.0x10^5$Hz is studied. As frequency increases, the dielectric loss falls and reaches a low value in the high frequency range of the spectrum, as seen in the Figure 6.The large magnitude of dielectric losses at lower frequencies might be attributed to grain boundary's high resistivity [19]. The PANI/$CoFe_2O_4$ mayuse as switch for electronic applications such as capacitors [20]. The dielectric losses in PANI/$CoFe_2O_4$ are reflected in conductivity measurements, where highly conductive materials cause large losses and vice versa.

Conclusion

In this study PANI/$CoFe_2O_4$ nanocomposite of 5, 10 and 15 weight percentage have been successfully synthesized by *In-situ* chemical oxidative polymerization method using ammonium dichromate as an oxidizing agent and the nano particle $CoFe_2O_4$ were synthesized by using co-precipitation method. Morphology, thermal, electrical and dielectric properties of synthesized samples was analyzed by SEM, TGA/DSC, AC and DC, Dielectric respectively. The average grain size of synthesized sample is about 70-85nm and thermal studies revealed that synthesized sample was stable at higher temperature. Electrical parameters indicated low conductivity of the samples and it encouraged us to study the dielectric properties of the sample. Synthesized sample showed good dielectric behavior and these may find applications in electronic devices.

References:

1. S. Ameen, M.S. Akhtar, S.G. Ansari, O.B. Yang and H.S.Shin, Superlattices Microst. 46, 872 (2009)

2. G.D. Prasanna, H.S. Jayanna and V.Prasad, J.Appl. Polym. Sci.120,2856(2011)

3. J.C. Chiang, A.G. Macdiarmid, Synth. Met. 13 (1986) 193–205.

4. R. Ansari, M.B. Keivani, Eur. J. Chem. 3 (2006) 202–217.

5. A. Tiwaria, R. Kumar, M. Prabaharan, R.R. Pandey, P. Kumari, A. Chaturvedi, A.K. Mishra, Polym. Adv. Technol. 21 (2010) 615–620.

6. T. Moa, H. Wang, S. Chen, Y. Yeh, Ceram. Int. 34 (2008) 1767–1771.

7. G.D. Prasanna, H.S. Jayanna, A.R. Lamani, S. Dash, Synt. Met. 161 (2011) 2306– 2311.

8. K. Lakshmi, H. John, K.T. Mathew, R. Joseph, K.E. George, Acta Mater. 57 (2009) 371–375.

9. C. Yang, H. Li, D. Xiong, Z. Cao, React. Funct. Polym. 69 (2009) 137–144.

10. R.T. Ma, H.T. Zhao, G. Zhang, Mater. Res. Bull. 45 (2010) 1064–1068.

11.I. Gul, A. Maqsood, Structural, magnetic and electrical properties of cobalt ferrites prepared by the sol-gel route, J.Alloy. Compd 465(2008)227-231.

12. R. Nongjai, S. Khan, K. Asokan, H. Ahmed. I. Khan, Magnetic and electrical properties of In doped cobalt ferrite nanoparticles, J. Appl. Phys. 112(2012) 084321.

13. Hong J, Xu D.M, Yu J.H, Gong P.J, Ma H.J, Yao S.D, 135608 Nanotechnol.18 (2007)

14. Park J.H ,Maltzahn G. V, Zhang L. L,Schwartz M.P, Ruoslahti E, Bhatia S.N, Sailor M.J, 1630-1635Adv.Mater. 20(2008)

15.M.R Vaezi, L.Nikzad, B.Yazdani,IJE Trans. B:Appl. 22(2009) 381-386

16. Prasanna GD, Jayanna HS, Lamani AR, et al. Polyaniline/CoFe2O4 nanocomposites: A

novel synthesis, characterization and magnetic properties. Synth Met 2011; 161: 2306–2311.

17. Bharati Nandapure, subhash kondawar, Mahesh Salunkhe and Arti Nandapure, "Nanostructure cobalt oxide reinforced conductive and magnetic polyaniline nanocomposites", Journal of Composite Materialsm,PP. 1-9 0(0) (2012)

18. J. Chen, C. Sorensen, K. Klabunde, G. Hadjipanayis, E. Devlin, A. Kostikas, Sizedependent magnetic properties of MnFe2O4 fine particles synthesized by coprecipitation, Phys. Rev. B 5

19. F. Alam, S.A. Ansari, W. Khan, M.E. Khan, A.H. Naqvi, Funct. Mater. Lett. 5 (2012) 1250026

20. W. Fan, B. Kabius, J.M. Hiller, S. Saha, J.A. Carlisle, O. Auciello, R.P.H. Chang, R. Ramesh, J. Appl. Phys. 94 (2003) 6192. 16. Prasanna GD, Jayanna HS, Lamani AR, et al. Polyaniline/CoFe2O4