International Journal of Engineering Technology Science and Research
IJETSR
www.ijetsr.com
ISSN 2394 – 3386
Volume 5, Issue 2
February 2018

Magnetic and Enhanced Microwave Absorption Properties of Ni-Co-Zn Ferrite/Polyaniline Nano Composites

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ABSTRACT:

Spinel structure $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite have been synthesized by sol- gel auto combustion technique and ferrite /polyaniline (PANI)composite was synthesized by in-situ polymerization The structural, Morphological and magnetic properties at room temperature of the product were characterized by X- Ray Diffraction (XRD), Field emission scanning electron microscopy (FE-SEM), Field emission gun transmission electron microscopy (FEG-TEM) and Vibrating Sample Magnetometer (VSM). X- ray patterns confirmed the formation of single phase cubic structure. The crystallite size of synthesized ferrite nanoparticle is within the range of 20 - 78 nm. The microwave absorbing properties of ferrite and ferrite/polyaniline composite was investigated by using Vector Network Analyser in the frequency range of 2GHz to 18GHz.The minimum value of reflection loss was -14.40dB at the frequency of 18 GHz for $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles (thickness 3.0mm) and -22.58dB at frequency of 18GHz for PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanocomposite (thickness 3.0mm). The microwave absorbing properties increase drastically by forming a nanocomposite with polyaniline.

Keywords:Spinel structure, ferrite nanoparticles, polyaniline, nanocomposites, microwave absorbing property, reflection loss.

INTRODUCTION

The Microwave absorption materials and shielding technology has received great attention in recent decades due to rapid advancement in science and technology of system has led to exponential growth of systems that operate at high frequencies in giga hertz, such as development in telecommunication systems, industry, security, military systems, microwave oven, medical equipment etc. also frequent applications of high frequencies increase the level of electromagnetic radiation pollution and effect on ecology and health of human being [1-3].

To protect from this hazardous electromagnetic radiation, there is need of developments in microwave absorbing materials with proper thickness, cost,efficiency, weight, stability, flexibility, electromagnetic and physical comparability. Ferrite and magnetic nanoparticles of mixed spinel ferrites absorbers are used due to their high resistivity, low dielectric loss, mechanical hardness, high Curie temperature and chemical stability [4].Hexaferrites are also extensively used for electromagnetic wave absorptionand interference suppression[6]. The performance of microwave absorption depends mostly on dielectric loss and magnetic loss of materials [7]. The requirement of absorbing materials are different for different application such as shielding material,Wire less systems, military electronic systems, navigation, aircraft technology and electronic devices. The intensive usage of microwaves and radio waves in such areas causes electromagnetic interference (EMI) and electromagnetic comparability (EMC) problems [8-10]. Moreover , maximum electromagnetic wave absorption materials are expected to have broad absorbing bandwidth,strong absorption capability, low density, thin absorber and strong absorption capability. However, traditionalabsorption materials still have same disadvantages. ferrite material are required to have thinabsorbent layers because of their small EM loss in giga hertz frequency range metallic magnetic nanoparticles perform high permeability at high frequency over gigahertz and the eddy current effect can be restrained due to the nanometre size lower than skin depth. Also metallic nanoparticles are self-ignited or easily oxidized in the air.Recently the Nanocomposite materials composed of dielectric materials have been considered as an effectiveness to

improve the microwave absorption properties. These nanocomposites can obtain not only the complementarity between dielectric and magnetic loss but also additional physical and chemical properties (11-13). Composite structure like nanoparticle with conducting polymers are also applied for to reduce the weight in large scale production in aerospace and aeronautic industries to an increasing degree(14). Conducting polymers nanocomposite have attracted significance attenuation in recent decades because of their potential application in various fields such as electromagnetic interference (EMI) shielding, bio sensor & microwave absorption Among the known conducting polymers, polyaniline (PANI) has been extensively studied due to its unique electrical properties and physicochemical behaviour, good environmental stability (15-18). Conducting polymer/spinel ferrite composites with an organized structure provide a new functional material between hybrid organic and inorganic materials (19). Coating of PANI on ferrite nanoparticles can enhance compatibility with organic ingredients, electric loss ,reduce susceptibility to leaching and probably avoid aggregation (20-23).

In this proper $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ferrite nanoparticles and $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite/PANI Nanocomposites were synthesized by sol-gel auto comparison method and in-situ polymerization method.The samples were characterized by various experimental technique. The magnetic and microwave absorption properties of nanocomposites where investigated.

2.EXPERIMENTAL

2.1Synthesis Of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ Ferrite

$Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite powderwas synthesized by a sol-gel auto-combustion method. The detail process can be described as follows. The stoichiometric amount citric acid, $Ni(NO_3)_2 . 6H_2O$, $Co(NO_3)_2 . 6H_2O$, $Zn(NO_3)_2 . 6H_2O$, and $Fe(NO_3)_2 . 9H_2O$ were first dissolved separately in deionized water. This obtained cationic solutions were mixed one into another and stirred continuously for one hour ii order to improve homogeneity. The molar ratio of nitrates to citric acid was 1.5:1. Ammonium hydroxide was then added dropwise to adjust the P^H value to about 7.0 then, the mixed solution was heated at 90^0C under constant stirring to transform into a dried gel burned in a self-propagating combustion way until all gels were burned completely out to form loose precursors. Finally $Ni_{0.3}Co_{0.2}Zn_{0.5}Fe_2O_4$ crystalline powder was obtained after calcining the loose precursors at 700^0C for 2 hours.

2.2Synthesis of Polyaniline/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ Ferrite Composite

Polyaniline/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite composite was prepared by in situ polymerization in an aqueous solution. Firstly, a certain amount of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite particle were suspended in a 70ml, 1M HCl solution and stirred for 30 min. to get well dispersed. Two milliliter aniline monomer was then added to the suspension and stirred for 30min. Ammonium peroxydisulfate(ASP) of 4.98gm (the molar ratio of ASP to aniline was 1:1) in a 40ml 1M HCl solution was then slowly dropped to the suspension mixture with a constant stirring. The polymerization was allowed to proceed for 12 hours at 0^0C to 5^0C. The composite was obtained by filtering and washing the suspension with 1M HCl and deionized water and dried under vacuum at 60^0C for 24 hours.

2.3Characterization

The resulting powder was characterized by X- ray powder diffraction (XRD) using a diffractometer (RIGAKU, Model D/max) with CuKα radiation of wavelength λ= 0.15418nm. Its morphology was studied with a field emission gun scanning electron microscope (FEG-SEM, model –JSM-7600F) and field emission gun transmission electron microscope (FEG-TEM-300kV,model- Tcnai G@F30). Magnetization measurements were taken at room temperature using a vibrating sample magnetometer. The samples used for EM parameter measurements were prepared by pressing the powder into a compact toroidal shape with outer diameters of 7.0mm and inner diameter of 3.0mm. The complex permittivity and complex permeability of the samples were measured by vector network analyser in the frequency range 2GHz – 18 GHz by using coaxial reflection/ transmission technique. The reflection loss of the samples with different thickness versus the frequency is studied.

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3.RESULT AND DISCUSSION

3.1 X- ray Diffraction Analysis

Fig.1. shows the XRD pattern of the synthesized samples. Fig.1.1 of PANI shows the amorphous nature in partially crystalline state with two diffraction peak 2θ = 20.41 and 25.61 due to the densely packed phenyl rings those exhibit an extensive interchain π-π orbital overlap and parallel and perpendicular periodicity of the PANI(13). Fig.1.3 shows the XRD pattern of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite, the diffraction peaks have been observed at 2θ value of 18.60 (d= 4.8416),30.37 (d = 2.9473), 35.45 (d= 2.5148), 37.29 (d= 2.4098), 43.37 (d = 2.0882), 53.516 (d =1.7103), 57.16 (d = 1.6135), 62.84 (d = 1.4789), 71.22 (d =1.3261), 74.19 (d = 1.2778) and 75.15 (d = 1.2650) which corresponds to (111),(220), (311), (222), (400), (422), (511), (440), (620), (533)and (622) Bragg's reflection of the spinel structured $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles respectively. No direction peaks from other crystalline forms have been detected, which indicates a high purity and crystallinity of as synthesized $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ nanoparticles. As for PANI/$Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanocomposites fig.1.2, the diffraction peaks of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ can be clearly distinguished for all the samples while the diffraction intensities of these peaks decrease with the reduction of the content of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ferrite nanoparticles. The crystallite size (D) of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles can be calculated by using Scherrer's equation

$$D = \frac{k}{\beta} \qquad (1)$$

Where λ is thee X-Ray wavelength, k the shape factor (= 0.89), θ is the Bragg angle and β is the full width at half maxima (in radian). The crystallite size of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanoparticle s has been calculated using above equation and estimates to be 20 - 68 nm, which is in accordance with the FEG -TEM.

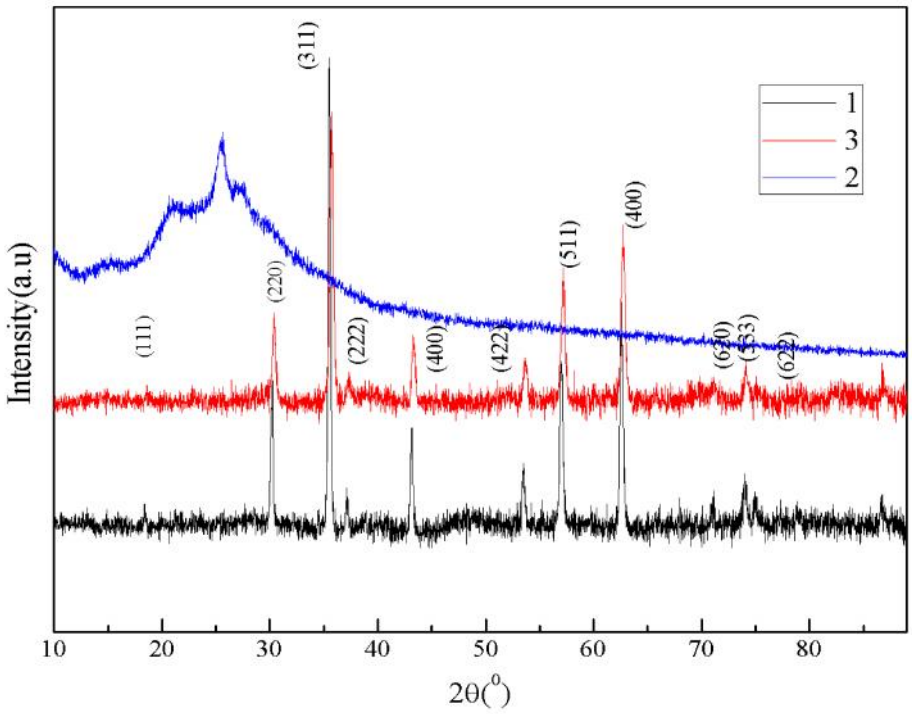

Fig.1. XRD diffraction patterns of (1) PANI (2)PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ (3) $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$

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3.2Morphology Investigation

3.2.1 SEM images

Fig.2, Fig. 3 and Fig.4 shows the FEG-SEM images for $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite, polyaniline and PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanocomposite respectively. Fig.2.1 shows the cubic structure of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles of size is about 20-68nm. Fig.2.2 shows the PANI as amorphous and fig. 2.3, it is found that the PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ nanocomposite still retains the morphology of PANI shape and it has seen ferrites nanoparticle coated with PANI. It is much unknown how to form spongy-shaped composite in the polymerization process. The SEM image clearly shows that the $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$.

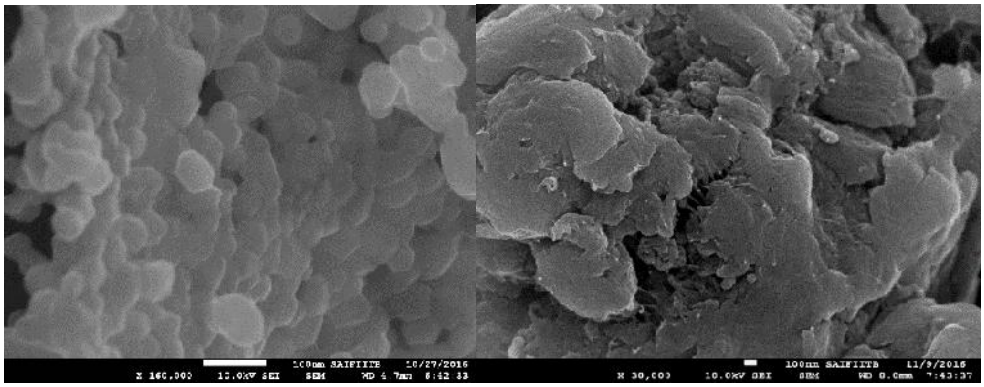

Fig.2 FEG-SEM image for

$Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferriteFig. 3 FEG-SEM image for polyaniline

Ferrite nanoparticles were distributed rather homogenously and ultra sonication is effective for dispersing ferrite nanoparticle in the polymer matrix.

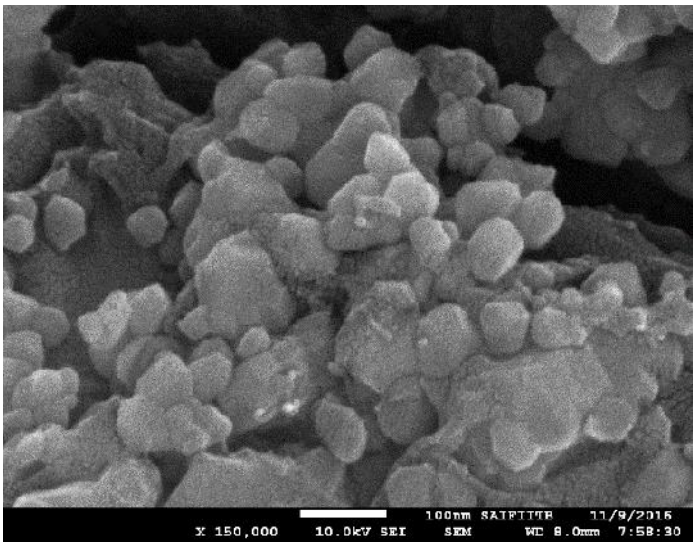

Fig.4 FEG-SEM images for PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nano composite.

3.2.2 TEM Analysis

Average particle size of the $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ferrite nanoparticles and PANI coated $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ferrite were measured using FEG-TEM analysis and micrographs for the ferrite powder and PANI coated ferrite were shown in fig.5 and fig 6. The photographs indicate that average particle size of

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www.ijetsr.com
ISSN 2394 – 3386
Volume 5, Issue 2
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the powders was in the range 20 to 78nm and for composites the particle size slightly increases and HR -TEM image clearly indicate the coating of PANI over ferrite nanoparticle as shown in fig. 7.

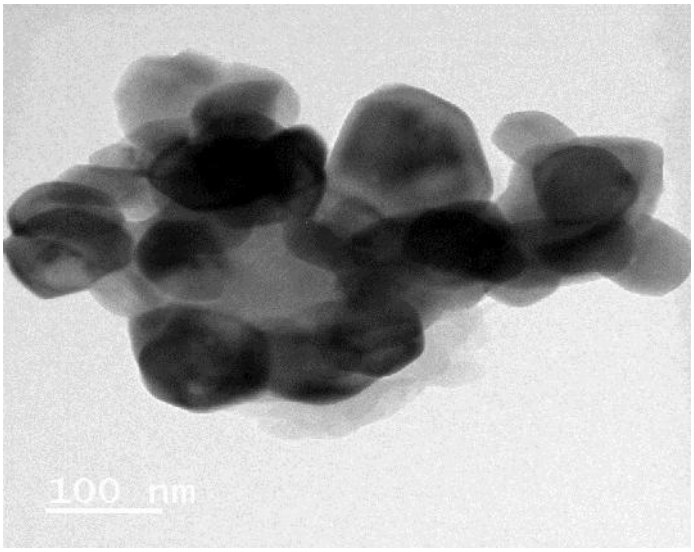

Fig. 5 TEM image of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles

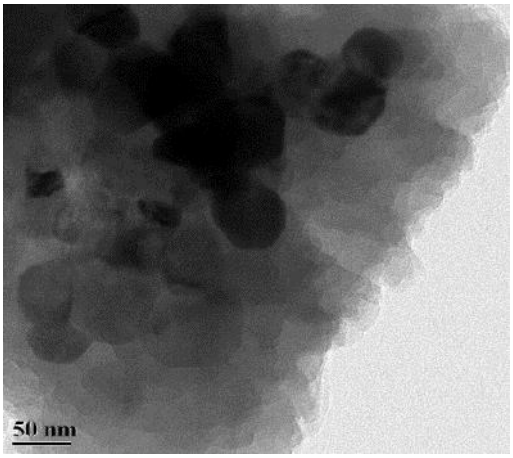

Fig.6 FEG-TEM of $PANI/Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$

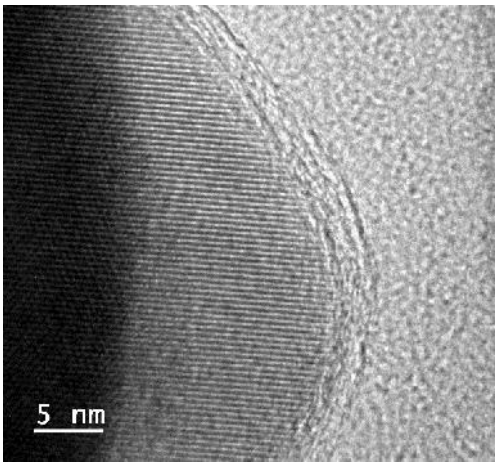

Fig .7 HR TEM Image of $PANI/Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$

3.4 MagneticProperties

The magnetic properties of the $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles and PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanocomposite were analysed at room temperature by using a vibrating sample magnetometer (VSM) with an applied field -20 kOe ≤ H ≤ 20 kOe.

Fig.8 shows the magnetization (M) versus the applied magnetic field (H) for $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles and PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanocomposite. It can be inferred from the hysteresis loops that all the composite magnetic spheres are magnetically soft at room temperature. The value of

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ISSN 2394 – 3386
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saturation magnetization (Ms) for $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite is about 68.43emu/g, and remnant magnetization.

(Mr) and coercivity field are 15.34 emu/g and 71.14Oe respectively.

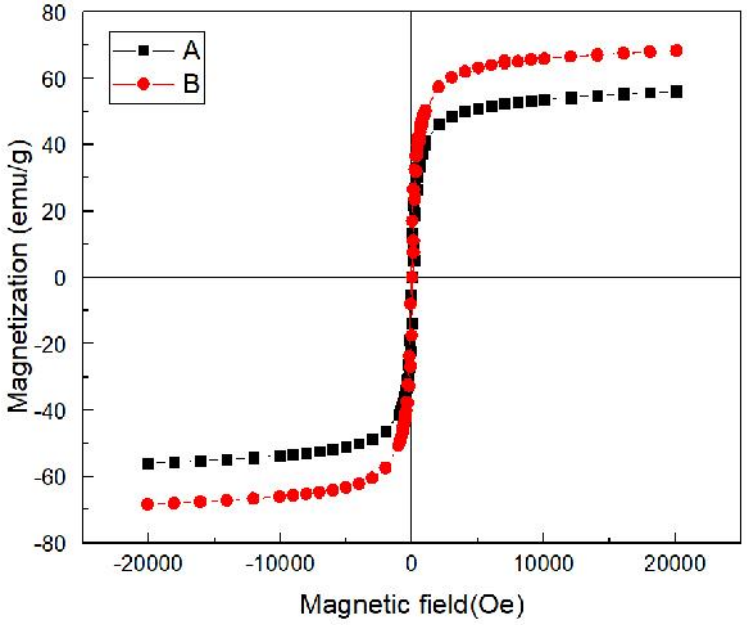

Fig.8variation of magnetization with the applied field measured at room temperature for A) PANI/$Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ and B) $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$

The value of saturation magnetization (Ms) for PANI/NiCoZn ferrite nanocomposite is about 56.11 emu/g, and remnant magnetization (Mr) and coactivity field are 12.33emu/g and 75.71Oe respectively, these values are lower than pure NiCoZn ferrite nanoparticles. So the magnetization curve of the sample shows weak ferromagnetic behaviour Withslender hysteresis. The Magnetic properties of nanocomposites containing magnetite or ferrite particles have been believed to be highly dependent on the sample shape, crystallinity and the value of magnetic particles, so that they can be adjusted to obtain optimum property.

3.4 Microwave Absorbing Properties

In order to investigate the microwave absorption characteristics, the measured permittivity and permeability of samples by vector network analyser are used to calculate the reflection loss (RL) by using following equation

$$RL = 20 \log_{10} \frac{|z-1|}{|z+1|}$$

Where the impedance (Z) of medium is

$$Z = \sqrt{\frac{\mu r}{\varepsilon r}} \tan h(-i\frac{2\pi}{\lambda} t \sqrt{\frac{\mu r}{\varepsilon r}})$$

Here μ_r and ε_r are the measured relative complex permeability and complex permittivity, respectively.λ is wavelength ofthe incident plane wave in free space and t is the thickness of the absorber.

The results of different thickness of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite and PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanocomposite is shown in fig.9 and Fig.10 respectively by using vector network analyser in the frequency range of 2GHz to 18GHz. The minimum value of reflection loss was -14.40dB at the frequency of 18GHz for $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles of thickness 3.0mmand -22.58dB at frequency of 18GHz for PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanocomposite of thickness 3.0mm. So microwave absorption is increased with PANI.

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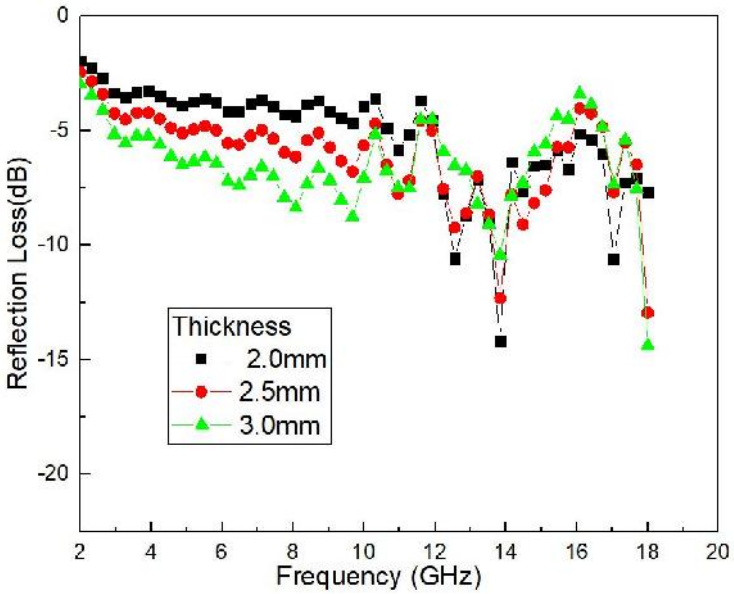

Fig.9. Absorption characteristics of $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles

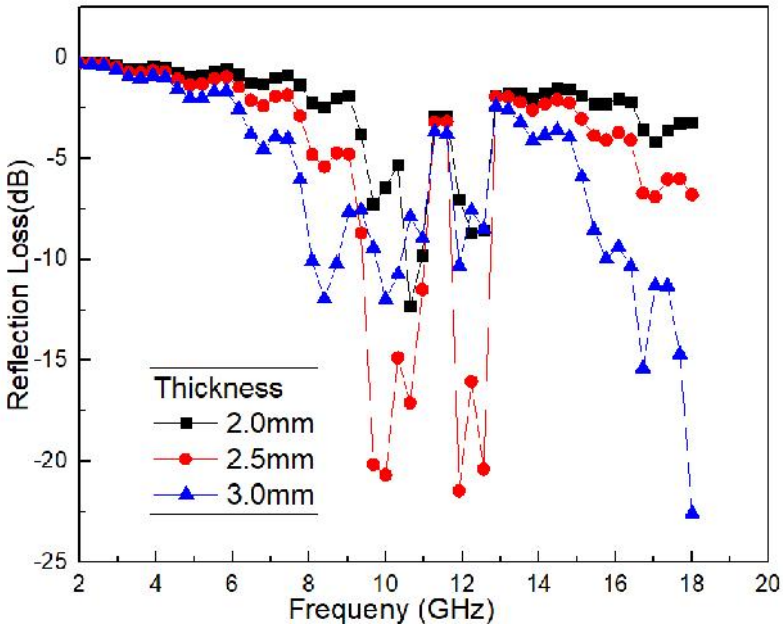

Fig.10 Absorption characteristics of PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanocomposite

4. CONCLUSIONS

$Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferritenano particle and PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanocomposite exhibiting electromagnetic properties were successfully synthesized by sol-gel auto combustion method and in situ polymerization method. XRD, FEG-SEM, FEG -TEM studies have established the formation of the PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ ferrite nanocomposites. Our result indicate that the composite exhibits excellent absorption performance over a broad band range in the radar band with good electromagnetic properties. PANI/ $Ni_{0.2}Co_{0.3}Zn_{0.5}Fe_2O_4$ nanocomposite improves electromagnetic properties compared with PANI or ferrite.

REFERENCES

1. O.akman, H.kavas, A.baykal, M.S.Topark, at.al.Magnetic metal nanoparticles coated polyacrylonitrile textiles as microwave absorber Journal of magnetism and magnetic materials 327.
2. Xiaohuren, guangliangxu, Electromagnetic and microwave absorbing properties of nicozn- ferrite doped with La^{3+}.J. Magn.Magn.Materials,354(2014) 44-48.
3. K.K Gupta, S M Abhas et.al, Microwave absorption in X and Ku band frequency of cotton fabric coated NiZnferrit and carbon formulation in polyurethane, J. Magn. Magn.Materials,362(2014) 216-225.
4. Yi Liu, Shicheng, et.al., Effect of heat treatment on microwave absorption properties of Ni- Zn- Mg –La ferrite nanoparticle, J. Magn.magn.Materials,349(2014)57-62.
5. Ch. Sujatha, K. venugopal Reddy, et.al, Effect of Co substitution of Mg and Zn on electromagnetic properties of NiCuZn ferrites, J. Phy. And Chem.of Solids 74 (2013)917-923.
6. Muhammad Waqas Mukhtar, Muhammad Irfan,et.al., Synthesis and properties of Pr substituted MgZn ferrites for core materials and high frequency applications, J. Magn.magn.Materials,381(2015)173-178.
7. C.A. Stergiou, G. Litsardakis, Electromagnetic properties of Ni and la doped strontium hexaferrites in the microwave region, J. of Alloys and Compounds 509(2011)6609-6615.
8. Le. Chen, Chunhu Lu et.al, Infrared emissivities and microwave absorption properties of perovskite $Sm_{0.5}$ $Sr_{0.5}$ Co_{1-x} Fe_xO_3 ($0<x<0.5$) , J. of Alloys and Compounds 509(2011)8756-8760.
9. Imran Sadiq, ShahzadNaseem,et.al., Temperature dependnt magnetic and microwave absorption properties of doubly substituted nanosized material, J. Magn.Magn.Materials,385(2015)236-242.
10. Niandu Wu, Xianguo Liu ,et.al., Effect of particle size on the magnetic and microwave absorption properties of carbon – coated nickel nanocapsules, J. of Alloys and Compounds656(2016)628-634.
11. S. J. Yan, S.L. Dai, H.Y Ding, et.al, Influence of Ni/Co molar ratio on electromagnetic properties and microwave absorption performance for Ni/Co paraffin composites, J. Magn.Magn.Mater.358(2014)170-176.
12. L.l. Zhang, X.X Yu, H. R. Hu, et.al. Facile synthesis of iron oxide/ reduced graphine oxide composite application for electromagnetic wave absorption at high temperature, Sci. Rep. 5(2015)92-98.
13. S. J Yan, L. Zhen, et.al, microwave absorption properties of $FeNi_3$ Submicrometre spheres and SiO_2 @ $FeNi_3$ core - shell structure, J. Phys. Appl. Phys. 43(2010) 245003.
14. D. Lu, X. L. Dong, H. Huang, et.al., Microwave absorption properties of the core/ Shell- type iron nickel nanoparticle, J. Magn.Magn.Mater. 320(2008)1106-1111.
15. M. Jallali, S. Dauterstedt, A. Michaud, Electromagnetic Shielding of polymer matrix composites with metallic nanoparticle, Composites Part: B 44(2011)1420-1426.
16. E.F. Fang , H. J. Choi,W. S. Ahn, Electroactive response of mesoporous silica and its nanocomposites with conducting polymers. Compos. Sci. technol.69(2009) 2088-2093.
17. S.Geeta, K.K.S. Kumar, S. Meenaxi et.al, Synergetic effect of conducting polymer composites reinforced E- Glass fabric for the control of electromagnetic radiation. Compos.Sci. Technol. 70 (2010) 1017-1022.
18. J. Q. Kan, X. H. Pan, C. Chen, Polyaniline – uricase biosensors prepared with template process, Biosens.Bioelectron.19(2004) 1635-1640.
19. W. Zhang, h. Xiao, S. Y. Fu, preparation and characterization of novel polypyrole – nanotube/polyaniline free standing composite films via facile solvent – evaporation method, Compos. Sci. technol. 72(2012)1812-1817.
20. E. Lahiff, T. Woods, w. Blau, G.G.Wallace, Synthesis and characterization of controllably functionalized polyaniline nanofiber, Synth. Met. 159(2009)07410748.
21. Deng –Aoli, Hong- Bin Wang, Ju-Min Zhao, Fabrication and electromagnetic Characteristics of microwave absorbers containing PPY and Carbonyl iron composites. Mat. Chem. Phys. 130(2011)437-441.
22. Namita Gandhi, Kuldeep Singh, et.al, Thermal, Dielectric and microwave absorption properties of polyaniline-CoFe2O4 nanocomposites. J. Compos. Sci. technol.71(2011)1754-1760.
23. Shi-Yuan Tong,Jenn- Ming W, Yu- Ting Huang et.al, Design and characteristics of flexible radio wave absorber conststed of functional NiCuZn ferrite –polymer composites. J. Alloys and compounds 509(2011)2263-2268.