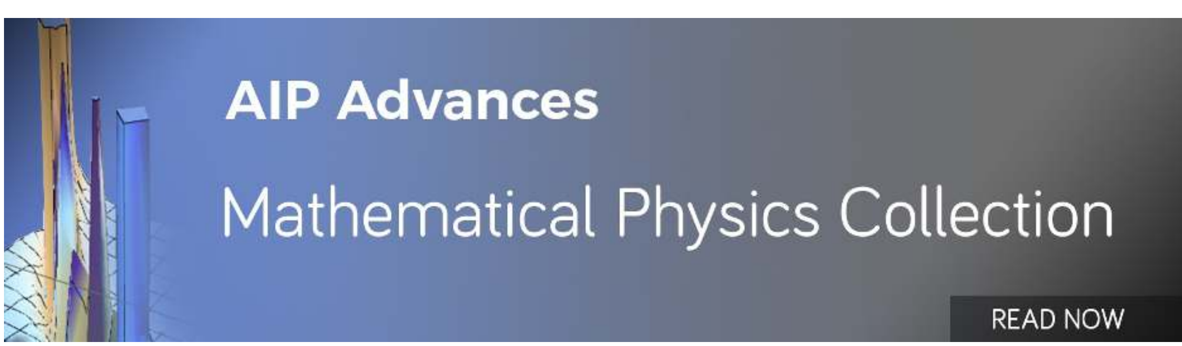
AIP Advances

Magnetization and thickness dependent microwave attenuation behaviour of Ferrite-PANI composites and embedded composite-fabrics prepared by *in situ* polymerization

Cite as: AIP Advances **11**, 015106 (2021); https://doi.org/10.1063/9.0000022
Submitted: 07 October 2020 • Accepted: 23 November 2020 • Published Online: 06 January 2021

Sumit Kumar, Vivek Verma and Rajan Walia



Magnetization and thickness dependent microwave attenuation behaviour of Ferrite-PANI composites and embedded composite-fabrics prepared by *in situ* polymerization

Cite as: AIP Advances 11, 015106 (2021); doi: 10.1063/9.0000022
Presented: 2 November 2019 • Submitted: 7 October 2020 •
Accepted: 23 November 2020 • Published Online: 6 January 2021

View Online Export Citation CrossMark

Sumit Kumar,[1,2,a)] Vivek Verma,[2] and Rajan Walia[3]

AFFILIATIONS

[1] Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India
[2] Department of Physics, Hindu College, University of Delhi, Delhi 110007, India
[3] Department of Physics, Deen Dayal Upadhyaya Gorakhpur University, Gorakhpur, Uttar Pradesh 273009, India

Note: This paper was presented at the 65th Annual Conference on Magnetism and Magnetic Materials.
[a)] **Author to whom correspondence should be addressed:** Sumit95.mittal@gmail.com

ABSTRACT

Ultrahigh efficient and effective electromagnetic-interference (EMI) shielding composites have been fabricated with the combination of Polyaniline and zinc-cobalt ferrites ($Co_{1-x}Zn_xFe_2O_4$, $0.1 \le x \le 0.4$). Ferrite nanoparticles synthesized via the sol-gel method were functionalized to polyaniline via *in situ* polymerization. Average crystallite sizes of the nanoparticles were estimated using Debye–Scherrer and Rietveld method and found to be in between 20-30 nm. FTIR spectra revealed the formation of interactions between the PANI molecules and the ferrite nanoparticles. Substitution of the nonmagnetic Zn ions considerably changes the magnetic properties of cobalt ferrites as observed from the M-H loops recorded by VSM at room temperature. The EMI-shielding performance of the fabricated composites was examined at various thicknesses with the polymer filler ratio of 1:1 in X-band frequency region using a vector network analyser. The EMI shielding performance of composites was found to be increasing with the thickness of composites where a thickness of 3.0 mm achieved an SE of ~ 100 dB for the $Co_{0.7}Zn_{0.3}Fe_2O_4$-PANI composite. Composite absorbers were deposited on cotton fabrics for protective clothing by *in situ* incorporation during the synthesis of composites which displayed relatively high EMI shielding effectiveness (SE) (40-45 dB) at a thickness of only 0.30 mm for the fabrics. The PANI-Ferrite nanocomposites can be established as promising high capacity electromagnetic shielding materials because of the dipole polarization and the magnetic losses with low cost, lightweight, high durability and good flexibility.

INTRODUCTION

Due to rapid increase in technology, usage and sensitivity of electronic devices which leads to the existence of many undesired radiations in the environment, the increasing electromagnetic interference (EMI) pollution is becoming a consequential risk to daily life.[1,2] To overcome the problems caused by electromagnetic interference, there is an urgent need to develop advance shielding materials with strong absorption over a wide range of frequency. The traditional electromagnetic interference attenuation constituents such as carbonyl iron or iron oxides (e.g. Fe_2O_3 and Fe_3O_4) have bulkiness or high-density restrictions to their practical application for shielding phenomena.[3,4] With recent progress in the field of nanoscience, electrically conducting polymer which acts as host matrices to nanocomposites have emerged out as highly effective and efficient materials to shield an electronic device or system from the undesired electromagnetic waves emitted by a nearby source.[5,6] Thus, an amalgamation of magnetic materials with conducting polymer matrix possess great potential for EMI compatibility from numerous EM radiation sources due to the presence of both dielectric and magnetic losses.[7,8] Polyaniline (PANI) can be considered probably the most studied and experimentally observed conducting polymer among all due to numerous factors which includes: facile formation, cost of synthesis, high eco-friendly solidity, excellent conductive behaviour and various applications.[9,10] Nanoferrites epitomize a significant kind of materials having notable characteristics due to which they have been widely studied and used for several purposes such as swapping circuits, recording devices, sensing application, biotechnological applications, EMI Shielding.[11–13] Cobalt Ferrite possesses significant physical properties like high magnetic saturation behaviour with large coercivity and anisotropy energy, great tensile strength and chemically steady behaviour. Therefore, Co–Zn mixed ferrites have diverse properties as Zn substitution causes important structural and physical changes as per the requirement of various practical applications which includes shielding of devices.

In this work, a simple method to design the lightweight, flexible with minimal thickness and chemically stable fabrics, one is the cloth which is generally used by the national security persons for different purposes while other is typically used white cotton cloth, deposited with zinc doped cobalt ferrite and polyaniline nanocomposites during the *in situ* polymerisation of composite materials is projected which serve efficiently for high-performance EMI shielding materials. Direct deposition or coating of the composite materials on the fabrics acts as a more suitable and convenient method due to their low cost, labour saving and simplicity of processing than the spinning methods. Therefore, by keeping in mind the above aspects, excellent EMI shielding fabrics should be fabricated through depositing the Ferrite-PANI composite materials on the surface of the substrate.

Therefore, the purpose of present work is to examine the structural analysis and magnetic behaviour of zinc doped Cobalt nano ferrites, $Co_{1-x}Zn_xFe_2O_4$ (with Zn from 0.1 to 0.4) prepared by gel auto-combustion method. The effect of the magnetic nature of fillers, filler ratio, the thickness of composites and their deposition on fabrics in the modification of shielding effectiveness (SE) was inspected, and the related shielding mechanism is discussed.

EXPERIMENTAL SECTION

Zinc doped cobalt ferrite nanoparticles ($Co_{1-x}Zn_xFe_2O_4$ with Zn = 0.1 - 0.4) were synthesized by using the sol-gel process under similar parameters for all compositions as per our previously reported work.[14] PANI/$Co_{1-x}Zn_xFe_2O_4$ ($0.1 \le x \le 0.4$) composite samples were synthesized by using chemical oxidative *in situ* polymerization technique[15] in presence of ferrite nanoparticles with 50% weight ratio to aniline monomer. 0.3M DBSA (serving as both surfactant and dopant) and ferrite nanoparticles were homogenized by using the homogenizer and 0.1M of aniline (An) was further dissolved and supersonic stirring was sustained for 1 h to form a suspension or emulsion kind of solution. The oxidant ammonium persulfate (0.1M) was added very carefully in a controlled way maintaining the temperature of reactor below 0°C with dynamic stirring for 5–6 h to above emulsion. The green polymer precipitates so gained were then cured with isopropyl alcohol under dynamic stirring for 2–3 h. During the synthesis of nanocomposites, composite materials get uniformly deposited on cloth samples as rotator moves continuously within the solution for the entire duration of the synthesis process.

X-ray diffraction investigation

The typical XRD patterns of $Co_{1-x}Zn_xFe_2O_4$ (x=0.1, 0.2, 0.3, 0.4) nanoferrites recorded in 2θ range of 20-80° are presented in Figure 1. The XRD pattern displays that all characteristic peaks well indexed to (220), (311), (222), (400), (422), (511) and (440) atomic planes in nanoferrites along with their corresponding interplanar spacing mentioned with the peaks.

The average crystallite size of nanoferrites was computed using Debye–Scherrer method and Williamson-Hall method.[16,17] The change in d values with Zn^{2+} ions content is given with the size ranging from 20-35 nm showing that size decreases with an increase in zinc content.

Figure 2 shows the Rietveld refinement graphs of XRD patterns of present $Co_{1-x}Zn_xFe_2O_4$ nanoferrites having experimentally observed intensity, theoretically calculated intensity and corresponding Bragg peak positions refined theoretically using the FullPROF software.[18] It can be understood that the values of χ^2 are 0.748, 0.798, 0.781, and 0.847 which are less than 1 which indicates that quality of refinement processed for experimental data is in good agreement with theoretical model applied to the samples.

The FTIR spectra of composite samples were recorded in wavenumber region of 400–2500 cm^{-1} and are presented in figure 1. It is clear from figure that spectra have characteristics peaks associated with both ferrites and PANI polymer which conclude that there is a strong interface among ferrite nanoparticles and PANI in nanocomposites. The cubic spinel ferrites have two basic absorption bands, the first one corresponds to vibration of molecules at tetrahedral sites, which has been observed near 530 cm^{-1} with peak shift for increasing Zn content and the second one is due to vibrations at octahedral sites, here observed at a lower frequency near 400 cm^{-1}.[19] The FTIR spectra characteristic peaks of PANI are observed at 1560, 1480, 1290, 1235, 1100 and 790 cm^{-1} as depicted by figure 1, ascribed

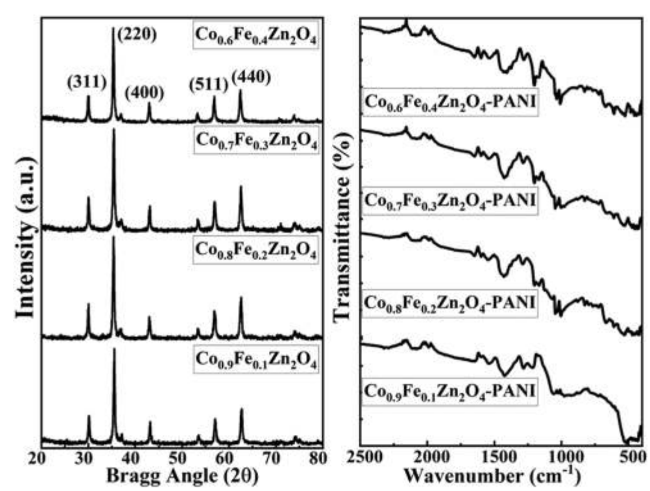


Figure 1. X-ray diffraction (XRD) plots of $Co_{1-x}Zn_xFe_2O_4$ (x = 0.1, 0.2, 0.3 and 0.4) ferrite nanoparticles well indexed with the corresponding miller planes and FTIR spectra of Ferrite-PANI nanocomposites.

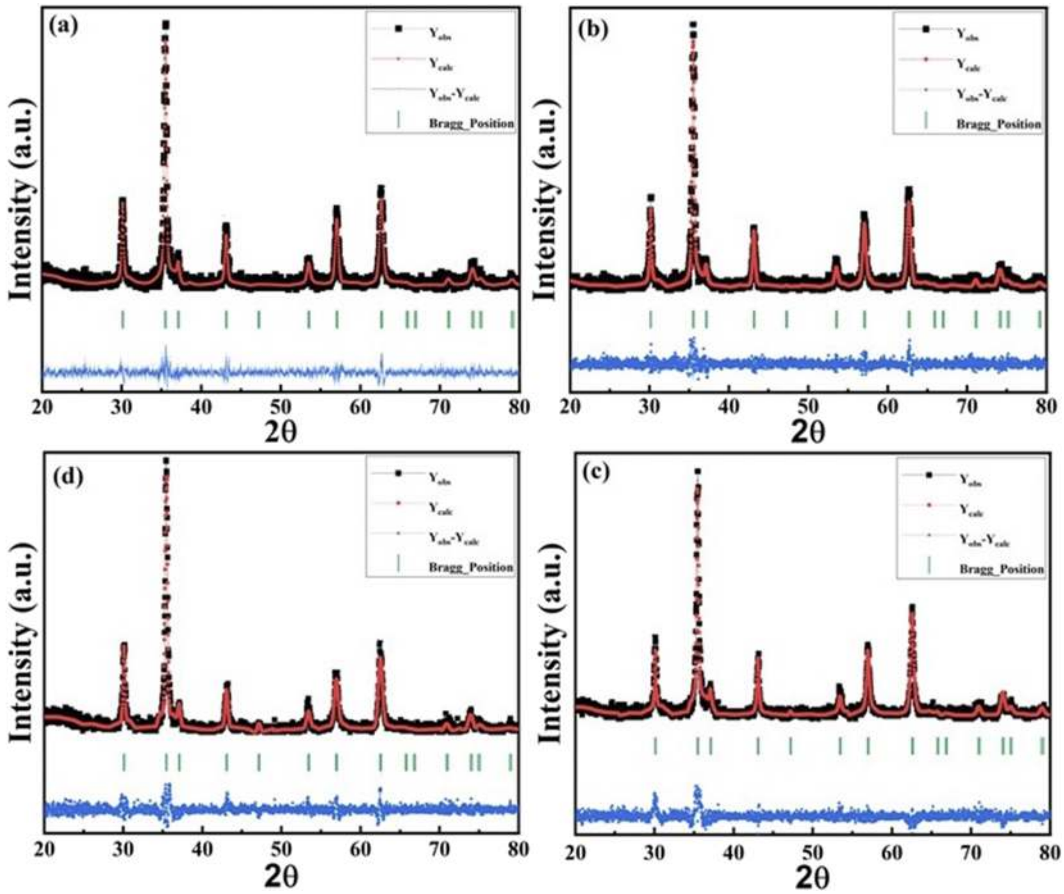


Figure 2. Rietveld refinement curves for (a) $Co_{0.9}Zn_{0.1}Fe_2O_4$ (b) $Co_{0.8}Zn_{0.2}Fe_2O_4$ (c) $Co_{0.7}Zn_{0.3}Fe_2O_4$ (d) $Co_{0.6}Zn_{0.4}Fe_2O_4$, depicting the observed and calculated XRD intensity, Bragg positions and the intensity difference.

to double carbon (C=C) stretching bonds of quinoid and benzenoid rings of structural monomer, C–N vibrations of a benzenoid ring, stretching mode of N=Q=N bonds and plane distortion of C–H in 1,4-disubstituted benzene ring respectively.[20]

Magnetic measurements

Magnetic measurements for the zinc doped cobalt nanoferrites and their composites with polyaniline show the typical hysteresis loops as shown in figure 3. The observed magnetization measurements for ferrite nanoparticles show that saturation magnetization values first escalate up to Zn = 0.3 form the value 70 emu/gm to 76 emu/gm (Ms = 70, 72, 76 and 55 emu/gm for Zn = 0.1-0.4 respectively) and then decreases while the coercivity decreases with increase in Zn content from 1185 Oe for Zn = 0.1 to 227 Oe for Zn = 0.4. According to Néel's two sublattice model, the magnetic moments of tetrahedral A-sites and octahedral B-sites are antiparallel and not equivalent, due to which magnetic moment M arises in terms of difference of magnetic moments of A and B site.[21] The replacement of Co ions with nonmagnetic Zn^{2+} ions at tetrahedral sites decreases the net magnetic moment A sublattice, which leads to an upsurge in a total magnetic moment with Zn substitution. As we further increase Zn content the magnetic Co ions occupying A-sites get reduced which weakens the exchange interactions between A and B sites. So, the canted spins system leads to a decrease in magnetic moment with further increase in Zn content for x > 0.3.[22] It is observed that values M_S for PANI/Ferrite nanocomposites decreases as compared to pure ferrite nanoparticles and also variation follows the same behavior as depicted by pure ferrite nanoparticles The diamagnetic nature serving as dead layers on ferrite surfaces and specific surface morphology of PANI plays a vital role in the extensive decrease of magnetization after the encapsulation of ferrite nanoparticles to PANI layers.

Electromagnetic shielding investigations

The shielding which is defined as a reduction of undesired or unnecessarily interfering electromagnetic signals with a device/instrument and the effectiveness of a shield (SE) can be measured as

$$SE = SE_R + SE_A + SE_M$$

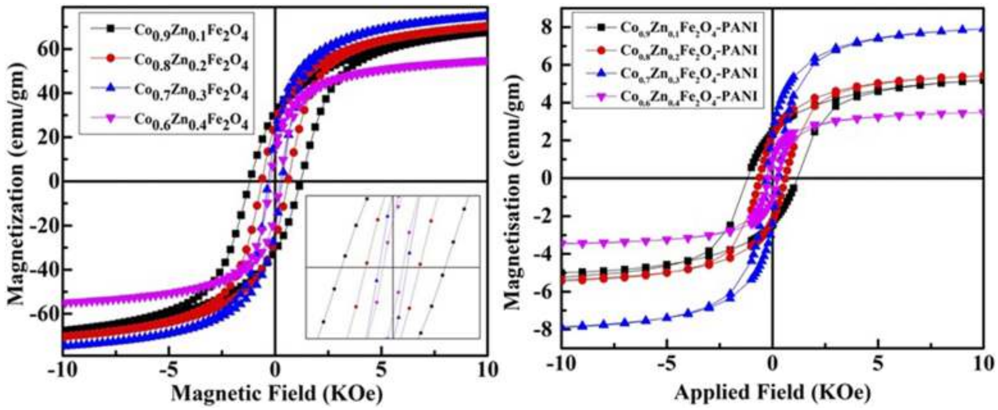


Figure 3. Vibrating sample magnetometer plots of Zinc doped cobalt ferrite and polyaniline composites recorded at room temperature showing a change in magnetization with the applied field.

where SE_R, SE_A and SE_M signify the shielding effectiveness due to reflection, absorption and multiple reflections.[23]

Practically, the shielding attenuation capacity is generally determined using network analyser instruments with help of scattering parameters (S_{11}, S_{12}, S_{21} and S_{22}). Therefore, the shielding effectiveness due to reflection (SE_R) and shielding by absorption (SE_A) are defined as:[24]

$$SE_R = -10\log(1 - R) = -10\log\left(1 - |S_{11}|^2\right)$$

$$SE_A = -10\log 1 - A_{eff}) = -10\log\left(\frac{T}{(1 - R)}\right) = 10\log\left(\frac{(1 - |S_{11}|^2)}{|S_{21}|^2}\right)$$

$$SE_T = SE_R + SE_A = -10\log\left(|S_{21}|^2\right)$$

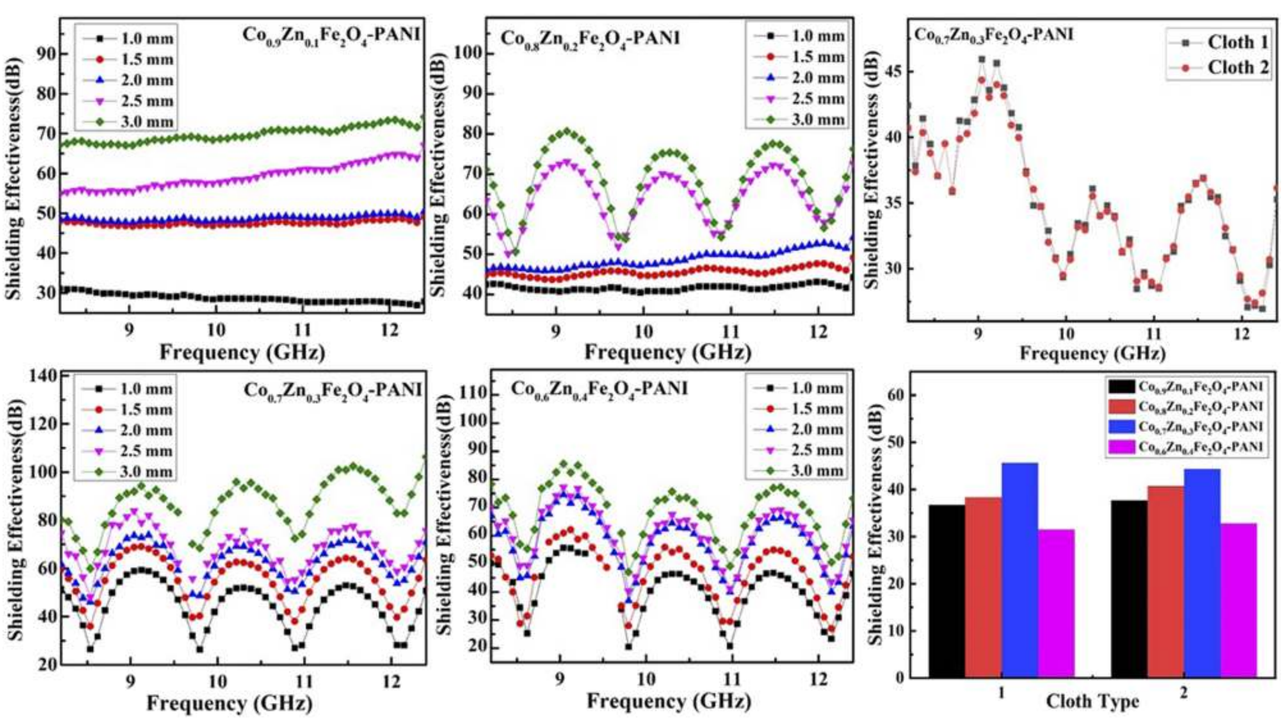


Figure 4. Dependence of shielding effectiveness (SET) as a function of frequency with the magnetization and sample thicknesses of the CZFO-PANI composites and SE values for the fabrics deposited with the composites and the frequency dependence of SE for the deposition of $Co_{0.7}Zn_{0.3}Fe_2O_4$-PANI.

Figure 4 shows EMI SE curves of nanocomposites in the X-band region (8 – 12 GHz) with varying thickness of samples ranging from 1 mm to 3 mm for each composite sample. The highest value of EMI SE is observed for $Co_{0.7}Zn_{0.3}Fe_2O_4$-PANI composite and is found to be 106 dB, while EMI SE of other composites (Zn = 0.1, 0.2 and 0.4) is 74, 81 and 86 dB respectively. It can be observed that the SE values improved up to Zn = 0.3 and then start decreasing for a particular thickness following the magnetic behaviour of pure ferrite and nanocomposite samples. The main cause behind reflection phenomena is impedance mismatching between incident EM waves and shielding material,[25] while for efficient absorption of incident radiations, there should be high dielectric and/or magnetic losses. The magnetic losses not only depend on conducting nature of materials but also on magnetic permeability.[26] In $Co_{0.7}Zn_{0.3}Fe_2O_4$-PANI composite, ferrite fillers have the highest magnetization which causes impedance mismatching due to the low electrical nature of conducting polymer and high magnetic permeability due to magnetic filler. From figure 4, it can also be observed that with an increase in the thickness of a sample, composites show a rise in EMI SE values. As if we consider $Co_{0.7}Zn_{0.3}Fe_2O_4$-PANI composite, EMI SE values increased from 60 dB to 106 dB with a rise in thickness from 1 mm to 3 mm. The variation in SE values with thickness show a gradual increase with an increase in the thickness of samples, as for Zn = 0.1, the SE value increased from 31 dB to 74 dB while for Zn = 0.2, the value increased from 44 to 81 dB. This can be attributed to fact that transmission of EM waves reduce with higher thicknesses o sample as wave has to propagate through a large distance which causes more loss or dissipation of EM wave energy.[27] The absorption loss occurring in a shield is directly proportional to the thickness of shield given by relation,[28] $SE_A = 8.7^{*}d/\delta$, where d represents thickness of sample and delta stands for skin depth.

All synthesized nanocomposites were deposited on two different kinds of clothes stated earlier. The average thickness of clothes is measured to be 0.30 mm. From figure 4, it is clear that the highest SE values of 45 dB are shown by clothes deposited with $Co_{0.7}Zn_{0.3}Fe_2O_4$-PANI composite material yielding the same SE pattern as shown by composite materials depending on their magnetic behavior. Also for other composites deposited fabrics, the SE values are more than 35 dB for each fabric indicating the high attenuation of incident EM radiations. As we dipped fabrics into composite materials, the deposition of materials modified their surface with a rough topology which helps in the reflection of incident EM waves. The deposited materials got embedded into sunken regions of the fabrics which lead to the formation of conductive paths on surface which helps in dissipation of EM energy in form of heat or leakage current. All of these factors resulted in a high performance and efficient shielding fabrics with their use to maximize the processability of various EMI shielding applications for both commercial and military purposes.

CONCLUSIONS

The XRD analysis of spinel ferrite $Co_{1-x}Zn_xFe_2O_4$ (x= 0.1, 0.2, 0.3, and 0.4) nanoparticles, synthesized by the sol-gel process has established the existence of a single-phase cubic structure. FTIR results have shown the bond vibration characteristic bands for both the ferrite nanopowders and the polyaniline present in the composite samples prepared by *in situ* polymerization. This study delivers capable and highly efficient EMI-shielding materials by incorporation of CoZn ferrite nanoparticles into polyaniline matrix. Synthesized composite with the presence of highly magnetic CoZn ferrite (Zn = 0.3) has depicted the highest EMI SE of 106 dB. The results also depicted that the shielding response of the composite materials was heightened by a rise in the magnetization and the sample thickness. The current study demonstrates a capable approach to prepare flexible, lightweight, and highly efficient X-band EMI shielding fabric based on deposition during *in situ* polymerization. The resultant shielding fabrics showed a high SE of 45 dB which considerably meets requirements for commercial EMI shielding applications.

ACKNOWLEDGMENTS

Authors of this work are grateful to the Physics Department, Hindu College, University of Delhi and Head, Department of Physics and Astrophysics, University of Delhi. We acknowledge the University Science Instrumental Centre (USIC) and Prof. Vinay Gupta, University of Delhi for the characterization facilities and valuable suggestions regarding the present work. Author Sumit Kumar is thankful to the Council of Scientific and Industrial Research (CSIR) for providing the junior research fellowship (File Number: 09/045(1578)/2018-EMR-I) for the necessary financial support and to carry out this research.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] Y. L. Cheng, J. M. Dai, X. B. Zhu, D. J. Wu, and Y. P. Sun, "Preparation, magnetic and microwave absorption properties of $La_{0.55}Sr_{0.5}MnO_3/La(OH)_3$ com," Mater Res Bull **45**, 663–667 (2010).

[2] D. Micheli, R. Pastore, C. Apollo, M. Marchetti, G. Gradoni, V. M. Primiani *et al.*, "Broadband electromagnetic absorbers using carbon nanostructure based composites," IEEE Trans Micr Theory Tech **59**, 2633–46 (2011).

[3] L. Wang, H. Wu, Z. Shen *et al.*, "Enhanced microwave absorption properties of Ni-doped ordered mesoporous carbon/polyaniline nanocomposites," Mat Sci Eng B **177**, 1649–1654 (2012).

[4] Ö. Yavuz, M. K. Ram, M. Aldissi *et al.*, "Synthesis and the physical properties of MnZn ferrite and NiMnZn ferrite polyaniline nanocomposite particles," J Mater Chem **15**, 810–817 (2005).

[5] Y. Wu, Z. Y. Wang, X. Liu, X. Shen, Q. B. Zheng, Q. Xue, and J.-K. Kim, "Ultralight graphene foam/conductive polymer composites for exceptional electromagnetic interference shielding," ACS Appl. Mater. Interfaces **9**, 9059–9069 (2017).

[6] L. Zhang, M. Liu, S. Roy, E. K. Chu, K. Y. See, and X. Hu, "Phthalonitrile-based carbon foam with high specific mechanical strength and superior electromagnetic interference shielding performance," ACS Appl. Mater. Interfaces **8**, 7422–7430 (2016).

[7] H.-M. Xiao and S.-Y. Fu, "Synthesis and physical properties of electromagnetic polypyrrole composites via addition of magnetic crystals," Cryst Eng Commun **16**(11), 2097 (2014).

[8] S. P. Gairola, V. Verma, L. Kumar, M. A. Dar, S. Annapoorni, and R. K.Kotnala, "Enhanced microwave absorption properties in polyaniline and nano-ferrite composite in X-band," Synth Met **160**(21–22), 2315 (2010).

[9] N. Gospodinova and L. Terlemezyan, "Conducting polymers prepared by oxidative polymerization: Polyaniline," Prog Polym Sci **23**, 1443–1484 (1998).

[10] C. L. Yuan, Y. S. Hong, and C. H. Lin, "Synthesis and characterization of Sr(ZnZr)x Fe12–2xO19–PANI composites," J Magn Magn Mater **323**, 1851–1854 (2011).

[11] S. Verma, J. Chand, and M. Singh, Adv. Mat. Lett. **4**, 310–316 (2013).

[12] A. Mandal and C. K. Das, J. Electron Mater. **42**, 121–128 (2013).

[13] L. M. Salah, A. M. Moustafa, and I. S. A. Farag, Ceram. Int. **38**, 5605–5611 (2012).

[14] S. Kumar, A. Ohlan, P. Kumar, and V. Verma, "Improved electromagnetic interference shielding response of polyaniline containing magnetic nano-ferrites," J. of Superconductivity and Novel Mag. **33**, 1187–1198 (2019).

[15] J. Jiang, L.-H. Ai, and L.-Y. Liu, "Poly(aniline-co-o-toluidine)/BaFe12O19 composite: Preparation and characterization," Mater Lett **64**, 888–890 (2010).

[16] G. K. Williamson and W. H. Hall, Acta Metallurg **1**, 22–31 (1953).

[17] P. P. Hankare, U. B. Sankpal, R. P. Patil, I. S. Mulla, R. Sasikala, A. K. Tripathi, and K. M. Garadkar, J. Alloys Comp. **496**, 256–260 (2010).

[18] V. A. M. Brabers, Phys. Stat. Sol. **33**, 563–572 (1969).

[19] J. Jiang, "Facile synthesis and characterization of polyaniline/NiFe2O4 nanocomposite in w/o microemulsion," J Macromol Sci Part B: Phy **47**, 242–249 (2008).

[20] P. S. Aghav, V. N. Dhage, M. L. Mane, D. R. Shengule, R. G. Dorik, and K. M. Jadhav, Phys. B: Condens. Matter **406**, 4350–4354 (2011).

[21] S. Bhukal, T. Namgyal, S. Mor, S. Bansal, and S. Singhal, J. Mol. Str. **1012**, 162–167 (2012).

[22] R. C. Kambale, P. A. Shaikh, S. S. Kamble, and Y. D. Kolekar, J. Alloys Comp. **478**, 599–603 (2009).

[23] P. Saini, V. Choudhary, B. P. Singh *et al.*, "Enhanced microwave absorption behavior of polyaniline-CNT/polystyrene blend," Synth Met **161**, 1522–1526 (2011).

[24] D. R. Mane, D. D. Birajdar, S. Patil, S. E. Shirsath, and R. H. Kadam, J. Sol–Gel Sci. Technol. **58**, 70–79 (2011).

[25] M. Wan, *Conducting Polymers with Micro or Nanometer Structure* (Springer, Berlin, Heidelberg, New York, 2008).

[26] M. Gholampoor, F. Movassagh-Alangh, and H. Salimkhani, "Fabrication of nano-Fe3O4 3D structure on carbon fibers as a microwave absorber and EMI shielding composite by modified EPD method," Solid State Sci **64**, 51 (2017).

[27] N. C. Das, D. Khastgir, T. K. Chaki, and A. Chakraborty, "Electromagnetic interference shielding effectiveness of carbon black and carbon fibre filled EVA and NR based composites," Compos. A **31**, 1069–1081 (2000).

[28] J. Huo, L. Wang, and H. Yu, "Polymeric nanocomposites for electromagnetic wave absorption," J. Mater. Sci. **44**, 3917–3927 (2009).