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Zinc substitution effect on the structural, spectroscopic and electrical properties of nanocrystalline MnFe$_2$O$_4$ spinel ferrite

C. Murugesan $^{a, b}$, K. Ugendar $^c$, L. Okrasa $^d$, Jun Shen $^{a, *}$, G. Chandrasekaran $^{b, **}$

$^a$ College of Mechatronics and Control Engineering, Shenzen University, Shenzen, China
$^b$ Department of Physics, Pondicherry University, Puducherry, 605014, India
$^c$ Department of Applied Physics, Jabalpur Engineering College, Jabalpur, 482011, MP, India
$^d$ Department of Molecular Physics, Lodz University of Technology, Zeromskiego 116, 90-924, Lodz, Poland

** Corresponding author.
E-mail addresses: junshen@szu.edu.cn (J. Shen), chandgc@gmail.com (G. Chandrasekaran).

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1. Introduction

Nanomaterials with dimensions of 1 nm–100 nm show paradigm change in chemical, physical, electrical, magnetic, and optical properties compared with its bulk counterpart [1–6]. The ultimate goal of nanoscience is to exploit these unusual properties to develop next-generation devices. Based on the area of application, the field of nanoscience has expanded and rechristened as nanoelectronics, nanomagnetism, nanophotonics, and nanomechanics [7–9]. In the field of nanomagnetism, the spinel ferrites are important materials because they exhibit unusual magnetic and electrical properties in comparison with their bulk counterpart [4,10–12]. Nanocrystalline spinel ferrites have been demonstrated as useful material for hyperthermia [13,14], detection of COVID-19 [15], visible light-enabled photodegradation [16] and, the catalyst for the synthesis of chalcones [17]. The molecular formula of spinel-type ferrite is MFe$_2$O$_4$ (M = Co, Ni, Mn, Mg, or other divalent cations) [18]. Two types of interstitial sites exist such as tetrahedral site coordinates 4 surrounding O ions and the octahedral site coordinates 6 surrounding O ions [19]. The important properties of ferrites are determined by the distribution of cations within these interstitial sites. Depending on the occupancy of divalent cations and the Fe$^{3+}$ ions in interstitial sites, the spinel ferrites are generally categorized as normal, inverse, and mixed. Among these three types, mixed ferrites are considered significant materials because of their wide range of tunability in properties. In recent decades, several investigations have been done to explore and enhance the magnetic and electrical properties of end member ferrites by substituting different divalent and trivalent cations using various synthesis methods [16,20–34]. Among the spinel
ferrites, the Zn substituted ferrites are attracted special interest due to the strong tetrahedral site preference of Zn$^{2+}$ ion. Choodamani et al. [25] prepared the Zn substituted MgFe$_2$O$_4$. The evaluated crystallite sizes were in the range of 47–80 nm. The dielectric constant, tan δ, and electrical conductivity were the lowest for x = 0.50 sample. The saturation magnetization of the ferrites increases up to x = 0.5 with the Zn concentration. In our previous work, we investigated the nanocrystalline Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ mixed ferrites. The size of the crystallites was in the range of 9.6–31 nm. The magnetization of the samples increases up to x = 0.2 (44.16 emu/g). The prepared ferrites exhibit superparamagnetic behavior for x ≥ 0.4 concentration of Zn [35]. Andhare et al. [27] prepared the Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ mixed ferrite nanoparticles. The crystallite size, lattice constant, and X-ray density were increases with zinc substitution. The energy band gap of prepared ferrites was increasing from 2.258 eV to 2.8306 eV. The hysteresis curve of ferrites shows that the prepared ZnFe$_2$O$_4$ was magnetically softer than Co$_2$O$_4$. Anupama et al. [29] synthesized the nanocrystalline Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples through the

### Table 1

Crystallite size (D) and lattice constant (a) of nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$.

| x   | D (nm) | a (Å)  |
|-----|--------|--------|
| 0.0 | 8.5    | 8.358  |
| 0.2 | 8.2    | 8.362  |
| 0.4 | 9.4    | 8.419  |
| 0.6 | 10.5   | 8.427  |
| 0.8 | 11.5   | 8.429  |
| 1.0 | 19.6   | 8.435  |

Fig. 1. Rietveld refined XRD patterns of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ mixed ferrites [28].
combustion technique. The cubic structure of the prepared sample without the formation of impurity phases was confirmed using Rietveld refinement. The magnetic properties reveal that the highest value of magnetization obtained for $x = 0.4$. It is observed from the literature results that the Zn substitution significantly improves the properties of Mg, Cu, Co, and Ni based nano ferrites. Among the number of spinel-type ferrites, manganese ferrite ($\text{MnFe}_2\text{O}_4$) is an attractive ferrite with important applications in catalysis [36,37], gas sensor [38], MRI contrast agents [39], hyperthermia [40], transformer core [41,42], deflection yokes [43], and microwave device [44,45] because of the high value of magnetization and resistivity. The bulk $\text{MnFe}_2\text{O}_4$ is crystallized in cubic symmetry with $\text{Fd}_{3}\text{m}$ space group, in which 80% of Mn ions occupy the A sites, and 20% occupy the B sites [46]. Over the past few decades, researchers focused on the synthesis of various nano ferrites to explore the novel properties. The synthesis method and synthesis parameters have an important impact on the size of the particles which

| Structural parameters | $x = 0.0$ | $x = 0.2$ | $x = 0.4$ | $x = 0.6$ | $x = 0.8$ | $x = 1.0$ |
|-----------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Goodness of fit ($\chi^2$) | 8.491 | 8.886 | 8.075 | 8.121 | 8.119 | 7.837 |
| Lattice Constant (Å) | 8.334 | 8.349 | 8.403 | 8.418 | 8.436 | 8.438 |
| Bond length (Å) | O–B: 2.034(2) | 2.019(6) | 2.002(8) | 2.048(7) | 2.034(5) | 2.076(4) |
| Bond Angle (degree) | O–A: 1.960(10) | 1.929(10) | 2.000(8) | 1.922(5) | 1.960(4) | 1.885(3) |
| O–B–O | 85.48 | 85.95 | 83.88 | 86.71 | 85.56 | 88.12 |
| Cation occupancy | Mn (A site): 0.8718 | 0.6504 | 0.4836 | 0.3251 | 0.1604 | 0 |
| Zn (A site): 0 | 0.1701 | 0.3196 | 0.4795 | 0.6399 | 0.8073 |
| Fe (A site): 0.2765 | 0.2113 | 0.2036 | 0.1992 | 0.1996 | 0.2001 |
| Mn (B site): 0.0942 | 0.0671 | 0.0633 | 0.0387 | 0.0194 | 0 |
| Zn (B site): 0 | 0.0186 | 0.0413 | 0.0599 | 0.0809 | 0.0991 |
| Fe (B site): 0.8895 | 0.8973 | 0.8790 | 0.8996 | 0.9055 | 0.8990 |
| O | 1.0405 | 0.8959 | 0.9123 | 0.9370 | 0.9687 | 1.0227 |

Fig. 2. FE-SEM images of $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ mixed ferrites.
subsequently results into the change in properties for the same ferrite \([32, 47, 48]\). Since different synthesis methods yield different magnetic and electrical properties, in this work a simple and low-cost solvent-free synthesis method is used to synthesize nano-sized Zn substituted \(\text{MnFe}_2\text{O}_4\) with the chemical formula of \(\text{Mn}_\text{1-xZn}_\text{xFe}_2\text{O}_4\). The advantage of this synthesis route is that it does not involve any solvent to dissolve the precursor. Since the metal nitrates used during the synthesis are hygroscopic in nature, they tend to form a homogeneous mixture so that the solvent evaporation time can be minimized. The total synthesis process completed within an hour. In our previous investigation the structural and magnetic properties of the same compounds were reported \([28]\). In this work, the structural, morphological, spectroscopic, dielectric, ac conductivity, and impedance properties of the Mn–Zn ferrites were systematically studied and the obtained results are discussed in detail in the following sections.

2. Experimental details

2.1. Synthesis

Nanocrystalline \(\text{Mn}_\text{1-xZn}_\text{xFe}_2\text{O}_4\) (where \(x = 0.0\) to 1.0 in steps of 0.2) ferrites were synthesized through a solvent-free combustion reaction method. To synthesize \(\text{Mn}_\text{1-xZn}_\text{xFe}_2\text{O}_4\), nitrates of manganese, zinc, iron, and citric acid were used as precursor materials. The reactants

\[ \text{Mn(NO}_3\text{)}_2 + \text{Zn(NO}_3\text{)}_2 + \text{Fe(NO}_3\text{)}_3 + \text{C}_\text{6H}_\text{8O}_7 \rightarrow \text{Mn}_\text{1-xZn}_\text{xFe}_2\text{O}_4 + 3\text{H}_\text{2} \text{O} \]

The reaction mixture was heated to 100°C in a muffle furnace and the synthesized powders were calcined at 400°C for 2 h. The synthesized powders were characterized by X-ray diffraction, transmission electron microscopy, and selected area electron diffraction. The details of the experimental setup and characterization methods are discussed in the following sections.

Fig. 3. The TEM images and SAED patterns of \(\text{Mn}_\text{1-xZn}_\text{xFe}_2\text{O}_4\) (where \(x = 0.0, 0.4\) and 1.0) mixed ferrites.
were weighed and then mixed for 30 min using a magnetic stirrer. Then the nitrate and citric acid mixture were heat-treated at 75 °C until it forms a dry gel. Since the metal nitrates are hygroscopic in nature, the mixed metal nitrates form gel during mixing. The obtained dried gel was heated continuously until self-combusted. The resultant ferrite powder was heat-treated for 1 h at 300 °C and then used for further characterization [28, 49].

2.2. Characterization

The X-ray diffraction (XRD) pattern of the ferrites was recorded using a powder X-ray diffractometer (Ultima IV, RIGAKU) by employing Cu-Kα1 (Wavelength-1.5406 Å) radiation. Rietveld refinement was carried out using the GSAS program and its EXPGUI user interface. The surface morphology image of the ferrites was examined using Carl Zeiss SUPRA 55 field emission scanning electron microscope (FE-SEM). Particle morphology was obtained using transmission electron microscopy (TEM) observations using a JEOL JEM-2100F microscope that operates at 200 kV. The spectra of oxidation states at the surface were recorded using a Thermo Fisher ESCALAB 250xi photoelectron spectroscopy (XPS). The pass energy for a wide survey and narrow spectra is 100 eV and 30 eV, respectively. The AC electrical properties were measured using a broadband dielectric spectrometer (BDS) Alpha Analyser Concept 80, Novocontrol.

3. Results and discussion

3.1. X-ray diffraction analysis

The Rietveld refined powder XRD patterns of spinel Mn1-xZnxFe2O4 ferrites are shown in Fig. 1. The broadening of diffraction peaks shows that the prepared ferrite samples are smaller sized [28]. No additional reflection peaks correspond to any secondary phase was observed in nanocrystalline Mn1-xZnxFe2O4. The values of crystallite sizes are calculated using Scherrer’s formula [49] and given in Table 1. The size of the nanocrystalline MnFe2O4 is 8.5 nm. Moreover, no significant change in crystallite size was observed for the initial x = 0.2 substitution. For further substitution, the size of the crystallites increases slowly up to x = 0.8 and suddenly reaches to 19.6 nm for x = 1.0. This finding indicates that the Mn and Zn ratio has a major influence on the crystallites size [50]. The lattice constant values of nanocrystalline Mn1-xZnxFe2O4 are determined using the relation given in Ref. [49] and are given in Table 1. The Zn substitution increases the values of the lattice constant gradually. Nevertheless, the Zn2+ (0.74 Å) ionic radius is larger than that of the Mn3+ (0.645 Å), an increased lattice constant value is observed for Zn-substituted samples. The Rietveld refinement was carried out for all the samples and the Mn1-xZnxFe2O4 are seen to crystallize in spinel structure with the space group Fd3m. The structural parameters of Mn1-xZnxFe2O4 ferrites such as goodness of fit, lattice constant, bond length, bond angle, and cation occupancy obtained from the Rietveld refinement are given in Table 2. The lattice constant values

Fig. 4. The particle size distribution for the TEM images of Mn1-xZnxFe2O4 (where x = 0.0, 0.4, and 1.0) mixed ferrites fitted for the Lorentzian shape.
are almost similar to that of the value calculated theoretically. The bond length O–B, O–A, and the bond angle A-O-B, B-O-B, and A-B-O of MnFe₂O₄ are slightly affected for the Zn substituted samples which confirm the substitution of Zn. The cation occupancy in different sites also was refined and given in Table 2 which indicates the change in cation distribution with Zn concentration.

3.2. Surface morphological analysis

3.2.1. FE-SEM analysis

The surface morphology images of Mn₁₋ₓZnₓFe₂O₄ ferrites are shown in Fig. 2. The images confirm the nano size of the samples, and the prepared samples are roughly spherical in shape. Furthermore, the substitution of Zn does not greatly affect the surface morphology of nanocrystalline Mn₁₋ₓZnₓFe₂O₄ up to x = 0.8.

3.2.2. TEM analysis

The TEM images for selected samples of Mn₁₋ₓZnₓFe₂O₄ (x = 0.0, 0.4 and 1.0) are shown in Fig. 3. The particles are aggregated, and the images further showed that the particles of x = 1.0 sample have bigger sizes than other samples, as observed in FE-SEM analysis.

The selected area electron diffraction (SAED) patterns of the Mn₁₋ₓZnₓFe₂O₄ (where x = 0.0, 0.4, and 1.0) nanoparticles presented in Fig. 3 shows the concentric rings and bright spots over the rings, which point out the polycrystalline nature of the prepared ferrites. The size distribution from the TEM images was calculated and fitted for the Lorentzian shape as shown in Fig. 4. The calculated values of particle size of the samples x = 0.0, x = 0.4 and x = 1.0 are 7.54, 8.71 and 17.73 nm,

Fig. 5. XPS survey spectra of Mn₁₋ₓZnₓFe₂O₄ mixed ferrite nanoparticles.
respectively. The obtained values of particle size are agreed well with the XRD results.

3.3. X-ray photoelectron spectroscopy analysis

The XPS wide-scan spectra of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles are shown in Fig. 5. Given that the binding energy varies for different elements, the binding energy values are used to find out the elements present in the samples. The survey scan of the samples shows the presence of elements, such as carbon, oxygen, iron, manganese, and zinc.

3.3.1. Mn 2p peak

The high-resolution Mn 2p spectra of MnFe$_2$O$_4$ are shown in Fig. 6. The XPS spectra that correspond to Mn 2p shows two major peaks around 641.6 eV (Mn 2p$_{3/2}$) and 653.4 eV (Mn 2p$_{1/2}$) for MnFe$_2$O$_4$. The peak position of the Mn 2p spectra was fitted using the Lorentzian–Gaussian model [51]. No satellite peak is observed between Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$. This provides clear evidence for the absence of manganese in Mn$^{2+}$ state at the surfaces [37]. The XPS spectra of Zn substituted samples are shown in Fig. 7. The substitution of Zn has not resulted in the emergence of new peaks, which in-turn confirms the incorporation of Zn into MnFe$_2$O$_4$.

3.3.2. Zn 2p peak

Fig. 8 shows the high-resolution Zn 2p spectra of Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ ferrite nanoparticles. The peak position of the Zn ions in Zn 2p spectra was fitted using the Lorentzian–Gaussian model and shown in Fig. 8. Two peaks for Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ with the binding energy values of 1021.16eV and 1044.24eV are observed, indicating the presence of Zn$^{2+}$ ion [52]. Fig. 9 shows that no large change is observed in the position of the peaks implying that the ionic state of Zn remains the same for the
high concentration of Zn. Furthermore, these spectra confirm that the Zn atom is fully dissolved in the spinel-structured MnFe$_2$O$_4$.

3.3.3. Fe 2p peak

The high-resolution Fe 2p spectra of MnFe$_2$O$_4$ nanoparticles are shown in Fig. 10. The XPS spectra show two peaks for Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ with the binding energy values of 710.4 eV and 724.2 eV respectively. In addition to that two satellite peaks appear at binding energies of 718.6 and 732.7 eV, indicating the presence of Fe$^{3+}$ cations [37]. The high-resolution XPS spectra of nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites are shown in Fig. 11. The substitution of Zn does not result in the appearance of new peaks, indicating that Zn does not change the ionic state of Fe present in nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$.

3.3.4. O 1s peak

Fig. 12 shows the O 1s high-resolution spectra of MnFe$_2$O$_4$ fitted for the Lorentzian–Gaussian model. Two major peaks for O 1s with the binding energy values of 530.78 eV and 529.54 eV are observed. The peak at 529.54 eV corresponds to the metal cations doubly bonded with metal-oxygen atoms. The peak observed at 530.78 eV corresponds to the cation that is covalently bonded to two atoms [51]. The XPS spectra of nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ are shown in Fig. 13. The substitution of Zn increases the binding energy of nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites.

3.4. AC electrical properties of nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$

3.4.1. Dielectric constant

The frequency dependant dielectric constant ($\varepsilon'$) of nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ is shown in Fig. 14. The dielectric constant values are
almost constant at lower frequencies and decreases at higher frequencies. The dielectric dispersion at the lower frequency region is due to the space charge effect that arises from the grain size, Fe\textsuperscript{2+} ions, and oxygen vacancies present in the samples \cite{25}. The electrical conduction in the spinel arises from the charge carriers hopping between the ions, and the dielectric polarization is also explained through the same mechanism \cite{53, 54}. The dielectric polarization in MnFe\textsubscript{2}O\textsubscript{4} is attributed to the hopping of electron between Fe\textsuperscript{2+}→Fe\textsuperscript{3+} and the hole hopping between Mn\textsuperscript{3+}↔Mn\textsuperscript{2+} ions in the octahedral site; in ZnFe\textsubscript{2}O\textsubscript{4}, polarization arises from the hopping of electron between Fe\textsuperscript{2+}→Fe\textsuperscript{3+} cations \cite{12, 25}. These charge carriers hopping between Fe\textsuperscript{2+}→Fe\textsuperscript{3+} ions cannot cooperate at higher frequencies with the external electric field, thereby reducing polarization \cite{54}. The substitution of Zn decreases the dielectric constant by up to x = 0.8, and the nanocrystalline Mn\textsubscript{0.2}Zn\textsubscript{0.8}Fe\textsubscript{2}O\textsubscript{4} sample has the lowest value. However, ZnFe\textsubscript{2}O\textsubscript{4} exhibits a higher dielectric constant than Mn\textsubscript{0.2}Zn\textsubscript{0.8}Fe\textsubscript{2}O\textsubscript{4} and also show slightly different dielectric relaxation behavior than the other samples. Such behavior may arise due to the presence of more number of Fe\textsuperscript{2+} ions in octahedral sites and higher grain size of the ZnFe\textsubscript{2}O\textsubscript{4} \cite{25}.

3.4.2. Dielectric loss tangent

Frequency-dependent dielectric loss tangent (tan δ) of nanocrystalline Mn\textsubscript{1-x}Zn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} is shown in Fig. 15. Initially, tan δ decreases with frequency, and a relaxation peak emerges at particular frequencies. When the charge carrier’s hopping frequency between Fe\textsuperscript{2+}→Fe\textsuperscript{3+} and Mn\textsuperscript{3+}↔Mn\textsuperscript{2+} is larger than that of the applied field, the charge carriers are able to follow the electric field, due to that more absorption occurs at lower frequencies, thereby incurring more loss. However, at higher frequencies, the hopping frequency of the charge carriers cannot follow the external field. Thus, less absorption occurs, and hence less loss is obtained. In addition to that, the dielectric loss also occurs from the dipole relaxation, which dissipates energy \cite{55}. Relaxation peaks in tan δ arise when the charge carrier’s hopping frequency is same as the frequency of the applied field. The substitution of Zn decreases tan δ, and the Mn\textsubscript{0.2}Zn\textsubscript{0.8}Fe\textsubscript{2}O\textsubscript{4} sample has the lowest value among all the samples.

3.4.3. AC conductivity

The frequency-dependent real part of ac electrical conductivity (σ’) of Mn\textsubscript{1-x}Zn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} mixed ferrites is shown in Fig. 16. At lower frequencies, conductivity increases slowly whereas rapidly increases at higher frequencies. At lower frequencies, the resistive natured grain boundaries are more active, and hence low conductivity value is observed. The high conductive nature of grains become highly active at higher frequencies, thereby increasing the hopping of charge carrier between the ions, and conductivity is also increased at high frequencies \cite{56, 57}. When the concentration of Zn increases, the value of conductivity gradually decreases, and the Mn\textsubscript{0.2}Zn\textsubscript{0.8}Fe\textsubscript{2}O\textsubscript{4} sample has the lowest value of conductivity among all the samples.

The ac electrical conductivity of Mn\textsubscript{1-x}Zn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} ferrites at various temperatures are measured and shown in Fig. 17. Conductivity increases with the temperature, which shows the semiconducting behavior of the samples. The temperature-dependent reciprocal ac conductivity is shown in Fig. 18, and conductivity reveals the Arrhenius-type temperature dependence. The activation energy for the electrical conduction process is calculated from the least square straight-line fit, and the observed values are depicted in Table 3. The values of activation energy show a strong dependence on Zn concentration. The calculated values of
activation energy (0.43 eV–0.62 eV) confirm that the electron hopping is main responsible for the process of electrical conduction in the samples [58]. Mn$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ sample has the highest value of activation energy because of its low conductivity.

3.4.4. Impedance

The Cole–Cole plots of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites are shown in Fig. 19. The plot shows two overlapped depressed semicircles that characterize the grain boundary and grain contribution of the samples [59]. The Cole–Cole plots were modeled using \((R_gCPE_g)(R_{gb}CPE_{gb})\) equivalent circuit model and the values are obtained by fitting Cole–Cole plots for the proposed circuit at 303 K and presented in Table 3. \(R_{gb}\) values are higher than those of \(R_g\) values, whereas the CPE\(_g\) values are higher than those of CPE\(_{gb}\) values. This analysis shows that the contribution of grain boundary is higher compared with the grain to the resistance. Furthermore, the values of grain boundary and grain resistance increase with Zn, and the sample Mn$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ has the highest resistance value because of its low conductivity.

3.4.4. Impedance

The Cole–Cole plots of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites are shown in Fig. 19. The plot shows two overlapped depressed semicircles that characterize the grain boundary and grain contribution of the samples [59]. The Cole–Cole plots were modeled using \((R_gCPE_g)(R_{gb}CPE_{gb})\) equivalent circuit model and the values are obtained by fitting Cole–Cole plots for the proposed circuit at 303 K and presented in Table 3. \(R_{gb}\) values are higher than those of \(R_g\) values, whereas the CPE\(_g\) values are higher than those of CPE\(_{gb}\) values. This analysis shows that the contribution of grain boundary is higher compared with the grain to the resistance. Furthermore, the values of grain boundary and grain resistance increase with Zn, and the sample Mn$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ has the highest resistance value because of its low conductivity. The Cole–Cole plot of the nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites are measured at different temperatures and shown in Fig. 20. The radius of the semicircle decreases with the
increase in temperature because of the increment in electrical conductivity. The values of $R_g$ and $R_{gb}$ are obtained by fitting the plot to the proposed model. The values are plotted and shown in Fig. 21. The $R_g$ and $R_{gb}$ values increase with Zn substitution. The activation energy calculated using the Arrhenius relation for the grain and grain boundary resistance, and given in Table 3. Among all samples, the $x = 0.8$ composition has the highest value of activation energy because of its high resistance.

4. Conclusion

The nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ mixed ferrites were successfully synthesized using the combustion reaction method. All samples are single-phase and no extra phase was observed for Zn substitution. Studies on surface morphology analysis indicate that the synthesized ferrites are nano size and spherical shaped. Further, the SAED patterns point out the polycrystalline nature of the prepared ferrites. The X-ray photoelectron spectra show the presence of atoms Mn, Zn, Fe, and O in the Mn 2p, Zn 2p, Fe 2p, and O 1s states. The values of dielectric constant, $\tan \delta$, and ac electrical conductivity gradually decreases with Zn substitution up to $x = 0.8$. The activation energy of the nano ferrites increases from 0.44 eV ($x = 0.0$) to 0.62 eV ($x = 0.8$). The impedance study shows that the role of the grain boundary is predominant for electrical resistance, and the highest values of grain ($4.42 \times 10^8 \Omega$) and grain boundary ($4.37 \times 10^9 \Omega$) resistance are observed in the nanocrystalline Mn$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ sample. The obtained results in the present

| $X$ | $E_a$ (eV) | $R_g$ (Ω) | $R_{gb}$ (Ω) | CPE$_g$ (F) | $n_g$ | CPE$_{gb}$ (F) | $n_{gb}$ | $E_{a(g)}$ (eV) | $E_{a(gb)}$ (eV) |
|-----|------------|-----------|-------------|--------------|-------|----------------|---------|----------------|-----------------|
| 0.0 | 0.43       | $4.69 \times 10^4$ | $2.51 \times 10^6$ | $3.62 \times 10^{-11}$ | 0.83  | $6.46 \times 10^{-11}$ | 0.93  | 0.42           | 0.45            |
| 0.2 | 0.48       | $8.44 \times 10^5$ | $1.09 \times 10^7$ | $1.57 \times 10^{-10}$ | 0.76  | $2.05 \times 10^{-11}$ | 0.99  | 0.46           | 0.48            |
| 0.4 | 0.53       | $1.43 \times 10^7$ | $1.09 \times 10^8$ | $2.69 \times 10^{-10}$ | 0.68  | $3.05 \times 10^{-11}$ | 0.97  | 0.53           | 0.54            |
| 0.6 | 0.55       | $4.13 \times 10^7$ | $1.21 \times 10^8$ | $6.72 \times 10^{-11}$ | 0.77  | $3.56 \times 10^{-12}$ | 0.96  | 0.53           | 0.57            |
| 0.8 | 0.62       | $4.42 \times 10^7$ | $2.57 \times 10^8$ | $4.63 \times 10^{-11}$ | 0.80  | $2.51 \times 10^{-11}$ | 0.94  | 0.59           | 0.63            |
| 1.0 | 0.50       | $1.11 \times 10^8$ | $1.11 \times 10^9$ | $-3.34 \times 10^{-11}$ | $-3.44 \times 10^{-11}$ | 0.86  | $-3.44 \times 10^{-11}$ | 0.97  | 0.53           | 0.57            |

Fig. 19. Cole-Cole plots of nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ at 303 K.
investigation suggest that the prepared Zn substituted MnFe$_2$O$_4$ ferrite Mn$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ nanoparticles are useful candidate material for high-frequency electronic device applications.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Fig. 21. Grain resistance (a) and grain boundary resistance (b) of nanocrystalline Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ at different temperatures.

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