Original Article

Enhancement of Néel temperature and electrical resistivity of Mn–Ni–Zn ferrites by Gd\(^{3+}\) substitution

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**ABSTRACT**

Structural, magnetic, and dielectric properties of various Mn\(_{0.5}\)Ni\(_{0.4}\)Zn\(_{0.1}\)Fe\(_{2}\)\(_{0.8}\)Gd\(_{x}\)O\(_{4}\) sintered at 1200 °C were investigated thoroughly. The samples were synthesized by standard solid state reaction technique. The crystal structure was characterized by X-ray diffraction (XRD), which has confirmed the formation of single phase spinel structure. Bulk density, average grain size and initial permeability are found to decrease with increasing Gd content. For Gd substituted compositions, the value of Néel temperature is found to increase considerably, about 200 °C higher than that of the parent composition. The value of magnetic loss and dielectric loss are observed to decrease with the substitution of Gd\(^{3+}\) for the frequencies greater than 0.54 MHz and 10 kHz respectively. It is found that the AC resistivity (\(\rho_{AC}\)) increases with the substitution of Gd\(^{3+}\) and the highest value of \(\rho_{AC}\) is observed for the composition with \(x = 0.03\), about 600 times greater than that of parent composition.

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1. Introduction

Spinel ferrites exhibit remarkable electrical and magnetic properties by virtue of their unique electronic and crystalline structure [1-6]. These ferrites are used for various applications such as recording heads, transformers, inductors, converters, antennas, and electromagnetic wave absorbers [7-9]. But for high performance, permeability, Néel temperature and resistivity of these materials need to be increased. Most other technologically useful magnetic materials such as iron and soft magnetic alloys have low electrical resistivity. This makes them ineffective for applications at high frequencies. The low electrical resistivity of these materials allows eddy currents to flow within the materials themselves, thereby producing heat and waste energy [10,11].

Ni–Zn ferrites have been promising materials for high frequencies applications because of their high resistivity and consequently low eddy current losses but they have relatively low initial permeability at high frequencies. On the other hand, Mn–Zn ferrites are known to possess high initial permeability but low resistivity [6,12]. Many authors studied the...
combination of Ni–Zn and Mn–Zn ferrites in order to obtain favorable magnetic properties with low losses especially at high frequencies [6,12–15]. Eltabey et al. [16] have reported the sample with the chemical formula Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_2$O$_4$ possess the optimum properties for promising applications. Furthermore, it was noticed clearly that the properties of Mn–Ni–Zn ferrites are predominantly governed by the type of substituted ions [7,8,16].

Accordingly, this research work communicates the electrical and magnetic properties of Gd$^{3+}$ substituted Mn–Ni–Zn ferrites. The choice of this system is made so as to yield large electrical resistivity, high permeability and high Néel temperature. Among the rare-earth cations, Gd$^{3+}$ is chosen because of its high magnetic moment ($7\mu_B$) and consequently, it is expected the improvement of various magnetic properties [17]. In addition, Hemeda et al. [18] have reported Gd$^{3+}$ increases the electrical resistivity of spinel ferrites, which makes them promising candidates for high frequency applications where eddy current losses have a higher contribution.

2. Experimental

2.1. Sample synthesis

Various polycrystalline Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_2$O$_4$ with $x = 0.0, 0.015, 0.03, 0.06$ and $0.1$ were synthesized by the standard solid state reaction method. As raw materials, commercially available powders of MnCO$_3$ (99.9%), NiO (99.9%), ZnO (99.9%), Gd$_2$O$_3$ (99.95%) and Fe$_2$O$_3$ (99.9%) were used. Stoichiometric amounts of required powders were weighted and mixed thoroughly by hand milling for 4 h. During hand milling, few drops of acetone were added to increase the degree of mixing. Then the well mixed powders were calcined at 900°C in a closed alumina crucible for 5 h. The calcined powders were grinded thoroughly again for 3 h to obtain a homogeneous mixture. Later the powders were mixed with 10% polyvinyl alcohol (PVA) as a binder for granulation and then pressed uniaxially at a pressure of about 45 MPa into pellet shaped (about 13 mm diameter, 1.5–2.0 mm thickness) and toroid shaped (about 13 mm outer diameter, 6–7 mm inner diameter, and 2.0–2.5 mm thickness) samples. Finally, the samples were sintered in air for 3 h at 1200°C. The rate of heating and cooling was maintained 10 and 5°C/min, respectively for both calcination and sintering.

2.2. Characterizations

The structural characterization was carried out using an X-ray diffractometer (Phillips PANalytical X’PERT-PRO) with CuK$_\alpha$ radiation ($\lambda = 1.541\text{Å}$) at room temperature. XRD patterns of all compositions were measured over a range of $2\theta$ from 20° to 60° using a step size 0.04°. The bulk density ($\rho_b$) for each composition was calculated using the relation, $\rho_b = m/(\pi r^2 t)$, where $m$ is the mass, $r$ is the radius and $t$ is the thickness of the pellet. The theoretical density ($\rho_{th}$) was calculated using the relation, $\rho_{th} = 8M/(N_a a_0^3)$, where $N_a$ is the Avogadro’s number, $a_0$ is the lattice constant, and $M$ is the molecular weight of the composition. The porosity ($P$) was calculated using the formula, $P = [(\rho_{th} - \rho_b)/\rho_{th}] \times 100$. Surface morphology and micro-structural analysis were performed by Field Emission Scanning Electron Microscope (FESEM, Model no.: JEOLESM-7600F). Average grain sizes (grain diameter) of all compositions were determined from FESEM micrographs by linear intercept technique [19]. The real part ($\mu'$) and imaginary part ($\mu''$) of the complex initial permeability were measured as a function of frequency within the range of 100 Hz to 120 MHz using a WAYNE KERR 650B Impedance Analyzer. The values of $\mu'_1$ and $\mu''_1$ were calculated using the relations: $\mu'_1 = L_0/L$ and $\mu''_1 = \mu''_0 \tan \delta_m$, where $L_0$ is the self inductance of the sample core and $L_0$ is the inductance of the winding coil without the sample core and $\tan \delta_m$ is the magnetic loss tangent. $L_0$ is derived geometrically using the relation, $L_0 = \mu_0 N^2 S/d$, where $\mu_0$ is the permeability in vacuum, $N$ is the number of turns of the coil ($N = 5$), $S$ is the cross-sectional area and $d = (d_1 + d_2)/2$ is the mean diameter of the toroid-shaped sample, where $d_1$ and $d_2$ are the inner and outer diameter of the toroid-shaped sample, respectively [20]. The relative quality factor (RQF) was calculated from the relation, $RQF = \mu'/\tan \delta_m$. The temperature dependent permeability was measured using WAYNE KERR Impedance Analyzer at fixed frequency (10 kHz) and the Néel temperature ($T_N$) of each composition was determined from this measurement. The dielectric measurements were carried out at room temperature within the frequency range of 100 Hz to 120 MHz by using Impedance Analyzer. For dielectric measurements samples were painted with conducting silver paste on both sides to ensure good electrical contacts. The real part of dielectric constant ($\varepsilon'$) and AC resistivity ($\rho_{AC}$) were calculated using the formula: $\varepsilon' = C/\varepsilon A$ and $\rho_{AC} = 1/(\varepsilon \omega \varepsilon \tan \delta_e)$, where $C$ is the capacitance of the pellet, $A$ is the cross-sectional area of the electrode, $\varepsilon_0$ is the permittivity in free space, $\omega$ is the angular frequency and $\tan \delta_e$ is the dielectric loss tangent.

3. Results and discussion

3.1. Structural analysis, density and porosity

The X-ray diffraction (XRD) has been carried out to verify the phase formation of polycrystalline Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_2$O$_4$ with $x = 0.0, 0.015, 0.03, 0.06$ and $0.1$. Fig. 1 shows the XRD
patterns of various Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_{2-x}$Gd$_x$O$_4$ sintered at 1200 °C for the angle of 2θ from 20° to 60°. The patterns clearly show the formation of spinel structure for each composition. All the peaks in the XRD pattern for all samples matched well with characteristic reflections of spinel structure reported earlier [21,22]. The peaks observed in the XRD patterns are well indexed with their Miller indices for (220), (311), (222), (400), (422), and (511) crystal planes of spinel ferrites. It is observed that there is no noticeable variation of these XRD patterns with the earlier reported XRD patterns for same composition sintered at 1250 °C [23].

The values of lattice parameter ($a_0$) of all the peaks obtained for each reflected plane are plotted against Nelson–Riley function, $F(\theta) = \frac{1}{2}\frac{[\cos^2 \theta/\sin \theta] + (\cos^2 \theta/\theta)]}{\theta}$, where $\theta$ is the Bragg’s angle. A straight line fit is obtained and the value of exact lattice parameter ($a_0$) for each composition is estimated from the extrapolation of the line to $F(\theta)=0$. The estimated values of $a_0$ for various Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_{2-x}$Gd$_x$O$_4$ are plotted as a function of Gd content, as shown in Fig. 2(a). It is seen that the exact lattice parameter decreases with the Gd content up to $x=0.03$, then it increases with the increase of Gd content. Similar trend has been found for Nd substituted Mn–Ni–Zn ferrites [16]. For $x < 0.03$, it is assumed that some rare earth ions reside at the grain boundaries and they hinder the grain growth and may exert a pressure on the grains and lead the exact lattice parameter to decrease. On the other side, for the compositions with higher concentration of Gd$^{3+}$ ($x > 0.03$), some of the Gd$^{3+}$ (radius = 0.97 Å) that substitute Fe$^{3+}$ (radius = 0.64 Å) in the unit cell may cause the increase in the exact lattice parameter, which in turn compensates the decrease due to the grain boundaries pressure.

The variation of bulk density and porosity with Gd content for various Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_{2-x}$Gd$_x$O$_4$ is shown in Fig. 2(b). It is observed that bulk density decreases with the increase of Gd content in Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_{2-x}$Gd$_x$O$_4$ and porosity shows opposite trend. It is possible to explain this phenomenon with the help of SEM analysis. From the SEM micrographs, it is seen that the number of pores and hence pore volume increase with the increase of Gd content which will be discussed in next section.

### 3.2. Surface morphology

The FESEM micrographs of various Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_{2-x}$Gd$_x$O$_4$ with $x = 0.0, 0.03$, and 0.1 sintered at 1200 °C are shown in Fig. 3. Average grain sizes (grain diameter) of various compositions are measured from FESEM micrographs by linear intercept technique. To do this, several random horizontal and vertical lines are drawn on the FESEM images. Then, the number of intersected grains is counted, and the length of the line traversed along the grains is measured. Finally, the average grain size is calculated by the formula simply the ratio of total length of the lines and total number of grains. It is clear from the FESEM images that average grain size decreases with increasing Gd substitution. This may be due to the interaction of grain boundary and pores. Hankare et al. [24] reported that when many pores are present, and the sintering temperature is not too high, grain growth is inhibited. It is observed that the porosity increases with increasing Gd substitution, as shown in Fig. 2(b). Thus, grain growth is impeded due to the presence of many pores.

### 3.3. Frequency dependent initial permeability

The frequency dependent real part of complex initial permeability spectra for various Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_{2-x}$Gd$_x$O$_4$ sintered at 1200 °C is shown in Fig. 4. The frequency response of $\mu'_i$ of these compositions remains fairly constant up to a certain frequency, beyond which it increases slightly to form a hump and then drops rapidly to a very small value. The wide frequency range with constant value of $\mu'_i$ is named as the zone of utility of ferrites and it is desirable for various applications. The value of $\mu'_i$ for Gd substituted compositions is found to decrease noticeably compared to that of parent composition and with the increase of Gd content, $\mu'_i$ goes down slowly, as shown in Fig. 4. This is perhaps due to decrease in density, decrease in grain size and increase in porosity with Gd content. The initial permeability of ferrites depends on many factors such as chemical composition, impurity contents, stoichiometry, grain size, magnetization, density and porosity [25,26]. It is well known that the initial

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Fig. 3 – FESEM micrographs for various Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_{2-x}$GdxO$_4$.

The permeability of magnetic materials is originated because of the spin rotation and domain wall motion [27,28]. So, it can be expressed as: \[ \mu' = 1 + \chi_w + \chi_{\text{spin}}, \]
where \( \chi_w = 3\pi M_S^2 D/4\gamma \) and \( \chi_{\text{spin}} = 2\pi M_S^2/K_u \) indicate the magnetic susceptibility of domain wall motion and spin rotation, respectively, and where \( M_S \) is the saturation magnetization, \( K_u \) is the anisotropy constant, \( D \) is the average grain diameter, and \( \gamma \) is the domain wall energy.

Accordingly, the domain wall motion is influenced by the average grain size and enhanced with the increase of grain size. It is generally believed that smaller the grain size, lower the initial permeability. In microstructure studies of the present ferrite system, it is observed that average grain diameter and bulk density decrease with the increase of Gd content. Therefore, variation of the initial permeability is found to correlate...
with bulk density, average grain size and porosity of these compositions.

Fig. 5 shows the variation of $\mu'_1$ (measured at frequency 1 MHz) and resonance frequency ($f_r$) as a function of Gd content for various Mn$_{0.5}$Ni$_{1-x}$Zn$_x$Fe$_2$-B$_{3-x}$Gd$_x$O$_4$ sintered at 1200 °C in air. It is observed that, as $\mu'_1$ decreases, resonance frequency increases with the increase of Gd content. An inversely proportional relation of $\mu'_1$ and $f_r$ confirms the Snoek’s relation, $f_r$/$\mu'_1$ = constant [29]. Initial permeability in ferrites is due to domain wall displacement and remains constant with frequency as long as there is no phase lag between the applied field and the domain wall displacement. In ferrites, two resonance peaks are normally observed: one at comparably lower frequency (10–100 MHz), which is due to the domain wall oscillations [30] and the other at higher frequencies (~1 GHz) due to Larmor precession of electron spins [31]. In the present study, the resonance frequency of domain wall oscillations is found in the range of 10.23–27.39 MHz. Maximum value of resonance frequency ($f_r$ = 27.39 MHz) is observed for the composite Mn$_{0.5}$Ni$_{0.7}$Zn$_{0.3}$Fe$_{1.94}$Gd$_{0.06}$O$_4$ sintered at 1200 °C and the corresponding value of $\mu'_1$ is 74.

3.4. Magnetic loss tangent and relative quality factor

The magnetic loss tangent ($\tan \delta_M = \mu'_2/\mu'_1$) is a measure of the inefficiency of the magnetic system and it is highly desirable to have this parameter as low as possible from application point of view. Fig. 6(a) shows the variation of $\tan \delta_M$ with frequency for various Mn$_{0.5}$Ni$_{1-x}$Zn$_x$Fe$_2$-B$_{3-x}$Gd$_x$O$_4$ sintered at 1200 °C. It is observed that the $\tan \delta_M$ decreases with increasing frequency up to a certain frequency, beyond which it increases with the increase of frequency. It is also observed that the values of $\tan \delta_M$ for Gd substituted compositions are comparably less than the parent composition at frequency greater than 0.54 MHz. The magnetic loss can be split up into three components: hysteresis losses, eddy current losses and residual losses. This gives the formula $\tan \delta_M = \tan \delta_h + \tan \delta_e + \tan \delta_r$ [20]. As the initial permeability is measured in presence of low applied magnetic field, so, hysteresis losses vanish at very low field strengths. Thus, at low field the remaining magnetic loss is due to eddy current losses only because residual losses are independent of frequency. Eddy current losses increase with frequency and can be expressed as $P_e \sim f^2/\rho$, where $P_e$ is the energy loss per unit volume and $\rho$ is the resistivity [25,28]. Therefore, one can conclude that at high frequency, the low value of $\tan \delta_M$ for Gd substituted compositions is due to the increase of resistivity with Gd content. In the present study, AC resistivity is found to increase with increasing Gd content which will be discussed in section 3.8.

The variation of relative quality factor (RQF = $\mu'_2/\tan \delta_M$) as a function of frequency for various Mn$_{0.5}$Ni$_{1-x}$Zn$_x$Fe$_2$-B$_{3-x}$Gd$_x$O$_4$ sintered at 1200 °C is shown in Fig. 6(b). For practical application RQF is often used as a measure of performance. It is observed that RQF increases with an increase in frequency showing a peak and then decreases with further increase in frequency. It is also observed that for Gd substituted compositions RQF decreases slightly compared to parent composition and the peak associated with the RQF shifting to higher frequencies. The maximum RQF values for various Gd substituted compositions are found in the range of 2378–2866. Among all the Gd substituted samples, highest value of RQF (=2866) is observed for Mn$_{0.5}$Ni$_{0.5}$Zn$_{0.5}$Fe$_{2.97}$Gd$_{0.03}$O$_4$ sample.

3.5. Temperature dependent permeability and Néel temperature

The real part of initial permeability ($\mu'_1$) as a function of temperature for various Mn$_{0.5}$Ni$_{1-x}$Zn$_x$Fe$_2$-B$_{3-x}$Gd$_x$O$_4$ is shown in Fig. 7(a). The temperature dependent $\mu'_1$ was measured at a constant frequency (10 kHz). It is observed that, $\mu'_1$ slowly decreases with temperature and then drops sharply at a certain temperature, known as Néel temperature ($T_N$). This result could be explained according to Globus relation, which is given by $\mu'_1 \propto M_s^2 D/\sqrt{K_1}$, where $M_s$ is the saturation magnetization, $D$ is the average grain size and $K_1$ is the anisotropy constant. It was reported that for Mn–Zn ferrites, the anisotropy constant is independent of temperature for temperatures higher than the room temperature [32]. Thus, the decrease in initial permeability with temperature can be attributed to the decrease in $M_s$. At $T_N$, saturation magnetization drops rapidly with temperature leading to the rapid decrease in $\mu'_1$. The rapid decrease of $\mu'_1$ with temperature suggests phase formation and good homogeneity of the present ferrite samples, which have been confirmed by X-ray diffraction analysis.

The values of $T_N$ were measured from the extrapolation of the linear part at the sudden decrease in initial permeability.
with temperature for all investigated samples. The variation of $T_N$ and exact lattice parameter ($a_0$) with Gd content is shown in Fig. 7(b). It is clear that, $T_N$ increases significantly with increasing Gd content (about 200 °C for the sample with $x = 0.03$ higher than that with $x = 0$). For $x > 0.03$, $T_N$ decreases but its value is still much higher than that of the parent composition. One can notice from Fig. 7(b) that $T_N$ and $a_0$ behave in an opposite manner, which is in agreement with the previously reported results [33–35]. The increase in $T_N$ for $0 < x < 0.03$ with Gd-concentration could be understood in view of the behavior of the exact lattice parameter. The value of $a_0$ decreases with increase of the Gd-content and so there will be increased of the A-B interaction between the moments. This in turn increases the value of $T_N$. On the other hand, for $x \geq 0.03$, the increase in the value of $a_0$ leads the A-B interaction between the moments to decrease and hence there is a decrease in the $T_N$.

### 3.6 Dielectric property

The effect of frequency on the $\varepsilon'$ is shown in Fig. 8(a) for various $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{Zn}_{0.5}\text{F}_{2-x}\text{Gd}_x\text{O}_4$. It is observed from the figure that at lower frequencies, $\varepsilon'$ decreases with the increase of frequency. For $x = 0$, the values of $\varepsilon'$ are decreased more rapidly than other samples. At higher frequencies, the values of $\varepsilon'$ are so small that they become almost independent of frequency. The observed variation in dielectric constant can be explained on the basis of space charge polarization. It is known that ferrite materials consist of well-conducting grains separated by poorly conducting grain boundaries. As the grain boundaries have large resistance, the electrons file up there and produce large space charge polarization [36]. As a result, at lower frequencies $\varepsilon'$ have larger values. Beyond a certain frequency the electron exchange between Fe$^{2+}$ and Fe$^{3+}$ cannot follow the ac electrical field [37] and therefore, their contribution to the polarization decreases. Also, the presence of Ni$^{2+}$/Ni$^{3+}$, which gives rise to p-type carriers, contributes to the net polarization though it is small. So, the dielectric constant attains a constant value above certain high frequency.

The variation of tanδ with frequency is shown in Fig. 8(b). The tanδ for all the samples is found to be larger at lower frequencies and decreases with the frequency. At lower frequencies, which corresponds to high resistance (due to the grain boundaries), more energy is required for electron transfer between Fe$^{2+}$ and Fe$^{3+}$, thus the value of tanδ is high. At higher frequencies, which corresponds to low resistance (due to the grains), less energy is required for electron exchange [38]. From the figure it is clear that anomalous relaxation peak is observed only for the sample with $x = 0$. All other samples (with the addition of Gd) have not shown any anomalous behavior or peaking behavior. The peaking behavior is explained by Rezlescu model [37,39]. According to this model, the peaking behavior is obtained when the frequency of charge...
hopping between the Fe$^{3+}$ and Fe$^{3+}$ exactly matches with the frequency of the external applied field. It is found from Fig. 8(b), the dielectric loss tangent (tanδ) value for the Gd substituted samples was decreased considerably at frequency greater than 10 kHz.

### 3.7. Complex impedance spectra analysis

Fig. 9(a) shows the variation of real components of complex impedance ($Z'$) with frequency at room temperature for all compositions. It is observed that the value of $Z'$ gradually decreases with increasing frequency. The decrease in $Z'$ indicates that the conduction is increasing with frequency. At lower frequencies, it is found that the value of $Z'$ increases with increase of Gd content up to $x = 0.03$ and beyond this value of $x$, $Z'$ decreases with Gd content. The higher values of $Z'$ at lower frequencies mean the polarization is larger. It is because all kinds of polarization are present at lower frequencies. It is also observed that the value of $Z'$ for all compositions coincide at frequency about 1 MHz. At higher frequencies, the lower values of $Z'$ for all compositions indicates possible release of space charge polarization at the boundaries of homogeneous phases in the composites under the applied external field [40].

Fig. 9(b) shows the Cole–Cole plot, $Z'$ versus $Z''$, where $Z''$ is the imaginary components of complex impedance. Three semicircles are found for parent composition, while only one semicircle has been found for Gd substituted compositions. In general, the plot could be composed of three semicircles, depending upon the electrical properties of the material. The semicircle at lower frequency represents the sum of resistance of grains and grain boundaries, while the semicircle at higher frequency corresponds to the resistance of grains only. The third semicircle is also observed in some materials which could be due to the electrode effect. All Gd substituted compositions exhibit a single semicircular arc starting from the origin. The absence of second and third semicircles in the Cole–Cole plots indicates that the materials have only grain effect to the conductivity mechanism. It is also seen that the diameter of semicircle increases with increase of Gd content and reaches its maximum value at $x = 0.03$. For $x > 0.03$, the diameter of semicircle goes down. The diameter of semicircle corresponds to the resistance of the grain [41].

### 3.8. AC resistivity

The AC resistivity of all present compositions is calculated from the experimental data using the relation [7]:

$$\rho_{ac} = \frac{1}{\varepsilon_{o} \varepsilon' \omega \tan \delta}$$

where $\omega$ is the angular frequency, $\varepsilon_{o}$ is the permittivity in vacuum, tanδ is the dielectric loss tangent and $\varepsilon'$ is the real part of dielectric constant. The variation of AC resistivity with frequency for various Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_{2-x}$Gd$_{x}$O$_4$ at room temperature is shown in Fig. 10. It is observed that the value of $\rho_{ac}$ decreases with increasing frequency beyond a particular frequency (hopping frequency). Below this frequency...
frequency, it shows almost frequency independent nature. In the low frequency region, grain boundaries with high resistance are effective, giving a constant plateau region. At higher frequencies, the decrease in resistivity is due to grain effect and increased hopping of charge carriers between Fe$^{2+}$ and Fe$^{3+}$ ions at the adjacent octahedral sites [42]. Fig. 10 shows that the AC resistivity values for Gd substituted compositions are much higher than that of the parent composition. Similar result has been reported earlier for Gd substitution on Ni-ferrites [18]. The increase in resistivity with Gd substitution is due to the decrease in the magnitude of electronic exchange, which is dependent on the concentration of Fe$^{3+}$/Fe$^{2+}$ pairs present on B-site. It is also seen that the value of $\rho_{ac}$ increases with the increase of Gd content up to $x=0.03$ and then decreases for the compositions $x>0.03$. The observed variation of $\rho_{ac}$ with Gd content is found similar with the result of RQF and Néel temperature of these compositions. The highest value of AC resistivity (3.698 × 10$^6$ $\Omega$ × $m$) is observed among all the present compositions.

4. Conclusions

Various Mn$_{0.5}$Ni$_{0.1}$Zn$_{0.4}$Fe$_{2−x}$Gd$_x$O$_4$ were successfully prepared by standard solid state reaction technique. The XRD patterns for these compositions confirm the formation of spinel structure. With the increase of Gd content, the RQF decreases slightly and the peak associated with this shifted to higher frequencies. The value of Néel temperature increases with the substitution of Gd$^{3+}$ to record about 200 °C, for the sample with $x=0.03$, higher than that of the parent composition. Impedance spectroscopy analysis indicates that the Gd substituted compositions have only grain effect to the conduction mechanism. Frequency dependent complex impedance analysis shows that Z" increases with increase of Gd content up to $x=0.03$ and beyond this value of $x$, Z" decreases but its value is still much higher than that of parent composition. AC resistivity is found to increase considerably with the substitution of Gd$^{3+}$. Considering the above facts, these ferrites can be suitable for the applications in high-frequency microwave devices.

**Conflicts of interest**

The authors declare no conflicts of interest.

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