Dielectric properties of superparamagnetic titanium doped nanophased Mn–Zn ferrites for high frequency applications

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Abstract

Effect of Ti⁴⁺ ions on Structural, Dielectric and Magnetic properties of nanophased Mn₀.₅Zn₀.₅TixFe₂₋₄x₁₈₋₃ₓ/(x = 0.0, 0.01, 0.02, 0.03, 0.04 and 0.05) ferrites synthesized by hydrothermal method is studied. XRD peaks reveal pure spinel phase without extra peaks. Lattice parameter a is found to vary non-linearly with dopant concentration (x). An overall decrease in Crystallite Size (D) (varying from 78 nm–41 nm) with x is witnessed. Values of dielectric constant (ε`) and loss factor (tan δ) of Ti⁴⁺ doped Mn–Zn ferrites are lower than that of the undoped sample. Increase of AC resistivity (ρ) by an order of 10 in Ti⁴⁺ doped Mn–Zn ferrites is ensued due to locking of Ti⁴⁺–Fe²⁺ pairs. Lowered values of Ms is attributed to spin canting due to growth of nanosized grains, weakening of exchange interactions by non-magnetic Ti⁴⁺ doping and lower values of x-ray density. Transition from single to multi-domain region of Mn–Zn–Ti ferrites is clearly evinced from the plot of Coercivity (Hc) with D. Reduced value of coercivity to zero up to a critical size of ~49 nm indicates the existence of superparamagnetism in these ferrites. Superparamagnetism first ever reported in the present case of Ti⁴⁺ doped Mn–Zn ferrites synthesized by hydrothermal method. Relatively lowered values of ε`(29–18), tan δ (of the order of 10⁻²–10⁻³), higher values of ρ (10⁶ Ω—cm) and lowered values of Hc obtained with Ti⁴⁺ doping improve the eddy current losses and direct these materials for high frequency applications.

1. Introduction

Mn–Zn ferrites are an important class of soft ceramic magnetic materials, with relatively low cost, low core losses, high electrical resistivity and high initial permeability and have a wide range of applications [1] in electronic or electrical peripherals. Rapid development in power electronic devices towards miniaturization tends to increase the operating frequency of the Mn–Zn ferrites to relatively higher values resulting in dramatic increase in power losses. One of the key strategies to improve the electromagnetic properties is to synthesize [2] the nanoferrites from their bulk counterparts. Occurrence of new physical phenomena like quantum confinement and larger surface to volume ratio in the nano regime along with improved power losses and enhanced electrical resistivity are reported [3, 4] in nanophased Mn–Zn ferrites. Owing to these phenomena, they have enormous technological and biomedical applications in ferrofluids, magnetocaloric refrigeration, Magnetic Resonance Imaging (MRI) and guided drug delivery. Although nanoparticles of pure metals like Fe, Co and Ni are found [5, 6] to exhibit superparamagnetism, they have limited applications due to their chemical unstability and relatively lower sizes of few nanometers. On the other hand, magnetic metal oxides such as spinel ferrites have a great potential for applications as they are relatively inert and their properties can be improved [7] by addition of dopants. Single domain particles are formed for critical size varying from 10–40 nm resulting in an increase of coercivity with increase in crystallite size. In this single domain region, reduced coercivity to nearly
zero is referred to as superparamagnetism (SPM). Beyond the critical size, coercivity decreases with increase in crystallite size reflecting upon the multi-domain nature of the ferrites. Occurrence of SPM is reported [8–12] in MnFe$_2$O$_4$, MnZnFe$_2$O$_4$, Lanthanum and Gadolinium doped Mn–Zn ferrites by other researchers.

Among a wide variety of techniques that exist for the synthesis of ferrites, Hydrothermal synthesis is proven [13] to be relatively user friendly and cost-effective technique which needs comparatively lower sintering temperatures, less energy and has an advantage of producing less agglomerated particles of controlled size. It is well recognized [14] in the field of electroceramics that the nature and the amount of dopant is one of the most important operational parameters towards tailoring or improving properties and performance of the product. TiO$_2$ is an effective additive in improving [1] electromagnetic properties by replacing Fe$^{3+}$ ions with Ti$^{4+}$ ions at octahedral sites of the spinel lattice. Simultaneous codoping of TiO$_2$, CaCO$_3$ and SiO in the Mn–Zn ferrite lattice is found [15] to lead to the formation of Fe$^{2+}$–Ti$^{4+}$ pairs replacing Fe$^{3+}$ ions in the octahedral B-sites hindering the electron hopping, thus resulting in an increase of dc electrical resistivity and improved power losses of the material. An overall increase in ac resistivity and decrease in saturation magnetisation is observed [16] with increase in Ti$^{4+}$ concentration in Mn$_{1−x}$Fe$_{2x}$TiO$_4$ ferrites. Addition of Ti$^{4+}$ ions in Ni–Zn ferrites is reported [17] to exhibit improved values of electrical resistivity while it is found to exhibit an adverse effect on saturation magnetization. Higher values of electrical resistivity are obtained [18] in Cobalt and Titanium doped Mn–Zn ferrites.

Incorporation of tetravalent ions like TiO$_2$ or SnO$_2$ into ferrites is reported [19] to be capable of development of high resistivity ferrites as they form stable bonds with Fe$^{2+}$ ions and they impede the process of electron hopping. Moreover, it is also reported [1] that addition of pentavalent ions is useful in producing high conductivity ferrites whereas tetravalent ions have the ability to produce ferrites of comparatively higher values of electrical resistivity. In our previous work, for both the cases of Sb$^{5+}$ and Nb$^{5+}$ doped nanocrystalline Ni–Zn ferrites synthesized [20, 21] by hydrothermal method, we have obtained XRD patterns with pure spinel phase, exhibiting relatively larger values of saturation magnetisation (M$_s$), higher values of ac resistivity (ρ) and lower loss factor (tan δ) values which are viable for high frequency applications. When similar dopants, i.e., Sb$^{5+}$ and Nb$^{5+}$ are introduced [22, 23] into nanophased Mn–Zn ferrites, XRD patterns show certain hematite peaks along with spinel phase accompanied by higher values of ρ and lower values of tan δ and M$_s$. Titanium ions dissolve [24] in the lattice and occupy regular tetrahedral and octahedral positions of the lattice and change the dielectric and magnetic properties. Electrical resistivity is found to be improved by formation of a liquid phase at the grain boundaries but addition of Ti$^{4+}$ has a negative effect on the values of M$_s$. Even though extensive research work is carried out on bulk Ti$^{4+}$ doped Mn–Zn ferrites, synthesis of nanophased Ti$^{4+}$ doped Mn–Zn ferrites by hydrothermal method and their dielectric and magnetic response to investigate the property of superparamagnetism has not been elaborated so far. In view of the above reports on Ti$^{4+}$ doped ferrites and other pentavalent Sh$^{5+}$ and Nb$^{5+}$ doped ferrites, a humble attempt is made to synthesize nanophased Mn$_{0.5}$Zn$_{0.5}$Ti$_x$Fe$_{2−4x/3}$O$_4$ ferrites by hydrothermal method at lower dopant concentrations i.e., for x varying from 0–0.05 insteps of 0.01 and characterize them for possible applications.

2. Experimental

2.1. Preparation

Nanophased Mn$_{0.5}$Zn$_{0.5}$Ti$_x$Fe$_{2−4x/3}$ (x = 0.0, 0.01, 0.02, 0.03, 0.04 and 0.05) are prepared using hydrothermal method. The starting precursors are A.R.Grade Mn(NO$_3$)$_2$·6H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O and TiO$_2$.Stoichiometric quantities of the required materials are dissolved in deionised water and using Ammonia solution, pH of 8 is obtained. The solution is then thoroughly mixed using magnetic stirrer for nearly one hour and is then heated in a autoclave at a temperature of 200 °C for four hours. After allowing to cool naturally, the solution is taken out and cleaned using deionised water. Hot air oven is used to dry the sample at 60 °C for 24 h. The material is then taken out and powdered using an agate mortar. The powder is then sintered at a temperature of 500 °C for 6 h. Pellets of 12 mm diameter are prepared at a pressure of 5Tons. The pellets are then sintered at a temperature of 1000 °C for 6 h. The sintered pellets are used for structural, electrical and Magnetic characterization.

2.2. Structural Studies

XRD studies were carried out with a Bruker (Germany, Model: D8) x-ray Diffractometer operated with CuK$_{α}$ radiation with λ = 1.5406 Å. The lattice parameter (a) corresponding to the observed prominent reflections (identified with the help of standard JCPDS Card No. 10–0467) is estimated using the equation

\[
\text{a} = \frac{\lambda}{\sin \theta}
\]

where \(\lambda\) is the wavelength of the x-ray source and \(\theta\) is the Bragg angle.
\[ a = d\sqrt{(h^2 + k^2 + l^2)} \]  

where, \( d \) is experimentally observed inter-planar spacing and \((h k l)\) are the Miller indices of the planes.

The theoretical density \( (\rho_t) \) for the samples was estimated by an equation

\[ \rho_t = \frac{ZM}{Na^3} \]

where, \( Z \) refers to the number of molecules per unit cell in the spinel structure, \( M \) is the Molar mass of the sample, \( a \) is the lattice parameter of the ferrite and \( N \) is the Avogadro’s number.

Crystallite (D) size was determined by Scherrer formula given by

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

where, \( k \) was taken as a constant (~1, i.e., unity in the wake of shape of the crystal), \( \lambda \) was the wavelength of x-rays and \( \beta \) was full width at half maximum.

### 2.3. Dielectric studies

The dielectric response of all samples was measured using LCR meter Hioki 3532–50, LCR Hi TESTER, in the frequency range of 40 Hz to 5 MHz over a temperature range of 200 °C.

The dielectric constant \( (\varepsilon'(\omega)) \) at various frequencies was calculated using the measured capacitance value at the strong accumulation region from the following relation,

\[ \varepsilon' = \frac{Cd}{\varepsilon_0 A} \]

where, \( C \) is the capacitance (Farads), \( d \) is thickness of the sample (2.87 mm–6.5 mm), \( A \) is the cross-sectional area of the flat surface (11.30 mm²–11.32 mm²) and \( \varepsilon_0 \) is the permittivity of free space \( (8.85 \times 10^{-12} \text{ F m}^{-1}) \).

The loss factor \( (\tan \delta) \) is determined by the equation given by

\[ \tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \]

where, \( \varepsilon'(\omega) \) is the real part of permittivity and \( \varepsilon''(\omega) \) is the imaginary of permittivity.

The a.c. conductivity of the samples at desired frequencies can be estimated using the equation

\[ \sigma_{a.c.} = \varepsilon_0 \cdot \tan \delta \]

where, \( \varepsilon'(\omega) \) is the real part of permittivity, \( \varepsilon_0 \) is the permittivity of free space \( (8.85 \times 10^{-12} \text{ F m}^{-1}) \), \( \cdot = 2\pi f \) is the angular frequency and \( \tan \delta \) is the dielectric loss factor.

### 2.4. Magnetic studies

The magnetic studies were done using Microsense (EZ) Vibrating Sample Magnetometer. In the spirit of Neel’s two-sub lattice \([25]\) model, local spins for the \( Ti^{4+} \) doped \( Mn-Zn \) ferrites, viz., local magnetic moments \([26, 27]\) were estimated in terms of Bohr’s magneton \( n_B \) by

\[ n_B = \frac{M_s}{5585} \left( \frac{M_s}{\rho} \right) \]

where, \( M_s \) denotes the molar mass of the sample,
\( M_s \) denotes the saturation magnetization and \( \rho \) denotes the theoretical density.

The values of magnetic moment \( (\mu_B) \) is calculated using the equation

\[ \mu_B = \sqrt{n(n+1)} \]

where, \( n \) denotes the no. of unpaired electrons of the element.

### 3. Results and discussion

#### 3.1. Structural characterization

XRD Patterns of the \( Mn_{0.3}Zn_{0.3}Ti_xFe_{2-4x}/3O_4 \) ferrites for ‘x’ varying from 0 to 0.05 in steps of 0.01 sintered at 1000 °C are presented in figure 1. From figure 1, it is observed that the present \( Ti^{4+} \) doped \( Mn-Zn \) ferrites are found to assume pure spinel structure without any additional peaks by matching with standard JCPDS data.
In our earlier reports [22, 23] of Sb$^{5+}$ doped and Nb$^{5+}$ doped Mn–Zn ferrites synthesized by hydrothermal method, the ferrites are sintered at 800 °C and an extra hematite phase is observed along with the spinel phase. But, in the present case of Ti$^{4+}$ doped nanocrystalline Mn–Zn ferrites sintered at 1000 °C, XRD patterns exhibit pure spinel phase with no additional hematite peaks and it is attributed [28] to high temperature sintering conditions of 1000 °C. Relative broadening of XRD peaks evince the formation of nanocrystalline ferrites. The values of lattice parameter (a) determined from XRD data are provided in table 1 and its variation with dopant concentration (x) is presented in figure 1(a). The values of a are found to vary from 8.3030 Å to 8.926 Å. From figure 1(a), it is observed that at lower concentrations (i.e., up to x = 0.02), a is found to decrease with x. For intermediate concentrations, i.e., from x = 0.02 to x = 0.04, the values of a exhibit an increasing trend. Beyond x = 0.04, again a decreasing trend of a with x is witnessed. Mn–Zn ferrite is a mixed spinel ferrite, with Mn$^{2+}$, Zn$^{2+}$, and Fe$^{3+}$ ions are reported to occupy both tetrahedral (A-sites) and octahedral sites (B-sites), whereas Mn$^{3+}$ and Fe$^{2+}$ ions occupy octahedral sites only. Ti$^{4+}$ ions are reported [29] to have a tendency to enter both A- and B-sites. The ionic radius of Ti$^{4+}$ (0.63 Å) is less than that of Fe$^{3+}$ ions (0.69 Å) at A—sites. So, the initial decrease of a with x up to x = 0.02 is attributed to the replacement of Ti$^{4+}$ ions with Fe$^{3+}$ ions at A-sites. As the ionic radius of Ti$^{4+}$ (0.74 Å) ions at B-sites is larger than that of Fe$^{3+}$ (0.69 Å) ions, they tend to replace Fe$^{3+}$ ions at B-sites resulting in increase of lattice parameter. Again, the decrease in a for x = 0.05 is explained by the influence of repulsion parameter (b) and Madelung Constant (M). The lattice parameter a is proportional [30] to (b/M). At higher concentrations, more Ti$^{4+}$ enter into B-sites, thus pushing more charge from B-sites to A-sites resulting in an increase of M. Thus, b/M decreases. Hence, lattice constant decreases for x = 0.05. It is also reported [31] that in case of ferrites that are neither completely normal spinel nor inverse spinel, the lattice parameter a is found to exhibit a non-linear behavior with dopant concentration (x). Thus, the non-linear behavior of lattice constant of nanocrystalline Mn–Zn ferrites with Titanium concentration in the present case can also be attributed to the mixed spinel structure of Mn–Zn–Ti ferrites.

The crystallite size (D) is calculated using the (311) peak and the values are provided in table 1. The values of D are found to be in the range of 78 nm–41 nm. An overall decreasing trend of D with x is presented in figure 1(a). In case of Sb$^{5+}$ doped nanocrystalline Mn–Zn ferrites, the crystallite size is reported [22] to be in the range of 46 nm–14 nm for Sb$^{5+}$ doped ferrites, while case of Nb$^{5+}$ doped ferrites, D is found [23] to vary from 50 nm–14 nm. Relatively larger values of D in the present case of Ti$^{4+}$ doped Mn–Zn ferrites as compared to that of reported [22, 23] values of other high valency doped Mn–Zn ferrites is attributed to higher sintering temperature of 1000 °C employed in the present case. The crystallite size is reported [32] to increase from 74 nm–137 nm in Ni–Ti doped Mn ferrites synthesized by standard ceramic method and sintered at 1300 °C. Decrease in D with Ti$^{4+}$ doping in the present case of Mn–Zn ferrites vouches for the successful substitution of dopant by the present hydrothermal method adopted in the synthesis of the ferrites.

The representative FESEM Micrographs for x = 0.00, x = 0.01 and x = 0.05 are presented in figures 2(a)–(c). The images are clear and less electrostatically distorted. Well crystallized grains with almost uniform size can be

**Figure 1.** XRD patterns for Titanium doped Mn–Zn nano ferrites. (a) Variation of Lattice parameter (a) and Grain size (D) with Titanium concentration (x) in nano phased Mn–Zn nano ferrites.
observed. Decrease in particle size with increase in Ti⁴⁺ dopant concentration can be clearly observed from SEM micrographs. An overall view of structural properties indicate that the present hydrothermal method is successful in synthesizing single phase nanocrystalline Titanium doped Mn–Zn ferrites.

3.2. Dielectric studies

Variation of Dielectric constant ($\varepsilon'$) is found to exhibit (figure 3) a non-linear behavior with $x$. However, an overall decreasing trend of $\varepsilon'$ with increase in $x$ can be witnessed due to reduced [31] hopping probability between Fe³⁺ and Fe²⁺ ions by replacement of Ti⁴⁺ ions with Fe³⁺ ions at B-sites. Relatively lower values of $\varepsilon'$ ranging from 29–18 are obtained in the present case of Titanium doped nanocrystalline Mn–Zn ferrites. From figure 3, a correlative trend between $\varepsilon'$ and $D$ with $x$ is observed. Increasing values of $\varepsilon'$ with $D$ are attributed [33, 34] to the increasing number of iron ions at octahedral sites with $D$. Thus, the anomalies in the values of $\varepsilon'$ with $x$ are correlated to grain size. Similar grain size dependence of dielectric constant is also reported [22, 23] in Sb⁵⁺ and Nb⁵⁺ doped Mn–Zn ferrites. Moreover, the variation of dielectric constant is found [19] to be inverse to that of lattice parameter, except for $x = 0.02$ which is ascribed to the relatively higher density of the sample. The values of $\varepsilon'$ in bulk Mn–Zn ferrites synthesized by ceramic method are found [35] to be of the order of (17–32) x 10⁵ at room temperature while for nanocrystalline Mn–Zn ferrites, the values of $\varepsilon'$ are reported [36] to be reduced by an order of 10⁴ and they are found to be 85, 79, 395 for crystallite sizes of 65 nm, 59 nm and 11 nm, respectively. In case of Ti⁴⁺ doped nanocrystalline Ni-Zn ferrites, the values of $\varepsilon'$ are reported [37] to be of the order of 10⁴. In our previous work of Sb⁵⁺ and Nb⁵⁺ doped nanocrystalline Mn–Zn ferrites synthesized [21, 23] by hydrothermal method, the order of magnitude of $\varepsilon'$ is 10². At room temperature, Ti⁴⁺ doped Manganese ferrites are found [38] to have values of $\varepsilon'$ ranging from 10 to 100 at 1 MHz frequency. In the present case, the values of $\varepsilon'$ are as low as of the order of 29–18. As reported [24] by other researchers earlier, Titanium is found to improve the values of $\varepsilon'$ in the present synthesized Mn–Zn–Ti ferrites and make these materials viable for high frequency microwave applications.

Variation of dielectric constant ($\varepsilon'$) with varying ac frequency from 100 mHz–4 MHz is shown in figure 3(a). $\varepsilon'$ is found to witness a decreasing trend with frequency since the electron exchange between Fe²⁺ ↔ Fe³⁺ of
| Composition | Lattice parameter (Å) | Crystallite size (nm) | X-ray density (gm/cm³) | Permittivity ε′ | Dielectric loss ε″ | Loss factor (tan δ) | ac Conductivity (σ x 10⁻⁷)Ω⁻¹ cm⁻¹ | Mₛ x 10⁻¹ (emu/gm) | H_c (Oe) | M_r x 10⁻² (emu/gm) | Magnetic Moment (μ₀) |
|-------------|-----------------------|-----------------------|------------------------|-----------------|-------------------|-------------------|-----------------------------------|------------------|----------|-------------------|---------------------|
| x = 0.00    | 8.6305                | 78                    | 3.55                   | 29              | 1.74              | 0.060             | 10.09                             | 0.70             | 0.05                | 0.31               | 0.0006               |
| x = 0.01    | 8.6435                | 49                    | 3.53                   | 24              | 0.63              | 0.026             | 4.46                              | 0.27             | 0.36                | 1.94               | 0.0002               |
| x = 0.02    | 8.303                 | 44                    | 3.98                   | 27              | 0.98              | 0.036             | 6.32                              | 15.5             | 0.40                | 2.19               | 0.0112               |
| x = 0.03    | 8.7593                | 50                    | 3.39                   | 25              | 0.17              | 0.006             | 1.15                              | 16.9             | 1140                | 61.8               | 0.0153               |
| x = 0.04    | 8.9255                | 41                    | 3.20                   | 21              | 0.34              | 0.016             | 2.17                              | 0.70             | 112                 | 0.31               | 0.0006               |
| x = 0.05    | 8.7422                | 43                    | 3.40                   | 18              | 0.15              | 0.008             | 1.36                              | 0.27             | 0.36                | 1.94               | 0.0002               |

Mₛ = Saturation magnetization.
H_c = Coercivity.
M_r = Retentivity.
Mn–Zn ferrites does not follow [39] the AC field resulting in decrease of polarization. Variation of dielectric loss factor (tan δ) as a function of frequency for varying Ti⁴⁺ concentrations in nanocrystalline Mn–Zn ferrites (figure 3(b)) exhibits a steep decrease with frequency at lower frequencies while a marginal decrease is witnessed at higher frequencies, as reported [40].

From the values of tan δ (table 1), a non-linear variation of tan δ with magnitude of dopant (x) is observed and the values of all the Ti⁴⁺ doped samples are lower as compared to that of undoped sample. The decrease in tan δ with Ti⁴⁺ doping can be attributed to decrease in dielectric constant. The magnitude of values of tan δ is reported [35] to range from 1.59–2.31 at room temperature in case of bulk Mn–Zn ferrites and in nanocrystalline Mn–Zn ferrites, the values are improved [36] and are found to be in the range of 0.2–0.4. In our earlier reports [22, 23] on higher valency Sb⁵⁺ and Nb⁵⁺ doped nanocrystalline Mn–Zn ferrites sintered at 800 °C, lower values of tan δ of the order of 10⁻²–10⁻³ are obtained. Similar, lowered values of tan δ, i.e., of the order of 10⁻² are also exhibited by the present Ti⁴⁺ doped nanocrystalline Mn–Zn ferrites. Observed lower values of tan δ leads to reduced power losses and thus make these materials usable for high frequency applications. Thus, we can conclude that the values of tan δ are improved with Ti⁴⁺ doping in nanocrystalline Mn–Zn ferrites.

### 3.3. Conductivity mechanism

Figure 4 exhibits the variation of ac Conductivity (σ) with frequency for pure and Titanium doped nanocrystalline Mn–Zn ferrites. All the samples are found to exhibit an increase in conductivity with frequency in agreement [41, 42] with the report of other ferrite samples.

Variation of ac Conductivity (σ) with dopant concentration (x) is presented in inset figure 4(a) and the values are provided in table 1. An overall decreasing trend of σ with x can be viewed from figure 4(a). From table 1, the electrical resistivity (ρ) is found to rise by an order of 10 with increase in Ti⁴⁺ concentration due to hindered [34] hopping between Fe³⁺ and Fe⁵⁺ ions by pushing away of Fe³⁺ ions to octahedral sites by Ti⁴⁺ ions. Similar increase in ρ is witnessed with increase in Ti⁴⁺ concentration in Ni–Zn ferrites also [43].

Conductivity is found to exhibit an overall decreasing trend with in Ti⁴⁺ doped ferrites, as Ti⁴⁺ ions form [24] locking Ti⁴⁺–Fe³⁺ ion pairs to reduce conductivity. From the overview of above reports [16–19, 24], the authors sincerely attempted in presenting the conductivity mechanism in Ti⁴⁺ doped nanophased Mn–Zn ferrites in a pictorial form in figures 4(c) and (d). Thus, the increase in values of ρ results in improved power losses required for pushing the operating frequency of the devices to higher frequencies. Also, several other underlying reasons for enhanced power losses with Ti⁴⁺ doping are also discussed. Under an applied ac field, low-melting insulating phases at the boundaries [15] are formed due to reduction of ohmic currents causing improved power losses. Generally, the electrical conductivity of Mn–Zn ferrites is reported [44] to increase monotonously with increase in concentration of Fe²⁺ ions. Moreover, at higher sintering temperatures, partial reduction of Fe³⁺ to Fe²⁺ ions take place. Hence, from the above factors, the values of ac conductivity...
should witness an increase in the present case of ferrites sintered at relatively higher temperature of 1000 °C. But, on the contrary, the electrical conductivity is found to decrease. The possible reason may be due to formation [45] of very small amount of Fe$^{2+}$ ions owing to evaporation of Zinc at relatively higher sintering temperatures.

In our previous reports of similar high valency doped Sb$^{5+}$ and Nb$^{5+}$ doped nanocrystalline Mn–Zn ferrites, both sintered at 800 °C, the values of $\sigma$ are found to vary from $1.65 \times 10^{-7} \text{ cm}^{-1}$–$1.83 \times 10^{-8} \text{ cm}^{-1}$, $1.66 \times 10^{-8} \text{ cm}^{-1}$–$10^{-9} \Omega^{-1} \text{ cm}^{-1}$, respectively. In case of nanophased Mn–Zn ferrites synthesized [15] by ball mill method and codoped with TiO$_2$ (varying from 0–3000 ppm), CaCO$_3$ (500ppm) and SiO$_2$(100ppm), the values of dc resistivity are found to get enhanced with increasing TiO$_2$ content. The ac values of electrical conductivity in the present Ti$^{4+}$ doped nanocrystalline Mn–Zn ferrites sintered at 1000 °C are found to decrease from $1.09 \times 10^{-6} \text{ cm}^{-1}$–$1.15 \times 10^{-7} \text{ cm}^{-1}$. As the sintering temperature of the present ferrites is obviously lower than that of the reported [22, 23] Sb$^{5+}$ or Nb$^{5+}$ doped Mn–Zn ferrites, larger values of tan $\delta$ and $\sigma$ are expected due to zinc losses prevailing [46] at relatively higher sintering temperatures of 1000 °C. On the contrary, improved values of tan $\delta$ and $\rho$ are obtained.

3.4. Magnetic studies

The variation of Saturation Magnetisation ($M_s$) with applied field is shown in figure 5 and the variation of $M_s$ with dopant concentration ($x$) is exhibited in figure 5(a). The values of Saturation magnetization ($M_s$), Coercivity ($H_C$) and Retentivity ($M_r$) are given in table 1. From figure 5, it is observed that $M_s$ is found to increase with $x$ up to $x = 0.02$ and beyond $x = 0.02$, it witnesses a decrease with $x$. Magnetisation of a material is reported [24] to depend mainly upon nature of the dopant, grain size and density or porosity of a material. Initially, the variation of $M_s$ with $x$ can be explained using Neels’ two sublattice model. The values of magnetic moment ($\mu_B$) are determined from equation (8). As the magnetic moment of Ti$^{4+}$ ($0.4 \mu_B$) ions is less than that of Fe$^{3+}$ (5.92 $\mu_B$) ions, an overall decrease in $M_s$ is witnessed with increase in $x$. It is reported [29] that Ti$^{4+}$ ions have a tendency to enter A-sites for lower concentrations and at higher concentrations, they subsequently occupy B-sites.

**Figure 4.** Frequency variation of ac conductivity with Titanium doping in Mn–Zn nano ferrites. (a) Inset graph of variation of ac Conductivity and dopant concentration with Titanium doping in Mn–Zn nano ferrites. (b) Inset graph of Conductivity Mechanism in pure Mn–Zn ferrites. (c) Inset graph of Conductivity Mechanism in Titanium doped Mn–Zn ferrites.
For \( x \leq 0.02 \), Ti\(^{4+}\) ions tend to replace Fe\(^{3+}\) ions at A-sites resulting in decrease of magnetization at A-site. So, the net magnetization (\( M_B-M_A \)) increases thereby causing a rise in the values of \( M_s \). At higher doping levels, i.e., for \( x \geq 0.02 \), Titanium ions are argued to replace Fe\(^{3+}\) ions at B-sites causing a reduction in net magnetisation (\( M_B-M_A \)). Thus, the values of \( M_s \) witness a decreasing trend with \( x \). The values of magnetic moment of bulk Mn\(_{0.98+1/2}\)Zn\(_{0.05-2x}\)Fe\(_{2x}\)O\(_4\) (for \( x \) varying from 0.0–0.4 in steps of 0.1) synthesized by conventional ceramic technique are found [29] to decrease from 3.15 \( \mu_B \)–0.92 \( \mu_B \). In the present case of Ti\(^{4+}\) doped nanocrystalline Mn–Zn ferrites, the values of magnetic moment are comparatively lower than their bulk counterparts i.e., of the order of 0.001 \( \mu_B \)–0.015 \( \mu_B \). Eventhough Ti\(^{4+}\) ions are found to be successful in improving the loss properties, several researchers reported deteriorating values of \( M_s \) with Ti\(^{4+}\) doping. Ni–Cu–Zn doped with Ti\(^{4+}\) ions are found to witness a sudden fall in values of \( M_s \) (i.e., from 1.5 emu–0.1 emu gm\(^{-1}\)) and it is attributed to the breaking of domain structure of the material due to introduction of tetravalent titanium ions. A decrease in \( M_s \) is also reported [49] in Mg\(_{0.05}\)Mn\(_{0.05}\)Fe\(_{2-2x}\)Ti\(_{2x}\)O\(_4\) with increase in substitution of Ti\(^{4+}\) ions and it is due to dilution of sublattice by non-magnetic Ti\(^{4+}\) ions resulting in weakening of exchange interaction in the system. With increase in TiO\(_2\) additions in Ni–Zn soft ferrites, the values of \( M_s \) are found [50] to reduce with decrease in Fe\(^{3+}\) ions due to their replacement by Ti\(^{4+}\) ions. Similar decreasing trend of \( M_s \) with \( x \) is also observed in the present case Ti\(^{4+}\) doped nanophased Mn–Zn ferrites. Secondly, the lower values of \( M_s \) are correlated tonanosized grains obtained in Mn–Zn ferrites with Ti\(^{4+}\) doping. In nanoparticles an inert or dead layer is formed at the surface which prevents the spins to align along the field direction. In addition to this due to large surface to volume ratio in nanomaterials there will be spin glass like layer (canted spins) [51, 52] at the surface which reduces the values of \( M_s \). These canted spins are representative of triangular spin arrangements on the B-Site resulting in a fall of \( M_s \).Lower values of \( M_s \) is also attributed to the lower sintering temperature of 900 °C. Increase in sintering temperature leads to increment in density, grain size. The increase in grain size in turn results in increase of \( M_s \). Magnetic properties in nanophased ferrites can also be correlated [53–55] to finite size effects related to the number of exchange-coupled spins within nanoparticles, reduced symmetry of atoms at the surface and inter-particle interactions of agglomerated magnetic nanoparticles. It is also reported that in case of superparamagnetic nano iron clusters, sintering temperature is reported to weaken the inter-particle interactions causing increased values of \( M_s \). Magnetic properties of ferrites are also reported [55] to depend upon the shapes of the nanophased samples. \( M_s \) is found to decrease with increasing thickness off the sample. Hence, in the present case of Ti\(^{4+}\) doped ferrites, the values of \( M_s \) can be increased by raising the sintering temperatures to reduce the agglomerating trends which inturn reduce the interparticle interactions. Coating with insulating thick silica shell can also increase the values of \( M_s \). Finally, the observed lower values of \( M_s \) are explained in terms of density. Generally, the magnetic properties of a material are reported [56] to be dependent on the porosity or density of the material. The demagnetizing factor is directly proportional to porosity of the material. Hence, the...
materials with relatively higher values of porosity or lower values of density are prone to exhibit lower values of $M_s$. Thus, the values of $M_s$ for the present Ti$^{4+}$ doped nanocrystalline Mn–Zn ferrites are also attributed to relatively lower values of density obtained in the present samples. Thus, the competing factors like nature of the dopant, grain size, interparticle interactions and density can be considered as the major factors for the observed lower values of $M_s$.

The nanosized Ti$^{4+}$ doped nanocrystalline manganese zinc ferrite powder is found to exhibit superparamagnetic behaviour. Complex domain structure is exhibited [57] by large-grain-size ferrites. As the grain size is reduced, the number of domains decreases, and a transition from a polydomain to a single-domain occurs. As the particle size decreases beyond a certain limit, formation of domain wall structure is not thermodynamically favoured and thus the magnetic nanoparticles consist of all spins aligned in the same direction and at a critical particle diameter all the particles will be in a single domain. As the particle size continues to decrease and reaches a critical size where thermal energy exceeds the magnetic anisotropy energy barrier, the magnetization and demagnetization measured in a finite time interval is zero. This particle size represents the critical size for superparamagnetic behaviour and such particles are superparamagnetic. The corresponding magnetization curve of the superparamagnetic material exhibits a saturation of magnetization and no hysteresis around the origin. These particles may show a type of magnetic Brownian movement and tend to behave similar to a paramagnetic atom with a very large magnetic moment. In a single-domain particle, all the spins are aligned in the same direction and the particle is uniformly magnetized. Because there are no domain walls to move, the magnetization will be reversed through spin rotation rather than through the motion of domain walls. This results in large coercivity of the nanoparticles. Relatively larger values of $H_c$ are observed in the present case of Ti$^{4+}$ doped nanocrystalline Mn–Zn ferrites. The variation of $H_c$ with crystallite size ($D$) is provided in figure 5(c). An overall view of figure 5(c) reveals that the values of $H_c$ are found to increase with $D$ up to a critical size of 50 nm. Beyond $D = 62$ nm, the values of $H_c$ are found to increase with $D$. Under this critical diameter which typicaly lies in the range of a few tens of nanometers (and depends on the type of material), the particle will consist of a single domain. Beyond $D = 62$ nm, the Ti$^{4+}$ doped Mn–Zn ferrites exhibit multidomain structure. From figure 5(c), the values of $H_c$ are approaching to nearly zero values at a critical size of $\sim 49$ nm exhibiting superparamagnetism. The particle size limit incase of MnFe$_2$O$_4$ is reported [8, 9] to be 42 nm and 42.9 nm, respectively, below which the ferrites exhibit superparamagnetic behavior. Hydrothermally synthesized [10] nanosized Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ exhibit superparamagnetism for grain sizes less than 100 nm beyond which they exhibit ferromagnetism.

Superparamagnetism is witnessed [11, 12] in La$^{3+}$ doped Mn–Zn ferrites for a critical size of nearly 57.14 nm and for Gd$^{3+}$ doped Mn–Zn ferrites for a critical size of around 45 nm. Hence, the critical range of $D (\sim 49$ nm$)$ in Ti$^{4+}$ doped nanocrystalline Mn–Zn ferrites is found to agree with reported values. Surface modified magnetic nanoparticles (MNPs) added with calcium salt of poly (T–glutamic acid) are found [58] to exhibit superparamagnetism at room temperature. Superparamagnetic magnetic nanoparticles modified with sodium and calcium salts of poly (γ—glutamic acid) are reported [59] to be utilized in magnetic driving and bacterial biofilm and cell targeting in vivo applications due to their antibacterial and cytotoxic effects. Iron oxide nanoparticles synthesized by coprecipitation of iron salts in alkali media followed by coating with glycol chitosan are found to inhibit [60] the growth of bacteria and are potential nanomaterials for in vivo applications due to their biocompatibility and antibacterial properties. Thus, the phenomena of superparamagnetism observed at relatively higher critical sizes in the present Mn–Zn–Ti ferrites make these materials usable for technological and biomedical applications.

Hence an overall view of the above structural, dielectric and magnetic studies indicatethat addition of Titanium ions into Mn–Zn is found to produce nanophased ferrites with

(i) Relatively Lower values of dielectric constant ($\varepsilon$) and tan δ of the order of $10^{-2}$–$10^{-3}$
(ii) Increased electrical resistivity ($\rho$) with increasing Ti$^{4+}$ concentration
(iii) Higher values of $\rho$ of the order of $10^6$ $\Omega$–cm
(iv) superparamagnetic state at a critical size of $\sim 49$ nm

Thus, these materials can be best suitable for high frequency, biomedical and biotechnology applications.

### 3.5. Applications of nanoferrites

#### 3.5.1. Conventional applications of ferrites

Ferrites find a wide range of applications in electronic industry due to interesting electrical and magnetic properties. The properties of ferrites are found [59, 60] to be improved by reducing their size to the nanoscale and introduction of selective dopants in the host lattice. Mn–Zn ferrites with high permeability and low losses are the major requirements for targeted applications. Low losses and high resistivity coupled with good magnetic properties make these materials suitable as cores for inductors and transformers in carrier telephony technology,
domestic television receivers as core materials for line time base transformers. Enhanced electrical resistance and improved dielectric losses obtained in the present TiO\textsubscript{2} doped Mn–Zn ferrites make them usable in switching power supply transformers, fly back transformers or deflection yoke, domestic radio transformers, various inductance elements, impedance elements for EMI countermeasure and electromagnetic wave absorbers.

3.5.2. Biological applications
The basic requirements for biotechnology applications are explained Superparamagnetism observed in the present Ti\textsuperscript{4+} doped Mn–Zn nanoferites make [59] them suitable for biomedical and biotechnology applications like hyperthermia, magnetic resonance imaging contrast agents, and targeted drug delivery. Biomedical applications require particles that are biocompatible, less toxic and relatively smaller size.

In magnetic drug delivery, the drug molecules are attached to a functionalized magnetic nanoparticle and guided to a chosen site using an external magnetic field and they stay at that site until therapy is complete and after that they are removed. Nanoferites with good superparamagnetic properties like Fe\textsubscript{3}O\textsubscript{4} are gaining increasing attention in the field of targeted drug delivery and cell imaging.

Hyperthermia treatment is considered to be a treatment along with chemotherapy, radiotherapy and surgery in cancer therapy. When a varying magnetic field is applied to a superparamagnetic nanoparticle, heat is generated by magnetic hysteresis loss, Neel relaxation and the Brownian relaxation effect. This results in a rise of temperature up to nearly 40 °C–45 °C. As the tumor cells are more sensitive to heat than normal cells, they are destroyed. Nanoferites and fluorescent magnetic nanocomposites have been widely used in \textit{vivo} as magnetic resonance imaging (MRI) contrast agents for molecular and cell imaging. Magnetic separation can be used as a quick and simple method for capturing specific proteins or biomolecules efficiently and reliably without using expensive liquid chromatography or other techniques.

For biological applications, the nanoparticles should be biocompatible and non-toxic, preferably sufficiently small (10–50) nm leading to large surface to volume ratio that results in improving efficiency of coating (and also the attachment of ligands) in reducing agglomeration and better targeting. Smaller nanoparticles remain in the circulation after injection and pass through the capillary systems of organs and tissues avoiding vessel embolism and they avoid precipitation due to gravitational forces. They should also possess higher values of $M_s$ to control the movement of particles, close to the target pathologic tissue in the blood with moderate external magnetic field.

3.6. Conclusions
Influence of Ti\textsuperscript{4+} ions on Structural, dielectric and magnetic properties of nanophased Mn–Zn ferrites synthesized by hydrothermal method infer that:

- Formation of pure spinel phase of nanophased Mn–Zn–Ti ferrites without any extra peaks is ascribed to the relatively higher sintering temperature of 1000 °C.
- Non-linear variation of lattice parameter (a) with x is explained by occupancy of Ti\textsuperscript{4+} ions in both tetrahedral and octahedral sites.
- Replacement of Ti\textsuperscript{4+} ions with Fe\textsuperscript{3+} ions in Mn–Zn ferrites results in an overall decreasing trend of $\mu$ with x.
- Dielectric parameter $\varepsilon'$ is found to exhibit grain size ($\phi$) dependent behavior. Improved dielectric properties and reduced power losses anticipated with increasing Ti\textsuperscript{4+} concentration are attributed to hindered hopping mechanism by locking of Ti\textsuperscript{4+} – Fe\textsuperscript{3+} pairs.
- Reduced values of $M_s$ with doping x due to spin canting mechanism and triangular spin arrangement in nanosized grains and lowered density of the samples.
- Attainment of zero value of $H_C$ upto a critical size of ~49 nm denotes the superparamagnetic nature of nanophased Mn–Zn–Ti ferrites.
- Lowered values of $\tan \delta$ and higher values of $\rho$ render these materials usable for high frequency applications.

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