TEMPERATURE DEPENDENT STRUCTURAL AND ELECTRICAL ANALYSIS OF Mn-Zn NANO FERRITES

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Abstract
Mn-Zn ferrite powders (Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$) were prepared by the chemical co-precipitation method. The effect of annealing temperature on the crystalline phase formation and dielectric properties were investigated by X-ray diffraction and impedance analyzer respectively. The DTA/TGA analysis was carried out to know decomposition mechanism. Ferrites decomposed to Fe$_3$O$_4$ above 873 K annealing temperature. Particle size increased with increasing annealing temperature between 7-13 nm. The resistivity decreased with increase in temperature showing semiconductor like behaviour. The measured dc resistivity for samples at 573 K was found to be 2.86×10$^5$ Ω- cm and 4.02×10$^5$ Ω- cm. The dc conductivity data are explained using Mott’s variable range hopping (VRH) model and different related parameters were calculated. Dielectric constant decreased with increasing frequency and temperature. Relaxation peak occurred for loss tangent versus frequency curves. The ac conductivity explained using small polaron tunnelling (SPT) model.

Keywords: X-ray diffraction, DC electrical resistivity, dielectric constant, loss tangent, VRH Model.

1. Introduction
The field of spinel ferrites attracted researchers and engineers because of their potential applications in various fields and the interesting physics involved in it$^1$-$^3$. Even after more than half of the century the scientist, researchers, technologist, and engineers are still excited in various types of bulk as well as nano-crystalline ferrite materials. The recent trend is focused on the doped ferrites prepared using various synthesis techniques with different cation concentrations which in turn affects the various properties like, electrical, dielectric, and magnetic behaviour. The magnetic and electrical properties of soft ferrites could be easily tuned by suitable addition of divalent or trivalent cations in the spinel structure. Therefore spinel ferrites become the important class of commercially available ferrites extensively used in microwaves and electrical industries$^2$-$^3$. Mn–Zn ferrites are very important soft magnetic materials because of their high initial magnetic permeability, saturation magnetization, electrical resistivity and low power losses. These materials are extensively used as inductors, transformers, antenna rods, loading coils, deflection yokes, choke coils, recording heads, magnetic amplifiers, electromagnetic interference devices (EMI), power transformers and splitters$^4$-$^6$. Moreover, Mn–Zn ferrites are very important in biomedicine as magnetic carriers for bio-separation, enzymes and proteins.

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immobilization. Recently, with the development of high frequency, low power miniaturized electronic devices, special focus has been placed on the preparation of high performance Mn–Zn ferrite powders. To prepare high electromagnetic performance Mn–Zn ferrites, various synthesizing methods have been reported recently, including co-precipitation, alcohol dehydration, hydrothermal synthesis, spray drying, and sol–gel methods\textsuperscript{7-12}.

In the present work Mn-Zn ferrite powders were synthesized using co-precipitation method. The as-prepared powders were annealed at different temperatures ranging from 673 K to 923 K for 2 h in air. Structural and dielectric properties of annealed Mn-Zn ferrites were investigated using different techniques.

2. Experimental details
2.1 Sample preparation
Nanocrystalline Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) particles were synthesized by chemical co-precipitation method\textsuperscript{13,14}. The starting materials used were of AR grade Mn(NO\(_3\))\(_2\).4H\(_2\)O, Zn(NO\(_3\))\(_2\).H\(_2\)O and Fe\(_2\)(NO\(_3\))\(_3\).9H\(_2\)O. For synthesis, 0.05molar solutions of Mn(NO\(_3\))\(_2\). 4H\(_2\)O, 0.05 molar Zn(NO\(_3\))\(_2\).H\(_2\)O and 0.2 molar Fe\(_2\)(NO\(_3\))\(_3\).9H\(_2\)O were mixed in their stoichiometric ratio and homogenized at 358 K. To this, 3 molar ammonia solution was added dropwise with constant stirring. The pH of the solution was maintained between 10.5-11. The mixture was then heated at 363 K for about 1h. The precipitates were thoroughly washed with distilled water until the washings were free from sodium and chloride ions. The product was dried in an electric oven at 378 K overnight to remove water contents. Ferrite powders were heated at 673 K (MZ4), 773 K (MZ5) and 923 K (MZ65) separately. These were then pelletized in circular disks of 13mm diameter by applying a uniaxial load of 5kN using hydraulic press. The samples were then characterized through various characterization techniques.

2.2 Sample Characterizations
The structure was determined through the X-ray diffraction (XRD) analysis. XRD patterns were taken using Cu K\(\alpha\) (\(\lambda = 1.5406 \ \text{Å}\)) radiation at room temperature. The estimated average crystallite size, lattice parameter, mass density, X-ray density, measured density and porosity were calculated using simple formulae\textsuperscript{15,16}. The dc electrical resistivity was obtained by a simple two-probe method within temperature range 300–573 K The relation between electrical resistivity (\(\rho\)) and temperature\textsuperscript{17} may be expressed as:

\[
\rho = \rho_o \exp({\Delta E / k_B T})
\]

where \(\Delta E\) is the activation energy in (eV) for conduction, \(k_B\) is the Boltzmann constant and \(T\) is the temperature in Kelvin (K). The value of the dielectric constant was calculated using the relation between the capacitance, \(C_0\), and the dimensions of the sample. The capacitance and dielectric loss were recorded simultaneously using a WAYNE KERR LCR METER (6440B) in the frequency range from 50 Hz to 5 MHz at different selected temperatures. The samples were pressed into circular disc shaped pellets, and placed in specially designed sample holder. The real part of the dielectric constant (\(\varepsilon'\)) was calculated by the relation\textsuperscript{15,18}:

\[
\varepsilon' = \frac{Cd}{\varepsilon_o A}
\]
where $C$ is the capacitance in Farad, $d$ the thickness of the pellets in m, $A$ the cross-sectional area of a flat surface of the pellet sample in m$^2$ and where $\varepsilon_0$ is the permittivity of free space, equal to $8.854 \times 10^{-12}$ F/m. The dielectric loss tangent ($\tan \delta$) can be determined in terms of real and imaginary parts of dielectric constant as:

$$\tan \delta = D = \frac{\varepsilon''}{\varepsilon'}$$ (3)

The ac conductivity was calculated from dielectric constant and dielectric loss tangent ($\tan \delta$) as

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon' \tan \delta$$ (4)

where $\sigma_{ac}$ is the ac conductivity and $\omega$ is the angular frequency.

3. Results and Discussion

3.1 TGA/DTA analysis

Thermogravimetry analysis (Figure 1) shows that maximum weight loss occurs upto 518 K. The observed weight loss is due to desorption of water from sample. The DTA curve show endothermic peak around 373 K due to dehydration. Second peak in DTA curve is oxidation exothermic peak showing formation of ferrite sample. The possible reaction taking place during co-precipitation reaction can be written as:

$$0.5\text{Mn(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} + 0.5\text{ZnNO}_3 \cdot 3\text{H}_2\text{O} + 2\text{Fe}_2\text{(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} + 8\text{NaOH} \rightarrow \text{Mn}_0.5\text{Zn}_0.5\text{Fe}_2\text{O}_4 \cdot n\text{H}_2\text{O} + (4-n)\text{H}_2\text{O}$$

Large exothermic peak around 518 K shows formation of Mn-Zn ferrite nanocrystal. Weight loss also occurs at 518 K which confirms formation of Mn-Zn ferrite nanocrystal. No significant weight loss is observed over 673 K implying the presence of only Mn-Zn ferrite.

3.2 Phase identification

Figure 2 shows XRD patterns of the nano-crystalline Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrite powder samples annealed at different temperatures, ranging from 673 K to 923 K for 2 h in air. The as-prepared sample (MZ0) has pure spinel structure (JCPDS 74-2400), which indicates that one can obtain pure Mn-Zn ferrite phase by co-precipitation method using low temperature synthesis. At low (673 K) annealing temperature, powders also have pure cubic spinel structure. However above 923 K, the annealed powders contain additional XRD reflections which are due to Fe$_3$O$_4$. Figure 3 shows the effect of annealing temperature on the crystallite sizes of the annealed powders. The average crystallite sizes were determined using Scherrer’s formula. The particle size remained within the range 7 to 13 nm for the studied samples and increased with annealing temperature. The lattice constant $a$, measured density $D_m$, X-ray density $D_x$ and porosity $P$ are tabulated in Table 1. At high sintering temperature the measured density observed to decrease slightly which is due to grain growth. According to Lange and Kellet grain growth and densification are related. The formation of pores within the grain or grain boundaries may be responsible for the observed decrease in density (Figure 4). At higher temperatures the intergranular porosity increases because of discontinuous grain growth. With high rate of grain growth, pores may be left behind by moving the grain boundaries as a result pores are trapped inside grains. This discontinuous growth of the grains rises with temperature, contributing towards reduction of bulk density (Figure 4).
This result agrees with the result obtained for Ni–Zn ferrites.  

3.3 Electrical Properties

The electrical and dielectric properties give valuable information about the behaviour of electric charge carriers which leads to good understanding and explanation of conduction mechanism in ferrites. The high values of electrical resistivity is one of the important properties of ferrites which are suitable for high-frequency applications. The resistivity of the ferrites, in general, depends on several factors such as the density, porosity, grain size, chemical composition, etc. Figure 6 illustrates the variation of dc electrical resistivity of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ measured as a function of temperature. The measured dc resistivity for samples at 573 K is found to be $2.86 \times 10^5$ Ω·cm and $4.02 \times 10^5$ Ω·cm. From Figure 5, it is evident that dc electrical resistivity exhibits semiconductor like behaviour, i.e. decreasing resistivity with increasing temperature for all the samples. The conduction mechanism in these ferrites can be explained by a hopping mechanism. The activation energy of all the samples was determined from the slope of the ln $\rho$ versus $(1/k_B T)$. The activation energy ($\Delta E$) of the studied specimens was found to be $0.7 \pm 0.05$ eV and $0.77 \pm 0.09$ eV.

The temperature variation of dc conductivity $\sigma_{dc}(T)$ of samples were measured in the temperature range (293K-573 K). The semi conducting behaviour of $\sigma_{dc}(T)$ is represented by Arrhenius equation of activation:

$$\sigma_{dc} = \sigma_o \exp\left(-\frac{\Delta E}{k_B T}\right)$$  \hspace{1cm} (5)

where $\Delta E$ is the activation energy. The value of the pre-exponential $\sigma_o$ indicates whether the conduction is occurred by the extended states or by the localised states. The value of $\sigma_o$ is in the range of $10^5$-$10^4$ S/cm for the extended states conduction and a smaller for the conduction by hopping between localised states. In the present work, the values of $\sigma_o$ are small; of the order of $10^{12}$-$10^{18}$ S/cm, which indicates that the conduction takes place by hopping mechanism. This result is confirmed by small values of $\Delta E$, which is 0.55 eV and 0.57 eV for two samples. In the low temperature range, it is possible to suppose that the hopping process would be governed by a Mott’s variable-range-hopping (VRH) mechanism expressed by the following expression:

$$\sigma_{dc} = \sigma_o \exp\left[-\left(\frac{T_o}{T}\right)^{1/4}\right]$$  \hspace{1cm} (6)

where $\sigma_o$ is a pre-exponential factor, $T_o$ is the degree of disorder $T_o = \lambda \alpha^2 / k_B N(E_F)$, $N(E_F)$ is the density of the localized states at the Fermi level $E_F$, $\lambda$ is a dimensionless constant (about 16) and $\alpha^{-1}(\alpha = 10^7$ cm$^{-1}$) represents the degree of localisation. The hopping distance $R$ and the average hopping energy $W$ are given by

$$R = \left[9/8k_BT N(E_F)\right]^{1/4}$$  \hspace{1cm} (7)

and

$$W = 3/[4\pi R^3 N(E_F)]$$  \hspace{1cm} (8)

Figure 6 shows the Mott’s VRH plot: ln $(\sigma_{dc})$ vs. $T^{-1/4}$ for the samples. Deviation from straight line at higher temperature may be due to other conduction mechanism which arises with higher temperature. Degree of
disorder, hopping distance and average hopping energy increases with increase in annealing temperature.

3.3.1 Dielectric Studies
Dielectric constant ($\varepsilon'$) in ferrites is contributed by several structural and micro-structural factors. The frequency dependence of the dielectric constant for MZ4 sample has been studied at 313 K to 373 K in the frequency range 50Hz to 5MHz. Figure 7 shows the variation of real and complex part of dielectric constant with frequency at some representative temperatures. It is clear that the sample exhibit the dielectric dispersion where both real ($\varepsilon'$) and imaginary part ($\varepsilon''$) decrease as the frequency increases from 50 Hz–5MHz. The dielectric constant decreases rapidly in low frequency region and slows down in high frequency region, almost approaches to frequency independent behaviour. The phenomenon of dielectric dispersion in ferrites has been explained on the basis of Maxwell–Wagner model\textsuperscript{28,29} and Koop's phenomenological theory\textsuperscript{30} of dielectrics. This model, suggests that dielectric medium is made of well conducting grains, separated by poorly conducting grain boundaries. It has been observed that in ferrites the permittivity is directly proportional to the square root of conductivity\textsuperscript{31}. Therefore the grains are highly conductive and have high values of permittivity, while as the grain boundaries are less conductive and have smaller values of permittivity. At lower frequencies the grain boundaries are more effective than grains in electrical conduction. Thinner the grain boundary, higher is the value of dielectric constant. The higher values of the dielectric constant($\varepsilon'$) observed at lower frequencies are also explained on the basis of interficial/space polarization due to inhomogeneous dielectric structure\textsuperscript{32,33}. The inhomogeneities present in the system can be porosity and grain structure. At high frequencies ($10^5$ Hz), independent value of dielectric constant with temperature is due to atomic and electronic polarizations. At each temperature, decrease in the dielectric constant with frequency is observed, showing lower dipolar response of the ac field\textsuperscript{34}. The variation of dielectric loss factor (tan$\delta$) is shown in Figure 8. It is observed that the loss tangent decreases initially with increasing frequency followed by the appearance of the relaxation peak. The appearance of relaxation peak can be explained according to the Debye relaxation theory\textsuperscript{35}. The loss peak occurs when the applied field is in phase with the dielectrics and the condition $\omega\tau=1$ is satisfied, where $\omega=2\pi f$, $f$ being the frequency of the applied field. Singh et al.\textsuperscript{36} have observed a similar relaxation peak at a frequency of 1 kHz for Mn substituted Ni–Zn ferrites synthesized by the citrate precursor method. In the present investigation, the relaxation peak appears at frequency 1kHz. The shifting of the relaxation peak towards lower frequency side with an increase in temperature is due to the strengthening of the dipole–dipole interactions causing hindrance to the rotation of the dipoles\textsuperscript{36}. Therefore the resonance between rotation of the dipoles and applied field takes place at lower frequency.

3.3.2 AC conductivity
It has been found that conductivity is decreasing function of frequency in the case of band conduction and increasing function of frequency in case of conduction by hopping. Generally total conductivity is the sum of
band and hopping conduction, related by the formula\(^{(9)}\):

\[
\sigma_{\text{total}} = \sigma_{dc}(T) + \sigma_{ac}(\omega, T)
\]

The dc conductivity is frequency independent term also known as band conduction and ac conductivity, due to hopping process at octahedral site, depends on frequency \((\omega = 2\pi f)\). For semiconductors and disordered systems the ac conductivity follows the power law \(^{(38)}\):

\[
\sigma_{ac}(\omega, T) = A\omega^s
\]

where A is pre exponential factor and s is the frequency exponent \((s \leq 1)\). From \(\ln \sigma_{ac} vs \ln \omega\) plot, the slope directly gives the value of dimensionless frequency exponent \(s\).

The ac conductivity \((\sigma_{ac})\) was studied over a frequency range of 50Hz-5MHz, for the sample. The \(\sigma_{ac}\) was calculated from dielectric data using relation given in equation \((4)\). At low frequency, ac conductivity is weakly dependent on frequency due to non equilibrium occupancy of trap charges\(^{(39)}\).

At higher frequency occupancy of trap charges decreases making more conductive states available for hopping of electrons and holes. The trend in conductivity with temperature supports our results of dielectric constant as both conductivity and dielectric run in parallel.

Frequency exponent measures the correlation between \(\sigma_{ac}\) and \(\omega\). Value of \(s\) is 0 for random hopping of carriers and tends to 1 as the correlation between \(\sigma_{ac}\) and \(\omega\) increases. In present study, value of \(s\) varies between 0.28 to 0.70. The values are within acceptable range, reported by different researchers. Value of frequency exponent \((s)\) increases in the high frequency region with temperature. Small polaron tunnelling (SPT) is usually associated with increase in \(s\) with temperature, indicating the activated behaviour of polarons\(^{(40)}\).

![Figure 1 DTA/TGA curve for as-prepared sample (MZ0).](image-url)
Figure 2 XRD of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ annealed at different temperatures. ‘o’ shows peaks of Fe$_3$O$_4$.

Figure 3 Increase in particle size with temperature.
Figure 4 Change in porosity and density with temperature.

Figure 5 Variation of dc resistivity with temperature.
Figure 6 Variation of dc conductivity with temperature.

Figure 7 Variation of dielectric constant and imaginary part (inset) with frequency at given temperatures.
Figure 8. Variation of loss tangent with frequency at given temperatures.

Figure 9. Plot of $\ln \sigma_{ac} (\text{S-m}^{-1})$ with respect to $\ln \omega (\text{Hz})$. 
Table 1. Effect of annealing temperature on lattice constant, measured density and porosity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice constant(a)Å</th>
<th>XRD Density(Dx) g-cm⁻³</th>
<th>Measured Density(Dm) g-cm⁻³</th>
<th>Porosity(fractional)</th>
<th>Crystallite Size nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MZ0</td>
<td>8.439</td>
<td>5.21</td>
<td>3.85</td>
<td>0.26</td>
<td>7</td>
</tr>
<tr>
<td>MZ4</td>
<td>8.439</td>
<td>5.21</td>
<td>3.68</td>
<td>0.27</td>
<td>11</td>
</tr>
<tr>
<td>MZ5</td>
<td>8.438</td>
<td>5.21</td>
<td>3.62</td>
<td>0.30</td>
<td>12</td>
</tr>
<tr>
<td>MZ65</td>
<td>8.431</td>
<td>5.23</td>
<td>3.50</td>
<td>0.33</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 2. Parameters of Mott’s VRH model at 300K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T₀(K)</th>
<th>N(E_F)(eV⁻¹cm⁻³)</th>
<th>R(nm)</th>
<th>W(meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MZ4</td>
<td>1×10¹⁰</td>
<td>1.86×10¹⁶</td>
<td>28</td>
<td>554</td>
</tr>
<tr>
<td>MZ5</td>
<td>1.46×10¹⁰</td>
<td>1.27×10¹⁶</td>
<td>32</td>
<td>574</td>
</tr>
</tbody>
</table>

4. Conclusions
Nanocrystalline Mn₀.₅Zn₀.₅Fe₂O₄ particles were synthesized by chemical co-precipitation method. The particle size remains within the range of 7nm to 13nm. Good quality ferrite can be obtained even at low temperature i.e. 673 K. At higher temperature additional peaks of Fe₃O₄ were observed. The calculated values of activation energies for samples agreed with the experimental observations within experimental error. The dielectric constant decreases rapidly with increase in frequency and then approaches a constant value. Relaxation peak occurs for loss tangent versus frequency curve and shifts towards lower frequency with high annealing temperature showing resonance phenomena i.e. hopping frequency of electrons and that of applied field become equal approximately. The ac conductivity increases up to a maximum value and starts decreasing due to hindrance in the hopping mechanism at higher frequency. Resistivity decreases with increase in temperature, showing semiconductor like behaviour. Variable range hopping (VRH) model fits in low temperature range to explain change in dc conductivity with temperature. Small polaron tunnelling (SPT) model fits for change in ac conductivity with temperature.

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References