Substitutional effect on structural, magnetic and dielectric properties of (Zn, Mg)\(_x\)Co\(_{1-x}\)Fe\(_2\)O\(_4\) mixed Ferrites

In this chapter, we discuss the structural, magnetic and dielectric properties of \(A_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4\) (\(A = \text{Zn, Mg}; x = 0.0, 0.5\)) ferrite as synthesized by chemical co-precipitation method. Rietveld-refined X-ray powder diffraction patterns at room temperature confirmed the formation of single-phase cubic (FCC) structure with \(Fd\bar{3}m\) space group. Raman analysis reveals the doublet-like nature of \(A_{1g}\) mode and small shift in Raman modes and increment in the line width has been observed. The magnetic measurement infers that the saturation value (\(M_s\)) is maximum for CoFe\(_2\)O\(_4\) as compared to Zn and Mg doped cobalt ferrites. The variation of permittivity and ac conductivity as a function of frequency shows that dispersion is attributed to the hopping of charge carriers. The minimum value of loss tangent (\(\sim 0.04\)) at 5 KHz makes \(A_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4\) most suitable material for microwave application. Temperature dependent dielectric constant and loss tangent shows an increasing trend with increasing temperature. The activation energy (\(E_a\)) for CoFe\(_2\)O\(_4\), Co\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) and Co\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) are found to be 0.81 eV, 0.76 eV and 0.63 eV respectively. The electrical modulus study clearly tells the presence of non-Debye type of dielectric relaxation in the present material.

Papers published with this chapter:

1. Dielectric relaxation behavior of \(A_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4\) (\(A = \text{Zn, Mg}\)) mixed ferrites.
   
   Kavita Verma, Ashwini Kumar and Dinesh Varshney

2. Substitutional effect on structural and magnetic properties of \(A_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4\) (\(A = \text{Zn, Mg} \text{ and } x = 0.0, 0.5\)) ferrites.
   
   Dinesh Varshney, Kavita Verma and Ashwini Kumar
   2011 *Journal of Molecular Structure* (Elsevier - U.S.A), 1006, Pp. 447-452

"Science is not only compatible with spirituality - It is a profound source of spirituality."

Carl Sagan
4.1 Introduction

Spinel ferrites are magnetic materials with a general formula \((M_{1-x}Fe_x)[Fe_{2-M}M]O_4\), the round and square brackets denote the tetrahedral (A) and octahedral (B) interstitial sites. M is the divalent (Mn\(^{2+}\), Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), etc.) and Fe is the trivalent (Fe\(^{3+}\)) metal cation occupying the FCC lattice formed by O\(^{2-}\) anions. The magnetic properties of a spinel are sensitive to the types of cation and their distribution amongst the two interstitial sites of spinel lattice [1]. The cation distribution between A-site and B-site depends on the ionic radii, the type of bonding and the preparation method. Changing the variables as temperature, pressure, magneto-crystalline anisotropy, and composition of metal ions may influence the cation distribution.

CoFe\(_2\)O\(_4\) is typically an inverse spinel ferrite in which Fe\(^{3+}\) ions are occupied equally, with their spin in the opposite direction, in the tetrahedral (A) and octahedral (B) sites. The magnetic property is mainly dependent on the Co\(^{2+}\) (3d\(^7\)) ions that have an orbital moment of 3.7 \(\mu_B\) per formula unit. It has a coercivity of \(-0.75-0.98\) kOe along with 80-emu/g magnetization at room temperature and is a good candidate for the magnetic recording application [2]. Magnetic coercivity of any material depends on several factors like magnetocrystalline anisotropy, shape anisotropy, strains, defects, size of the particles, doping, nature of the surface, and interface [3-7]. A number of efforts have been made to increase the coercivity in cobalt ferrite using different strategies. However, the maximum coercivity reported so far in the powders of CoFe\(_2\)O\(_4\) is 5.3 kOe for the samples prepared by chemical route. Such a large coercivity is attributed to small particle size and large residual strain [8]. The maximum room temperature coercivity reported in CoFe\(_2\)O\(_4\) particles synthesized by mechanical milling process is 5.1 kOe. This large coercivity is attributed to the high strain and defects produced in CoFe\(_2\)O\(_4\) powders by milling [4].

Conversely, ZnFe\(_2\)O\(_4\) is a normal spinel, where Zn\(^{2+}\) preferably occupies the tetrahedral sites due to their affinity for sp\(^3\) bonding with oxygen anions leaving all the ferric ions on the octahedral sites. ZnFe\(_2\)O\(_4\) is antiferromagnetic in nature due to low Neel temperature and is paramagnetic at room temperature due to weak super exchange interaction attributed to 90° angle in Fe\(^{3+}\)-O-Fe\(^{3+}\) [9]. Thus, ZnFe\(_2\)O\(_4\) exhibits lower magnetic moment (\(-5\) emu/g) at room temperature. However, on vacuum thermal annealed at 1000° C and cooled to room temperature it becomes magnetically ordered with a large magnetic moment (\(-62\) emu/g). This change is attributed to the change in the cation distribution from the normal to mixed spinel type, where Fe\(^{3+}\) and Zn\(^{2+}\) occupy both sites under vacuum thermal annealing [10].

On the other hand, MgFe\(_2\)O\(_4\) is a soft magnetic n-type semiconducting material, and is very important member of ferrite family. The cation distribution in MgFe\(_2\)O\(_4\), upon which many physical and chemical properties depend, is a
complex function of processing parameters and mostly depends on the preparation method of the material. The earlier reported cation distribution reveals that Mg$^{2+}$ ions exist in both sites but have a strong preference for the octahedral site [11]. The magnetic moment of Mg$^{2+}$ is zero, so the magnetic couplings in MgFe$_2$O$_4$ purely originate from the magnetic moment of Fe cations and may be relatively weaker. Thus, the magnetic anisotropy in MgFe$_2$O$_4$ could be lower than that of other spinel ferrites.

Previously, Padalia and co-workers have estimated the valance state of Co as Co$^{2+}$ and Fe as Fe$^{3+}$ in Zn doped Cobalt ferrites using X-ray fine structure method. Additionally the bond length estimated from fine structure method was found close to those obtained from crystallographic data [12]. Furthermore, Amulevicius et al. explore the dependence of average hyperfine field and temperature dependent magnetic anisotropy of mixed ferrites using multilevel relaxation model [13]. The vibrational method as Raman spectroscopy and Fourier transform infrared spectroscopy is the powerful probe to reveal the vibrational and structural properties. At room temperature five Raman active modes of Fe$_3$O$_4$ at 670 cm$^{-1}$ ($A_{1g}$), 410 cm$^{-1}$ ($E_g$), 193 cm$^{-1}$ ($T_{2g}(1)$), 540 cm$^{-1}$ ($T_{2g}(2)$), and 300 cm$^{-1}$ ($T_{2g}(3)$) are predicted according to group theory [14]. Although the X-ray powder diffraction pattern of CoFe$_2$O$_4$ and Fe$_3$O$_4$ are quite similar, their Raman spectra are quite different.

Apart from magnetic properties, studies of electric and dielectric behaviour are equally important from both fundamental and applied point of view. Cobalt ferrite is also treated as a good as dielectric material. It was reported that the dielectric constant increases with increasing calcination temperature of CoFe$_2$O$_4$ synthesized by chemical auto combustion route method [15]. Moreover, the dielectric constant and dielectric loss is found to reduced significantly due to substitution of La$^{3+}$ ion in CoFe$_2$O$_4$, whereas the DC resistivity was found to be 30 times more as compared to pure CoFe$_2$O$_4$ [16]. Also the dielectric loss of Al$^{3+}$ substituted CoFe$_2$O$_4$ was found to decrease with Al$^{3+}$ ion concentration [17].

In the present investigation, we aim to study the effect of Zn and Mg substitution on structural, magnetic and dielectric properties of $A_x$Co$_{1-x}$Fe$_2$O$_4$ ($A$ = Zn, Mg and $x = 0.0, 0.5$) samples. The chemical co-precipitation method has been used to synthesize Zn and Mg doped cobalt ferrites. Detailed analysis of the structural, magnetic and dielectric properties of as prepared ferrites are discussed through X-ray diffraction, Raman spectroscopy, Vibrating sample magnetometer, and Dielectric and impedance spectroscopy.

4.2 Experimental details

4.2.1 Synthesis of samples

For the synthesis of $A_x$Co$_{1-x}$Fe$_2$O$_4$ ($A$ = Zn, Mg and $x = 0.0, 0.5$) samples through chemical co-precipitation technique all the reagents were commercial products with analytical grade without further purification. The chemical reagents for this
experiment Fe(NO₃)₃ 9H₂O, Co(NO₃)₂ 6H₂O, Zn(NO₃)₂ 6H₂O, Mg(NO₃)₂ 6H₂O, and sodium hydroxide were used. The deionized water was used during the experiments. The aqueous solution of Co, Zn, Fe and Mg salts were freshly prepared by taking Fe(NO₃)₃ 9H₂O, Co(NO₃)₂ 6H₂O, Zn(NO₃)₂ 6H₂O, and Mg(NO₃)₂ 6H₂O in appropriate molar ratio. This mixture was heated until the temperature reached 70° C. On vigorous stirring, the pH of the above solution was raised to 12 rapidly, by the addition of 6 M NaOH. The particles settled at the bottom were collected and the top water layer with excess salts was discarded. The particles have been washed repeatedly with distilled water to remove salt impurities. Later, the washed particles were treated with acetone dried at room temperature and further calcined at 700° C for 5 h.

4.2.2 Characterizations

The crystal structure and type of phases were identified by means of X-ray powder diffraction (XRD) at room temperature, using Bruker D8 Advance X-ray diffractometer with CuKα₁ (1.5406 Å) radiation. The data was collected with a scanning speed of 2°/min. with a step size of 0.02° over the angular range 2θ (10° < 2θ < 90°) generating X-ray by 40 kV and 40 mA power settings. The Raman measurements on as synthesized samples were carried out on LABRAM-HR spectrometer with a 488 nm excitation source equipped with a Peltier cooled charge coupled device detector. Fourier Transform Infrared (FT-IR) spectra were recorded in the frequency range of 2000–400 cm⁻¹ employing KBr disc technique using Bruker Germany make spectrometer model vertex-70. DC magnetization measurements on all the samples were performed using a vibrating sample magnetometer (VSM, Lakeshore 7300 model, USA) as a function of magnetic field from 0 to ±10,000 Oe.

Microstructure and surface morphology of the samples have examined by scanning electron micro-scope [SEM: JEOL-JSM-6390]. Frequency dependent dielectric measurements of the present samples were evaluated with impedance analyzer model-Novoc control tech Germany alpha ATB works over the wide range of frequency (3 μHz–20 MHz) and in the ac voltage range (100 mV–3 V). The dielectric constant (ε') and loss tangent (tan δ) were measured as a function of temperature (room temperature to 673 K) in air atmosphere using a Hewlett Packard 4192A (Berkshire, U.K.) impedance analyzer. For dielectric measurements sintered pellets were polished with zero grain emery paper, and coated with high purity silver paste on adjacent faces as electrodes and then dried for 2 h at 150 °C to make the parallel plate capacitor geometry.

4.3 Results and discussion

4.3.1 Structural Analysis (XRD)

The of X-ray diffraction pattern of AₓCo₁₋ₓFe₂O₄ (A = Zn, Mg and x = 0.0, 0.5) samples are shown in Figure 4.3.1.1. From the X-ray diffraction pattern, it has
been observed that all the reflection peaks of pure as well as doped compound matches well with Joint Committee for Powder Diffraction Set (JCPDS) Card No. 22-1086 for CoFe₂O₄ ferrite. Furthermore, there is no change in peak positions for all the three samples, which indicate that all the samples crystallize in single-phase cubic structure with \( Fd\bar{3}m \) space group. The crystallite sizes of the synthesized samples were determined from the x-ray diffraction data using Debye–Scherrer formalism:

\[
t = \frac{0.9 \lambda}{\beta \cos \theta}
\]

where, \( t \) is the crystallite size, \( \beta \) is the full width half maximum (FWHM) of the most intense peak (311) measured in radians, \( \lambda \) is the X-ray wavelength of the CuK\( \alpha_1 \) (1.5406 Å) and \( \theta \) is the Bragg’s angle in Eq. (4.1). The crystallite sizes are estimated as 41.5 nm, 45.9 nm and 45.0 nm for CoFe₂O₄, Co₀.₅Mg₀.₅Fe₂O₄ and Co₀.₅Zn₀.₅Fe₂O₄ respectively.

Fig. 4.3.1.1: X-ray powder diffraction pattern for AₓCo₁₋ₓFe₂O₄ (A = Zn, Mg and \( x = 0.0, 0.5 \)) ferrite samples.

The Rietveld refinement of X-ray powder diffraction pattern for AₓCo₁₋ₓFe₂O₄ (A = Zn, Mg and \( x = 0.0, 0.5 \)) samples at room temperature were performed using FullPROOF program and are shown in Fig. 4.3.1.2. The performed pattern for the structural modal with space group \( Fd\bar{3}m \) (227) reproduce adequately all the observed reflections and gave practically identical reliability factor. There is a good agreement between observed and calculated pattern using the Rietveld
analysis, which is confirmed by observing the difference pattern. The refined parameters of as synthesized samples are summarized in Table 4.3.1.1. We also identify the residuals for the weighted pattern $R_{wp}$, the pattern $R_p$, Bragg's factor $R_{Bragg}$, structure factor $R_p$, and goodness of fit $\chi^2$. All these parameters were used as numerical criteria of the quality of the fit. The initial input parameters used for the Rietveld refinement were taken from the earlier reported data [18, 19]. The Refined cationic positions suggest that all the structures have completely different compositions corresponding to the chemical formula of the compound. The value of $\chi^2$ comes out to be ~1, which may be considered to be very good for estimations.

Fig. 4.3.1.2: Rietveld refined XRD pattern for $A_xCo_{1-x}Fe_2O_4$ ($A=Zn, Mg$ and $x=0.0, 0.5$) ferrite samples.
Table 4.3.1.1: Rietveld refined XRD parameters of $A_xCo_{1-x}Fe_2O_4$ ($A = Zn, Mg$ and $x = 0.0, 0.5$) ferrite samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$CoFe_2O_4$</th>
<th>$Co_{0.5}Zn_{0.5}Fe_2O_4$</th>
<th>$Co_{0.5}Mg_{0.5}Fe_2O_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group</td>
<td>$Fd3m$</td>
<td>$Fd3m$</td>
<td>$Fd3m$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell parameters ($\text{Å}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_0$</td>
<td>8.3554</td>
<td>8.3522</td>
<td>8.3221</td>
</tr>
<tr>
<td>$a_t$</td>
<td>8.3532</td>
<td>8.3501</td>
<td>8.3199</td>
</tr>
<tr>
<td>Cell Volume ($\text{Å}^3$)</td>
<td>583.31</td>
<td>582.85</td>
<td>576.36</td>
</tr>
<tr>
<td>Atomic Positions ($x = y = z$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Fe_1/Zn, Mg$</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>$Fe_2/Co$</td>
<td>0.625</td>
<td>0.625</td>
<td>0.625</td>
</tr>
<tr>
<td>O</td>
<td>0.247</td>
<td>0.247</td>
<td>0.247</td>
</tr>
<tr>
<td>$R$-factors (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_p$ (%)</td>
<td>43.9</td>
<td>25.4</td>
<td>30.1</td>
</tr>
<tr>
<td>$R_{wp}$ (%)</td>
<td>24.3</td>
<td>17.3</td>
<td>22.5</td>
</tr>
<tr>
<td>$R_{exp}$ (%)</td>
<td>23.1</td>
<td>16.0</td>
<td>21.2</td>
</tr>
<tr>
<td>$R_{Bragg}$ (%)</td>
<td>5.72</td>
<td>4.25</td>
<td>5.60</td>
</tr>
<tr>
<td>$R_f$ (%)</td>
<td>5.47</td>
<td>4.10</td>
<td>5.77</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>1.10</td>
<td>1.16</td>
<td>1.19</td>
</tr>
<tr>
<td>GOF-index</td>
<td>1.0</td>
<td>1.1</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The lattice constant of $CoFe_2O_4$ and $Co_{0.5}Zn_{0.5}Fe_2O_4$ matches well with each other due to similar ionic radii of $Co^{2+} (0.745 \, \text{Å})$ and $Zn^{2+} (0.740 \, \text{Å})$ [20]. Whereas the lattice constant of $Co_{0.5}Mg_{0.5}Fe_2O_4$ slightly reduces as compared to $CoFe_2O_4$, this is due to smaller ionic radii of $Mg^{2+} (0.720 \, \text{Å})$. The theoretical value of the lattice constant “$a_t$” for above three compositions has also been determined by considering the cation distribution in these systems estimated from the X-ray diffraction.

In order to determine the cation distribution we have used the intensities of (220), (422) and (400) planes as these planes are most sensitive to the cations on tetrahedral (A) and octahedral (B) sites [21, 22]. The relative integrated X-ray intensity “$I_{hkl}$” of a given diffraction line was calculated using the Buerger formula specified as [23].

\[
I_{hkl} = |F_{hkl}|^2 \cdot P \cdot L_p
\]  

(4.2)

where, $I_{hkl}$ is the relative integral intensity, $F_{hkl}$ the structure factor, $P$ the multiplicity factor, $L_p$ refers to Lorentz polarization factor. It is worth mentioning...
that ions distributed over tetrahedral (A) and octahedral (B) sites. As reported earlier the intensities corresponding to (220) and (422) reflections are most sensitive to cations on tetrahedral sites, while those of (222) reflection to cation on octahedral sites. As seen from the Fig. 4.3.1.1., that the intensities of (220), (422), (440) and (222) reflections decrease with substitution of Zn$^{2+}$ and Mg$^{2+}$ ions indicating that both the ions enters in the tetrahedral (A) sites. Further the intensity ratios of $I_{220}/I_{440}$, and $I_{422}/I_{220}$, for all the three samples were calculated to determine the cation distributions. The values of intensity ratios and cation distribution are summarized in Table 4.3.1.2.

**Table 4.3.1.2: Cation distribution and values of intensity ratio of $A_xCo_{1-x}Fe_2O_4$ (A = Zn, Mg and $x = 0.0, 0.5$) ferrite samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>A-Site</th>
<th>B-Site</th>
<th>$I_{(220)}/I_{(400)}$</th>
<th>Obs.</th>
<th>Cal.</th>
<th>$I_{(422)}/I_{(220)}$</th>
<th>Obs.</th>
<th>Cal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A = Co</td>
<td>$x = 0.0$</td>
<td>$(Co_{0.1}Fe_{0.9})$</td>
<td>[Co$<em>{0.9}$Fe$</em>{1.1}$]</td>
<td>1.0646</td>
<td>1.0454</td>
<td>0.8458</td>
<td>0.7543</td>
<td></td>
</tr>
<tr>
<td>A = Zn</td>
<td>$x = 0.5$</td>
<td>$(Zn_{0.5}Fe_{0.5})$</td>
<td>[Co$<em>{0.5}$Fe$</em>{1.5}$]</td>
<td>1.5786</td>
<td>1.6172</td>
<td>0.7651</td>
<td>0.5422</td>
<td></td>
</tr>
<tr>
<td>A = Mg</td>
<td>$x = 0.5$</td>
<td>$(Mg_{0.1}Fe_{0.9})$</td>
<td>[Mg$<em>{0.4}$Co$</em>{0.5}$Fe$_{1.1}$]</td>
<td>1.0502</td>
<td>1.0322</td>
<td>0.8273</td>
<td>0.7143</td>
<td></td>
</tr>
</tbody>
</table>

The obtained values are in good agreement with the earlier reported data [24]. On the basis of estimated cation distribution, the value of theoretical lattice constant “$a_t$” for all the three samples has been determined using the relation [25]:

$$a_t = \frac{8}{3\sqrt{3}} \left( r_a + r_0 \right) + \sqrt{3} \left( r_b + r_0 \right)$$  \hspace{1cm} (4.3)

where, $r_a$, $r_b$ are the radii of tetrahedral (A) and octahedral (B) sites, respectively, and $r_0$ is the radius of the oxygen ion O$^{2-}$ (1.48 Å). It has been observed that the theoretically and experimentally observed values of lattice parameters are nearly equal and are shown in Table 4.3.1.1.

Another important factor that influences physical properties of ferrite system is the jump length “$L$”. The probability of the electron that are hopping between the A and B sites are less as compared to that are hopping between B and B sites. The reason being that the distance between the two metal ions placed at B-site is smaller than the distance if one is placed at A-site and other is at B-site. The jump length “$L$” of the tetrahedral (A) and octahedral (B) sites is determined from the relation given as [26]:

Materials Science Laboratory 69 Debi Ahilya Vishwavidyalaya, INDORE
Chapter 4

The values of jump length are found to be as for CoFe$_2$O$_4$ ($L_A$=3.6178 Å, $L_B$=2.9540 Å), Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ($L_A$=3.6165 Å, $L_B$=2.9532 Å) and Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ ($L_A$=3.6034 Å, $L_B$=2.9421 Å). It has been observed that jump length of CoFe$_2$O$_4$ and Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ are quite similar whereas, the jump length of Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ reduces. This reduction in jump length is attributed to replacement of larger ionic radii (Fe$^{3+}$) by smaller ionic radii (Mg$^{2+}$). The obtained result matches well with the earlier reported data [11].

4.3.2 Microstructural Analysis (SEM)

Fig. 4.3.2 represents the SEM images of $A_x$Co$_{1-x}$Fe$_2$O$_4$ ($A$ = Zn, Mg and $x$ = 0.0, 0.5) ferrite samples sintered at 1250$^\circ$ C for 24 h. From the micrograph it is clear that sintered samples results in greater densification with less porosity. The average grain size was 3.2 μm for CoFe$_2$O$_4$. The grain size increases with doping concentration and was found to be 4.7 μm and 7.4 μm for Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ respectively.

![SEM micrograph of CoFe$_2$O$_4$ (a), Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (b) and Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (c) samples.](image-url)
4.3.3 Vibrational Analysis (Raman and FTIR)

The room temperature Raman spectra of $A_xCo_{1-x}Fe_2O_4$ ($A = Zn, Mg$ and $x = 0.0, 0.5$) samples within range of 150-800 cm$^{-1}$ is shown in Fig. 4.3.3.1. The observed spectra were least square fitted with Lorentzian line shape function in order to determine the natural frequency and line width. The thick smooth lines are fits to the Lorentzian functions.

![Raman Spectra](image)

**Fig. 4.3.3.1:** Room temperature Raman spectra of $A_xCo_{1-x}Fe_2O_4$ ($A = Zn, Mg$ and $x = 0.0, 0.5$) ferrite samples.

Raman modes of $A_xCo_{1-x}Fe_2O_4$ ($A = Zn, Mg$ and $x = 0.0, 0.5$) samples are illustrated in Table 4.3.3. It has been observed that Raman band at $\sim 690$ cm$^{-1}$ show a shoulder like feature at lower wave number side against the reported single band to that of Fe$_3$O$_4$ [14]. These bands are assigned to $A_{1g1}$ and $A_{1g2}$ modes reflecting the stretching vibration of Fe$^{3+}$ and O$^{2-}$ ions in tetrahedral site. The other low frequency modes are assigned to $T_{2g}$ and $E_g$ modes reflecting the vibration of that site.

The doublet like feature is due to the local cation distribution. In Fe$_3$O$_4$ whole of the tetrahedral and octahedral sites are occupied by Fe ions while in
CoFe$_2$O$_4$ the octahedral site are occupied by Co and Fe ions and tetrahedral site are occupied by only Fe ion. Due to difference in ionic radii of Co and Fe ions in CoFe$_2$O$_4$ the Fe-O, Co-O bond distance redistribute between both the sites resulting in doublet like structure.

Due to weak Raman signals and broadening the $T_{2g}(1)$ mode in CoFe$_2$O$_4$ plus $T_{2g}(1)$ and $T_{2g}(3)$ mode in Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ could not be observed in the spectra. Except $E_g$ mode all other modes of Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ shows a red shift and is attributed to higher atomic mass of Zn as compared to Co ion. Whereas, modes of Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ shows a blue shift owing to lower atomic mass Mg as compared to Co ion.

Another common feature observed in Raman modes of all the three samples is that the line width changes with the doping elements. The line width increases with Mg and Zn doping. This increase in line width is attributed to strong electron-phonon interaction and electronic disorder arising as random arrangement of Cations on the octahedral ($B$) site. The line width of $A_{1g}$ and $T_{2g}$ modes are also given in Table 4.3.3.

| Table 4.3.3: Raman parameters of $A_x$Co$_{1-x}$Fe$_2$O$_4$ ($A = Zn, Mg$ and $x = 0.0, 0.5$) samples. |
| Sample | CoFe$_2$O$_4$ | Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ |
| Assignment | Raman modes (cm$^{-1}$) | Line width | Raman modes (cm$^{-1}$) | Line width | Raman modes (cm$^{-1}$) | Line width |
| $A_{1g}(2)$ | 693.3 | 33.97 | 693.2 | 43.39 | 684.5 | 47.55 |
| $A_{1g}(1)$ | 619.2 | 69.88 | 632.7 | 121.72 | 629.4 | 139.02 |
| $T_{2g}(3)$ | 571.0 | 35.19 | 551.7 | 111.92 | -- | -- |
| $T_{2g}(2)$ | 470.5 | 44.80 | 468.5 | 55.59 | 476.61 | 83.72 |
| $E_g$ | 311.5 | 51.87 | 314.5 | 89.95 | 319.5 | 99.96 |
| $T_{2g}(1)$ | -- | -- | 207.7 | 27.26 | -- | -- |

The transmission IR spectra of as synthesized samples are shown in Fig. 4.3.3.2. It has been mentioned that two main broad metal-oxygen bands are seen in IR spectra of all spinel ferrites [27]. The band around 600 cm$^{-1}$ corresponds to vibration of tetrahedral metal-oxygen [Fe-O] bond and the band at 400 cm$^{-1}$ to vibration of octahedral metal oxygen bond.

Furthermore, the absorption band (in the range of 500–600 cm$^{-1}$) in the present study corresponds to vibration of Fe$^{3+}$–O$^{2-}$ bond of tetrahedral ($A$) site, while a band around 1630 cm$^{-1}$ assigned to the bending vibration of H$_2$O absorbed after calcinations [28, 29]. The IR spectra show the band around 1384 cm$^{-1}$ due to the presence of trapped NO$_3^-$ (nitrate) in as prepared samples [30].
4.3.4 Magnetic Analysis (VSM)

The field dependence magnetization of $A_xCo_{1-x}Fe_2O_4$ ($A = Zn, Mg$ and $x = 0.0, 0.5$) samples measured using vibrating sample magnetometer (VSM) at 300 K with an applied field of 10 KOe is shown in Fig. 4.3.4. The substitution of $Co^{2+}$ by $Zn^{2+}$ and $Mg^{2+}$ ions produces a mixed effect on magnetic properties of these ferrites and is reflected in the magnetic hysteresis loop. The hysteresis curve for Zn doped sample is typical S shaped with very low coercivity ($H_c \approx 75.01$ Oe) and retentivity ($M_R \approx 8.12$ emu/gm).

On the other hand $CoFe_2O_4$ represent highest coercivity ($H_c \approx 1202.22$ Oe) and retentivity ($M_R \approx 39.77$ emu/gm), whereas, Mg doped $CoFe_2O_4$ show less coercivity ($H_c \approx 849.98$ Oe) and retentivity ($M_R \approx 25.91$ emu/gm) as compared to pristine $CoFe_2O_4$. The highest coercivity of $CoFe_2O_4$ is attributed to larger magnetocrystalline anisotropy. The contribution to magnetocrystalline anisotropy from $Fe^{3+}$ having five unpaired electrons is different in all the three systems. However the $Zn^{2+}$ and $Mg^{2+}$ ions has no unpaired electrons and leads to zero total electron spin, the $Co^{2+}$ ion have three unpaired electron and have large magnetocrystalline anisotropy due to strong L-S coupling. Furthermore, $CoFe_2O_4$ has the highest Saturation value ($M_s \approx 84.95$ emu/gm) and this saturation value decreases on substitution of $Zn^{2+}$ ($M_s \approx 80.99$ emu/gm) and $Mg^{2+}$ ($M_s \approx 51.09$ emu/gm) ions at Co site.

The saturation value of the present $CoFe_2O_4$ is amongst the highest values reported so far. The $CoFe_2O_4$ prepared by the Layered double hydroxide method reported the maximum $M_s$ value of about 86.1 emu/gm as compared to the same sample prepared by ceramic method and wet chemical method ($M_s \approx 73$) [31].

Fig. 4.3.3.2: FT-IR spectra of $A_xCo_{1-x}Fe_2O_4$ ($A = Zn, Mg$ and $x = 0.0, 0.5$) ferrite samples.
Furthermore, CoFe$_2$O$_4$ synthesized by wet chemical coprecipitation method has the saturation value of 60 emu/gm for 1.3 min digestion time, which was 75% of the corresponding bulk value [32]. This value is slightly less than the same sample prepared by wet chemical method [33]. Moreover, in a series of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) prepared by sol-gel method $M_s$ value increases from 84.5 to 91.6 emu/g. on increasing the Zn concentration up to 40% [34].

![Room temperature magnetic hysteresis loop of $A_x$Co$_{1-x}$Fe$_2$O$_4$ ($A = \text{Zn, Mg}$ and $x = 0.0, 0.5$) ferrite samples.](image)

The difference in the value of ($M_s$) is attributed to the cation distribution in both the lattice sites. As discussed earlier CoFe$_2$O$_4$ forms inverse spinel ferrite with Co$^{2+}$ ions occupying the octahedral (B) site and Fe$^{3+}$ are equally distributed among tetrahedral (A) and octahedral (B) site. On the other hand Zn$^{2+}$ and Mg$^{2+}$ have a site preference for A-site. The replacement of Co$^{2+}$ with non-magnetic Zn$^{2+}$ and Mg$^{2+}$ ions causes a reduction in A-O-B super exchange interaction. This would further disturb some magnetic coupling and lead to an overall reduction in magnetism as to the large magnetic moment of Fe$^{3+}$ ions. The magnetic moment ($\mu_B$)/atom in Bohr magnetron is calculated from expression:

$$\mu_B = \frac{(M \times M_s)}{(N \times \beta)} \quad (4.5)$$

where $M$ is the molecular weight of the sample, $M_s$ is the value of saturation magnetization, $N$ is the Avogadro number, $\beta$ is the conversion factor ($\approx 9.27 \times 10^{-21}$). The values of magnetic moment are 4.46 $\mu_B$, 3.45 $\mu_B$ and 1.98 $\mu_B$ for CoFe$_2$O$_4$, Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ respectively. The substitution of
nonmagnetic Zn\textsuperscript{2+} and Mg\textsuperscript{2+} ions replacing the magnetic ions (Fe\textsuperscript{3+}) might have affected the exchange interaction between A- and B-site, leading to the decrease in magnetic moment. The experimental value CoFe\textsubscript{2}O\textsubscript{4} is much higher than the theoretical value (≈3 \(\mu_B\)) due to contribution from the orbital magnetic moment remaining unquenched by the crystalline field [1].

4.3.5 Dielectric Analysis

Fig. 4.3.5.1 shows the variation of frequency dependence of real and imaginary part of dielectric permittivity. All the three samples exhibit the dielectric dispersion where both real (\(\varepsilon'\)) and imaginary part (\(\varepsilon''\)) decreases as the frequency increases from 1 Hz to 1 MHz. In low frequency region the dielectric constant of Co\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} is much higher than the Co\textsubscript{0.5}Mg\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} and CoFe\textsubscript{2}O\textsubscript{4}. This difference is attributed to space charge polarization owing to inhomogeneous dielectric structure that might be due to porosity, stoichiometry and grain structure. But in the high frequency region, variation of dielectric constant is same for all the three samples. This is because at high region the contribution of dielectric constant mainly arises from electronic and ionic polarizations that are frequency independent.

Furthermore, the higher value of dielectric constant of Co\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} may also be due to the fact that Zn ions might be evaporated from the surface layer due to high sintering temperature and as a result ferrous ions (Fe\textsuperscript{2+}) have been formed. Some of the Fe\textsuperscript{2+} ions have been transformed to Fe\textsuperscript{3+} ions during the sintering process and this generates free electrons, which contribute to the net polarization. The large number of electrons that are generated during transformation process will raise the dielectric constant of the sample. Similar kind of behaviour is also observed in earlier reported data [35].
Moreover, in present system a part from \textit{n}-type charge carrier (\textit{Fe}^{3+}/\textit{Fe}^{2+}), the local displacement of \textit{p}-type (\textit{Co}^{3+}/\textit{Co}^{2+}) charge carrier in direction of external electric field also contributes to net polarization. In view of the fact that mobility of \textit{p}-type carrier is smaller than the \textit{n}-type charge carrier, the contribution to polarization from former is smaller and decreases more rapidly even at lower frequencies than from the later. As a result the net polarization decreases with increase in frequency. Hence, the dielectric constant decreases.

The variation of dielectric loss as a function of frequency for $A_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($A = \text{Zn, Mg and } x = 0.0, 0.5$) samples is shown in Fig. 4.3.5.2. Samples of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Co}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4$ exhibit loss peak according to Debye relaxation theory. This loss peak occurs when the jumping frequency of electron between \textit{Fe}^{2+} and \textit{Fe}^{3+} is equal to the frequency of applied field and the condition $\omega t = 1 (\omega = 2\pi f)$ is satisfied. Similar kind of behaviour is also observed in case of Mn Zn ferrite [36]. The value of the loss tangent is minimum ($\tan(\delta) = 0.04$) for $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Co}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4$ measured at a frequency of 5 kHz at room temperature and is comparable with earlier measured value of Mn-Zn ferrite [36, 37]. Henceforth, $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Co}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4$ are suitable materials for microwave application because of low dielectric loss.

![Fig. 4.3.5.2: Variation of loss tangent of $A_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($A = \text{Zn, Mg and } x = 0.0, 0.5$) ferrite samples with variable frequency.](image)

Fig. 4.3.5.3 shows the variation of ac conductivity of pure and Zn, Mg doped cobalt ferrite samples ($A_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($A = \text{Zn, Mg and } x = 0.0, 0.5$)). The ac conductivity gradually increases as the frequency of applied field increases. At lower frequencies the grain boundaries are more effective than grains in electrical conduction hence the hopping of \textit{Fe}^{2+} and \textit{Fe}^{3+} ions are bound at lower
Substitutional effect on structural, magnetic and dielectric... Chapter 4

frequencies. As the frequency of the applied field increases the conductive grains become more active and promote the conduction mechanism. Cobalt ferrite has two regions of conductivity, the low conductivity region containing Co\(^{2+}\) and Co\(^{3+}\) ions and high conductivity region containing Fe\(^{2+}\) and Fe\(^{3+}\) ions [38].

Fig. 4.3.5.3: Variation of ac conductivity for \(A_xCo_{1-x}Fe_2O_4\) (\(A=Zn, Mg\) and \(x = 0.0, 0.5\)) ferrite samples with logarithmic frequency.

The presence of Cobalt on octahedral site follows the charge exchange mechanism as:

\[
Co^{2+} + Fe^{3+} \leftrightarrow Co^{3+} + Fe^{2+}
\]  

(4.6)

Which, predominantly explain the conduction mechanism in CoFe\(_2\)O\(_4\). The conductivity of Co\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) is high as compared to Co\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) and CoFe\(_2\)O\(_4\) that might be due to the difference in the grain size. The conductivities of polycrystalline material decreases with decreasing grain size. Smaller grains imply large number of insulating grain boundaries and smaller grain-to-grain surface contact area, which act as a barrier to the flow of the electron [39]. The grain size of CoFe\(_2\)O\(_4\) (3.2 \(\mu m\)) is smaller than Co\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) (4.7 \(\mu m\)) and Co\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) (7.4 \(\mu m\)) as concluded from SEM measurement. Hence conductivity is high for Co\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) and low for Co\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) and CoFe\(_2\)O\(_4\).

Another factor that influences the electrical conductivity of the ferrites is the jump length (\(L\)) of the charge carrier. As calculated in above section 4.3.1 the jump length (\(L\)) decreases for Co\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) (\(L_A=3.6165 \text{ Å}, L_B=2.9532 \text{ Å}\)) and Co\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) (\(L_A=3.6034 \text{ Å}, L_B=2.9421 \text{ Å}\)) as compared to CoFe\(_2\)O\(_4\) (\(L_A=3.6178 \text{ Å}, L_B=2.9540 \text{ Å}\)). This suggests that charge carrier require less energy to jump from one cationic site to other and causes an increase in conductivity. Hence the
Substitutional effect on structural, magnetic and dielectric... Chapter 4

conductivity of Mg doped cobalt ferrite is highest as compared to parent and Zn doped cobalt ferrite.

The temperature dependent dielectric constant and loss tangent of pure and Zn, Mg doped cobalt ferrite \( (A_xCo_{1-x}Fe_2O_4 \ (A = Zn, Mg \ and \ x = 0.0, 0.5)) \) samples are shown is shown in Fig. 4.3.5.4 (a). Both dielectric constant and loss tangent enhances with increase of temperature and is attributed to the fact that hopping of charge carrier is thermally activated with increase of temperature causing the increase of dielectric polarization. The variation of dielectric loss tangent \( (\tan \delta) \) with temperature at a frequency of 10 kHz represent a peaking behaviour as shown in the inset of Fig. 4.3.5.4 (a).

![Fig. 4.3.5.4: (a) Temperature dependent dielectric constant of \( A_xCo_{1-x}Fe_2O_4 \ (A = Zn, Mg \ and \ x = 0.0, 0.5) \) samples at 10 KHz. Inset shows the variation of loss tangent \( (\tan \delta) \) with temperature. (b) Variation of dielectric relaxation time \( (\tau) \) with temperature for \( A_xCo_{1-x}Fe_2O_4 \ (A = Zn, Mg \ and \ x = 0.0, 0.5) \) samples](image-url)

The peak is attributed to the resonance effect arise due to the matching of the time period of the applied electric field with those of the corresponding relaxation phenomena. The variation of relaxation time \( (\tau) \) with temperature for \( A_xCo_{1-x}Fe_2O_4 \ (A = Zn, Mg \ and \ x = 0.0, 0.5) \) samples are shown in Fig. 4.3.5.4 (b). It clearly suggests that the temperature dependence of the relaxation time follows the Arrhenius law given by the relation:

\[
\tau = \tau_0 \exp\left(-\frac{E}{k_B T}\right)
\]

where, \( E \) is the activation energy of the relaxation process, \( k_B \) is the Boltzmann constant and \( \tau_0 \) is the maximum relaxation time. It is observed that the relaxation time decreases with the measuring temperature and is attributed to the thermal activation of hopping frequency of electrons between Fe\(^{2+}\) and Fe\(^{3+}\) ions. The values of activation energy \( (E_a) \) obtained from the slope of the fitted curves are found to be 0.81 eV, 0.76 eV and 0.63 eV for CoFe\(_2\)O\(_4\), Co\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) and...
Substitutional effect on structural, magnetic and dielectric... Chapter 4

C0.5Zn0.5Fe2O4 respectively. The activation energy decreases with the Mg and Zn dopant ions. This is in good agreement with the fact that lower activation energy is associated with higher dielectric constant and higher conductivity [40].

Fig 4.3.5.5: Variation of real part of impedance spectra (a) and imaginary part of impedance spectra (b) with variable frequency of as synthesized samples

Fig. 4.3.5.5 represents the variation of real (resistive) and imaginary (reactive) part of impedance as a function of frequency for A0.5Co1-xFe2O4 (A = Zn, Mg and x =0.0, 0.5) samples. The impedance decreases gradually with the increase of frequency. The maximum value of impedance is observed for parent CoFe2O4. In order to distinguish between the grain and grain boundary contribution the Nyquist plot of A0.5Co1-xFe2O4 (A = Zn, Mg and x = 0.0, 0.5) samples were recorded at room temperature and are shown in Fig. 4.3.5.6.

The impedance spectra of CoFe2O4 do not take the shape of the semicircle, but rather represent a straight line with large slope. This shows that grain

Fig. 4.3.5.6: Nyquist-plot of A0.5Co1-xFe2O4 (A= Zn, Mg and x = 0.0, 0.5) ferrite samples.
boundary impedance is out of measurement scale, suggesting the insulating behavior. Whereas, for \( \text{Co}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4 \) and \( \text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \), the slope of the line decreases and curve towards the real \((Z')\) axis. \( \text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) sample represents a flat semicircle at higher frequency and is attributed to electrical conduction by the interior of the grain only, whereas, the impedance spectra of \( \text{Co}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4 \) sample represent two semicircular arcs (shown in the inset of Fig 4.3.5.6).

The intercept of semicircle with \( Z' \) at lower frequency represents the sum of resistance of grain and grain boundaries, while the intercept at higher frequency represents the resistance of grain only. The diameter of each semicircle corresponds to resistance of the grain [41]. The diameter of the semicircle changes with different doping elements. The diameter first reduces with substitution of \( \text{Zn}^{2+} \) ion and further with \( \text{Mg}^{2+} \) ions in \( \text{CoFe}_2\text{O}_4 \) indicating a change in grain interior resistance.

The variation of real and imaginary part of electrical modulus as a function of frequency is shown in Fig. 4.3.5.7. The observed values of stretched exponent parameter \( \beta \) for all the samples is less than unity and are found to be 0.86, 0.79, 0.68 for \( \text{CoFe}_2\text{O}_4 \), \( \text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) and \( \text{Co}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4 \) respectively. The value of \( \beta \) helps to decide whether the relaxations present in the materials are of Debye or non-Debye type. For an ideal dielectric for which the dipole–dipole interaction is negligible, the value of \( \beta \) is equal to unity. But the value of \( \beta \) is always less than unity for such a system in which the dipole–dipole interaction is significant. The observed values of stretched exponent parameter confirm the non-Debye type of dielectric relaxations.

![Fig. 4.3.5.7: Frequency dependent real part of modulus (a) and imaginary part of modulus (b) of \( A_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4 \) (\( A = \text{Zn, Mg} \) and \( x = 0.0, 0.5 \)) ferrite samples.](image-url)
4.4 Conclusions

All the polycrystalline ferrite $A_xCo_{1-x}Fe_2O_4$ ($A = Zn, Mg$ and $x = 0.0, 0.5$) samples were successfully prepared by chemical co-precipitation method. The effect of Zn and Mg doping on structural, magnetic and dielectric properties of CoFe$_2$O$_4$ has been studied. X-ray diffraction confirms the formation of single-phase crystalline structure without any trace of impurity. All the three samples fitted with Rietveld refinement using FullPROOF program revealed the existence of cubic structure (space group $Fd\bar{3}m$). A slight reduction in the lattice parameter of Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ has been observed as compared to pure CoFe$_2$O$_4$ and Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrite. The value of theoretical lattice parameter and the lattice parameter calculated from Rietveld refinement are found to be in good agreement. The jump lengths of CoFe$_2$O$_4$ and Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ are quite similar to each other. Whereas, the jump lengths of Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ slightly reduce as compared to other two. Scanning electron micrograph reveals that the ferrite samples sintered at 1250° C for 24 h results in greater densification with grain sizes of about 3.2 μm, 4.7 μm and 7.4 μm for CoFe$_2$O$_4$, Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ respectively.

Evolution of Raman spectra reveals the five active phonon modes for all the three samples. Due to the cation distribution at both the sites, a doublet like feature has been observed for $A_{1g}$ mode in all the three samples. Red shift in Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ is attributed to higher atomic mass of Zn as compared to Co; whereas blue shift in Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ is due to lower mass of Mg. The line width of phonon modes are found to increase with Zn and Mg doping in CoFe$_2$O$_4$. The absorption band at about 500-600 cm$^{-1}$ in the IR spectra corresponds to the vibration of Fe$^{3+}$-O$^{2-}$ bond related to tetrahedral (A) site with some traces of NO$_3$ peak and hydroxyl group. Magnetic study concludes that saturation magnetization value ($M_s$) is maximum for CoFe$_2$O$_4$. This saturation value decreases on substitution of Zn$^{2+}$ and Mg$^{2+}$ ions at Co site.

The dielectric dispersion with frequency was observed and successfully explained on the basis of hopping mechanism. The lower value of dielectric loss for Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and Co$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ makes them suitable material for microwave application. The observed ac conductivity is appropriate in the light of electron hop- ping between Fe$^{2+}$ and Fe$^{3+}$ ions. Temperature dependent dielectric constant and loss tangent of all the three samples shows an increasing trend with increasing temperature. However, the activation energy decreases with the substitution of Mg and Zn ions in parent CoFe$_2$O$_4$. The impedance spectra suggest a grain interior contribution in the conduction process. The electrical modulus study reveals the presence of non-Debye type of dielectric relaxation in present system with decrease in stretched exponent parameter $\beta$ with Zn and Mg doping.
References


