CHAPTER 3

Structural phase stability and physical properties in

\( \text{Co}_2\text{FeO}_4 \) ferrite

### 3.1 Introduction

\( \text{Fe}_3\text{O}_4 \) (magnetite) derived compounds (\( \text{Fe}_{3-x}\text{M}_x\text{O}_4 \): \( \text{M} \) is magnetic or non-magnetic-\( \text{Co, Mn, Zn, etc.} \)) [1-3] have drawn a lot of research interests for their exhibition of many unusual physical properties [4-6], including high magnetic moment, magneto-resistance, and half metallic behavior. \( \text{Fe}_{3-x}\text{Co}_x\text{O}_4 \) could be more attractive due to typical anisotropy character of \( \text{Co} \) ions. Most of the reports [3, 7, 8] are limited to the \( \text{Fe} \) rich regions (\( x \leq 1 \)) of \( \text{Fe}_{3-x}\text{Co}_x\text{O}_4 \) series. Few reports [9] are only available for \( \text{Co} \) rich regions (\( x \geq 2 \)), although \( \text{Co} \)-rich regions have shown potential applications in chemical sensors [10, 11], catalytic activity [12] and photo-conductive materials [13-15]. \( \text{Co} \) rich spinels are also interesting in view of the diverse magnetic properties (ferrimagnet, antiferromagnet and antiferromagnetic spin glass) and magneto-transport phenomena (colossal magnetoresistance) in \( \text{Co}_x\text{Mn}_{3-x}\text{O}_4 \) (0 <\( x <3 \)) spinel oxides [16, 17]. This thesis work will focus on the study of \( \text{Co}_2\text{FeO}_4 \) composition. The probable reason of limited experimental work on \( \text{Co}_2\text{FeO}_4 \) could be the spinel phase stability over a small temperature range about 900°C [17, 18]. The distribution of cations in \( \text{Co}_2\text{FeO}_4 \) is sensitive on the preparation techniques [19-22]. The presence of multi valence cations in \( \text{B} \) sublattice may attribute to a good magnetic semiconducting property in \( \text{Co}_2\text{FeO}_4 \), although experimental results [15, 23-25] indicated an increase of band gap energy (0.14 eV to 1.1 eV) with the increase of \( \text{Co} \) content in \( \text{Fe}_{3-x}\text{Co}_x\text{O}_4 \). Most of the reports prepared \( \text{Co}_2\text{FeO}_4 \) using different chemical methods, e.g., coprecipitation [20, 26] and combustion reaction [27]. The fact is that physical properties may depend upon the preparation technique as well as particle morphology (size, shape) of the sample [28]. However, limited information on this aspect of \( \text{Co}_2\text{FeO}_4 \) can be obtained in literature due to lack of sufficient experimental work. Here, we emphasize on the understanding of structural phase stabilization, magnetic, dielectric and electric properties of mechanical alloyed \( \text{Co}_2\text{FeO}_4 \) nanoparticles.
3.2 Sample preparation

Stoichiometric amounts of high purity (>99.5) Fe$_2$O$_3$ and Co$_3$O$_4$ were mixed to obtain the required compound. The mixture was ground using mortar and pestle for 2 hours. The mixed powder was mechanical alloyed using Fritsch Planetary Micro Mill “P7”. The milling was carried out in a 50 ml silicon nitride bowl in atmospheric conditions. The mass ratio of the ball (10 mm Silicon Nitride and 5 mm Tungsten Carbide) and material was maintained to 4:1. The milling was continued at rotational speed 300 rpm. After 100 hours milling, up to 100 hours with intermediate stopping for proper mixing and monitoring the phase evolution of the alloyed compound, the alloyed powder was made into pellets of several batches. Each pellet was annealed at different temperatures in the range 700°C to 1000°C. The annealed samples have been denoted as SX, where X = 70, 80, 86, 90, 95 and 100 for annealing temperature (T$_{AN}$) at 700°C (3 hours), 800°C (6 hours), 860°C (12 hours), 900°C (12 hours), 950°C (12 hours) and 1000°C (3 hours), respectively. Moreover, there is no significant change in the XRD pattern when the mechanical alloyed sample is annealed at a particular temperature, e.g., 800°C and 1000°C, for annealing time 3 hours, 6 hours and 12 hours. The samples annealed at below and above of 900-950°C showed the splitting of two spinel phases.

3.3 Result and discussion

3.3.1 Structure and surface morphology

The X-ray diffraction (XRD) pattern of Co$_2$FeO$_4$ samples are shown in Fig. 3.1. The XRD pattern of 100 hours milled sample (data not shown) is largely dominated by spinel phase, along with an extra peak at about 2θ~33°. This extra peak is consistent with the most intensity peak (104) of the rhombohedral crystal structure with the space group R3C, arising from a small fraction of unreacted α-Fe$_2$O$_3$. There is no trace of peak lines from α-Fe$_2$O$_3$ phase after annealing the alloyed sample at ≥ 860°C temperatures. The XRD peaks of the annealed samples, except 900°C and 950°C, are splitted into two components. We are confirmed, from the comparative peak positions of XRD pattern of our samples and standard spinel compounds (Co$_3$O$_4$, CoFe$_2$O$_4$), that additional peak lines are not contributed due to Cu Kα$_2$ radiations. In fact, the splitted peaks are matching to the pattern of two cubic spinel phases with a shift in 2θ values.
Fig. 3.1 XRD pattern of the annealed samples in the range 10 – 90° (left-hand side) and in the range 34 – 37.5° (right-hand side) to indicate the splitting of 311 peak at $2\theta_1$ and $2\theta_2$ positions.

The splitting of XRD peaks is noted in Fig. 3.1 (left hand side: $2\theta$ range 10 to 90°) and clearly shown for (311) XRD peak alone in the right hand side of Fig. 3.1. The peak positions at higher and lower $2\theta$ values are denoted at $2\theta_2$ and $2\theta_1$, respectively. As the annealing temperature increases from 700°C to 1000°C, the peaks at $2\theta_1$ and $2\theta_2$ are coming closer to each other and there is no splitting at 900°C (S90) sample, suggesting a single phased compound. Although (311) XRD peak is not clearly spitted for 950°C (S95) sample (i.e., the
sample is appeared to be in single phase), but there is a tendency of minor splitting in other XRD lines of 950°C sample in comparison with 900°C sample. This indicates that a minor secondary phase may coexist at 950°C. The peaks correspond to 2θ₁ and 2θ₂ are again well separated for T_{AN} 1000°C, indicating the reappearance of phase separation in the material. The results are consistent with earlier reports [18, 19] that Co₂FeO₄ is stabilized into a single cubic spinel phase only at about 900°C (S90), although preparation technique of the reported works is completely different from mechanical alloying. Hence, the structural phase instability in the present material outside the 900-950°C regime is not due to the insufficient diffusion at lower temperature or evaporation of some elements at higher temperature, but due to intrinsic chemical stability of the material.

The lattice parameter was calculated by matching the XRD peaks at 2θ₁ and 2θ₂ separately with cubic spinel structure, considering the coexistence of two spinel phases in the pattern. The lattice parameter corresponds to 2θ₁ and 2θ₂ are denoted as a₁ and a₂, respectively. In Fig. 3.2 (a), the lattice parameter a₁ decreases as the annealing temperature increases from 700 to 900°C, unlike the increase of a₂. Both (a₁ and a₂) are coinciding for 900°C (S90) sample. In the absence of clear splitting for the 950°C (S95) sample, we have fitted the spectrum assuming the single phase. The lattice parameter of 950°C sample is little bit higher in comparison with 900°C sample. The lattice parameters a₁ and a₂, again, separated for the 1000°C sample with a₁ higher than a₂. The calculated lattice parameter a (~8.24 Å) for

![Fig. 3.2 Lattice parameters a₁ and a₂ and % of (311) peak height at 2θ₁ and 2θ₂ positions of annealed samples are shown in (a) and (b), respectively.]

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the 900°C sample is in good agreement with theoretical calculation ($a = 8.27$ Å) [9] and experimental work ($a = 8.24$ Å) [21]. The lattice parameter for single phased $\text{Co}_3\text{O}_4$ and $\text{CoFe}_2\text{O}_4$ is found ~ 8.082 Å and 8.40 Å, respectively. On the other hand, $a_1$ and $a_2$ are ~ 8.37 Å and 8.13 Å for S70 sample and ~ 8.31 Å and 8.16 Å for S100 sample. In between, the system stabilizes to a single phased cubic spinel structure of $\text{Co}_2\text{FeO}_4$ with $a$ ~8.24 Å. We suggest that $a_1$ (corresponds to peaks at $2\theta_1$) comes from Fe-rich cubic spinel structure and $a_2$ (corresponds to peaks at $2\theta_2$) comes from Co-rich cubic spinel structure. We have attempted to estimate the fraction of coexisting two phases from the relative peak heights at $2\theta_1$ and $2\theta_2$ positions, assuming that the addition of two peak heights will contribute to the total peak height of single phased cubic spinel structure. Fig. 3.2(b) shows the % height of splitted peaks at $2\theta_1$ and $2\theta_2$ with respect to (311), (004) and (333) peaks of single phased cubic spinel structure (S90 sample). We observed that Fe-rich phase increases from ~60% (S70) to 100% (S90 and S95) by decreasing the Co-rich phase from ~40% to 0%. For S100 sample, the Co-rich phase increases by decreasing the Fe-rich phase. The change of relative peak heights of the two phases with annealing temperature is nearly same for all the three peaks (Fig. 3.2b).

Fig. 3.3 SEM pictures (in a–c) of S80, S90 and S100 samples and corresponding EDX spectrum (in d–f).
The grain size (in Table 3.1) usually increased (∼25 nm to 45 nm) with annealing temperatures. SEM pictures of selected samples (Fig. 3.3 (a-c)) also indicated the increase of particle size with thermal annealing. The EDX spectrum of different samples in Fig. 3.3 (d-f) indicated the presence of Fe, Co and O as the major elements, along with a minor trace of silicon (Si) and Tungsten (W). The chemical inhomogeneity at different points in the EDX spectrum is noted for annealed samples, except S90 sample (Fig. 3e). The Co and Fe atoms are almost homogeneously distributed over the selected zone of S90 sample and the average atomic ratio (Co:Fe~1.96:1) is close to the expected value (2:1).

3.3.2 Magnetic properties

3.3.2.1 Temperature dependence of magnetization

Temperature (T) dependence of dc magnetization at 1 kOe is shown in Fig. 3.4(a-e). The magnetic irreversibility between MFC and MZFC is seen for all the samples. The mixed ferrimagnetic phase of the samples, except S90, is reflected in the magnetization plots. The paramagnetic to ferrimagnetic ordering temperature (\(T_{C1}\)) of one phase is determined from the inflection point of MZFC curves. The irreversibility between MFC and MZFC occurred at a temperature higher than \(T_{C1}\). We define the irreversibility point as the paramagnetic to ferrimagnetic transition temperature (\(T_{C2}\)) of the second ferrimagnetic phase (\(T_{C2} > T_{C1}\)). The coexistence of two magnetic phases is also indicated by two distinct curves in the MFC(T) data. The MFC curves continued to increase with decreasing the temperature below irreversibility point, but a change of slope is marked near to \(T_{C1}\) of the sample.

The magnetic irreversibility occurs at \(T \leq 450\) K for S90 sample and there is no change of slope in MFC (T) curve of the sample. The \(T_{C1}\) of S90 sample ∼ 453 K, determined from the inflection point of MZFC(T), is consistent with the reported value ∼ 450 K of single phased Co\(_2\)FeO\(_4\) [19]. From magnetization measurement using high temperature oven in Argon gas atmosphere, we noted that MZFC at 1k Oe exhibited blocking behavior below the temperature \(T_B\) (∼ 420 K for S80, ∼ 360 K for S86 and ∼ 400 K for S100 samples, respectively).
Fig. 3.4 MZFC and MFC vs T for S80, S86, S90, S95 and S100 samples (in a–e), measured at 1 k Oe. $T_{C1}$, $T_{C2}$ and $T_B$ are defined in text.

The magnetization of the samples at 1 k Oe using low temperature cryostat is nearly consistent with data using high temperature oven and the data at different fields are shown in Fig.3.5. We noted exception only for S100 sample that showed magnetic blocking at relatively lower temperature in compare with 1 k Oe data using high temperature oven. Fig. 3.5 (a-c) shows that $T_B$ of the samples is reduced when the applied magnetic field increases. The blocking of magnetization becomes very sharp with the increase of applied field and it can be attributed to the rotation of magnetic domains along the local anisotropy axis. Field dependence of $T_B$ for different samples is shown in Fig. 3.5 (d).
Fig. 3.5 (a-c) temperature dependence of magnetization for S86, S90 and S100 samples at different magnetic fields, (d) $T_B$ vs. applied magnetic field for the samples.

### 3.3.2.2 Field dependence of magnetization

Fig. 3.6 (a) shows the field ($H$) dependence of magnetization ($M$) curve at 300 K. The magnetization of the samples, after rapid increase within 5 k Oe, is tending to saturate at higher magnetic field. The feature suggests a typical long ranged ferrimagnetic character of the samples irrespective of structural phase stability. The spontaneous magnetization ($M_S$) at 300 K (in Table 3.1) shows a decreasing trend with the increase of $T_AN$ from 800°C to 900°C. After attaining the minimum value for S90 sample, the $M_S$ value again increases with $T_AN$. The variation of $M_S$ with $T_AN$ shows a close relation to the variation of lattice parameter $a_I$ (due to Fe rich spinel phase). The calculated magnetic moment 16 emu/g (~0.68 $\mu_B$ per formula unit of Co$_2$FeO$_4$) for S90 sample at 300 K is comparable to the reported value (0.70 $\mu_B$) for single phased compound [19]. The magnetic moment of S80 and S100 samples ~1.0 $\mu_B$ per formula unit of Co$_2$FeO$_4$ is well below of the magnetic moment ~4.2 $\mu_B$ per formula...
Fig. 3.6 Field dependence of magnetization at 300 K (in a). The M–H loops of the samples are shown in b–f.

unit of CoFe$_2$O$_4$. On the other hand, higher Curie temperature ($T_{C2}$) of the bi-phase samples, e.g., ~752 K for S80 and ~772 K for S100, are close to the Curie temperature ($T_C$ ~785 K) of single phase CoFe$_2$O$_4$ [29]. This means the ferrimagnetic phase with Curie temperature $T_{C2}$ is associated with the phase that may not be due to typical CoFe$_2$O$_4$, but definitely due to a Fe-rich spinel phase coexisting with Co-rich (low magnetic moment) phase in the compound.
The data in Fig. 3.6 (b-f) are shown within \( H = \pm 7 \) kOe for clarity of the feature. It is interesting to note that M-H loop for single phased (S90 and S95 samples) is more symmetric with small hysteresis loss in comparison with other annealed samples. Such interesting magnetic feature clearly reflects the undergoing competitive spin order of two ferrimagnetic domains, arising from the coexistence of two different type cubic spinel phases in the bi-phased samples. The coercivity (\( H_C \)) and remanent magnetization (\( M_R \)), in Table 3.1, show similar variation with \( T_{AN} \), except \( H_C \) and \( M_R \) attained minimum value for S95 and S90 samples, respectively. Small increase of \( M_R \) in S86 sample compared to S80 sample is most probably related to the more asymmetric shape of the M-H loop in S86 sample. \( M_R/M_S \) ratio is \( \sim 0.42, 0.55, 0.46, 0.40 \) and 0.44 for S80, S86, S90, S95 and S100 samples, respectively.

Fig. 3.7 Field dependence of \( dM/dH \) of the samples at 300 K. The separation of the peaks is represented by the field \( 2H_m \).
The variation of $dM/dH$ with applied magnetic field (Fig. 3.7) showed peaks, which are almost symmetric about the $H = 0$ axis. The peaks are separated by magnetic field $2H_m$, as shown for sample S80. It may be noted (Table 3.1) that the peak position at $H_m$, i.e., the inflection point in M-H curve, is very close to the coercivity ($H_C$) of the samples, except S86 sample that has shown more asymmetric M-H loop. We noted that the initial susceptibility $(dM/dH)_{H\rightarrow 0}$ of the sample is nearly half of the $dM/dH$ peak height at $H_m$, i.e, at the inflection point of the M-H curves. The peaks are comparatively narrowed for S90 and S95 samples. This, further, indicates that ferrimagnetic domains formed a better homogeneous structure in the temperature range 900-950°C and formed the single phased character of the compound.

Table 3.1. Grain size, Curie temperatures ($T_{C1}(K)$ and $T_{C2}(K)$), blocking temperature ($T_B(K)$), Spontaneous magnetization ($M_S$), coercivity ($H_C$), remanent magnetization ($M_R$) and critical field ($H_m$) of Co$_2$FeO$_4$ samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain Size (nm)</th>
<th>$T_{C1}$ (K)</th>
<th>$T_{C2}$ (K)</th>
<th>$T_B$ (K)</th>
<th>$M_S$ (emu/g)</th>
<th>$H_C$ (Oe)</th>
<th>$M_R$ (emu/g)</th>
<th>$H_m$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S80</td>
<td>25</td>
<td>645</td>
<td>752</td>
<td>423</td>
<td>23.5</td>
<td>696</td>
<td>9.85</td>
<td>700</td>
</tr>
<tr>
<td>S86</td>
<td>29</td>
<td>555</td>
<td>750</td>
<td>358</td>
<td>19</td>
<td>540</td>
<td>10.53</td>
<td>415</td>
</tr>
<tr>
<td>S90</td>
<td>31</td>
<td>453</td>
<td>--</td>
<td>--</td>
<td>19</td>
<td>280</td>
<td>7.28</td>
<td>300</td>
</tr>
<tr>
<td>S95</td>
<td>36</td>
<td>449</td>
<td>560</td>
<td>--</td>
<td>21.6</td>
<td>125</td>
<td>8.57</td>
<td>130</td>
</tr>
<tr>
<td>S100</td>
<td>42</td>
<td>581</td>
<td>772</td>
<td>396</td>
<td>22</td>
<td>430</td>
<td>9.75</td>
<td>460</td>
</tr>
</tbody>
</table>

### 3.3.3 Dielectric properties

#### 3.3.3.1 AC conductivity

Fig. 3.8 (a-d) shows the frequency ($\nu$) dependent real part ($\sigma'$) of the ac conductivity in the temperature range 273 K - 473 K with interval 10 K for S86, S90, S95 and S100 samples. The log-log plot of $\sigma'(\nu)$ shows three distinct regimes and indicated for sample S95. In regime 1, $\sigma'(\nu)$ is nearly frequency independent. In regime 2, $\sigma'(\nu)$ has increased with $\nu$. In regime 3, $\sigma'(\nu)$ is slower than the regime 2, suggesting a different kind of response of the bound charge carriers at higher frequencies. Regimes 1, 2 and 3 of ($\sigma'$) shifted to higher frequencies with increasing measurement temperature and above 450 K, ($\sigma'$) regime 3 is not visible. The conductivity of the single phased sample S90 is lower than two phased samples.
Fig. 3.8 (a-d) Log-log scale plot of real part of ac conductivity with frequency at different measurement temperatures for S86, S90, S95 and S100 samples.

To understand the ac conductivity dynamics, we write $\sigma'(\nu) = \sigma'_{dc}(T) + \sigma'(T,\nu)$. $\sigma_{dc}(T)$, the dc limit of $\sigma'(\nu)$, has been estimated by extrapolating the regime 1 at $\nu \to 0$ limit. $\sigma_{dc}$ of the samples has increased with measurement temperature for each samples and also with increasing the annealing temperature of the samples except S90. The values of $\sigma_{dc}$ at 303 K and 473 K are tabulated in Table 3.2. According to Jonscher power law [30], the frequency activated part [$\sigma'(T,\nu)$] is written $\sigma'(T,\nu) = \alpha T\nu^n$. Here, $\alpha(T)$ is the temperature dependent parameter and $n$ is the frequency exponent. For regime 2, the obtained values of $n$ ($n_1$) are in the range 0.66 to 0.96 for all samples. For regime 3, the exponent $n$ ($n_2$) is in the range 0.4 to 0.7. The range of exponents suggests small polaron hopping is dominating in the mechanism of electrical conductivity.
3.3.3.2 Complex impedance

Fig. 3.9 (a) shows the complex impedance ($Z''$ vs. $Z'$) plot of S100 sample at different temperatures. The solid lines represent the semi-circle fit to the experimental data (open symbol) and $R_{gb}$ indicates grain boundary contribution of resistance. Inset of Fig. 3.9 (a) shows the signature of second semicircle due to contribution from grain ($R_g$). All samples showed two semicircles at low temperature. By incorporating the dimension of the samples, we calculated resistivity from grain ($\rho_g$) and grain boundary ($\rho_{gb}$). As temperature increases, the resistivity ($\rho_g$) due to grains is disappeared whereas grain boundary contribution ($\rho_{gb}$) predominates. Both $\rho_g$ and $\rho_{gb}$ are monotonically decreased with the increase of temperature. This suggests the nature of semi-conducting behavior. The impedance analysis confirmed the highest $\rho_g$ and $\rho_{gb}$ for S90 sample in comparison with other samples. Fig. 3.9 (b) shows that thermal activated $\rho_g$ and $\rho_{gb}$ can be fitted by Arrhenius law: $\rho(T) = \rho_0 \exp(E_a/k_B T)$. The samples S86 and S90 showed two slopes for $\rho_{gb}$ (T). This indicates there are two different thermally activated processes at grain boundaries of these samples. We noted a different activated conductivity regime for the S90 sample with higher activation energy ($E_a \sim 1.02$ eV for $g_b$) at measurement temperature $> 413$ K. The activation energy ($E_a$) initially increased (0.95 eV and 0.69 eV for grain boundary and grain) up to sample S90 thereafter decreased.

![Complex impedance spectrum](image)

**Fig. 3.9 (a)** Complex impedance spectrum of sample S100 at different temperatures. Inset shows the eye view of the second semi-circle arc with fitted semicircle. (b) shows the Arrhenius plot and fit lines of the $\rho_g(T)$ and $\rho_{gb}(T)$ for selected samples.
with the increase of annealing temperature of the alloyed sample. The $E_a$ of grain boundary is larger than grain and shown in Table 3.2 for all samples.

### 3.3.3.3 Dielectric constant/relative permittivity

The dielectric constant (real: $\varepsilon'$, imaginary: $\varepsilon''$, total: $\varepsilon$) as a function of frequency is shown in Fig.3.10 for samples S90 and S95. Real part ($\varepsilon'$) rapidly decreases with increase of frequency in lower frequency regime. This is followed by a slow decrease at higher frequency regime. It may be noted that $\varepsilon$ at lower frequency regime is dominated by $\varepsilon''$. This is due to Maxwell-Wagner type interfacial polarization effect at the grain boundaries. $\varepsilon$ of the samples increases with measurement temperature due to thermal activated orientation of the electric moments. The values of $\varepsilon'$ at 1 kHz at measurement temperature 473 K is shown in Table 3.2. Interestingly, $\varepsilon'$ is the highest for the single phased S90 sample.

![Fig 3.10 Frequency dependent dielectric constant at different measurement temperature for the samples S90 (a-c) and S95 (d-f).](image)

Fig 3.10 Frequency dependent dielectric constant at different measurement temperature for the samples S90 (a-c) and S95 (d-f).
Table. 3.2 The values of conductivity ($\sigma$ (S/cm)), dielectric constant, dielectric loss ($\tan \delta$), activation energy ($E_a$) of grain boundary (gb) and grain (g) from impedance and modulus spectrum.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma'$ (S/cm)</th>
<th>1k Hz at 473K</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$303 K \times 10^{-10}$</td>
<td>$473 K \times 10^6$</td>
<td>$\varepsilon'$</td>
</tr>
<tr>
<td>S86</td>
<td>1.008</td>
<td>0.242</td>
<td>37.87</td>
</tr>
<tr>
<td>S90</td>
<td>0.224</td>
<td>0.218</td>
<td>99.48</td>
</tr>
<tr>
<td>S95</td>
<td>9.412</td>
<td>2.50</td>
<td>65.93</td>
</tr>
<tr>
<td>S100</td>
<td>36.67</td>
<td>4.56</td>
<td>116.1</td>
</tr>
</tbody>
</table>

3.3.3.4 Dielectric loss

Fig. 3.11 (a-d) shows the variation of dielectric loss ($\tan \delta$) for S86, S90, S95 and S100 samples, respectively. The dielectric loss decrease with the increase of applied frequency and the decrease is rapid at low frequencies, followed by a peak and remains constant at higher frequencies. As the temperature increases the dielectric loss curve shifted to higher frequency. The remarkable observation is that the loss peak height is not same for all measured samples except single phased sample S90.

Fig 3.11 (a-d) Dielectric loss functions of frequency and selected temperature for S86, S90, S95 and S100 samples.
At room temperature dielectric loss of all the samples is very low (0-0.4) over a wide frequency range. This suggests that these samples may have potential applications in audio, radio frequencies. Little bit higher dielectric loss (>1) at lower frequency can be explained by Maxwell-Wagner interfacial type of polarization effect [31, 32]. Dielectric loss of the single phased sample S90 is less than bi-phased samples.

**3.3.3.5 Electrical modulus**

Fig. 3.12 shows the frequency dependent real ($M'$) and imaginary ($M''$) part of the electrical modulus (M) for samples S86 (a-b) and S100 (c-d). All samples showed two-step feature in $M'(\nu)$ and associated two peaks in $M''(\nu)$ at lower and higher frequency side. Two relaxation peaks are not in equal magnitude except for sample S90. Two relaxation peaks in $M''$ moves towards higher frequencies during increase of the measurement temperature. These peaks indicate the transition from long range to short range mobility with increase in the frequency [33-35].

![Graph showing frequency dependent real and imaginary parts of electrical modulus](image)

**Fig 3.12** Real and imaginary electrical modulus spectra of samples S86 (a-b) and S100 (c-d) function of frequency and selected temperature.
The lower frequency side relaxation peak of $M''(\nu)$ is fitted for each sample using Kohlraush-William-Watt (KWW) stretched exponential equation (2.13). The continuous lines in Fig. 3.13 (a) are the fit data, whereas symbol corresponds to the experimental data. The obtained $\beta$ values are in the range of 0.65 to 0.9. The relaxation time $\tau$ resulting from $M''$ at low and high frequency peaks corresponds to dielectric relaxation from grain boundary and grain and plotted against inverse of temperature according to Arrhenius law in Fig. 3.13 (b). The activation energies of the grain and grain boundary contributions were calculated from the slopes of the plots and values are given in Table 3.2.

![Graph showing frequency dependent imaginary part of the electrical modulus at selected temperatures for S95 sample and continuous curves are showed fit data.](image)

![Graph showing variation of relaxation time ($\tau$) with temperature of grain and grain boundary for S86, S90, S95 and S100 samples.](image)

Fig. 3.13 (a) Frequency dependent imaginary part of the electrical modulus at selected temperatures for S95 sample and continuous curves are showed fit data. Fig. 3.13 (b) shows the variation of relaxation time ($\tau$) with temperature of grain and grain boundary for S86, S90, S95 and S100 samples. Solid lines show the least-square fit data.

A comparative plot of electrical, dielectric and magnetic parameters is shown in Fig. 3.14. The activation energy of grain boundary and grain is larger for single phased S90 sample than other annealed samples. The dielectric loss, spontaneous magnetization and dc limit of ac conductivity for S90 sample at 303 showed lower values than other annealed samples. It is clearly seen that all the physical parameters are not changing monotonically with increasing particle size of the compound Co$_2$FeO$_4$. The structural phase stability of the samples played a crucial role in changing the physical properties.
Fig. 3.14 A comparative plot of activation energies ($E_a$) of grain boundary and grain from impedance and modulus formalism, dielectric loss at 303 with 1 M Hz, spontaneous magnetization ($M_S$), dc limit of ac conductivity at 303 K for different annealed samples.

We understand that the decrease of conductivity in S90 sample may be due to the reducing number of $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ pairs and increasing number of $\text{Co}^{2+} \leftrightarrow \text{Co}^{3+}$ ion pairs (less magnetic in comparison with $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ pairs) in octahedral sites. This also explains the lowest magnetization in single phased S90 sample. The fact is that mobility of hole in the path ($\text{Co}^{2+} \leftrightarrow \text{Co}^{3+}$) is small compare with electron mobility in the path ($\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$). The electron
hopping between Fe$^{2+}$ and Fe$^{3+}$ ions (n type) and hole hopping between Co$^{3+}$ and Co$^{2+}$ (p-type) on B-sites are the prominent source for the creation of electric dipoles and dielectric polarization in ferrite. In is ferrite, the dielectric constant ($\epsilon'$) of S100 is higher than other annealed samples. Since grain boundaries are more resistive, the occurrence of electron exchange between Fe$^{3+}$ ⇔ Fe$^{2+}$ ions in B site requires more energy and showed high dielectric loss in low frequency region. On the other hand, exchange of electrons between Fe$^{3+}$ ⇔ Fe$^{2+}$ ions in B site requires less energy for highly conductive grains. This gives low dielectric loss at higher frequency. In higher frequency side, the ions are spatially confined to their potential well and can execute only localized motion.

### 3.3.4 Conclusions

- The present work successfully applied the novel technique of mechanical alloying to synthesize Co$_2$FeO$_4$ spinel oxide with subsequent annealing. The structural phase evolution of the synthesized compound with annealing temperature is consistent with earlier reports, based on solid state and chemical routed samples.
- The experimental results suggest that crystal structure of the samples, except 900$^0$C annealed sample, is separated into the structure of two cubic spinel phase, consisting of Co-rich and Fe-rich phase. The physical picture that might occur in this system is that Co atoms are not uniformly diffusing into the Fe lattice positions at the temperatures differing from 900$^0$C, resulting in the separation of Co-rich and Fe-rich cubic spinel structures in the same material.
- The blocking of MZFC below $T_B$ is related to the nano-sized grains of the samples. Magnetic blocking of the nano-sized grains is strongly affected by the phase stability of cubic spinel structure; rather than a simple grain size effect.
- The high temperature study indicated that the samples are ferrimagnet, irrespective of structural phase stability. The co-existence of two ferrimagnetic phases in the samples, except 900$^0$C, have confirmed the structural phase separation and a strong correlation between cubic spinel structure and magnetism in Co$_2$FeO$_4$ spinel oxide.
Analysis of dielectric data suggests that the samples are electrically heterogeneous at low resistive grains and high resistive grain boundaries. The single phased S90 sample showed lowest conductivity and S100 sample showed highest conductivity among the annealed samples. The electrical modulus shows the non-debye relaxation behavior for all samples.

Finally, magnetic, electric and dielectric properties are strongly correlated to the structural phase instability of the material.

References