Study on AC permeability and permittivity of manganese doped cobalt ferrite nanoparticles

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Abstract
This paper reports the significances of the negative real part of ac permeability and the transition of real part of ac permittivity. The paper also identifies the $\mu$ negative media and double negative media in the frequency range 3–120 MHz. The eddy current loss calculated from the measured complex permeability is found to diminish with increasing frequency which is an important factor to be considered for high frequency applications of these materials.

1. Introduction
Cobalt ferrites are reported to be the best example of hard ferrite materials because of their excellent chemical stability, mechanical hardness, reasonable saturation magnetization and high magneto-crystalline anisotropy [1]. They are now being used in high-density recording media, ferro-fluids, magnetic resonance imaging (MRI), biomedical diagnostics, radio frequency hyperthermia and drug delivery as reported elsewhere in literatures [1–12]. Cobalt ferrite is of inverse spinel structure with basic formula $B (AB) O_4$ where relatively larger oxygen ions ($O^2_\parallel$) form cubic closed pack (ccp) structure. It’s tetrahedral (A) and octahedral (B) sites formed by the oxygen ions ($O^2_\perp$) are occupied by metal ions ($Fe^{3+}$ and $Co^{3+}$ ions). The A site is occupied by $Fe^{3+}$ ions while the B site is occupied by $Fe^{3+}$ and $Co^{3+}$ ions in equal proportion. Recently, cobalt ferrites doped with metallic ions have attracted renewed attention for sensors and high frequency device applications through optimizing its electrical and magnetic properties. These applications are mostly based on tailoring the structural, magnetic and electrical properties through tuning the substitution level of dopants, sintering temperature and their particle sizes. Numerous investigations have been performed on structural, magnetic and electric properties substituting Co or Fe by metallic ions in $CoFe_2O_4$. It is found that the dielectric properties are strongly affected by the cation redistributions with the increase of Mn concentration in $Co_{1-x}Mn_xFe_2O_4$ improving their electro-magnetic resistive properties which is suitable for their high frequency applications [8]. The ac electrical properties are also reported to be strongly frequency dependent [9]. The frequency dependent impedance property of $CoMn_xFe_{2-x}O_4$ makes it a potential candidate for use in frequency band filter design [10]. The variation of electromagnetic parameters (complex permittivity $\varepsilon'' = \varepsilon' - j\varepsilon''$ and complex permeability $\mu'' = \mu' - j\mu''$) and microwave absorption properties is reported over the X-band frequency range with varying composition but there is no data on its behavior in the high frequency regime. Both the loss factors, the dielectric loss ($\varepsilon''$) which originates from the dissipating electric dipole moments and the magnetic loss ($\mu''$) originating from the dissipating magnetic moments are found to decrease with increasing x, whereas the dielectric constant ($\varepsilon'$) and magnetic permeability ($\mu'$) variations are reciprocal with Mn addition [13]. Hence the addition of Mn in cobalt ferrite may lead to modify the permeability and permittivity closer to their equal values by tuning the $Co/Fe$ ratio. The equality in values of permeability and permittivity is a requirement for the design of antenna as reported in the literature [14] and thus the doping of Mn in cobalt ferrite may make it suitable for the use in antenna design. Eddy current is also another important factor to be considered in the case of microwave applications, which is a part of magnetic loss and depends on the grain size. Based on the above mentioned properties of cobalt ferrites we have selected three cobalt based compositions of ferrites, namely $Co_{1-x}Mn_xFe_2O_4$.
(stoichiometric), CoMn$_x$Fe$_{2-x}$O$_y$ (stoichiometric) and Co$_{1-x}$Mn$_x$Fe$_{2-x}$O$_y$ (non-stoichiometric) with $x = 0.5$ for our comparative studies of the electric and magnetic properties and the effect of Mn substitution on those properties.

2. Experimental

The samples for the present research work have been prepared by the conventional solid state reaction route using the planetary ball milling technique. Reagent grade Co$_2$O$_3$, MnO$_2$ and Fe$_2$O$_3$ were mixed in desired proportion and hand milled for 2 h. The samples were then calcined at 550 °C before ball milling. After calcination at 550 °C, again the mixer was ball milled for 12 h. The compositions of the prepared samples were CoFe$_2$O$_4$ (parent), Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$, CoMn$_{0.5}$Fe$_{1.5}$O$_4$ and Co$_{1.5}$Mn$_{0.5}$Fe$_{1.5}$O$_4$.

The as-made samples were used for scaling the particle size using FE-SEM images and the EDS spectrum were used to confirm the presence of compositional elements. The synthesized powder samples were shaped in the form of toroid’s and disc using hydraulic press applying a pressure of 5000 psi. The samples were then sintered at 700 °C for 30 min. A Wayne Kerr Impedance Analyzer 6500B series has been used to measure the ac permeability and permittivity in the frequency range 3–120 MHz. The eddy current loss has been calculated from the measured value of complex permeability using the formula [15] as mentioned below:

$$W_{\text{eddy current loss}} = \omega \mu_r \mu_0 H^2 V \sin \delta$$

where, $V$ is the volume of the toroid

$$\mu_r = \mu' (\text{real part})$$

$$\sin \delta = \frac{\mu''}{\sqrt{\mu'^2 + \mu''^2}}$$

$H$ is the magnetic field as calculated from the flux density ($H = \frac{B}{\mu_0}$)

$B$ is the flux density as calculated from the flux ($B = \frac{\varphi}{A}$, $A$ is the facial area of the toroid), $\varphi$ is the flux as calculated from ($\varphi = \frac{\mu_0}{\mu} H A$, Where $v$ is the applied voltage and $f$ is frequency).

3. Result and discussion

3.1. Particle size, elemental composition and x-ray diffraction (XRD) pattern

Figure 1(a) shows the FE-SEM image of Co$_{1.5}$Mn$_{0.5}$Fe$_{1.5}$O$_4$. From the image it can be seen that the particles are agglomerated. The average particle size is estimated to be around 40 nm. Figure 1(b) shows the EDS spectrum showing the chemical compositions of the NPs. The spectrum confirms the existence of Co, Mn, Fe and O in the sample and did not contain any traceable impurity elements. The inset of figure 1(b) shows the elemental composition of synthesized NPs and it can be seen that Co and Mn are present in 19.56 and 4.84 weight percent which confirms the presence of metallic cations by 80% and 20%. These values are in accordance with the initial stoichiometric.

Figure 1(c) shows the x-ray diffraction (XRD) pattern of Co$_{1.5}$Mn$_{0.5}$Fe$_{1.5}$O$_4$. The (111), (220), (311), (400), (422), (511) and (440) planes are indexed in the spectrum which also corresponds to the reported articles [7–10]. The presence of these planes in the pattern confirms the crystallinity of the sample. The observed peaks at 27°, 41°, and 49° may be due to the presence of CoFe$_2$O$_4$ [11]. In addition, the extra peaks at 24°, and 33° are observed due to the presence of MnO and Fe$_2$O$_3$ [12].

3.2. AC permeability

Figures 2(a) and (b) show the frequency dependent real part ($\mu'$) and imaginary part ($\mu''$) of ac permeability respectively. Figure 2(a) exhibits the variation of $\mu'$ for the samples Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ and CoMn$_{0.5}$Fe$_{1.5}$O$_4$ to be almost constant in the frequency range 3–120 MHz, which is normal behavior and comes out from the contribution of the spin only. The negative real part $\mu'$ of ac permeability is significant below 25 MHz (snap shot) for the sample Co$_{1.5}$Mn$_{0.5}$Fe$_{1.5}$O$_4$ which is the signature of diamagnetic behavior and expected to originate from the formation of magnetic dipoles opposite to the applied magnetic field due to the dominance of antiferromagnetic effect of Mn$^{2+}$ ions on the B site. The imaginary part $\mu''$ of the ac permeability for Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ and CoMn$_{0.5}$Fe$_{1.5}$O$_4$ is observed to slight increase in the high frequency regime as seen in the figure 2(b). This behavior corresponds well with the real part which converges asymptotically in the high frequency regime to a single value. However, the imaginary part $\mu''$ of Co$_{1.5}$Mn$_{0.5}$Fe$_{1.5}$O$_4$ is found to decrease sharply below 25 MHz which also corresponds well as the imaginary part rises sharply to a maximum value around the same frequency regime. This behavior is attributed to the possible size effect of the magnetic particles.
whose magnetic moments resonates well at the higher frequency regime but remain nonresponsive in the lower frequency regime. It may be mentioned that the magnetic moment of a particle is strongly size dependent as their response to external frequency. It is our assumption that as the samples are ball milled for different time.

Figure 1. (a) FE-SEM micrograph (b) EDS Spectrum (c) XRD Pattern of Co$_{1.5}$Mn$_{0.5}$Fe$_{1.5}$O$_{4}$.

Figure 2. (a) Real part $\mu'$ and (b) Imaginary part $\mu''$ of AC permeability as a function of frequency.
durations not every elements are reduced to a certain minimum. Therefore we expect that the magnetic elements in this composition has a certain critical size distribution and has responded to the specific frequency band.

3.3. AC permittivity

Figures 3(a) and (b) show the frequency dependent real part ($\varepsilon'$) and imaginary part ($\varepsilon''$) of the ac permittivity respectively. Figure 3(a) demonstrates that the real part $\varepsilon'$ for $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{CoMn}_{0.5}\text{Fe}_{1.5}\text{O}_4$ reaches a negative value ($\varepsilon' < 0$) below 60 MHz and drops rapidly to a very high negative value at the lowest measurable frequency. Then it goes towards zero and remains almost constant due to only presence of electronic mechanism of polarization, which is independent of frequency [16]. The high values of negativity $\varepsilon'$ implies that there is some attraction between the similar charges at the lowest frequency and the material behaves as purely metallic at the low frequency regime. As one could easily rule out the possibility of electrostatic attractions between the similar charges, it is assumed that such attraction between the similar charges has its magnetic origin. We assume that at the low frequency regime there is spin flipping induced by the antiferromagnetic $\text{Mn}_x$ ions. It is proposed that the other possible cause is the ionic polarization opposite to the applied electric field for $\text{Fe}^{2+}$ ions in the $A$ site. The decreasing nature of negative $\varepsilon'$ arises from the transition of ionic polarization to the electronic contributions due to the dominance of $\text{Mn}_2^{2+}$ ions in the $B$ site. From the figure 3(b) the imaginary part $\varepsilon''$ of these samples is found to follow the same variations. However, the transition of $\varepsilon'$ and $\varepsilon''$ at 25 MHz is found to be significant for the $\text{Co}_{1.5}\text{Mn}_{0.5}\text{Fe}_{1.5}\text{O}_4$, which is assumed to have been originated from the change of interfacial polarization [17] of local charges across the grain boundaries. In addition, the larger ratio of $\text{Co}^{2+}$/$\text{Fe}^{2+}$ ions could induce an antiferromagnetic exchange effect of $\text{Mn}^{2+}$ on the $B$ sites.

3.4. Significances

The variation of electric and magnetic parameters namely $\mu'$ and $\varepsilon'$ with the change in frequency as shown in figures 2(a) and 3(a) could represent $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{CoMn}_{0.5}\text{Fe}_{1.5}\text{O}_4$ as the epsilon negative medium (ENG) below 25 MHz due to $\varepsilon' < 0$ and $\mu' > 0$ as per the classification of material [17]. However, the most significant behavior is observed in $\text{Co}_{1.5}\text{Mn}_{0.5}\text{Fe}_{1.5}\text{O}_4$, which has demonstrated $\mu$-negative (MNG) [18] below 25 MHz since $\varepsilon' > 0$ and $\mu' < 0$ and double negative (DNG) [18] media above 25 MHz because of $\varepsilon' < 0$ and $\mu' < 0$ [19] as evident from the figure 4(a). Besides, the eddy current loss ($W_{\text{eddy current loss}}$) in $\text{Co}_{1.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{CoMn}_{0.5}\text{Fe}_{1.5}\text{O}_4$ is found to be almost vanishing above 5 MHz and for $\text{Co}_{1.5}\text{Mn}_{0.5}\text{Fe}_{1.5}\text{O}_4$ above 25 MHz. But it's dispersion $\text{Co}_{1.5}\text{Mn}_{0.5}\text{Fe}_{1.5}\text{O}_4$ below 25 MHz exhibits an anomalous behavior, which may be caused due to the $\mu$-negative (MNG) in the low frequency regime. We propose the notion that the nano-sized grain in the sample may lead to cause a vanishing eddy current loss as it is proportional to the grain size [18]. However, if this vanishing eddy current loss is neglected then the resonant absorption of energy by the spin damping under the applied ac field may be the dominant operating dissipation mechanism in these samples above 5 MHz and 25 MHz respectively. This significant and unique frequency dependent behavior of permeability and almost vanishing eddy current loss is expected to make these material suitable for high frequency applications such as in the design of patch antenna [20].

![Figure 3](image-url)
4. Conclusion

We found that the average particle size of the synthesized Co$_{1.5}$Mn$_{0.5}$Fe$_{1.5}$O$_4$ is around 40 nm. The negative real part $\mu'$ of ac permeability is significant below 25 MHz (snap shot) for Co$_{1.5}$Mn$_{0.5}$Fe$_{1.5}$O$_4$, which might be a signature of diamagnetic behavior and expected to have been originate from the formation of magnetic dipoles opposite to the applied magnetic field caused due to the antiferromagnetic effect of Mn$^{2+}$ ions on the B site. The transition of real part of ac permittivity at 25 MHz is found to be significant for Co$_{1.5}$Mn$_{0.5}$Fe$_{1.5}$O$_4$, which is attributed to the transition of interfacial polarization of the accumulated local charges across the grain boundary. The negative real part $\mu'$ of ac permeability and positive real part $\varepsilon'$ of ac permittivity correspond to the $\mu'$-negative (MNG) region below 25 MHz and double negative (DNG) region above 25 MHz. The almost zero eddy current loss above 5 MHz and 25 MHz might make the material suitable for the patch antenna design. However, we appreciate that the findings in this paper are based on the real part $\mu'$ of ac permeability and the real part $\varepsilon'$ of the ac permittivity. Thus further investigations are suggested for determining the other associated and relevant parameters to ascertain the facts.

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