

## Significances of Complex Impedance in Stoichiometric and Non-Stoichiometric Compositions of Manganese Doped Cobalt Nanoferrites

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**Abstract:** This paper reports on the complex impedance in stoichiometric and non-stoichiometric manganese doped cobalt nanoferrites. The decreasing trend in their impedance with the frequency shows an increasing trend in their conductivity, which is their normal behavior. The stoichiometric composition shows only the short-range mobility of charge carriers wherein n-type ( $Fe^{2+}/Fe^{3+}$ ) charge carriers play a dominant role and the non-stoichiometric composition demonstrates both the long-range and short-range mobility of charge carriers in their respective Nyquist plot. The p-type ( $Co^{2+}/Co^{3+}$ ) charge carriers are found to play a predominant role in the conduction mechanism of the non-stoichiometric composition. Thus, the complex impedance marks a single metallic band in the stoichiometric composition and a double metallic band in the non-stoichiometric composition. This double metallic band may make this sample suitable to be used in the switching as well as actuator devices. Conversely, the higher conductivity in the single metallic band is expected to generate heat by the eddy current loss for the stoichiometric composition, which may make it suitable to be used in hyperthermia and medical science-related research.

**Keywords:** Complex impedance, short-range mobility, long-range mobility, metallic band

Cobalt ferrite is a magnetic semiconductor wherein cobalt ions ( $Co^{2+}/Co^{3+}$ ) are p-type charge carriers and iron ions ( $Fe^{2+}/Fe^{3+}$ ) n-type charge carriers. This cobalt ferrite is a chemically excellent stable material and having very high magnetocrystalline anisotropy energy due to the presence of cobalt ions [1, 2]. The tuning existing properties or tailoring new properties in cobalt ferrites are possible by doping manganese keeping its basic structure almost the same. Meanwhile, intensive investigations have been performed on this cobalt ferrite to optimize them for diversified applications [2, 3]. Recently, this material has got renewed attention to use in catalysis, environmental and medical science-related research [4]. Accordingly, manganese doped cobalt ferrites with stoichiometric composition  $Co_{1-x}Mn_xFe_2O_4$  (CMF) and non-stoichiometric composition  $Co_{1+x}Mn_xFe_{2-x}O_4$  (CFMZ) have been prepared by the conventional solid-state reaction route using the planetary ball milling technique at different weight percent i.e.  $x = 0.125, 0.25, 0.375$  and  $0.5$ . The laboratory graded oxide powders of cobalt, manganese,

and iron was used as the raw materials for synthesising the aforesaid compositions. The Waynekerr impedance analyzer 6500B series was used for their characterization and the results on the complex impedance have been presented in this brief communication to highlight the contribution of p-type and n-type charge carriers in their conduction mechanism at the room temperature. Generally, the impedance is defined as the obstruction to the alternating current in the circuit. Since ferrite materials are composed of layers, those are grain boundaries and grains, so while there may be a phase difference between the applied ac electric field and the current. This fact gives rise to the complex impedance, which is usually described by the complex formalism  $Z^* = Z' - jZ''$ , where  $Z'$  is the real part,  $Z''$  the imaginary part of complex impedance, and

$j = \sqrt{-1}$ . The real part  $Z'$  and the imaginary part  $Z''$  have been determined from the electric modulus formalism by using the relation  $Z' = M''/\omega\epsilon_0$  and  $Z'' = M'/\omega\epsilon_0$ , where  $M'$ ,  $M''$  and  $\epsilon_0$  are the real part, the imaginary part of electric modulus, and  $\epsilon_0$  is the dielectric constant in free space [5, 6].

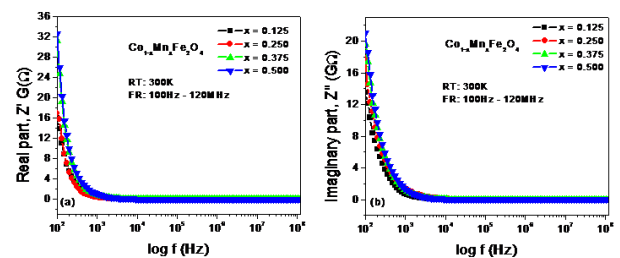


Fig.1: (a) Real part,  $Z'$  (b) Imaginary part,  $Z''$  as a function of frequency for the samples of the CMF system

Fig. 1 (a) and (b) show the variation of the real part  $Z'$  and imaginary part  $Z''$  of complex impedance for the samples of composition  $Co_{1-x}Mn_xFe_2O_4$  as a function of frequency on the logarithmic scale at the room temperature (RT). As seen in both Fig. 1(a) and (b), both the real and imaginary part of complex impedance decreases almost exponentially with the increase in the frequency of the applied ac field up to a certain frequency at around 1.5kHz and then remains non-responsive to the applied frequency. In the low-

frequency region, the higher values of both the real and imaginary parts of impedance may have originated from the space charge polarization mechanism in the grain boundaries of the investigated samples [1, 7, 8]. The decreasing trend below 1.5 kHz signifies the increasing trend of ac conductivity. This may have originated from the diffusion of charge carriers through grain boundaries that correspond to the long-range mobility of charge carriers due to the change of space charge polarization to the ionic polarization across the grain boundaries [9]. Above 1.5 kHz, the constancy in both the real and imaginary parts of impedance at lower values implies the increase in conductivity, which probably corresponds to the dc conductivity,  $\sigma_{dc}$  of the materials. This dc conductivity  $\sigma_{dc}$  may have arisen due to the localized hopping of charge carriers in the grains [7]. This localized hopping implies the short-range mobility of charge carriers. In the low-frequency region (<1.5 kHz), both the real and imaginary parts of impedance are found to increase with the Mn content, which may be due to the creation of oxygen vacancies by the Mn content while replacing the Fe ions in both tetrahedral and octahedral sites. These created vacancies generate the heterogeneity and thus pinning sites, which offer the higher scattering of charge carriers and leading to enhance the impedance.

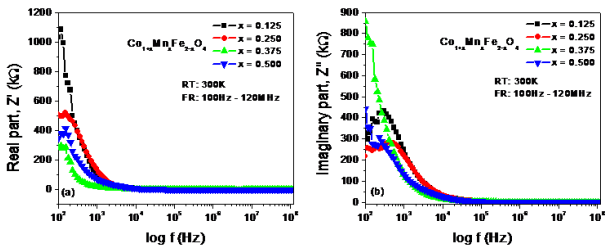


Fig.2: (a) Real part,  $Z'$  (b) Imaginary part,  $Z''$  as a function of frequency for the samples of CFMZ system

Fig. 2(a) and (b) shows the variation of the real part,  $Z'$  and the imaginary part,  $Z''$  of complex impedance for the samples of the composition  $Co_{1-x}Mn_xFe_{2-x}O_4$  as a function of frequency on the logarithmic scale over the frequency band 100 Hz - 120 MHz at the room temperature. As seen in Fig. 2(a) and (b) both the real part  $Z'$  and imaginary part  $Z''$  of complex impedance increase up to certain peak values and then decrease non-linearly (almost exponentially) with the increase in the frequency of applied ac electric field up to around 10kHz for the real part and 100kHz for the imaginary part of complex impedance. Finally, they become independent of frequency. The initial increase in the real part  $Z'$  as seen in Fig. 2(a) represents the anomalous behavior of dielectric constant in the lower frequency region due to the randomized accumulation of space charges across the grain boundaries. Each peak in  $Z'$  correspond to a particular frequency, which may be considered as the critical frequency, which set the boundary between anomalous and normal behavior of complex impedance and also marked to shift their

position with the change in concentration level  $x$  (Mn content) randomly, which may be due to the differences in the mobility of p-type ( $Co^{2+}$ ) and n-type ( $Fe^{3+}$ ) charge carriers. The decreasing trend in the real part  $Z'$  up to around 10 kHz implies the increase in ac conductivity  $\sigma_{ac}$ , which may come out from the diffusion of charge carriers through the grain boundaries and thus exhibits the long-range mobility of charge carriers (p-type and n-type) [9]. However, above 10 kHz, the constancy in the real part  $Z'$  signifies dc conductivity  $\sigma_{dc}$  according to Joncher's power law of conductivity [6]. This dc conductivity  $\sigma_{dc}$  is expected to cause by the hopping of localized charge carriers in the conductive grains. As seen in Fig. 2(b), the variation in the imaginary part  $Z''$  with the increase in the applied frequency of ac field implies the similar changes in conductivity wherein the non-responsive region is noticed above 100 kHz. Moreover, the peaks here exhibit the resonance effect where both the real and imaginary parts of complex impedance are almost equal. The corresponding frequency to each peak is known as characteristic frequency,  $f_{max}$ . This characteristic frequency,  $f_{max}$  is also noticed to shift their position with the change in concentration level,  $x$  but not in a regular fashion, which also may cause by the differences in the mobility of charge carriers. However, in the low-frequency regime, both the real and imaginary parts for both the composition are marked to differ randomly due to the deviation of cation distribution from their idealistic situation.

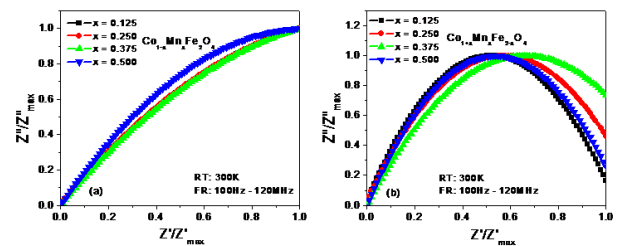


Fig.3: Nyquist plot Normalized values of the real part and imaginary parts of complex impedance for (a) CMF system (b) CFMZ system at RT

Fig.3 (a) and (b) show the Nyquist plot of complex impedance for the samples of compositions  $Co_{1-x}Mn_xFe_2O_4$  and  $Co_{1+x}Mn_xFe_{2-x}O_4$  respectively. The normalized scaling has been used in this plot to facilitate easy understanding and identifying the contributions of charge carriers in the samples of both stoichiometric and non-stoichiometric compositions. The arcs are observed for the sample of composition  $Co_{1-x}Mn_xFe_2O_4$  whereas a single non-Debye type semicircle is found to occur for the samples of  $Co_{1+x}Mn_xFe_{2-x}O_4$  as seen from Fig. 3(a) and (b) respectively. No peaks are observed in the Nyquist plot for the samples of  $Co_{1-x}Mn_xFe_2O_4$  as shown in Fig. 3(a). Whereas peaks are marked at around a particular frequency for the samples of  $Co_{1+x}Mn_xFe_{2-x}O_4$  as seen in Fig. 3(b), which may be the imaginary dividing line

between long-range mobility and short-range mobility of charge carriers [9]. The frequency band below the relaxation frequency corresponds to the long-range mobility of charge carriers. In this frequency band, the p-type ( $\text{Co}^{2+}/\text{Co}^{3+}$ ) charge carriers predominantly contribute to their conduction mechanism by diffusion process through the grain boundaries in the opposite direction due to the presence of additional Co content because of their non-stoichiometry and resulting in higher resistivity. Above this relaxation frequency, the band indicates the short-range mobility of charge carriers and the decreasing trend in the normalized value of the imaginary part,  $Z''$  is the signature of the short-range mobility of charge carriers wherein n-type ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) carriers are expected to be predominant in the electrical conduction by small polarons. Conversely, the decreasing trend in the normalized value of imaginary part  $Z''$  of complex impedance for the samples of  $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$  implies the higher ac conductivity  $\sigma_{ac}$ , which is expected to cause predominantly by the n-type ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) charge carriers by the faster hopping process in the conductive grains due to decrease in Co concentration by the Mn. Thus, double metallic bands are observed for the samples of  $\text{Co}_{1+x}\text{Mn}_x\text{Fe}_{2-x}\text{O}_4$  composition but a single metallic band is marked for the samples of  $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ . The double metallic bands may make the samples of composition  $\text{Co}_{1+x}\text{Mn}_x\text{Fe}_{2-x}\text{O}_4$  suitable to be used in switching as well as actuator devices. Whereas an eddy current loss as heat radiation may be generated due to the higher conductivity in the single metallic band and thus may make the stoichiometric sample suitable to be used in the hyperthermia or medical-related research. However, further investigations may also be required to ascertain and quantify the generated heat by the eddy current loss.

#### Acknowledgment

The authors are thankful to the ISP (International Science Programs), Uppsala University, Sweden for financial and technical support, and also to the department of physics, Bangladesh University of Engineering and Technology and the department of physics and mechanical engineering, Military Institute of Science and Technology for experimental support.

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