

# Dielectric and Magnetic Studies of Ni<sub>0.25</sub>Cu<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub>-NiO Composites

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## Abstract.

Transitional metal oxide (NiO) doped Ni<sub>0.25</sub>Cu<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub> ferrite composites with the basic composition (1-x) Ni<sub>0.25</sub>Cu<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub> + (x) NiO (here, x=0, 0.05, 0.1, 0.15) were synthesized mechanical grinding and for ferrites using nitrate-citrate method. Synthesized samples, were sintered at 950°C, were investigated for various properties through its structural, dielectric and magnetic studies. Phase of the synthesized samples were probed by X-ray diffraction (XRD) studies. Peaks observed in the XRD spectrum confirms the single phase spinel cubic structure for the Ni<sub>0.25</sub>Cu<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub> and for NiO face centered cubic structure and both the phases were present in the powder composite samples. Using SEM, surface morphology of the samples has been investigated. Using Hioki make LCR Hi-Tester 3250, various dielectric parameters such as dielectric permittivity ( $\epsilon'$ ), dielectric loss tangent ( $\tan \delta$ ) were investigated as a function of frequency and NiO concentration at room temperature, over the frequency range 100 Hz to 1 MHz. Frequency dependence of  $\epsilon'$  and  $\tan \delta$  is in accordance with the Maxwell-Wagner type interfacial polarization. Electrical conductivity ( $\sigma_{ac}$ ) is deduced from the measured dielectric data, and found that the conduction mechanism in ferrite and their composite samples are in conformity with the electron hopping model. Magnetic studies were completed using vibrating sample magnetometer (VSM), for the proposed ferrites, and their composites.

**Keywords:** Mechanical, Ferrites; Composites; permittivity.

## 1. INTRODUCTION

Magnetic oxides at nano regime are the ferrite spinels with excellent and tunable properties, such as its dielectric, magnetic properties and can be easily modified just by varying various synthesis methods. Extensive applications of composite materials led to their imperative technological applications and can be employed in numerous electronic and technological devices [1-4].

Ferrites are the oxide materials, mainly consisting of Fe<sub>2</sub>O<sub>3</sub>, have spinel cubic structure. Ferrites exhibit magnetic hysteresis (M-H curve) and also exhibit spontaneous magnetization. Various properties of magnetic spinel is because of distribution of divalent and trivalent metal ions among the available tetrahedral (A) and octahedral (B) sites [5]. For any materials of interest, its properties are highly dependent on preparation technique adopted, type of synthesis environment such as in inert or in open air atmosphere, type of organic fuel used, sintering time and temperature, etc.

Nickel ferrite belongs to inverse spinel with Ni<sup>+2</sup> at octahedral (B-site) and Fe<sup>+3</sup> ions distributed equally in both, tetrahedral (A-site) and octahedral sites (B-site). Nickel ferrites are used in numerous electronic device applications because of their high permeability, high electrical resistivity, mechanical hardness, and chemical stability [6-7].

Among metal oxides of technological importance, NiO is a transitional metal oxide which is antiferromagnetic in nature below 523 kelvin and is an excellent material for catalysis, energy conversion, in storage devices, gas sensors and electro-chromic films etc. [8-10]

Composites of mixed ferrites of Ni<sub>0.25</sub>Cu<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub> and Metal oxides such as NiO are the technologically important materials which are used in functional devices such as in field sensors, heterogeneous catalysis, and in various sensors [11].

In our present study, composite samples made up of ferrite phase and metal oxide (NiO) with the basic composition (1-x) Ni<sub>0.25</sub>Cu<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub> + (x) NiO (x=0, 0.05, 0.1, 0.15) were prepared using hybrid mechano synthesis for preparing composite materials and for synthesis of ferrite phase used nitrate-citrate auto-combustion method. Auto-combustion method is a self-propagating thermally-induced reaction of a gel, obtained from aqueous solutions containing metallic nitrates which acts as oxidizer and an organic fuel. Stoichiometric proportions between fuel and metallic nitrates are calculated according to the valencies of the reacting elements so as to provide the relation of oxidizer/fuel equal to one [12]. Here, metallic nitrates are preferred as starting materials which are also known as precursors, because of their water-soluble nature, have low ignition temperatures and are easy to prepare.

## 2. MATERIALS AND METHODS

Composites of  $\text{Ni}_{0.25}\text{Cu}_{0.75}\text{Fe}_2\text{O}_4$  and NiO were prepared using an hybrid method which includes both auto-combustion method and mechanical mixing. Precursors for starting the materials synthesis are Nickel Nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), Ferric Nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Copper Nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), Citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ), all chemicals are of AR Grade with purity more than 99%. Aqueous solutions of metallic nitrates and Citric acid, which is here taken as organic fuel needed for auto-combustion reaction and are taken as per the stoichiometry. Equi-molar citric acid was added into the aqueous solution of metallic nitrates. Aqueous solution containing redox mixture was taken in a silica crucible and is allowed in to a muffle furnace, which was already pre-heated to a temperature of  $550^\circ\text{C}$ . Redox mixture finally yields porous and fluffy voluminous ferrite powder. Obtained fluffy material was ground to get ferrite powders. As-burnt ash was sintered at  $950^\circ\text{C}$  for 4 hours to get better crystallization and homogeneous cation distribution in the proposed spinel and finally ground to get mixed  $\text{NiCuFe}_2\text{O}_4$  nano powders, similarly procedure is used for preparing NiO, later the nano powders of NiO and  $\text{Ni}_{0.25}\text{Cu}_{0.75}\text{Fe}_2\text{O}_4$  were mechanically mixed using agate mortar and pestle for prolonged hours of grinding.

Phase of the Pure NiO and their three composites samples were investigated by X-ray diffraction (XRD) studies using Bruker AXS D8 Advance X-ray diffractometer (using  $\text{Cu-K}_\alpha$  radiation,  $\lambda=1.5406 \text{ \AA}$ ), a working voltage of 40kV at 40mA of current. Diffraction data were collected in the  $2\theta$  range  $10-80^\circ$ . Morphology of the sintered samples has been investigated using Scanning Electron Microscope (Hitachi Hitech Model S-3400N). Parallel capacitance,  $C_p$  and dissipation factor,  $\tan\delta$  as a function of frequency in the range 100 Hz-1 MHz were measured using a precision LCR meter. Real and imaginary parts of dielectric permittivity ( $\epsilon'$ ) and ( $\epsilon''$ ) were computed using the formulae [13],

$$\epsilon' = Ct/\epsilon_0 A \quad (1)$$

$$\epsilon'' = \epsilon' \tan \delta \quad (2)$$

Where, t is the thickness and A the area of the pellet.

The ac conductivity,  $\sigma_{ac}$  was determined from the dielectric loss factor using a relation

$$\sigma_{ac} = \omega \epsilon_0 \epsilon'' \quad (3)$$

Where,  $\epsilon_0$  is the vacuum permittivity and  $\omega = 2\pi f$  with f being frequency.

## 3. RESULTS AND DISCUSSION

### 3.1 Phase and Surface Morphology

Presence of (111), (200), (220), (311), (222) planes in the diffraction patterns confirms the face centered cubic structure for the metal oxide NiO. Diffractograms of the proposed composites of the system  $(1-x) \text{Ni}_{0.25}\text{Cu}_{0.75}\text{Fe}_2\text{O}_4 + (x) \text{NiO}$  (where  $x=0.0, 0.05, 0.1, 0.15$ ) are presented in Figure 1. Presence of (220), (311), (400), (422), (511), (440) and (533) planes indexed for the cubic phase of spinel ferrites [ $\text{NiFe}_2\text{O}_4$ , Ref No: 00-066-0778, For NiO, Ref Code No: 01-078-4374 and JCPDS Card No: 25-0283 for  $\text{NiCuFe}_2\text{O}_4$ ]. From the X-ray diffractogram, it is clear that the composites are having both reflections corresponding to metal oxide (NiO) and ferrite phase ( $\text{NiCuFe}_2\text{O}_4$ ) which is shown with an asterisk (\*) symbol, as the NiO concentration increases the peak intensity corresponding to NiO also increases, there by confirming the presence of both the ferrite and NiO.

Microstructures were studied by placing the composite samples under Scanning electron microscope. Micrographs of the sintered samples are depicted in Fig. 2 (a-c), shows the surface structure for the proposed samples of metal oxide (NiO) doped  $\text{Ni}_{0.25}\text{Cu}_{0.75}\text{Fe}_2\text{O}_4$  ferrite. Optical micrographs shows that particles of transitional metal oxide (NiO) is well dispersed in the matrix of ferrite phase material ( $\text{Ni}_{0.25}\text{Cu}_{0.75}\text{Fe}_2\text{O}_4$ ) and also the particles with some agglomerated dense structure is noticed.

### 3.2 Dielectric studies

Dielectric permittivity ( $\epsilon'$ ) which is also known as dielectric constant and loss tangent ( $\tan\delta$ ) is the dielectric loss of the material. Main reason for the emergence of dielectric loss is the lag of the response of the synthesized materials to the external field.

Various dielectric parameters such as permittivity,  $\epsilon'$  and ac conductivity ( $\sigma_{ac}$ ) with frequency at room temperature for the proposed composite system is shown in Fig.3. From the Fig.3 (a), it is clear that  $\epsilon'$  decreases with increasing frequencies and remains almost independent at higher frequencies. Variation of dielectric constant with applied frequency is due to charge transport relaxation. This dielectric dispersion is common in ceramics like ferrites and is attributed to Maxwell and Wagner type of interfacial polarization [14-15], as the dielectric constant is a combined effect of dipolar, electronic, ionic and interfacial polarizations. Since ionic polarization decreases with frequency, at higher frequency cycle rates, the constituent electric dipoles are unable to follow the quick variations of the alternating applied electric field and hence, measured  $\epsilon'$  also decreased with frequency. Larger values of permittivity are related with space charge polarization at grain boundary and heterogeneous dielectric structure.

By electron exchange between  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$ , displacement of electrons takes place with the applied field and these electrons determine polarization. Polarization decreases with increase in frequency and for further increase, the electric exchange between  $\text{Fe}^{+2}/\text{Fe}^{+3}$  cannot follow the alternating field hence reaches the constant value [16-17].

Gradation in the dielectric loss for all the proposed series of samples upto the frequency range 1 MHz at room temperature is shown in Fig. 3(b). Values of loss tangent ( $\tan\delta$ ) represent the attenuation in magneto-electrics and polarization being unable to respond to applied external frequency. Similar nature of curves for both  $\epsilon'$  and  $\tan\delta$  are almost similar and may be correlated to the domain wall motion with the applied field. The electron exchange between  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  ions can correlate with the dielectric properties exhibited by proposed samples.

In order to understand the type of charge carriers and type of polarons responsible for conduction, ac conductivity,  $\sigma_{ac}$  were estimated as per  $\sigma_{ac} = \omega \epsilon_0 \epsilon''$ , with  $\epsilon_0$  is the permittivity of free space and  $\omega = 2\pi f$ .

For the synthesized composites, variation of  $\sigma_{ac}$  with frequency,  $\ln(\omega)$ , is shown in Fig.3 (c). Obtained plots are almost linear for the entire range of frequency except at lower frequencies. Linear variation of  $\sigma_{ac}$  with frequency confirms that, conduction in mixed spinel ferrite occurs by the hopping of charge carriers between the localized states which confirms the small polaron type of conduction [18]. Conduction mechanism in spinel ferrites can be explained based on the hopping of charge carriers between  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  ions on octahedral lattice sites. Increase in the frequency of the applied field accelerates the hopping of charge carriers thereby enhancing the overall conduction process, thereby increasing the conductivity. At higher frequencies,  $\sigma_{ac}$  remains constant because the hopping frequency of the charge carriers no longer follows the external applied field variations and lags behind it. However, the decrease in conductivity values at lower frequencies can be correlated to conduction by mixed polarons.

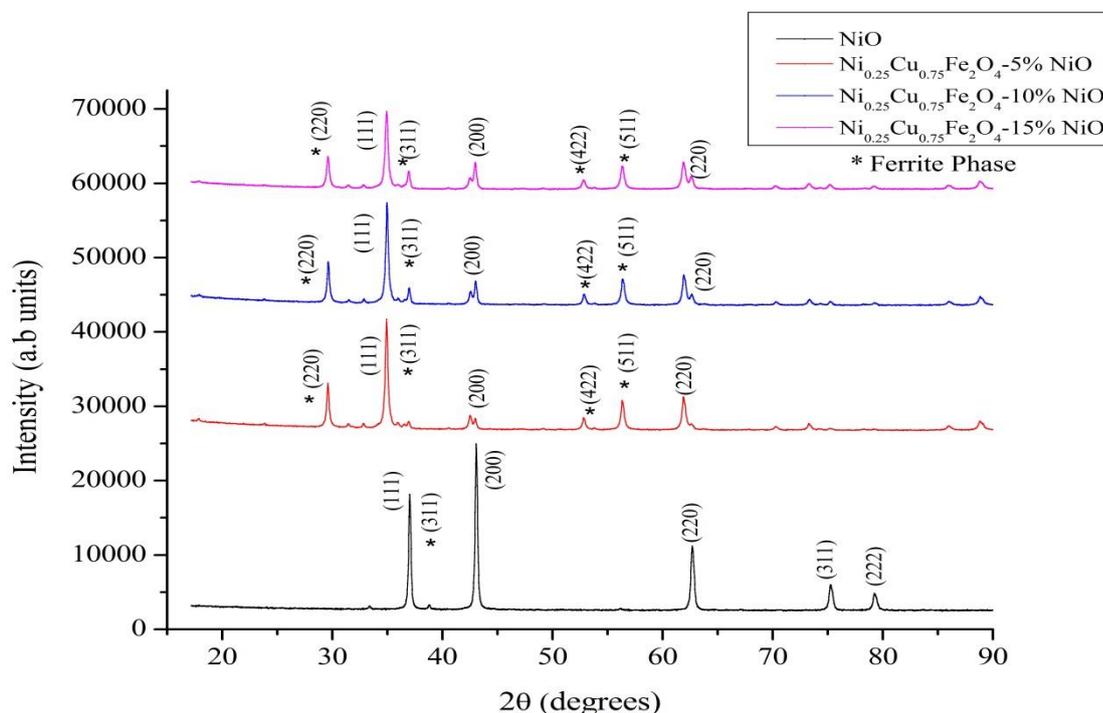


Fig. 1

Diffractogram of  $\text{Ni}_{0.25}\text{Cu}_{0.75}\text{Fe}_2\text{O}_4 - \text{NiO}$  Composite powder samples

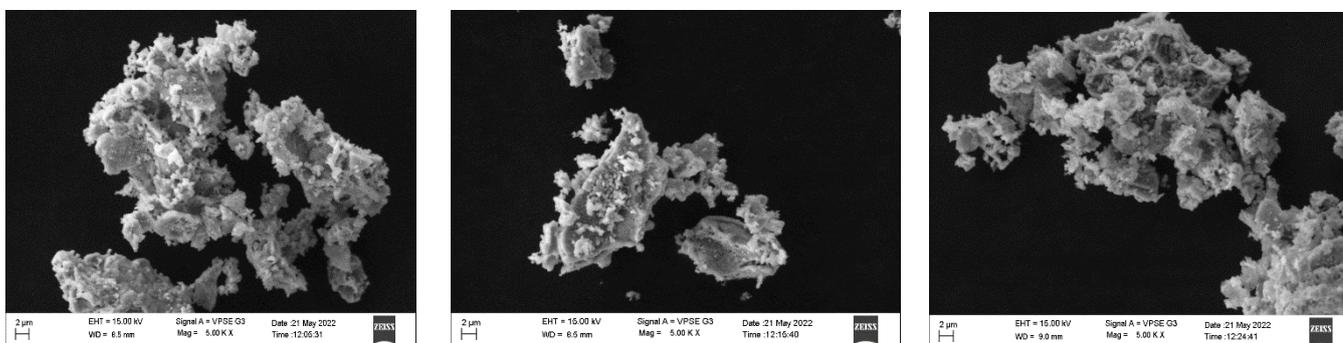


Fig. 2 Micrographs for (a) 5% doped  $\text{NiO-NiCuFe}_2\text{O}_4$  (b) 10% doped  $\text{NiO-NiCuFe}_2\text{O}_4$  and (c) 15% doped  $\text{NiO-NiCuFe}_2\text{O}_4$

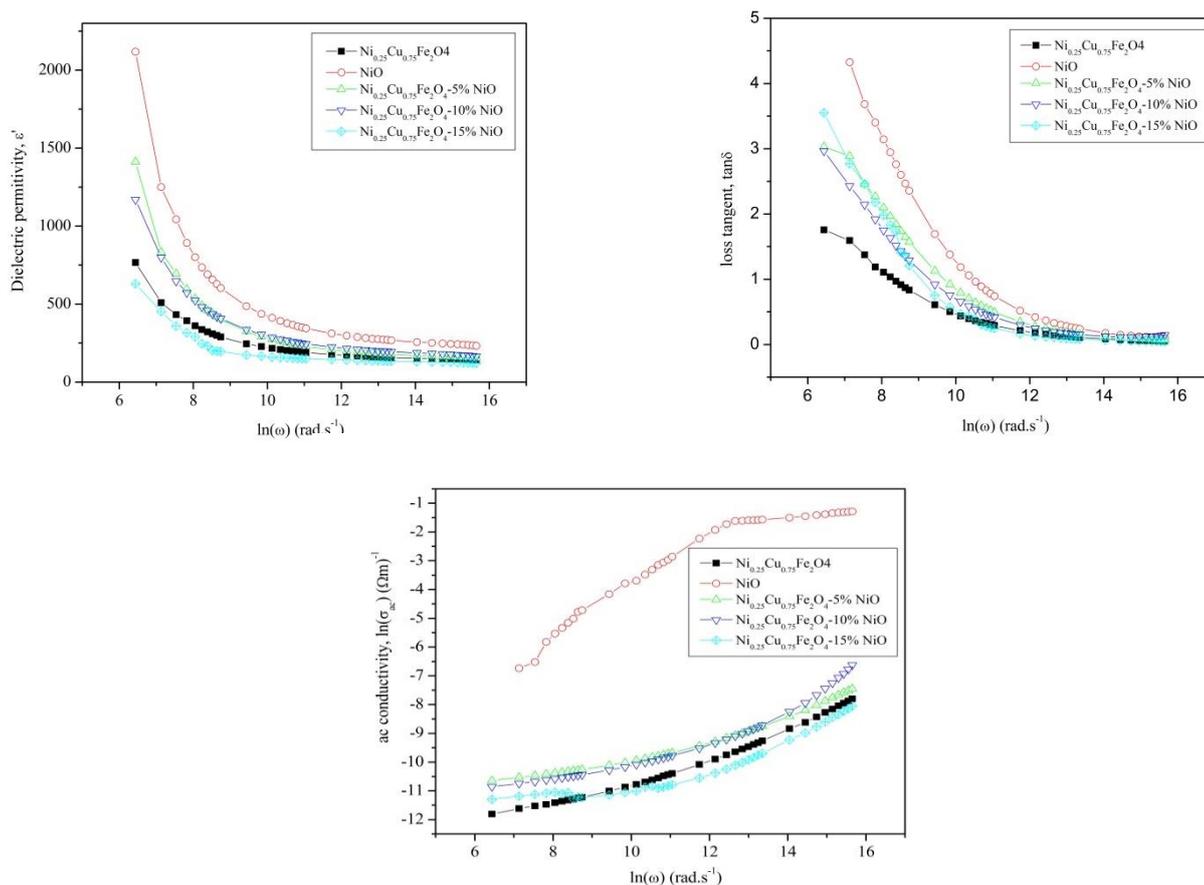


Fig.3 (a).Dielectric permittivity,  $\epsilon'$  with  $\ln(\omega)$  , (b) Tangent loss factor  $\tan\delta$  with  $\ln(\omega)$  and (c) AC conductivity,  $\sigma_{ac}$  with  $\ln(\omega)$ .

### 3.3 Magnetic studies

Magnetic hysteresis loops, at room temperature were recorded for all the Pure and doped composite samples. Magnetic hysteresis loops for all the samples sintered at 950°C are shown in Fig.4. Synthesized and sintered samples exhibited no hysteresis, which may be attributed to super paramagnetic nature of the samples. Various magnetic parameters such as saturation magnetization ( $M_s$ ), remanence magnetization ( $M_r$ ) and coercive fields ( $H_c$ ) were extracted from the obtained M-H loops. Extracted magnetic parameters for all the samples are listed in Table 1. Doping with NiO, it is observed that the magnetic properties of  $Ni_{0.25}Cu_{0.75}Fe_2O_4$  is random and may be attributed to the intrinsic properties of NiO, which has shown a  $M_s$  of 1.32 emu/g at RT.

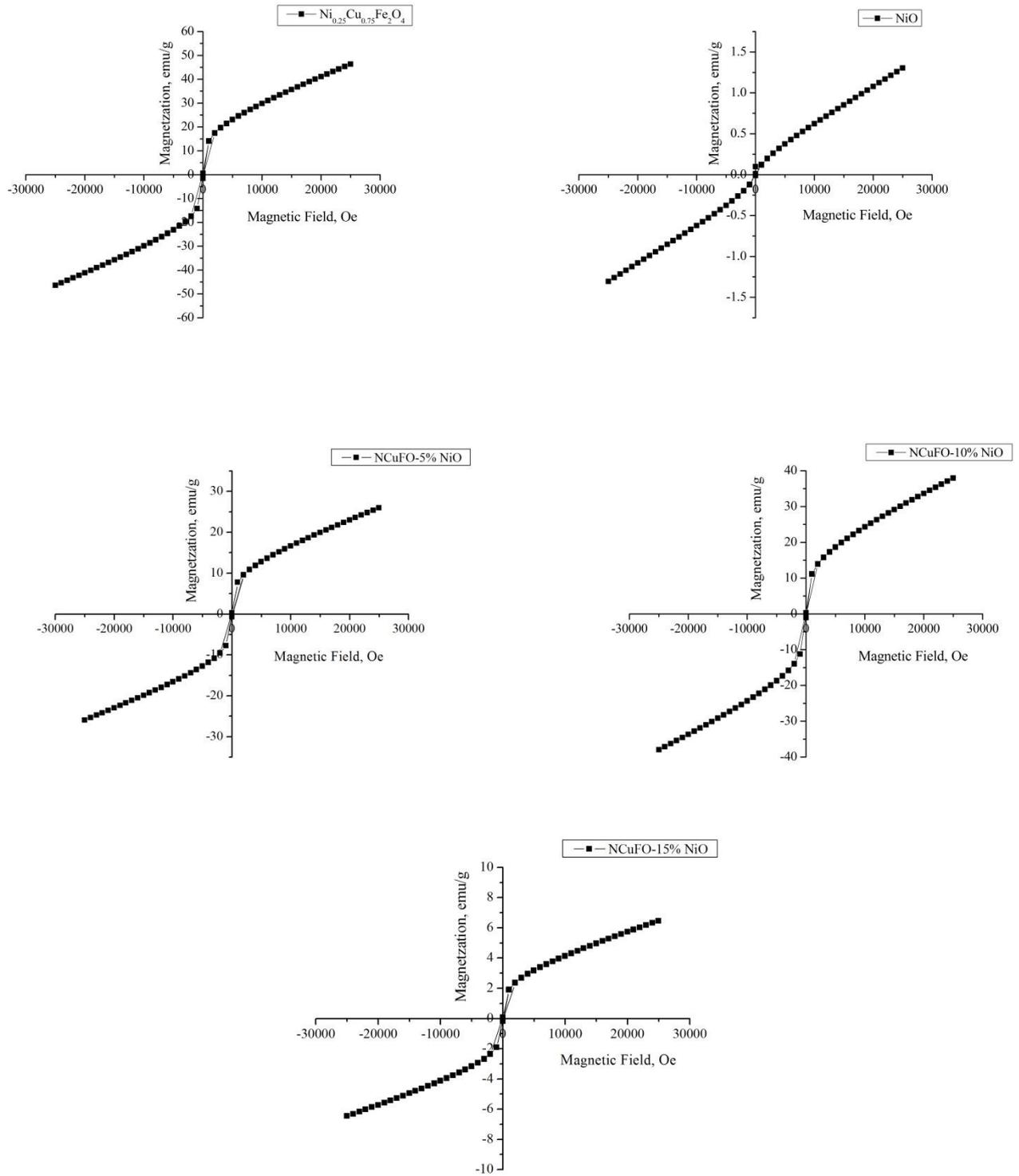


Fig.4. Magnetic Hysteresis loops of  $\text{Ni}_{0.25}\text{Cu}_{0.75}\text{Fe}_2\text{O}_4$ -  $\text{NiO}$  Composites

Table 1. Magnetic parameters extracted from M-H Loops.

Ferrite compositions	Saturation Magnetization ( $M_s$ -emu/g)	Remanance Magnetization ( $M_r$ -emu/g)	Coercive Field ( $H_c$ -Oe)
$Ni_{0.25}Cu_{0.75}Fe_2O_4$	46.38	0.6	97.13
$Ni_{0.25}Cu_{0.75}Fe_2O_4$ - 5% NiO	25.93	0.26	145.37
$Ni_{0.25}Cu_{0.75}Fe_2O_4$ - 10% NiO	37.96	0.34	88.23
$Ni_{0.25}Cu_{0.75}Fe_2O_4$ - 15% NiO	6.46	0.07	86.14
NiO	1.32	0.01	13.08

## CONCLUSIONS

Composites of the system  $(1-x) Ni_{0.25}Cu_{0.75}Fe_2O_4 + (x) NiO$  ( $x=0, 0.05, 0.1, 0.15$ ) prepared successfully using hybrid mechano synthesis method which involves both auto-combustion method and mechanical mixing. Composites and their constituent phases were confirmed from PXRD studies. Morphology of the composites reveals that the both NiO and  $Ni_{0.25}Cu_{0.75}Fe_2O_4$  particles well dispersed and forms agglomeration. Dielectric studies, confirms the dielectric dispersion for composites, and is attributed to Maxwell-Wagner two layer models and Koop's theory. A.C conductivity  $\ln(\sigma_{ac})$  of the proposed samples were plotted against  $\ln(\omega)$ , the plots are linear for almost entire range of frequency except at low frequencies. Linear variation of  $\sigma_{ac}$  with frequency indicates that the electrical conduction occurs because of the hopping of charge carriers between the localized states which confirms the conduction is due to small polarons. From magnetic studies, it is observed that, the composite samples with narrow hysteresis loop were synthesized with low values of coercivity. Hence, these composites are magnetically soft materials.

These characteristics of the proposed composite materials are of technologically important and can be implemented in smart functional device applications.

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Figures

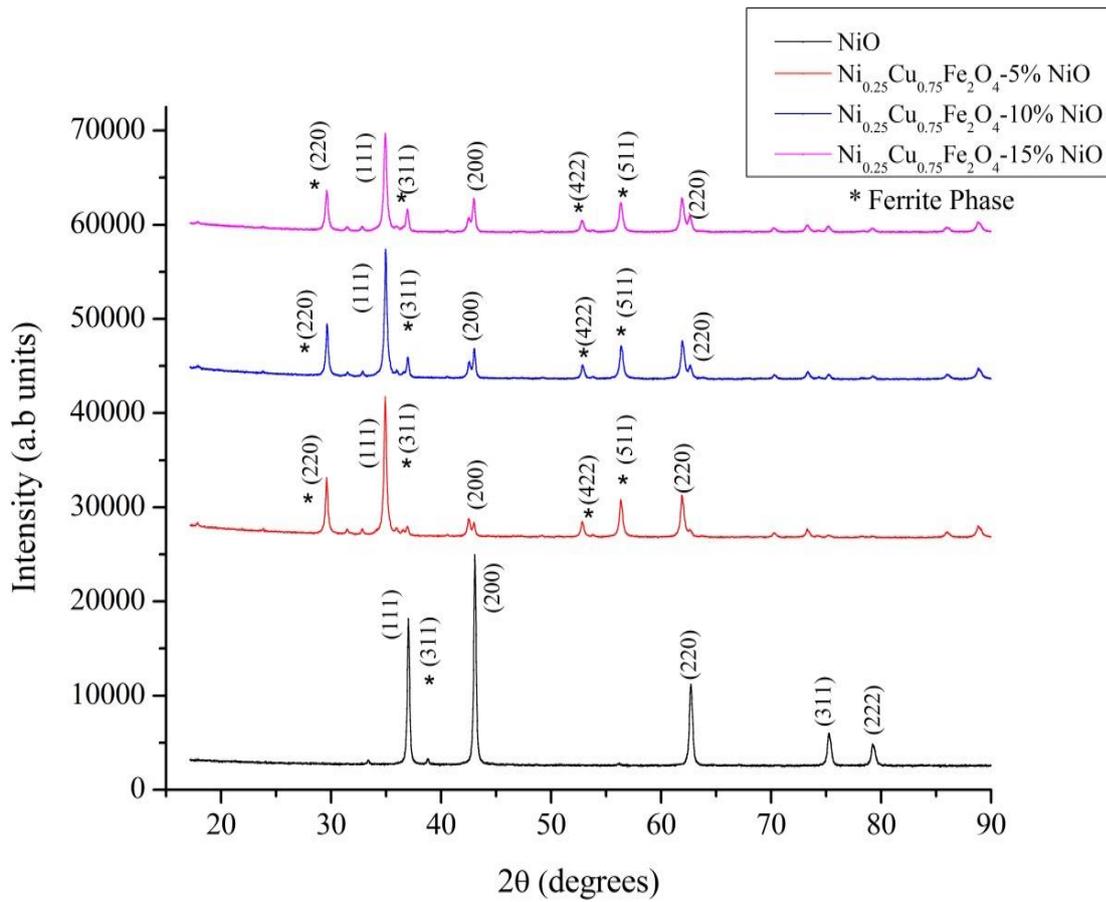


Fig. 1 Diffractogram of  $\text{Ni}_{0.25}\text{Cu}_{0.75}\text{Fe}_2\text{O}_4$  – NiO Composite powder samples

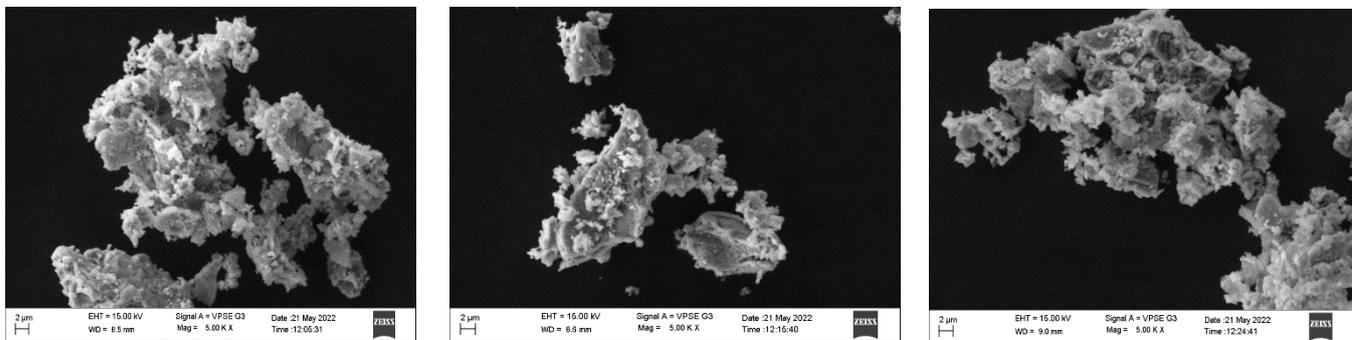


Fig. 2 Micrographs for (a) 5% doped NiO-NiCuFe<sub>2</sub>O<sub>4</sub> (b) 10% doped NiO-NiCuFe<sub>2</sub>O<sub>4</sub> and (c) 15% doped NiO-NiCuFe<sub>2</sub>O<sub>4</sub>

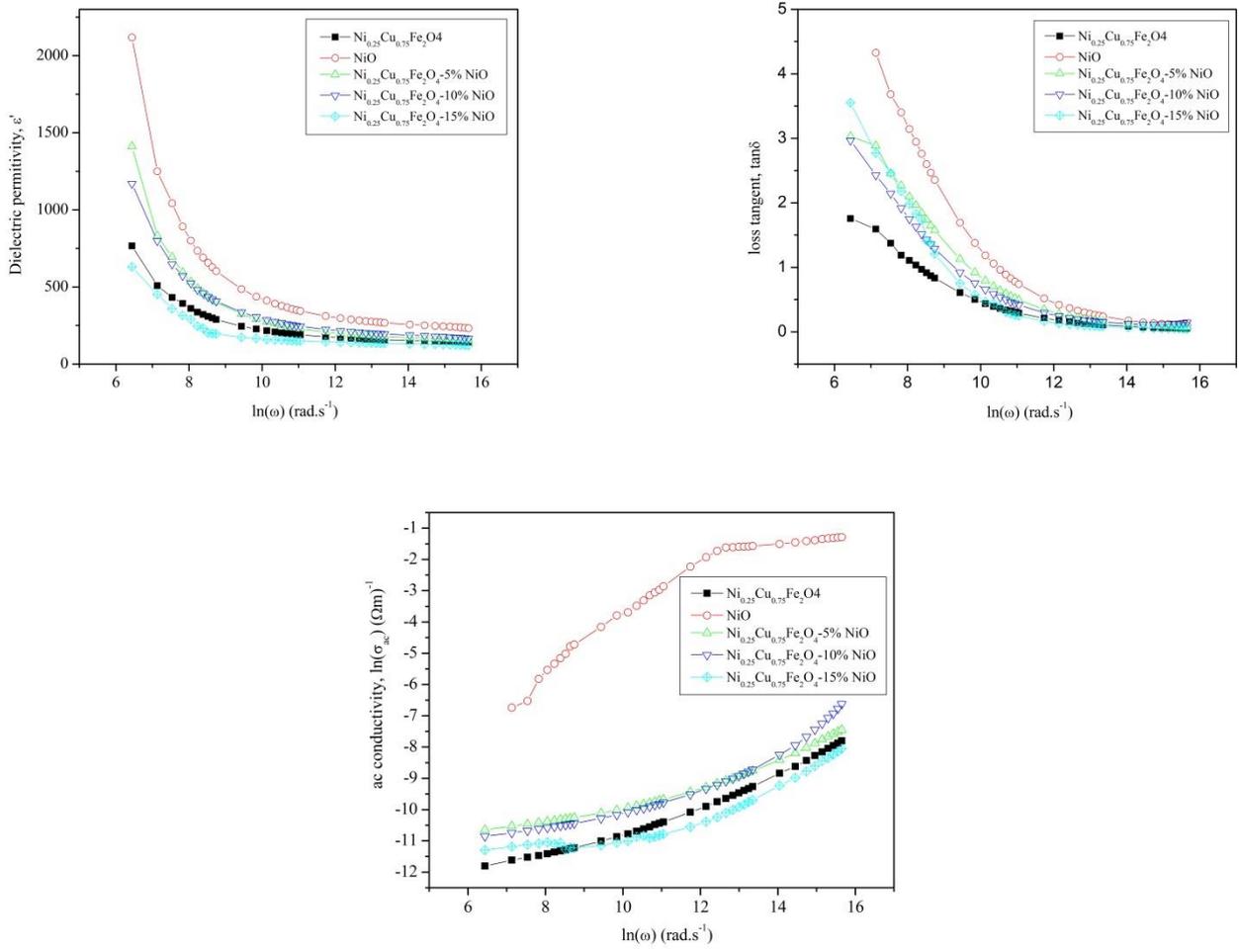


Fig.3 (a).Dielectric permittivity,  $\epsilon'$  with  $\ln(\omega)$  , (b) Tangent loss factor  $\tan\delta$  with  $\ln(\omega)$  and (c) AC conductivity,  $\sigma_{ac}$  with  $\ln(\omega)$ .

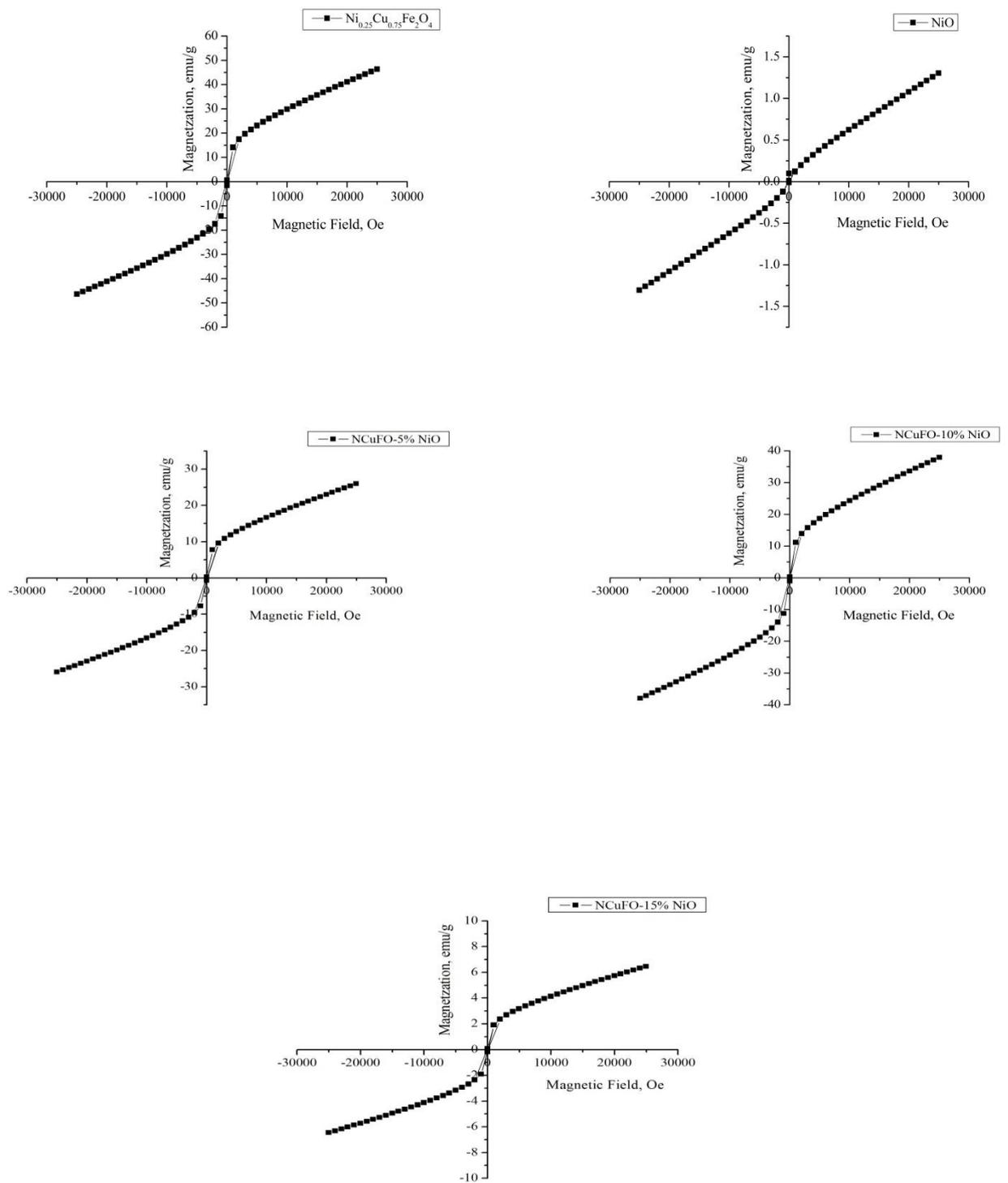


Fig.4. Magnetic Hysteresis loops of  $\text{Ni}_{0.25}\text{Cu}_{0.75}\text{Fe}_2\text{O}_4$ - NiO Composites

## Tables

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