



DIELECTRIC AND MAGNETIC STUDIES OF NiCuFe₂O₄ – NiO NANOCOMPOSITES

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Abstract:

This article presents the dielectric and magnetic studies of composites of two phases, ferrimagnetic and a transitional metal oxide. Transitional metal oxides such as NiO, if in limited proportions are doped with spinel structured magnetic oxides known as ferrites, then the resulting composites will exhibit excellent properties which are absent in their individual phases. Nanocomposites of ferrite Ni_{0.5}Cu_{0.5}Fe₂O₄ and transitional metal oxide, NiO with the basic composition (1-x) Ni_{0.5}Cu_{0.5}Fe₂O₄ + (x) NiO (here, x=0, 0.1, 0.15, 0.2) were synthesized using mechanical grinding method whereas, for the synthesis of ferrites, nitrate-citrate method was adopted. Synthesized samples were sintered at 900°C and investigated for various properties. 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_{0.5}Cu_{0.5}Fe₂O₄ and for NiO face centered cubic structure and both the phases were present in the powder composite samples. Using FESEM, surface morphology of the samples has been investigated. Composition and frequency dependent dielectric properties were studied using HIOKI make LCR meter model 3520-50 from 20Hz to 1MHz. For the proposed composite samples magnetic measurements were done at RT using Vibrating Sample Magnetometer (VSM).

Keywords: Dielectric; Nanocomposites; Magnetic; Composites.

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Introduction

Nano structured soft spinel ferrites have attracted great interest due to their excellent bio-compatibility, low toxicity and their magnetism as well as, because of their excellent tunable properties, such as its dielectric, magnetic properties and can be easily modified just by varying various synthesis methods and various factors such as the type of organic fuel used for the synthesis, P_H of the redox solution, composition of the metal ions, crystal structure, types of additives and sintering temperature etc [1-3]. These magnetic composite materials are currently considered among the widely

successful magnetic nanoparticles (MNPs) that can be extensively used for various technological and in medical applications such as electrochemical super-capacitor applications, lithium-ion batteries, contrast enhancement in magnetic resonance imaging, magnetic memories, magneto-calorific refrigerators, magnetic fluid hyperthermia and in many more technological devices and applications. [4-5].

Ferrites are the oxide materials, mainly consisting of Fe₂O₃, 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⁺² at octahedral (B-site) and Fe⁺³ 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 anti-ferromagnetic 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_{0.5}Cu_{0.5}Fe₂O₄ 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_{0.5}Cu_{0.5}Fe₂O₄ + (x) NiO (x=0, 0.1, 0.15, 0.2) 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.

Materials and methods

Composites of Ni_{0.5}Cu_{0.5}Fe₂O₄ and NiO were prepared using a hybrid method which includes both auto-combustion method and mechanical grinding of the two different phases. Precursors for starting the materials synthesis are Nickel Nitrate (Ni (NO₃)₂.6H₂O), Ferric Nitrate (Fe (NO₃)₂.9H₂O), Copper Nitrate (Cu (NO₃)₂.4H₂O), Citric acid (C₆H₈O₇.H₂O), 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°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 900°C for 4 hours to get better crystallization and homogeneous cation distribution in the proposed spinel and finally ground to get mixed Ni_{0.5}Cu_{0.5}Fe₂O₄ nano powders, similarly procedure is used for preparing NiO, later the nano-powders of NiO and Ni_{0.5}Cu_{0.5}Fe₂O₄ were mechanically mixed using agate mortar and pestle for prolonged hours of grinding. Synthesized composite samples of NiCuFe₂O₄-NiO composites are labeled as NCu-NiO-1, NCu-NiO-2 and NCu-NiO-3; where as pure samples are labeled as NiO and Ni_{0.5}Cu_{0.5}Fe₂O₄ as NCuFO.

Phase confirmation of the Pure NiO and their three composite samples were investigated using X-ray diffraction (XRD) studies using Bruker AXSD8 Advance X-ray diffractometer (using Cu-K_α radiation, λ=1.5406 Å), a working voltage of 40kV at 40mA of current. Diffraction data were collected in the 2θ range 10-80°. Morphology of the sintered samples has been investigated using Field Emission Scanning Electron Microscope (JEOL Model 7610FPLUS). Magnetic measurements were performed using vibrating sample

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magnetometer VSM, Lakeshore Model: 7400, USA. Parallel capacitance, C_p and dissipation factor, tanδ 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 (ε') and (ε'') 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, σ_{ac} was determined from the dielectric loss factor using a relation

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

Where, ε₀ is the vacuum permittivity and ω = 2πf with f being frequency.

Results and discussion

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) Ni_{0.5}Cu_{0.5}Fe₂O₄ + (x) NiO (where x=0.0, 0.1, 0.15, 0.2) are presented in Figure 1(a) and Fig 1(b). Presence of (220), (311), (400), (422), (511),

(440) and (533) planes indexed for the cubic phase of spinel ferrites [NiFe₂O₄, Ref No: 00-066-0778, For NiO, Ref Code No: 01-078-4374 and JCPDS Card No: 25-0283 for Ni_{0.5}Cu_{0.5}Fe₂O₄]. From the X-ray diffractogram, it is clear that the composites are having both reflections corresponding to metal oxide (NiO) and ferrite phase (Ni_{0.5}Cu_{0.5}Fe₂O₄), here the reflections corresponding to NiO 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 phase and NiO phase.

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 Ni_{0.5}Cu_{0.5}Fe₂O₄ ferrite. Grains of two different phases distributed inhomogeneously in the micrographs of the composites. Addition of NiO to Ni_{0.5}Cu_{0.5}Fe₂O₄ produced irregular grains. This may be attributed to the filling of pores between the Ni_{0.5}Cu_{0.5}Fe₂O₄ grains by the NiO particles and their segregation at the grain boundaries.

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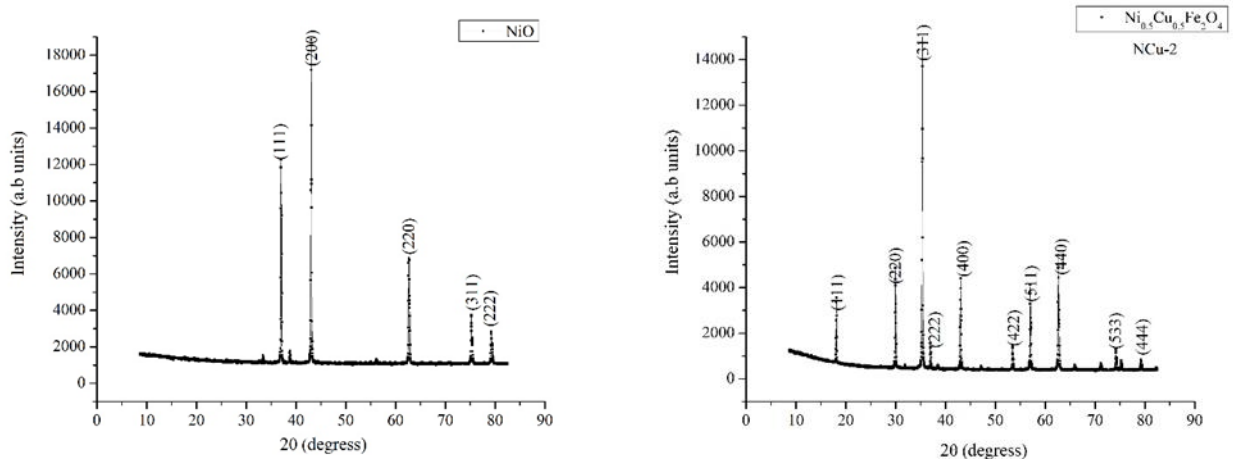


Fig.1 (a). Diffractogram of Pure NiO and Pure Ni_{0.5}Cu_{0.5}Fe₂O₄.

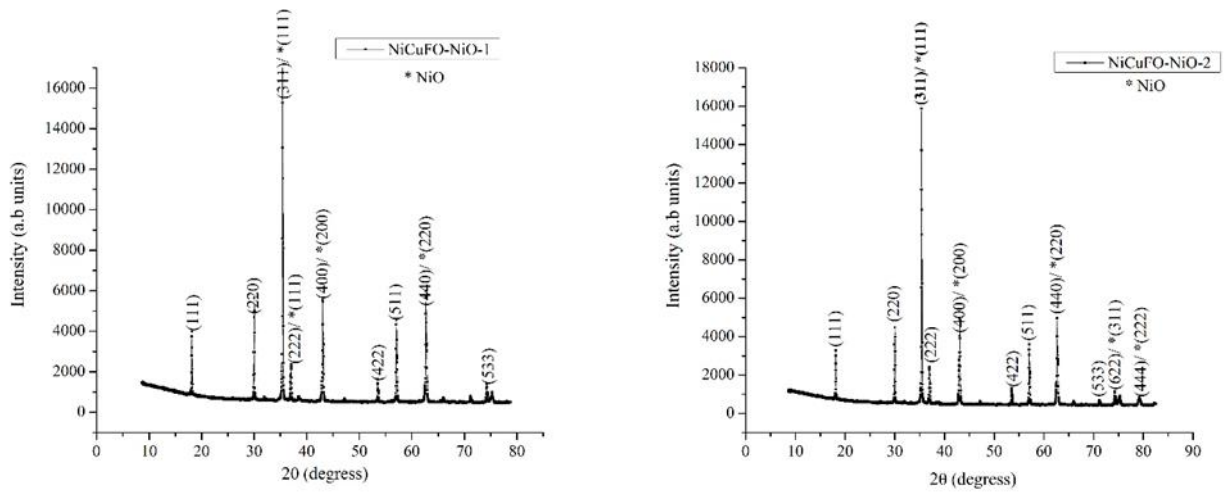


Fig. 1(b). Diffractogram of 10 wt% (NiCuFO-NiO-1) and 15 wt % NiO in Ni_{0.5}Cu_{0.5}Fe₂O₄ (NiCuFO-NiO-2)

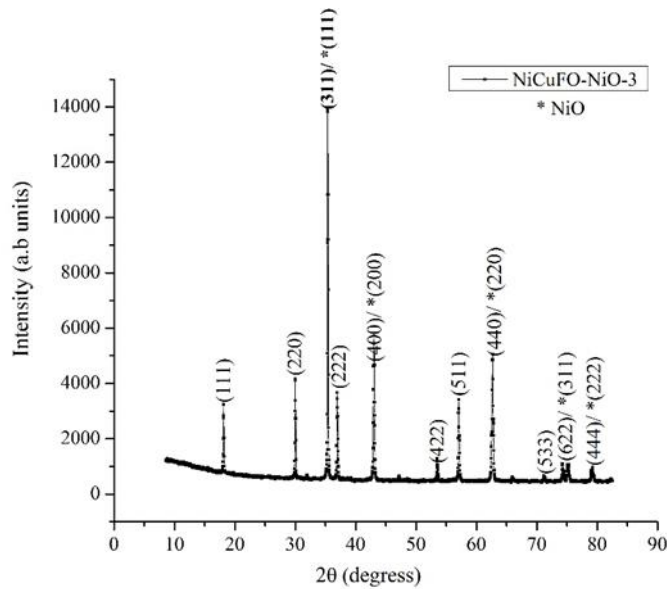


Fig. 1(c). Diffractogram of 20 wt % NiO in Ni_{0.5}Cu_{0.5}Fe₂O₄ (NiCuFO-NiO-3).

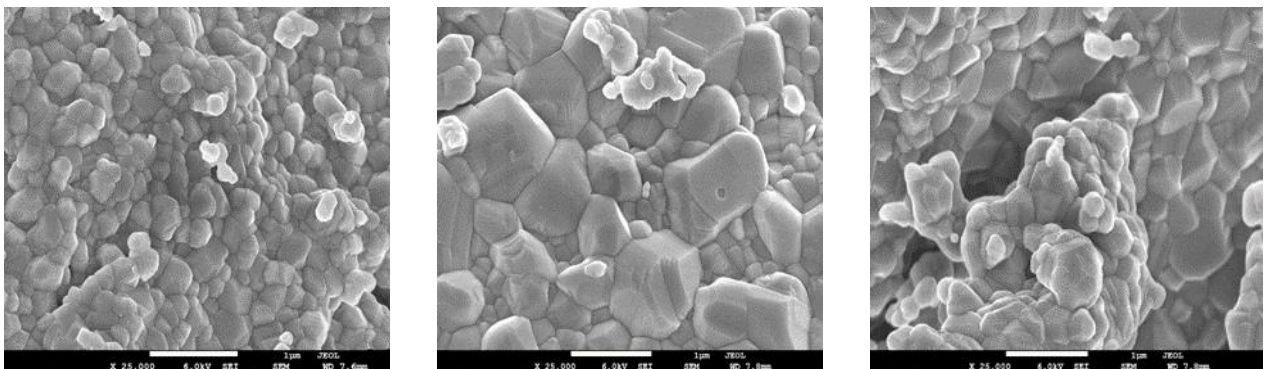


Fig. 2 Micrographs for NiO – Ni_{0.5}Cu_{0.5}Fe₂O₄ Composites for (a) 10 wt% doped (b) 15wt % doped and (c) 20 wt % doped

Dielectric studies

Dielectric permittivity (ϵ') 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, ϵ' and ac conductivity (σ_{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 ϵ' 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 ϵ' 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 Fe⁺² and 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 Fe⁺²/Fe⁺³ cannot follow the alternating field hence reaches the constant value [16-17].

Variation in the dielectric loss for all the proposed series of samples upto the

frequency range of 1 MHz at room temperature is shown in Fig. 3(c). Values of loss tangent ($\tan\delta$) represent the attenuation in these proposed ceramics and polarization being unable to respond to applied external frequency. Similar nature of curves for both ϵ' and $\tan\delta$ are almost similar and may be correlated to the domain wall motion with the applied field, the electron exchange between Fe⁺² and 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, σ_{ac} were estimated as per $\sigma_{ac} = \omega \epsilon_0 \epsilon''$, with ϵ_0 is the permittivity of free space and $\omega = 2\pi f$.

For the synthesized composites, variation of σ_{ac} with frequency, $\ln(\omega)$, is shown in Fig.3 (d). Obtained plots are almost linear for the entire range of frequency except at lower frequencies. Linear variation of σ_{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 Fe⁺² and 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, σ_{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.

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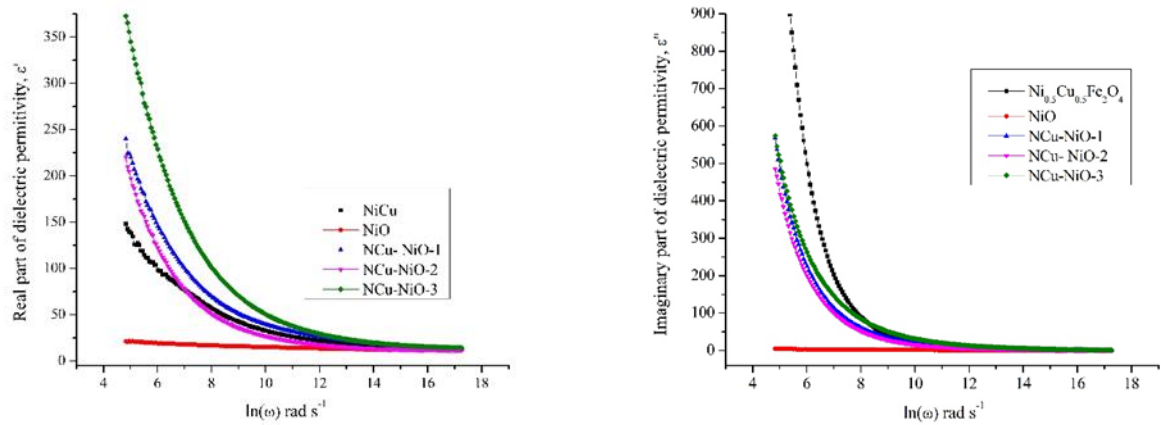


Fig.3 Variation of (a). Real Part of Dielectric constant, ϵ' with $\ln(\omega)$ and (b) Imaginary Part of Dielectric constant, ϵ'' with $\ln(\omega)$.

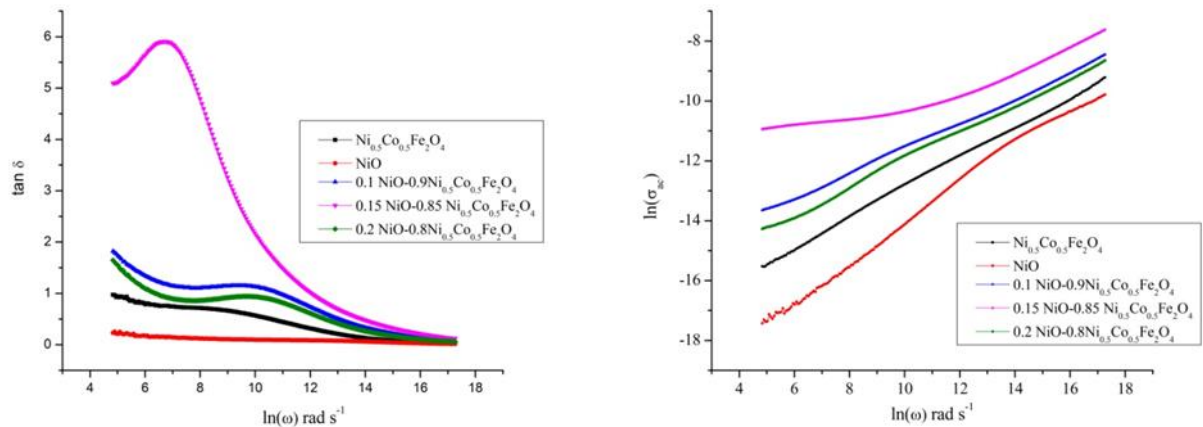


Fig.3 Variation of (c) Tangent loss factor $\tan \delta$ with $\ln(\omega)$ and (d) AC conductivity, $\ln(\sigma_{ac})$ with $\ln(\omega)$.

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 900°C are shown in Fig.4 (a) and Fig.4 (b). Proposed 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 field (H_c) were extracted from the obtained M-H loops [13-20]. Extracted magnetic parameters for all the samples are listed in Table 2. Doping with NiO, it is observed that the magnetic properties of Ni_{0.5}Cu_{0.5}Fe₂O₄ gets decreases as the anti-ferromagnetic NiO content increases and it may be attributed to the intrinsic properties of NiO, which has shown M_s of 1.20 emu/g at RT.

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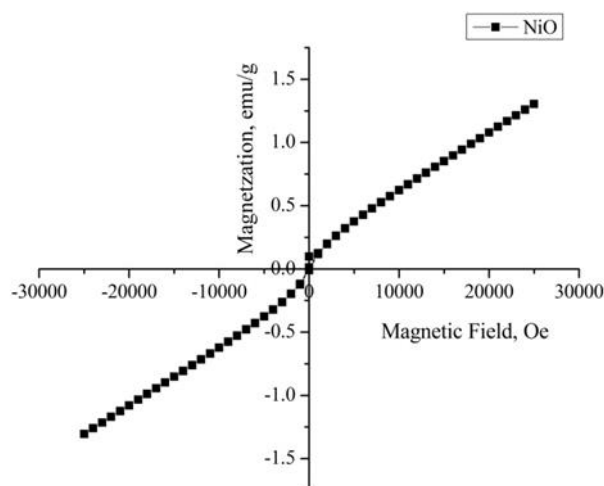


Fig.4 (a). Plots of magnetic hysteresis loop for the pure NiOnano-powder at RT.

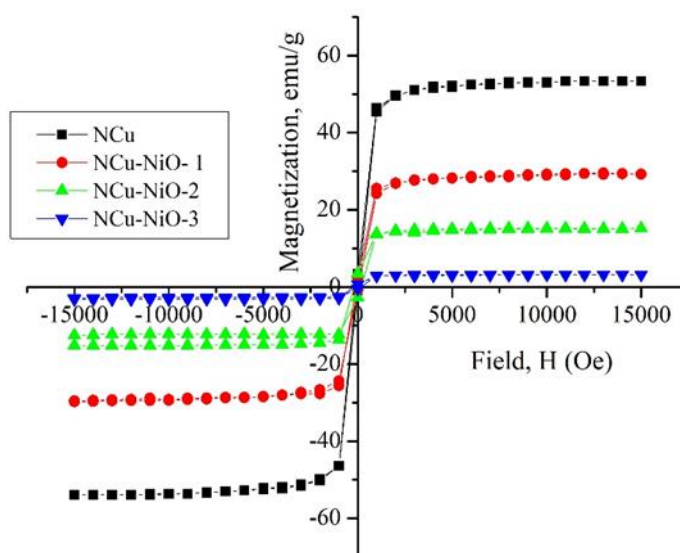


Fig.4 (b). Magnetic Hysteresis loops of Ni_{0.5}Cu_{0.5}Fe₂O₄- NiO Composites.

Table 2. Magnetic parameters obtained from M-H Loops.

Sample	Saturation Magnetization Ms (emu/g)	Remanent Magnetization Mr (emu/g)	Coercive Field Hc (Oe)
Ni _{0.5} Cu _{0.5} Fe ₂ O ₄	50.22	9.16	34.76
NiO	1.20	0.12	81.19
NCu-NiO-1	25.44	0.34	142.21
NCu-NiO-2	15.18	3.48	171.26
NCu-NiO-3	3.14	0.72	155.56

Conclusions

Composites of the system (1-x) Ni_{0.5}Cu_{0.5}Fe₂O₄+ (x) NiO (x=0, 0.1, 0.15, 0.2) were 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_{0.5}Cu_{0.5}Fe₂O₄ particles well dispersed and forms agglomeration. 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.

Finally, it is concluded that, a series of samples of NiCuFe₂O₄-NiO composites have been studied for structural, dielectric and magnetic properties.

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

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