

Magnetic and Gas Sensing Studies of NiO doped $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$

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Abstract:

To nano-structured ferrites, if transitional metal oxides such as NiO, are doped then the resulting composites will exhibit excellent properties which are absent in their individual phases. Nano-composites of ferrite $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ and transitional metal oxide, NiO with the basic composition $(1-x)\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4 + (x)\text{NiO}$ (here, $x=0, 0.1, 0.15, 0.2$) were synthesized mechanical grinding and for the synthesis of ferrites, used nitrate-citrate method. Synthesized samples were sintered at 900°C and 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 $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ 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 dependent magnetic studies of proposed nano-composite were performed at 300 K by applying an external magnetic field. Magnetic studies for the proposed samples were completed using vibrating sample magnetometer (VSM-Lakeshore, USA, Model: 7404).

Keywords: Gas Sensing; Nano-powders; Magnetic; Composites.

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_2O_3 , 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 $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ 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 $(1-x)\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4 + (x)\text{NiO}$ ($x=0, 0.1, 0.15, 0.2$) 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.

2. MATERIALS AND METHODS

Composites of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ 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 ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), Cobalt Nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 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 500°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 $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ nano powders, similarly procedure is used for preparing NiO, later

the nano-powders of NiO and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ were mechanically mixed using agate mortar and pestle for prolonged hours of grinding. Proposed composite samples are labeled as NiCo-NiO-1, NiCo-NiO-2 and NiCo-NiO-3; where as pure samples are labeled as NiO and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ as NCO.

Phase of the Pure NiO and their three composite 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 2θ range $10-80^\circ$. Morphology of the sintered samples has been investigated using Field Emission Scanning Electron Microscope (JEOL Model 7610FPLUS).

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 $(1-x)\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4 + (x)\text{NiO}$ (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 [NiFe_2O_4 , Ref No: 00-066-0778, For NiO, Ref Code No: 01-078-4374 and JCPDS Card No: 01-088-380 for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$]. From the X-ray diffractogram, it is clear that the composites are having both reflections corresponding to metal oxide (NiO) and ferrite phase ($\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$), 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 $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite. Grains of two different phases distributed in-homogeneously in the micrographs of the composites. Addition of NiO to $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ produced irregular grains. This may be attributed to the filling of pores between the $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ grains by the NiO particles and their segregation at the grain boundaries.

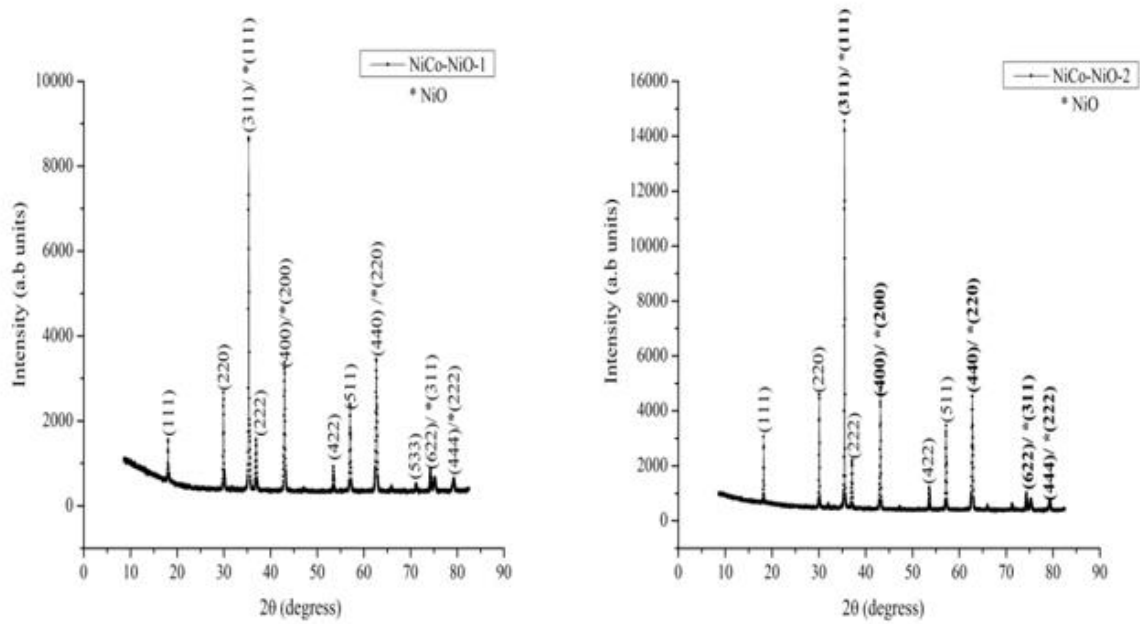


Fig.1 (a). Diffractogram of 0.1 wt % and 0.15 wt % NiO in $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$.

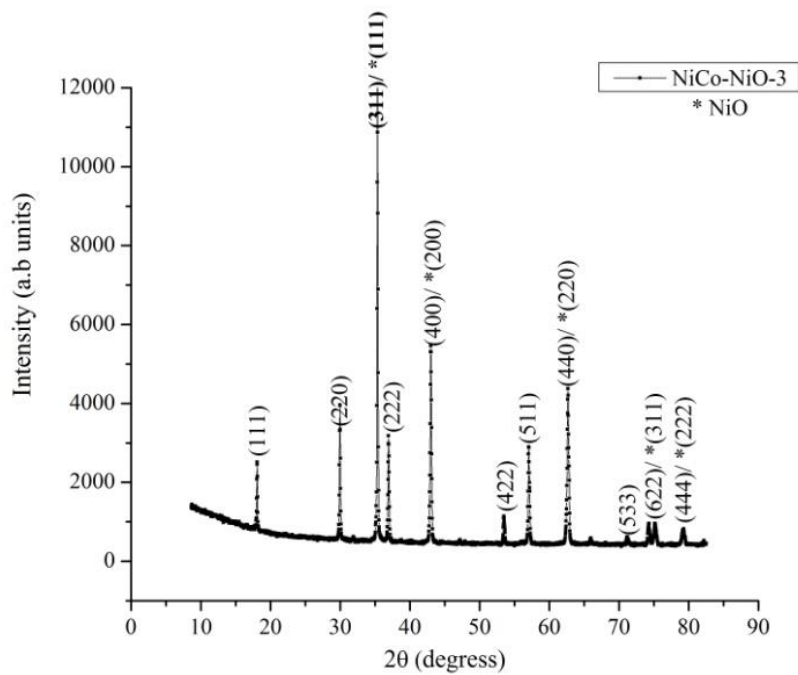


Fig. 1(b). Diffractogram of 0.2 wt % NiO in $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$.

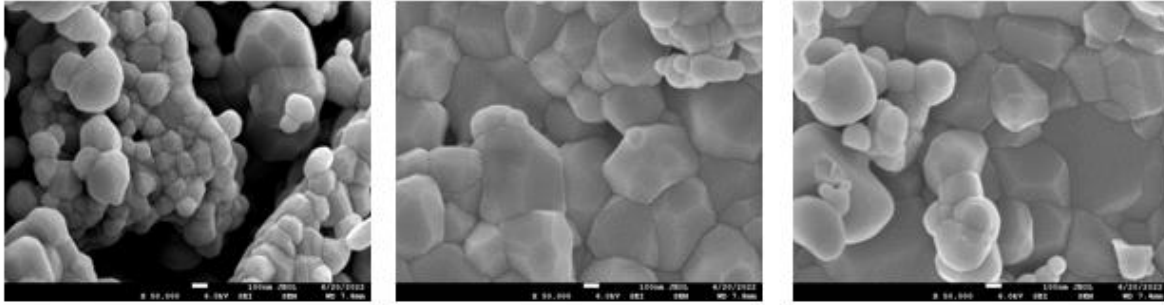
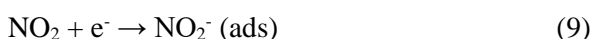
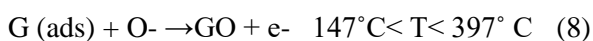
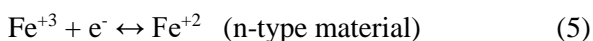
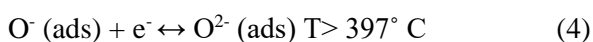
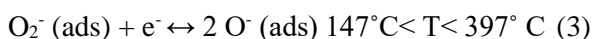
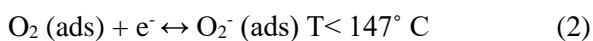


Fig. 2 Micrographs for NiO – Ni_{0.5}Co_{0.5}Fe₂O₄ Composites for (a) 10 wt % doped (b) 15wt % doped and (c) 20 wt % doped

3.2 Gas Sensing Studies

In this, the potentiality of the spinel structure ferrites doped with NiO is explored for gas sensing particularly for NO₂ gas (for 100ppm). Change of resistance usually mentioned as R_a/R_g, where R_a, the resistance in air, R_g, the resistance of the sensor after exposing to the gas, is the response which is the main performance of a gas sensor [21-22]. When Ni_{0.5}Co_{0.5}Fe₂O₄ – NiO based sensor is exposed to the air, the oxygen molecules in the air will chemisorb onto the metal oxide particle, capturing the electrons and transforms into O₂⁻, O⁻ or O₂ which specifically depends on temperature shown in equations (1) to (4). Mechanism of NO₂ detection of tested sensors (samples) at RT can be explained by the chemisorption and removal of the surface chemisorbed species.



Electron transfers that occur in equations (2) – (4) cause the formation of the depletion layer on the materials surface, making the conductive channel narrow with the the increase of R_a (Resistance in air). During the sensing process, the chemisorbed oxide particle can capture electrons, changing Fe⁺² to Fe⁺³, which is shown in equation (5). In p-type material, the hole becomes the carrier as per equation (6). On account of the dissociation effect of oxygen, the valency distribution and defects in the crystal structure changed, while a part of the conductive three-dimensional network structure is cut off, so that the R_a of the material increases [21-22].

When the reduced gas diffuses to the surface of the sensitive material, it will rapidly undergo a redox reaction, with the oxygen on the surface. During the reaction, electron captured by oxygen will return to the material, and the resistance will be altered means decreases. According to the sensing mechanism, the possible reacting processes to reduced gas are as per the equations (7) and (8). Detailed reaction will change with the operating temperature. Similar explanation follows for the remaining series of composite samples. Sensing response of pure Ni_{0.5}Co_{0.5}Fe₂O₄, NiO and their composites are mentioned from Fig. 3(a) to Fig.3(d). Obtained sensing parameters for NO₂ gas sensing is tabulated in Table.1.

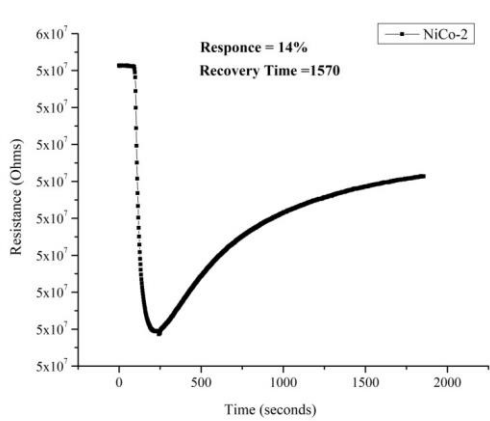


Fig.3 (a). Sensing response of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ (NiCo-2) Nano-ferrite.

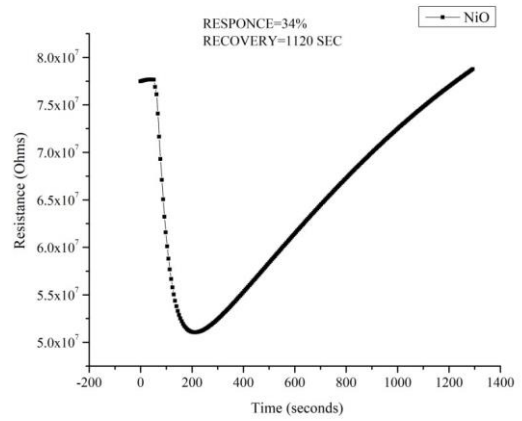


Fig.3 (b). Sensing response of pure NiO.

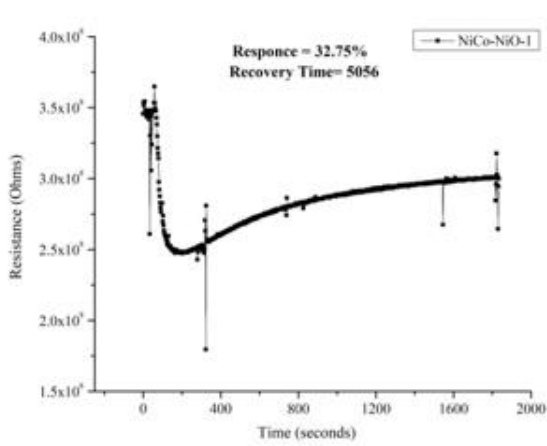


Fig.3 (c) Sensing response of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ – NiO Composites.

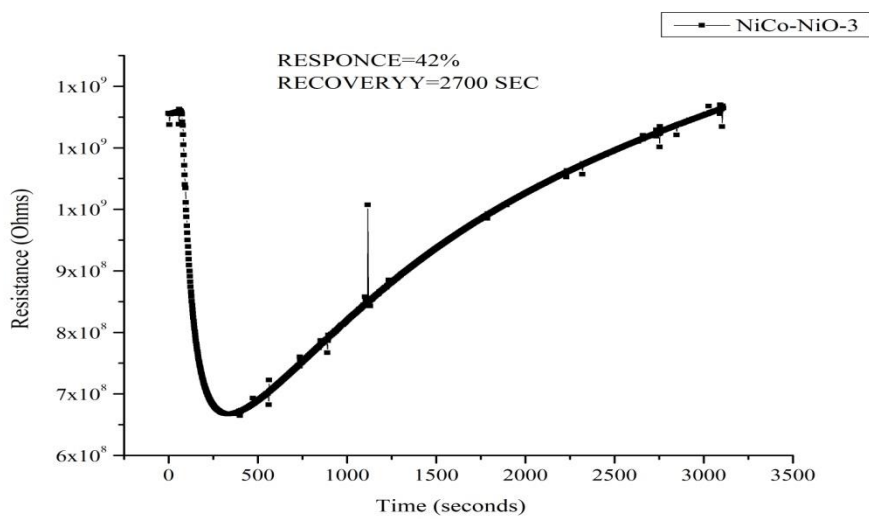
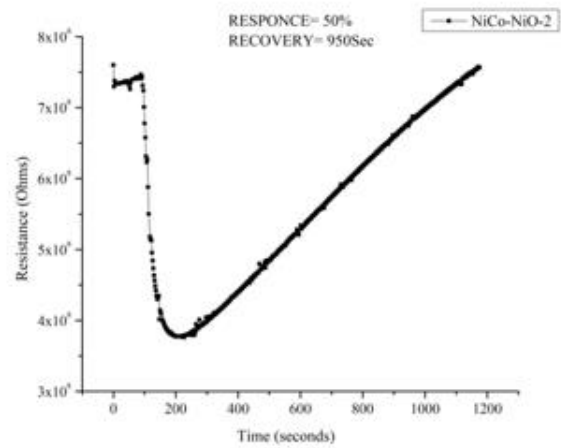


Fig.3 (d) Sensing response of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ – NiO Composite (NiCo-NiO-3).

Table.1 Gas Sensing parameters obtained from sensing curves for the $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ - NiO composite system.

Sample	Response of sensor in percentage	Recovery time in seconds
$\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	14	1750
NiO	34	1120
NCO-NiO-1	32.75	5056
NCO-NiO-2	50	950
NCO-NiO-3	42	2700

The desorption of NO_2^- (ads) is limiting at the decomposition of the NO_2 at the composite sample, which is determined by the extensive recovery time after the expose of the sensor (sample) to highly toxic NO_2 gas, the increase in sensitivity of samples can be explained by reversible oxidizing interaction of NO_2 molecules with the predominant surface adsorbed oxygen species O_2^- . Physisorbed NO_2 molecules form new surface acceptor levels deeper than surface oxygen ions. Therefore, bound electron is transferred from O_2^- ion to physisorbed NO_2 molecule and form NO_2^- species and increased band bending at the composite surface and thus can be explained the resistivity increase when sensor (sample) is placed in testing environment [23-25].

When compared to Pure $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$, the composites of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ - NiO have shown better response towards NO_2 gas, when pure ferrite is doped with NiO, especially second composite NCO-NiO-2 is having good response and short recovery time, which makes the material best suitable as NO_2 sensor. The gas sensing mechanism is already explained above; the performance of a gas sensor mainly depends on its porous structure, which can be seen clearly in the FESEM image of NCO-NiO-2.

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 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 $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ gets decreases as the anti-ferromagnetic NiO content increase and it may be attributed to the intrinsic properties of NiO, which has shown a M_s of 1.20 emu/g at RT.

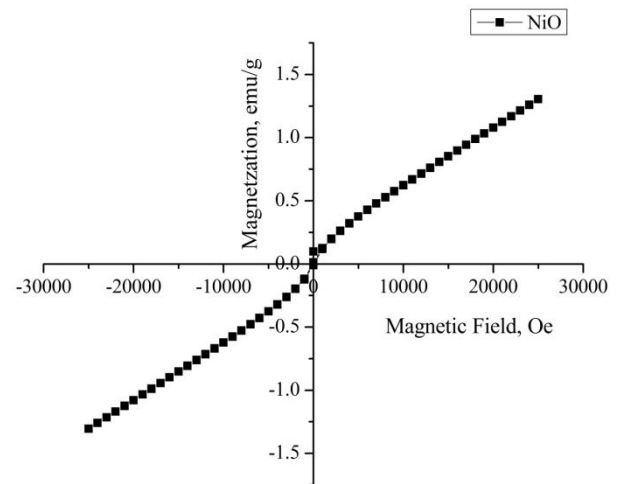


Fig.4 (a). Plots of magnetic hysteresis loop of pure NiO nano-powder at RT.

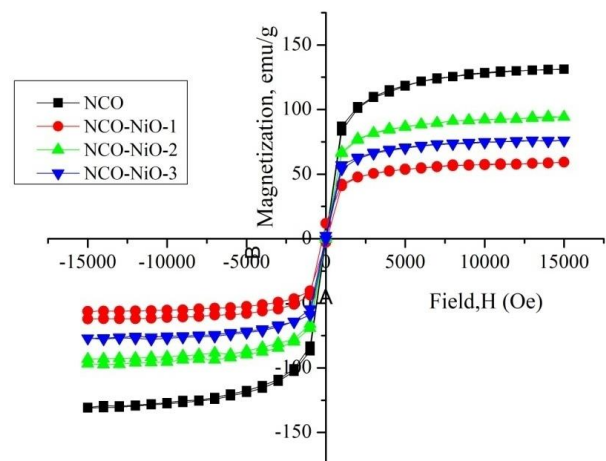


Fig.4 (b). Magnetic Hysteresis loops of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ - NiO Composites.

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

Sample	Saturation Magnetization Ms (emu/g)	Remanent Magnetization Mr (emu/g)	Coercive Field Hc (Oe)
Ni _{0.5} Co _{0.5} Fe ₂ O ₄	35.23	9.14	31.66
NiO	1.20	0.12	81.19
NCO-NiO-1	12.65	4.27	35.38
NCO-NiO-2	8.53	1.95	36.14
NCO-NiO-3	4.72	0.96	36.89

CONCLUSIONS

Composites of the system (1-x) Ni_{0.5}Co_{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}Co_{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. All the proposed samples responded to NO₂ gas, enabling them suitable candidates for NO₂ detection or sensing.

Finally, it is concluded that, three series of Ferrite-NiO composites have been studied for dielectric, magnetic and gas sensing 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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