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Comparative Study of Physical and Magnetic Properties due to Substitution of Ni^{2+} and Co^{2+} in CuCo and NiCu Nanocrystalline spinel Ferrite Respectively

A.M. Tamboli[1], Dr. S.M. Rathod[3], Dr. Gulam Rabbani[2]

Associate Professor, Department of Electronic Science, Poona College, Pune, Maharashtra, India[1].

Associate Professor, Department of Physics and Electronics, Maulana Azad College, Aurangabad, Maharashtra, India[2].

Associate Professor, Department of Physics, Abasaheb Garware College, Pune, Maharashtra, India[3].

ABSTRACT: Herein, the physical properties such as lattice constant a(Å), X-ray density d_x (gm/cm^3), bulk density (d_b) (gm/cm^3), porosity (%P), Particle size (t)and magnetic properties such as Saturation magnetization [Ms(emu/gm)], Magnetic moment [Mr(emu/gm)], Coercivity [Hc(Oe)], are reported for the series[Ni_xCu(constant) $Co_{0.8-x}$ Fe_2O_4] and[Co_xNi(constant) $Cu_{0.8-x}$ Fe_2O_4]where constant=0.2 with x=0.2, 0.4 and 0.6 of Nanocrystalline Spinel ferrites, synthesized by using pure metal nitrates with the help of Sol-Gel auto-combustion technique.The variation in the lattice constant a(Å), X-ray density d_x (gm/cm^3), bulk density (d_b) (gm/cm^3), porosity (%P), Particle size (t) and variation in the Saturation magnetization [Ms(emu/gm)], Magnetic moment [Mr(emu/gm)], Coercivity [Hc(Oe)] are studied at room temperature due to the effect of substitution 'x' of Ni^{2+} and Co^{2+} in [Ni_xCu(constant) $Co_{0.8-x}$ Fe_2O_4] and [Co_xNi(constant) $Cu_{0.8-x}$ Fe_2O_4] respectively. The NanocrystallinespinalStructural of ferrite material is confirmed by XRD and Fourier Transform Infrared Spectroscope (FT-IR). The magnetic properties are studied by using Vibrating Sample Magnetometer (VSM). The effect of substitution of Ni^{2+} and Co^{2+} on lattice constant a(Å), particle size and magnetic properties of the prepared ferrite material is discussed.

KEYWORDS : Sol-gel auto-combustion**,** X-ray diffraction, FT-IR, VSM meter.

I. INTRODUCTION

The physical and Magnetic properties of Nanocrystalline ferrite materials make them suitable for various magnetic storage applications and high frequency applications in the field of telecommunication andsignal processing. Ferrites can also be used as an electromagnetic noise and wave absorber, multilayer chip indicators (MLCIs), light weight transformer core and in frequency filters. Ferrites are widely used in microwave devices such as phase splitter, circulators, insulators, and phase shifters because of their excellent magnetic properties, high resistivity and low dielectric loss.[1-2]. The general formula of ferrite is MFe_2O_4 and electrical and magnetic propertiesof ferrites are dependent on the distribution of metal cation at tetrahedral A-site and at octahedral B-site [3-4]. Where M=Ni^{2+}, M=Cu^{2+}, M=Co^{2+}, M=Mg^{2+}, M=Zn^{2+} etc.

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II. MATERIALS AND METHODS

2.1 Synthesis

Pure AR grade ferric nitrate [$Fe(NO_3)_3.9H_2O$)], Copper nitrate [$Cu\ (NO_3)_2\ .6H_2O$], Nickel nitrate [$Ni(NO_3)_2.6H_2O$],Cobalt nitrate [$Co(NO_3)_2.6H_2O$], citric acid ($C_6H_8O_7$), ammonium hydroxide solution (NH_4OH) and distilled water were used to prepare the series [$Ni_xCu_{(constant)}\ Co_{0.8-x}\ Fe_2O_4$] and[$Co_xNi_{(constant)}Cu_{0.8-x}\ Fe_2O_4$]where constant=0.2 with x=0.2, 0.4 and 0.6 of ferritenanoparticles by sol-gel auto combustion synthesis technique. In this chemical process Citric acid is used as a Catalyst to boot the speed of reaction. All metal nitrates and citric acid were weighed accurately to have proper stoichiometric proportion required in the final product and all metal nitrates are dissolved in deionised water to form mixed solution. The mixed solutions of all the chemicals are stirred by using automatically rotating magnetic stirrer until the homogeneous solution is obtained. During the stirring process ammonium hydroxide solution was added drop by drop to obtain pH of liquid at 7. The mixed solution was simultaneously heated at 100 $^{\circ}$C for 2 hours to 4 hours such that formation of gel takes place. The transparent solution was heated at 100°C for 2 hours to 4 hours for removal of water and solution turns into a viscous brown gel. The temperature of the gel was further increased up to 140 $^{\circ}$C to 180 $^{\circ}$C such that combustion of the gel takes place and fine powder of [$Ni_xCu_{(constant)}\ Co_{0.8-x}\ Fe_2O_4$] and[$Co_xNi_{(constant)}Cu_{0.8-x}\ Fe_2O_4$]ferrite nanoparticles are obtained.

The powder was dried and annealed at 400 $^{\circ}$C for 4h in furnace having super kanthal ($MoSi_2$) heating elements and alumina insulation boards as chamber walls. Total six samples of ferrite materials are prepared out of that three samples of ferrite materials are prepared for [$Ni_xCu_{(constant)}\ Co_{0.8-x}\ Fe_2O_4$] and three for [$Co_xNi_{(constant)}Cu_{0.8-x}\ Fe_2O_4$]forconstant=0.2withx=0.2, 0.4 and0.6.Detail composition of all samples all six samples are represented by symbol A, B, C, D, E, A is shown in Table. No.1.

2.2 Characterization of Lattice Constant and Particle Size.

The phase analysis and gross structural analysis is done by using X-ray diffractometer (Cu $K\alpha_1$ radiation=1.5418 Å) and confirmation of single phase spinal structure is done. The average particle size of prepared powder has been calculated using Scherrer formula

$$t = 0.9\ \lambda / \beta \cos\theta \quad \text{----------} \quad (1)$$

Where;λ= Wave length of X-rays.

t = Particle size.

θ= Bragg's angle.

β = Full Width Half Maxima of the recorded peak θ and it is corrected for instrumental broadening.

The lattice parameter (a) is calculated from X-ray diffraction data by using formula

$$1/d^2 = 1/a^2 * (h^2 + k^2 + l^2) \quad \text{----------} \quad (2)$$

Using the XRD data, the interplaner spacing 'd' values for all the reflections were determined using Bragg's law. It is observed that due to the concentration of Ni^{2+} ions in place of Co^{2+} ions the Bragg's angle shifts towards higher angle and thereby interplaner spacing 'd' values decreases [1-3].The lattice constant is found to decrease with increase in Ni^{2+} concentration x. The variations in lattice constant as a function of Nickel concentration x can be understood on the basis of the ionic radius of the substituted cations. Since the ionic radius of Ni^{2+} ions (0.69Å) is less than that of Co^{2+} ions (0.745Å), the substitution is expected to decrease the lattice constant with increase in nickel concentration x[4-5] . When the smaller nickel ion enters, the lattice unit cell expands while preserving overall symmetry this is true as long as the lattice constant decreases with substituent concentration x.

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The values of lattice constant obtained from XRD data for varying nickel concentration x are given in Table 2. It can be seen from Table 2 that, the lattice constant decreases linearly with nickel concentration x and obeys Vegard's law [6-9]. The values of particle size obtained from Scherrer formula are given in Table 3. It can be seen from Table 3 that the particle size decreases with increase in Ni^{2+} substitution x.

It is observed that due to the concentration of Co^{2+} ions in place of Cu^{2+} ions the Bragg's angle shifts towards lower angle and thereby interplaner spacing 'd' values increases. The lattice constant is found to increase with increase in Co^{2+} concentration x. The variations in lattice constant as a function of Cobalt concentration x can be understood on the basis of the ionic radius of the substituted cations. Since the ionic radius of Co^{2+} ions (0.745Å) is greater than that of Cu^{2+} ions (0.73Å), the substitution is expected to increase the lattice constant with increase in Cobalt concentration x . When the larger Cobalt ions enters, the lattice unit cell expands while preserving overall symmetry this is true as long as the lattice constant increases with substituent concentration of Cobalt.

The values of lattice constant obtained from XRD data for varying Cobalt concentration x are given in below Table 4. It can be seen from Table 4 that the lattice constant increases with Cobalt concentration x and obeys Vegard's law [10-12]. The values of particle size for varying Cobalt concentration x is obtained from Scherrer formula and it is given in Table 5. It can be seen from Table 5 that the particle size increases with increase in Co^{2+} substitution x.

2.3 Characterization of Saturation magnetization [Ms (emu/gm)] and Coercivity [Hc(Oe)].

With increasing Ni^{2+} density 'x' in $[(Ni_x\ Cu_{(constant)}Co_{0.8-x})Fe_2O_4]$ for constant=0.2 with x=0.2,0.4 and 0.6 , Saturation magnetization [Ms (emu/gm)] of ferrite material increases and Coercivity [Hc(Oe)] decreases for three materials namely A, B and C. The total magnetization of the Spinel ferrites comes from the difference in the magnetization of B-sites and A-sites and it is also known that the octahedral (B) site has larger magnetic moment than the tetrahedral (A) site [13-20]. Table 6 shows the Values of [Ms (emu/gm)] and [Hc(Oe)]. Fig. 6 indicates variation in [Ms (emu/gm)] with substitution x of Ni^{2+} , Fig. 7 indicates variation in [Hc(Oe)] with substitution x of Ni^{2+} and Fig. 8 shows the Hysteresis loop of ferrite samples of A, B and C.

With increasing Co^{2+} density 'x' in $[Co_x\ (Ni_{(constant)}Cu_{0.8-x})Fe_2O_4]$ for constant=0.2 with x=0.2, 0.4 and 0.6, Saturation Magnetization [Ms (emu/gm)], Magnetic moment [Mr(emu/gm)] and Coercivity [Hc(Oe)] of ferrite material increases for three materials namely D, E and A. Table 7 shows the Values of [Ms (emu/gm)] and [Hc(Oe)]. Fig. 9 indicates variation in [Ms (emu/gm)] with substitution x of Co^{2+} , Fig. 10 indicates variation in [Hc(Oe)] with substitution x of Co^{2+} and Fig. 11 shows the Hysteresis loop of ferrite samples of D, E and A.

The FTIR spectroscopy confirms the single phase nature of the prepared sample. The peak 536.114 cm^{-1} gives the confirmation of Fe_2O_4.

III. RESULTS AND DISCUSSIONS

3.1: Structural and Magnetic properties analysis.

The XRD pattern of as-synthesized ferrite material of $[Ni_xCu(constant)\ Co_{0.8-x}\ Fe_2O_4]$is shown in Fig.1. The highest intensity peaks in all three specimens are observed at (311).The average grain (crystallite) size for all the composites is calculated using Scherer's formula with respect to the high intense peak plane (311) and Lattices Constant a (Å) is calculated by using the formula $1/d^2 = 1/a^2 * (h^2 + k^2 + l^2)$.It is observed that due to the concentration of Ni^{2+} ions in place of Co^{2+} ions the Bragg's angle shifts towards higher angle and thereby interplaner spacing 'd' values decreases. The lattice constant is found to decrease with increase in Nickel (Ni^{2+}) concentration x. The lattice constant is found to decrease with increase in Ni^{2+} concentration x.

With increasing Ni^{2+} density 'x' in $[(Ni_x\ Cu_{(constant)}Co_{0.8-x})Fe_2O_4]$ Saturation magnetization [Ms (emu/gm)] of ferrite material increases and Coercivity [Hc(Oe)] decreases for three materials namely A, B and C.

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It is observed that due to the increase concentration of Co^{2+} ions in Ni Cu the Bragg's angle shifts towards lower angle and thereby interplaner spacing's (d) values increases. The XRD pattern contains no secondary peaks and it gives the confirmation about pure spinal structure of sample.

When the larger Cobalt ions enters, the lattice unit cell expands while preserving overall symmetry this is true as long as the lattice constant increases with substituent concentration of Cobalt. It can be seen from Table 1.that, the lattice constant increases with increase of Cobalt (Co^{2+}) concentration x.

With increasing Co^{2+} density 'x' in $[Co_x (Ni_{(constant)}Cu_{0.8-x})Fe_2O_4]$,Saturation Magnetization [Ms (emu/gm)] and Coercivity [Hc(Oe)] of ferrite material increases for three materials namely D, E and A.

The FTIR spectroscopy confirms the single phase nature of the prepared sample. The peak 536.114 cm^{-1} gives the confirmation of Fe_2O_4.

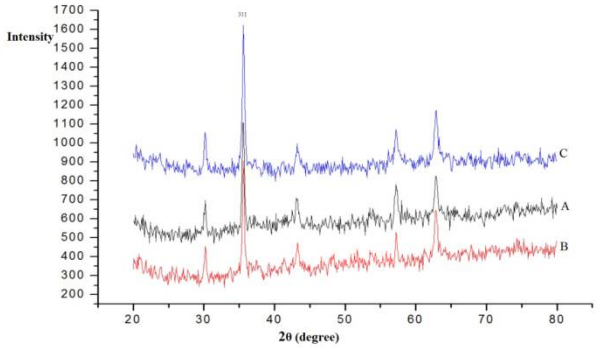

Fig. 1. XRD of Ferrite samples A, B and C

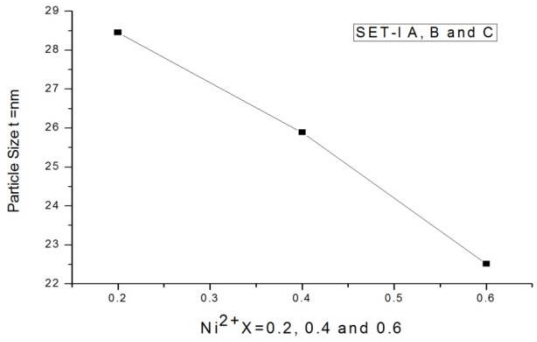

Fig. 2. Particle size (t) verses Ni^{2+} substitution x=0.2, 0.4 and 0.6.

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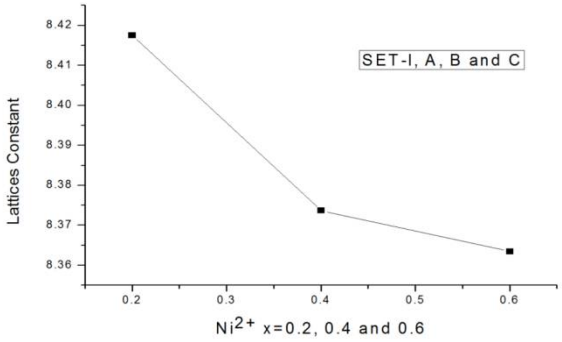

Fig. 3. Lattice Constant Verses Ni^{2+} substitution x=0.2, 0.4 and 0.6

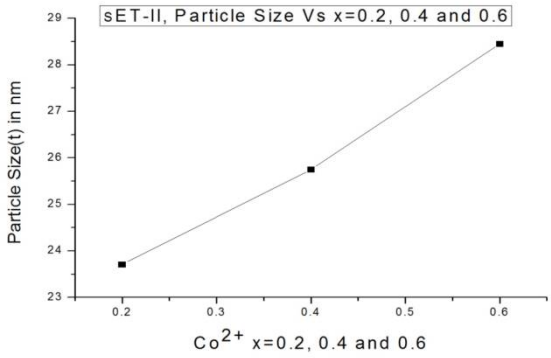

Fig. 4. Particle size (t) verses Co^{2+} substitution x in SET-II (D, E, A).

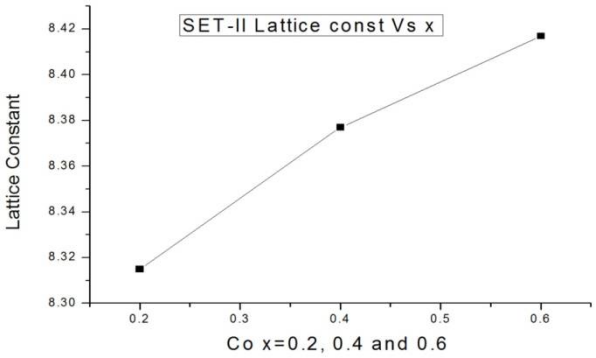

Fig. 5.Lattices Constant verses Co^{2+} substitution x in SET-II (D, E, A).

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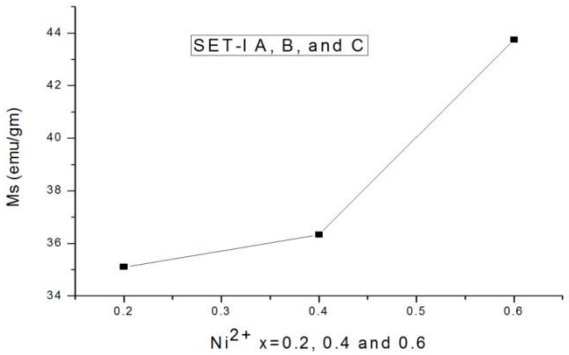

Fig. 6. Ms (emu/gm) Verses Ni^{2+} substitution x=0.2, 0.4 and 0.6.

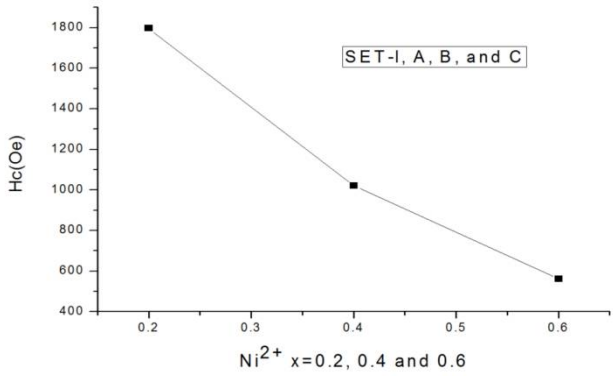

Fig. 7.Hc(Oe) Verses Ni^{2+} substitution x=0.2, 0.4 and 0.6.

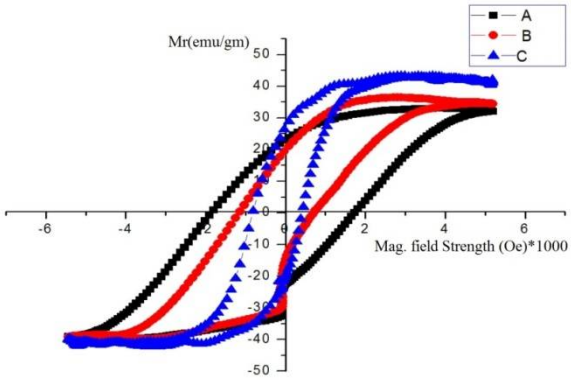

Fig. 8. Hysteresis Loop of three ferrite materials in SET-I (A,B,C).

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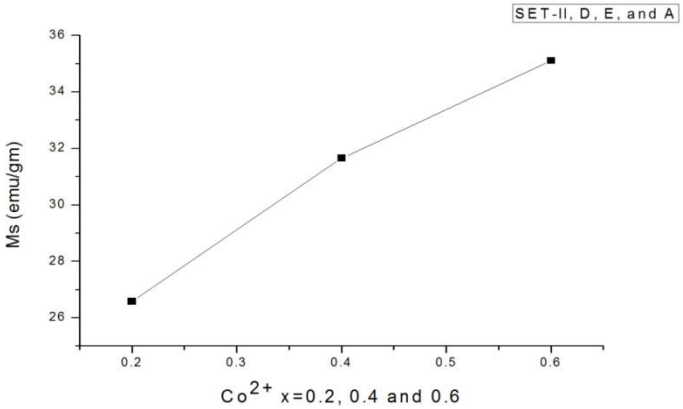

Fig. 9. Ms (emu/gm) Verses Co^{2+} substitution x=0.2, 0.4 and 0.6.

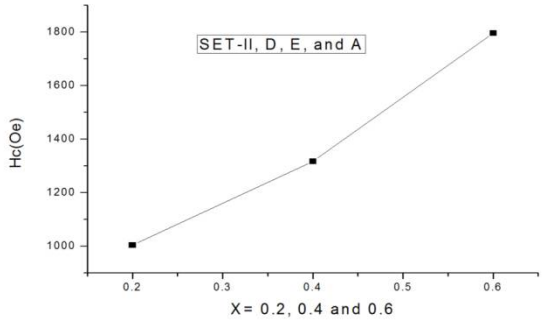

Fig. 10.Hc(Oe) Verses Co^{2+} substitution x=0.2, 0.4 and 0.6.

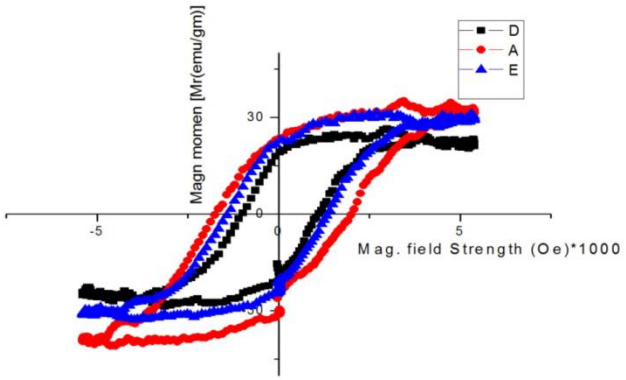

Fig. 11.Hysteresis Loop of three ferrite materials in SET-II (D, E, A).

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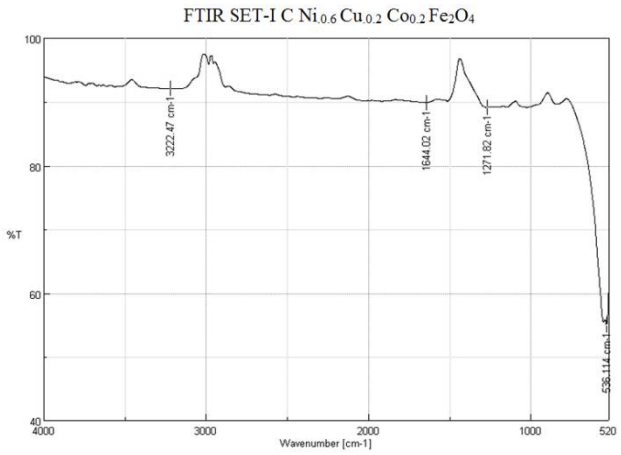

Fig. 12. FTIR graph for SET-I (C) $[(Ni_{.0.6}\,Cu_{.0.2}Co_{0.2})Fe_2O_4]$

Table 1.
Composition of Samples A, B, C, D, E, and A.

SET	Label	Ferrite Material
SET-I	A	$[(Ni_{.0.2}\,Cu_{.0.2}Co_{0.6})Fe_2O_4]$
	B	$[(Ni_{.0.4}\,Cu_{.0.2}Co_{0.4})Fe_2O_4]$
	C	$[(Ni_{.0.6}\,Cu_{.0.2}Co_{0.2})Fe_2O_4]$
SET-II	D	$[(Co_{0.2}\,Ni_{.0.2}\,Cu_{.0.6})Fe_2O_4]$
	E	$[(Co_{0.4}\,Ni_{.0.2}\,Cu_{.0.4})Fe_2O_4]$
	A	$[(Co_{0.6}\,Ni_{.0.2}\,Cu_{.0.2})Fe_2O_4]$

Table 2.
Variation of Particle size (t) and lattice constant a(Å) for SET-I(A,B,C).

Ferrite Sample and X	Particle Size t (nm)	Lattices Constant (Å)
(A) for X=0.2	28.45	8.417
(B) for X=0.4	25.89	8.374
(C) for X=0.6	22.52	8.364

Table 3.
Variation of Particle size (t) and Lattices Constant (Å) for SET-II (D, E, A).

Ferrite Sample and X	Particle Size t (nm)	Lattices Constant (Å)
(D) for X=0.2	23.71	8.315
(E) for X=0.4	25.75	8.377
(A) for X=0.6	28.45	8.417

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Table 4.
Comparison of VSM data for SET-I, A, B and C.

SAMPLE	Hc(Oe)	Ms (emu/gm)
(A) $Ni_{0.2}Cu_{0.2}Co_{0.6}Fe_2O_4$	1796.6049	035.1130
(B) $Ni_{0.4}Cu_{0.2}Co_{0.4}Fe_2O_4$	1022.1605	036.3335
(C) $Ni_{0.6}Cu_{0.2}Co_{0.2}Fe_2O_4$	560.8642	043.7550

Table 5.
Comparison of VSM data for SET-II, D, E and A.

SAMPLE	Hc(Oe)	Ms (emu/gm)
(D) $Ni_{0.2}Cu_{0.6}Co_{0.2}Fe_2O_4$	1004.9383	026.5841
(E) $Ni_{0.2}Cu_{0.4}Co_{0.4}Fe_2O_4$	1317.9630	031.6586
(A) $Ni_{0.2}Cu_{0.2}Co_{0.6}Fe_2O_4$	1796.6049	035.1130

IV. CONCLUSION

We have successfully implemented Sol Gel Auto combustion method andsuccessfully fabricated the Nanocrystalline Ferrite materials namely $[(Ni_{0.2}Cu_{0.2}Co_{0.6})Fe_2O_4]$, $[(Ni_{0.4}Cu_{0.2}Co_{0.4})Fe_2O_4]$, $[(Ni_{0.6}Cu_{0.2}Co_{0.2})Fe_2O_4]$,$[(Co_{0.2}Ni_{0.2}Cu_{0.6})Fe_2O_4]$,$[(Co_{0.4}Ni_{0.2}Cu_{0.4})Fe_2O_4]$ with good magnetic properties.

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