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Effect of concentration on dielectric properties of Co-Cu ferrite nano particles

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Abstract

Nano-sized Cobalt ferrites doped with copper as an additive element $\text{Co}_x\text{Cu}_{(1-x)}\text{Fe}_2\text{O}_4$ (where $x = 0, 0.2, 0.4, 0.6, 0.8, 1$) are synthesized using co-precipitation method. Cobalt-Copper ferrite samples sintered at 600°C are subjected to X-ray diffraction to calculate the average particle size and lattice parameters using Debye – Scherrer formula. The FT-IR spectra of these samples are recorded to ensure the presence of the metallic compounds. The variations of dielectric constant and dielectric loss for all the samples are studied as a function of frequency. The crystalline structure of composite nano particles are characterized by Transmission Electron Microscope (TEM).

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Keywords: Nano crystal; Co-precipitation; Lattice parameter; Transmission Electron Microscope; Ferrites.

1. Introduction

Studies on the properties of nano sized ferrite particles have drawn considerable interest in recent years because of their importance in the fundamental understanding of physical processes as well as their proposed applications for many technological purposes. Cobalt ferrite, a ferromagnetic ceramic has emerged as one of the important material due to its high electrical resistance and low eddy current losses. Cobalt ferrite nano particles have cubic spinel structure and have been extensively studied because of their interesting magnetic and electrical properties. Structural stability of the cobalt ferrite nano particles is essential in all technical applications.

In chemical methods of preparation of nano sized particles with desired physical properties, the structural and chemical properties of the constituents are of prime importance. Because of mixing at molecular level, good chemical homogeneity can be achieved. Also, these methods allow good control on the shape and size distribution during particle synthesis.

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Due to these reasons the chemical routes of preparation have emerged as very popular synthesis tools for nano particles of spinel ferrites. Among the various available preparation methods, to obtain nano crystalline ferrite particles, viz hydrothermal synthesis [1-4], coprecipitation [5-9], sol-gel [10-13], spraydrying [14], solid-state, microemulsion processes [15-17], and mechanical alloying [18-21], coprecipitation method is chosen in the present work for preparing Co-Cu mixed ferrites. As it is well known, co-precipitation is an economical way to produce homogenous nano ferrites. As prepared Cobalt-Copper ferrite samples are sintered at 600°C and are subjected to X-ray diffraction. The FT-IR spectra of these samples are recorded and the crystalline structure of the composite nano particles is characterized by Transmission Electron Microscope (TEM).

2. Experimental

Nano crystalline Cobalt ferrites $\text{Co}_x\text{Cu}_{(1-x)}\text{Fe}_2\text{O}_4$ ($x=0,0.2,0.4,0.6,0.8,1$) are prepared by coprecipitation method. The desired composition is obtained by taking stoichiometric amounts of Cobaltous Chloride [$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$], Cupric Chloride [$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$] and anhydrous Ferric Chloride [FeCl_3] dissolved in distilled water. The neutralization is carried out with sodium hydroxide solution. The pH of the solution is maintained at 10 and it is stirred for 2hrs. The precipitate is thoroughly washed with distilled water until they are free from impurities. The product is dried to remove water contents. The dried powder is mixed homogeneously and is sintered at 600°C.

Cobalt-Copper ferrite samples sintered at 600°C are subjected to X-ray diffraction to calculate the average particle size using Debye – Scherrer formula. The FT-IR spectra of these samples are recorded to ensure the presence of the metallic compounds. The variations of dielectric constant and dielectric loss for all the samples have been studied as a function of frequency. The crystalline structure of composite nano particles are characterized by Transmission Electron Microscope (TEM).

3. Results and Discussion

3.1 Structural Analysis

Fig.(1a-1c) represents the powder X-ray diffraction patterns of $\text{Co}_x\text{Cu}_{(1-x)}\text{Fe}_2\text{O}_4$ sintered at 600°C. All the peaks of $\text{CoCuFe}_2\text{O}_4$ and CuFe_2O_4 could be indexed with the standard pattern reported in the JCPDS card [22-23]. The XRD pattern reveals that the as prepared powder is a single phase ferrite with spinel structure. This indicates that Co-Cu ferrites can be directly formed with calcination [24]. The average crystallite sizes of prepared powders are calculated using the Debye-Scherrer formula and lattice parameters are estimated and reported in Table (1). It is seen that the powder of synthesized ferrites consists of nano crystalline particles with size in the range of 3–18 nm. Also it reveals that the addition of copper found to obstruct the grain growth which results in a decrease in the crystallite size. Recent reports [25-26] claim that there is a decrease in crystallite size with increase in Cu substitution for ferrite nanoparticles.

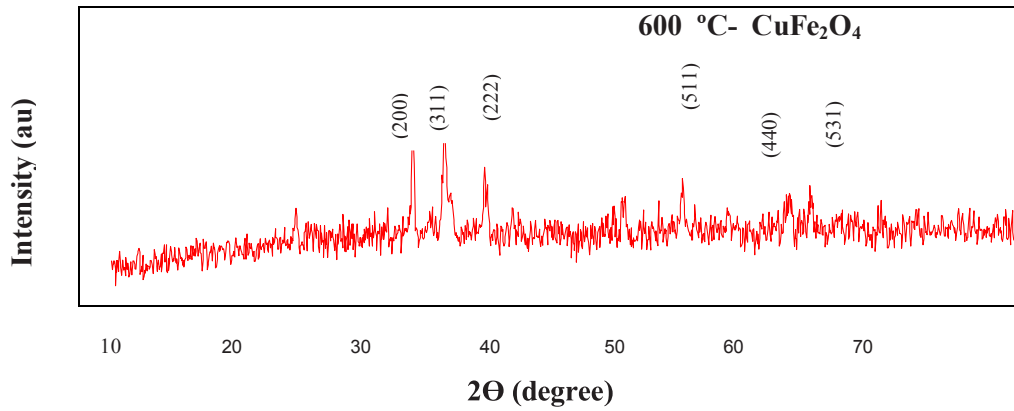


Figure (1.a). XRD pattern of CuFe₂O₄ nanoparticles by Co-precipitation method

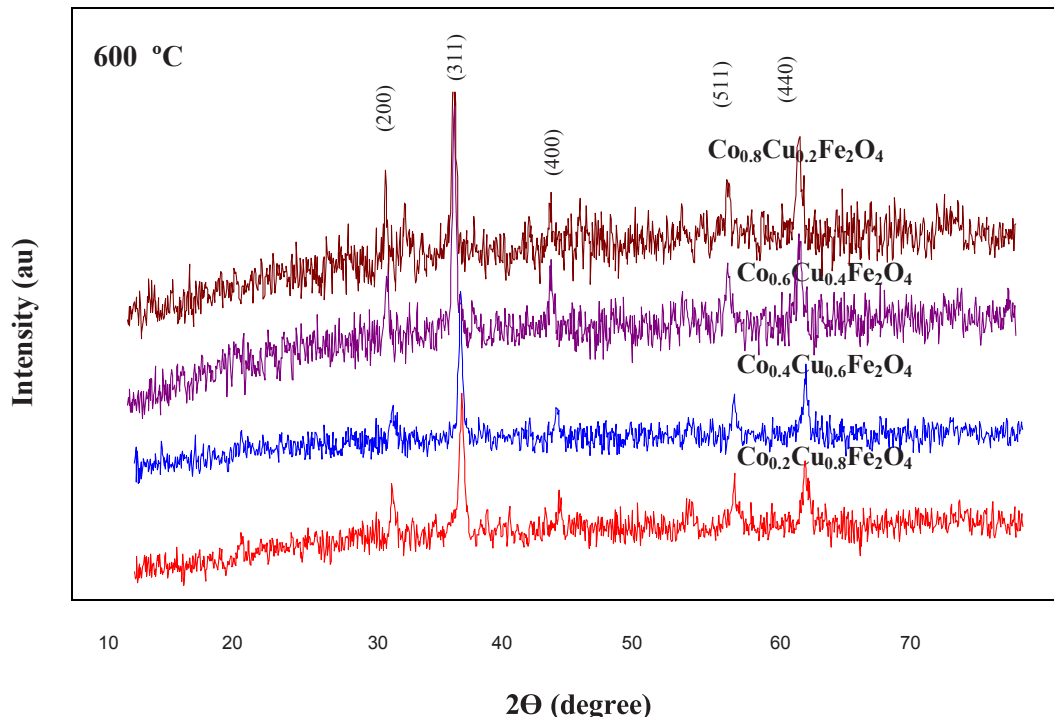


Figure (1.b). XRD pattern of Co_xCu_(1-x)Fe₂O₄ (x=0.8,0.6,0.4,0.2) nanoparticles by Co- precipitation method

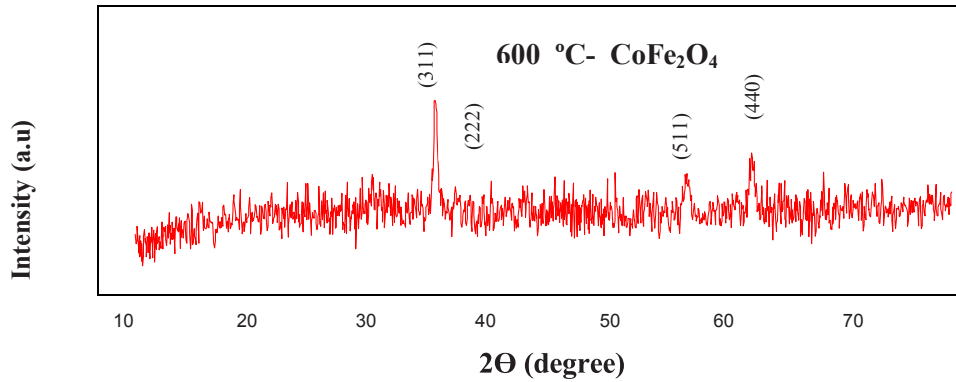


Figure (1.c). XRD pattern of CoFe_2O_4 nanoparticles by Co-precipitation method

Table. (1). Structural parameters of Nano crystalline $\text{Co}_x\text{Cu}_{(1-x)}\text{Fe}_2\text{O}_4$ ferrites

Composition	Crystallite size (nm)	Lattice parameter(Å)
CoFe_2O_4	6.11	8.08
$\text{Co}_{0.2}\text{Cu}_{0.8}\text{Fe}_2\text{O}_4$	3.71	8.14
$\text{Co}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$	5.30	8.22
$\text{Co}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$	6.15	8.17
$\text{Co}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$	17.29	8.18
CuFe_2O_4	18.16	8.12

3.2 IR Spectral Analysis

Fig.(2) shows the FT-IR spectra of $\text{Co}_x\text{Cu}_{(1-x)}\text{Fe}_2\text{O}_4$ nano crystalline particles sintered at 600°C . This spectra shows that the ferrites can be formed as continuously bonded crystals, via ionic, covalent or vander waals forces, to the nearest neighbours. In ferrite the metal ions are situated in two different sublattices, namely tetrahedral (A-sites) and octahedral (B-sites) according to the geometrical configuration of the oxygen nearest neighbours. The band around 500 cm^{-1} is attributed to stretching vibration of tetrahedral complexes and the band around 400 cm^{-1} to that of octahedral complexes [27].

This explains that the normal mode of vibration of tetrahedral cluster is higher than that of octahedral cluster. The absorption bands at 3400 cm^{-1} and 1630 cm^{-1} are ascribed to the O-H stretching modes and H-O-H bending vibration of the free or absorbed water. The band at 1380 cm^{-1} is associated with the anti-symmetric Cl^{3-} stretching vibrations directly arising from the residual chloride groups in the sample.

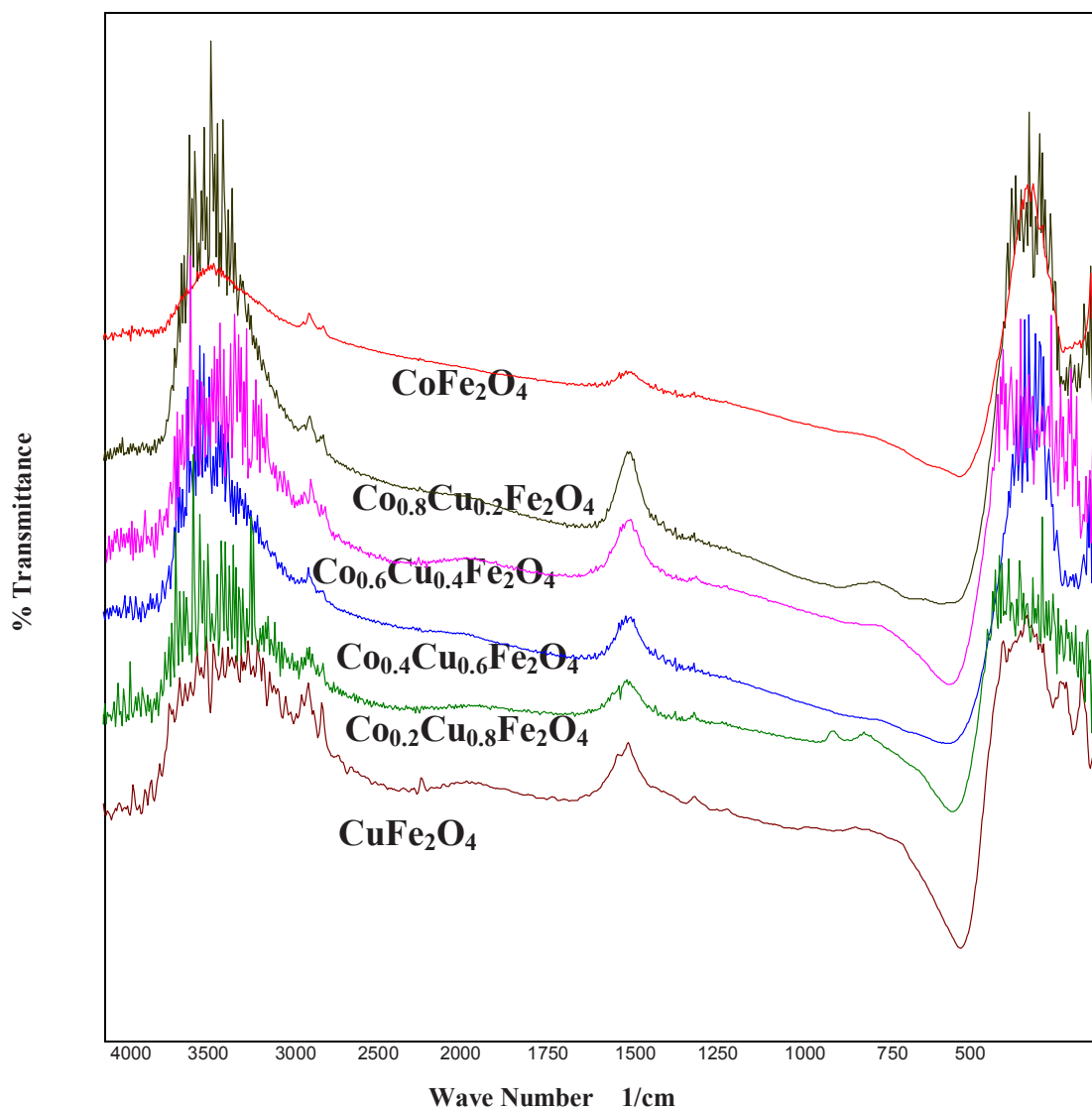


Figure. (2). FT-IR Spectrum of $\text{Co}_x\text{Cu}_{(1-x)}\text{Fe}_2\text{O}_4$ ($x=1,0.8,0.6,0.4,0.2,0$) Nano particles obtained by Co-precipitation method

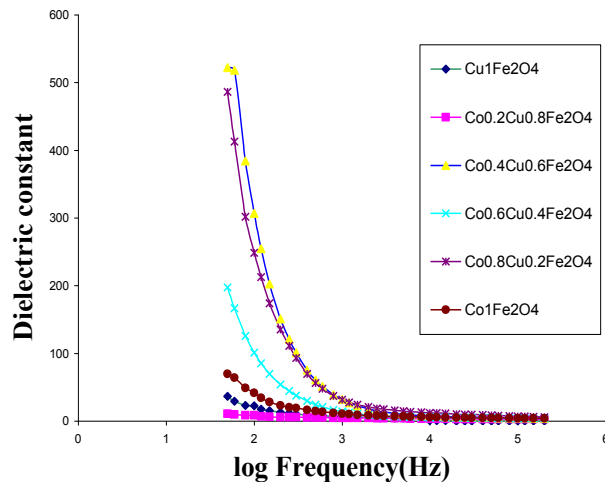
3.3 Dielectric Properties

The variation of the dielectric constant ϵ' and dissipation factor with respect to log frequency at an annealing temperature of 600 °C are shown in figure (3a & 3b). These variations can be explained on the basis of space charge polarization model of Wagner and Maxwell and are in agreement with the Koop's phenomenological theory. As these ions are polarized to the maximum extent, it is seen that the dielectric constant ϵ' , decreases with increase in frequency at all temperature as expected.

The dielectric constant starts to reach a steady state at 522.31. This steady state is retained for all the remaining higher orders of frequency, whereas samples with higher Cu substitution and lower Co

substitution at 600° C exhibit a decrease in dielectric constant value even at the stable state. These behaviours are expected because, the high thermal energy as well as the high frequency is enough to disturb the ordered dipoles, and thus it decreases the polarization and dielectric constant. Similarly the dielectric constant value varies from 522.31 to 10.44 at 600° C. This high value of dielectric constant is attained due to the lower particle size and higher value of crystallinity.

Variation of Dielectric Constant with respect to log Frequency



Variation of Dielectric Loss with respect to log Frequency

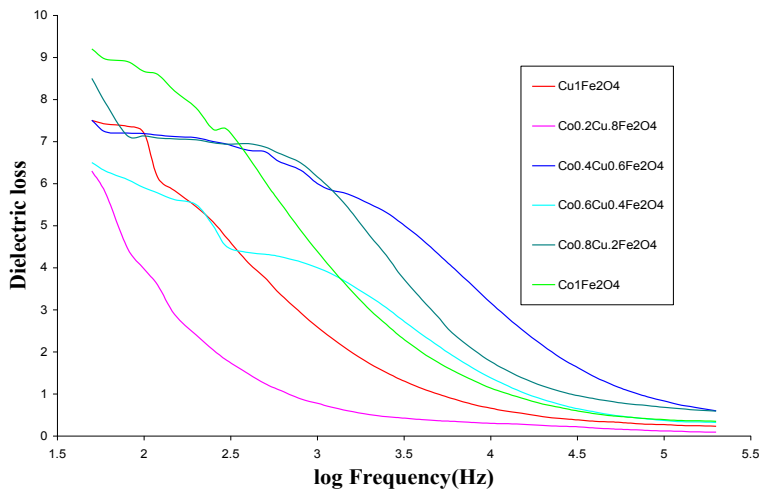
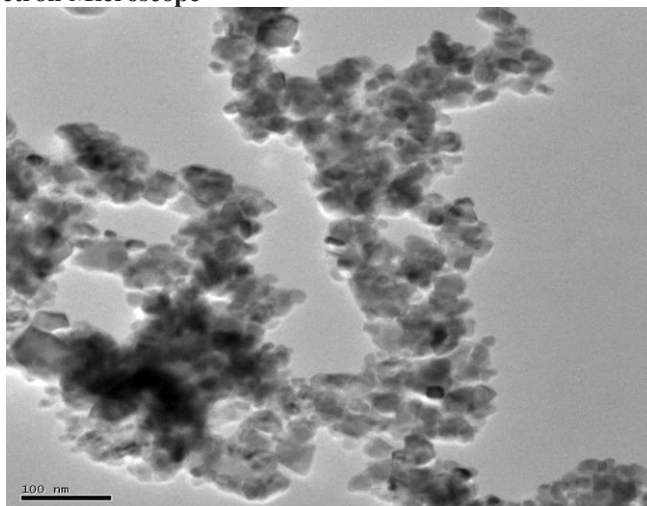


Figure. (3.a & 3.b). The variation of Dielectric Constant (ϵ') and the variation of Dielectric loss (ϵ'') with respect to Frequency (Hz) for Cu substituted Co ferrite nanoparticles

The dielectric constant decreases due to the electronic exchange which arises because of the local displacement of electrons in the direction of the applied electric field. This induces polarization in the ferrite [28]. Figure (3b) shows a high dielectric loss initially, which decreases at higher frequencies. The high loss can also be due to hopping conduction between Fe^{2+} and Fe^{3+} ions [29]. But a very low variation in the dielectric constant is observed for the CuFe_2O_4 .

3.4 Transmission Electron Microscope



Fig(4) The Transmission Electron Microscope (TEM) image of the $\text{Co}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$ nanoparticle

Fig (4) shows the TEM images of $\text{Co}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$ nanoparticles prepared by co-precipitation method. The image shows the small agglomerates of Co-Cu ferrite nano particles of size around 15-20nm.

4. Conclusion

$\text{Co}_x\text{Cu}_{(1-x)}\text{Fe}_2\text{O}_4$ nanoparticles are successfully prepared by co-precipitation method. The FT-IR spectra show main absorption bands at $\sim 500\text{ cm}^{-1}$ to 400 cm^{-1} corresponding to the vibration modes of all spinel compounds. The XRD pattern reveals that synthesized ferrites are made of nano crystalline particles with size in the range of 3–18nm. It is also observed that the crystallite size decreases with Cu substitution. The dielectric constant value varies from 522.31 to 10.44 at 600° C and this high value of dielectric constant is attained due to the lower particle size and higher value of crystallinity.

References

- [1] Pannaparayil, T., Marande, R., Komarneni, S., Magnetic properties of high density Mn-Zn ferrites, *J.Appl.Phys.* 69 (1991) 5349 – 5351.
- [2] Rozman, M., Drogenik, M., Hydrothermal synthesis of manganese zinc ferrites, *J. Am. Ceram. Soc* 78 (1995) 2449 -2455.

- [3] Komarneni, S., Fregeau, E., Breval, E., Roy, R., Hydrothermal preparation of ultra fine ferrites and their sintering, *J. Am. Ceram. Soc.* 71 (1998) c-26-c-28.
- [4] Sisk, M., Kilbride, I., barker, A. J., Production of manganese zinc ferrites via the hydrothermal decomposition of metal (III) acetates and citrates, *J. Mater. Sci. Lett* 14 (1995) 153-154.
- [5] Kiyama, M., The formation of manganese and cobalt ferrites by the air oxidation of aqueous suspensions and their properties, *Bull.Chem.Soc. Jpn.* 51 (1978) 134-138.
- [6] Katsura, T., Tamura, Y., Chyo, G.S., The formation of the oxidized $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{TiO}_4$ solid solution by the air oxidation of the aqueous suspension, *Bull.Chem.Soc. Jpn.* 52(1979) 96-100.
- [7] Kaneko, K., Kastura, T., The formation of Mg-bearing ferrite by the air oxidation of an aqueous suspension, *Bull.Chem.Soc. Jpn.* 52(1979) 1080-1085.
- [8] Kaneko, K., Takei, K., Tamura, Y., Kanzaki, T., Kastura, T., The formation of the cd-bearing ferrite by their air oxidation of an aqueous suspension, *Bull. Chem. Soc. Jpn.* 52 (1979) 1080-1085.
- [9] Tamura, Y., Rasyid, U., Kastura, T., Formation of a chromium bearing ferrite $\text{Cr}_0.42\text{Fe}_2.56\text{O}_4$ in aqueous suspension by nitrate oxidation, *J.Chem.Soc., Dalton Trans*, 53 (1980) 2125-2128.
- [10] Lee, J.G., Park, J.Y., Kim, C.S., Growth of ultra-fine cobalt ferrite particles by a sol-gel method and their magnetic properties, *J.Mater.Sci.* 33 (1998) 3965-3968.
- [11] Christoskova, S.G., Stoyanova, M., Georgieva, M., Low-temperature iron- modified cobalt oxide system. I. Preperation and Characterization, *Appl.Catal. A* 208 (2001) 235-242.
- [12] Arean, C.O., Mentruit, M.P., Platero, E.E., Xamena, F.X.L.I., Parra, J.B., Sol-gel method for preparing high surface area CoAl_2O_4 and $\text{Al}_2\text{O}_3\text{-CoAl}_2\text{O}_4$ spinels, *Mater. Lett.* 39 (1999) 22-27.
- [13] Kim, C.S., Yi, Y.S., Park, K.T., Namgung, H., Lee, J.G., Growth of ultrafine Co-Mn ferrite and magnetic properties by sol-gel method, *J. Appl. Phys.* 85 (1999) 5223-5225.
- [14] Yu, H.F., Gadalla, A.M., Preparation of $\text{Ni Fe}_2\text{O}_4$ powder by spray pyrolysis of nitrate aerosols in NH_3 , *J. Mater. Res.* 11 (1996) 663-670.
- [15] Mouden, N., Veillet, O., Pileni, M.P., Controlled preparation of nano size cobalt ferrite magnetic particles, *J. Magn. Magn. Mater.* 149 (1995)67-71.
- [16] Kommareddi, N.S., Tata, M., John, V.T., McPherson, G.L., Herman, M.F. , Lee, Y.S., O'Connor, O.J., Akkara, J.A., Kaplan, D.L., Synthesis of super paramagnetic polymer-ferrite composites using surfactant microstructures. *Chem.Mater.* 8 (1996) 801-809.
- [17] Lopez,-Quintela, M.A., Rivas, J., Chemical reactions in microemulsions: a powerful method to obtain ultrafine particles. *J.Colloid Interface Sci.* 158 (1993) 446-451.
- [18] Ding, J., McCormick, P.G., Street, P.G. R., Magnetic properties of mechanically alloyed CoFe_2O_4 , *Solid State Commun.* 95 (1995) 31-33.
- [19] Ding, J., Reynolds, T., Miao, W.F., McCormick, Street, High magnetic performance in mechanically alloyed co-substituted Fe_3O_4 , *Appl. Phys. Lett.* 65 (1994) 3135-3136.
- [20] Ding, J., McCormick, P.G., Street, R., Formation of spinel Mn-ferrite during mechanical alloying, *J.Magn. Magn. Mater.* 171 (1997) 309-314.
- [21] Shi, Y., Ding, J., Liu, X., Wang, J., $\text{Ni Fe}_2\text{O}_4$ ultrafine particles prepared by co-precipitation mechanical alloying *J. Magn. Magn. Mater.* 205 (1999) 249-254.
- [22] JCPDS Card No. #22 - 1086.
- [23] JCPDS Card No. #74 - 2081.
- [24] Zhenxing, y., Longtu, L., Zhou Hongguo, Z., and Zhilun, G., "Synthesis characterization of NiCuZn ferrite nano crystalline powders by auto combustion of nitrate – citrate gets", *Materials science And Engineering B*, .64(1999),.68-72.
- [25] Msomi, J., and Moyo, T., *J. Magn. Magn. Mater.* 321 (2009) 1246.
- [26] Gabal, M.A., Al Angari, Y.M., Kadi, M.W., "Structural and magnetic properties of nanocrystalline $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ prepared through oxalates precursors", *polyhedron*, vol.30 (2011) 1185-1190.
- [27] Kalaiselvan, R., Augustin, C.O., John, L., Berchmans, R.Saraswathi, "Combustion synthesis of CuFe_2O_4 ". *Materials Research Bulletin*, Vol.38 (2003), pp .41-54.

- [28]Jyotsenndu, G., Theerdhala, S., Saket, A., Gundu Rao Arun, K., Nigam, K., and dhirendra, B.,” synthesis of capped nanosized $Mn_{1-x}Zn_xFe_2O_4$ ($0 \leq x \leq 0.8$) by microwave refluxing for bio-medical applications”, *Journal of magnetism and magnetic materials*, Vol.293 (2005), pp.55-61.
- [29]Mukesh, H., Dimri, C., Subhash, C., Kashyap Dube, D.C., “Electrical and Magnetic Properties of Barium Hexaferrite nanoparticles prepared by Citrate Precursor method”, *Ceramics International* 30(2004) 1623-1623.