Original Research Article

Effect of temperature on Structural, Magnetic and Dielectric Properties of Cobalt ferrite Nanoparticles Prepared via Co-precipitation Method

Abstract

Nano-crystalline cobalt ferrite powders have been synthesized by coprecipitation method and characterized to investigate the effect of thermal treament on the structural, dielectric, and magnetic properties of the prepared sample. The structural/morphological, dielectric, and magnetic properties of the products were determined by X-raydiffraction (XRD), transmission electron microscopy (TEM), open ended coaxial probe and vibrating sample magnetometer (VSM). Results from analysis confirms that thermal heat influences the magnitude of magnetization, dielectric and surface morhpology of samples. The variation of dielectric properties with frequency reveals that the variation in magnitude is due to Maxwell–Wagner type of interfacial polarization as well as hopping of charge from Fe^{2+} to Fe^{3+} and from Co^{2+} to Co^{3+} ions at B-sites.

Keywords: nanoparticles, ferrites, spinel, cobalt ferrite, permittivity

Introduction

Magnetic nanostructured materials have gained great interest from scientists due to their unusual physical properties compared to their bulk form. They have very large areas of applications in technology, such as electronic devices, microwave devices, transformer cores, magnetic devices, switching devices, recording tapes, permanent magnets, hard disc recording media, flexible recording media, read–write heads, active components of ferrofluids, magnetic drug delivery, catalysis, color imaging, magnetic refrigeration, detoxification of biological fluids, magnetically controlled transport of anti-cancer drugs, magnetic resonance imaging (MRI) contrast enhancement and magnetic cell separation [1].

The ferrite nanoparticles have a spinel structure and the general spinel structure is in the form AB_2O_4. Cobalt ferrite is a partially inverted spinel structure with cobalt atoms predominantly in the octahedral sites [2] and it is a well-known hard magnetic material, which has been studied in detail due to its high coercivity (5400 Oe), high chemical stability, good electrical insulation, significant mechanical hardness and moderate saturation magnetization (80 emu/g) at room temperature.

Nanoferrites are simultaneously good magnetic and dielectric materials. These properties of ferrites are governed by the choice of the cations and their distribution between tetrahedral and octahedral sites of the spinel lattice. The properties of the nanoferrites are also affected by the preparation conditions, chemical composition, sintering temperature, doping additives, and the method of preparation [3]. Several chemical and physical methods such as spray pyrolysis, sol-gel, coprecipitation, combustion technique and high energy milling have been used for the fabrication of stoichiometric and chemically pure nanoferrite materials [4]. Among the available synthesis methods, sol-gel method has attracted much attention due to its inherent advantages of low processing temperature and homogenous reactant distribution. The products obtained by this method exhibit high crystalline quality, narrow size distribution, and uniform shape [5]. The effect of rare-earth ions inclusion into the ferrite spinel structure has been reported in many literatures, however little has been reported on the effect of calcination temperature on dielectric and magnetic properties. Rashad et al, [6] indicated the change in the magnetic properties of samarium substituted $CoFe_2O_4$ synthesized by citrate precursor method and the results revealed that the saturation magnetization and coercivity are decreased with the addition of Sm^{3+} ions. Peng et al. [7] have reported an increase in crystallite size of cobalt ferrite nanoparticles by the doping of gadolinium. Guo et al, [8] have reported that the substitution of Sm^{3+} in $NiFe_2O_4$ increases the lattice parameter and reduces the crystallite size of the materials. Tahar et al, [9] have investigated the effect of Sm^{3+} and Gd^{3+} substitution on the magnetic properties of cobalt ferrite synthesized by forced hydrolysis in polyol and reported that particle size increased slightly with rare earth substitution.

In this work we investigated the effect of temperature on structural, magnetic, and dielectric properties of $CoFe_2O_4$ nanoparticles synthetized via coprecipitation method.

Experimental

Synthesis

Required amount of iron nitrate and cobalt nitrate were dissolved in 100 ml of distilled water at room temperature and stirred for 15 min continously. During constant stirring, 100 ml of ammonia solution was added in drops form. The droppings were done so as to get a solution with pH about 12. The mixture solution/precipitate were dried in an oven at 80 – 100 ^{0}C for 48 hrs. The obtained dry powder were then calcined at in a furnace at 600 ^{0}C and 900 ^{0}C for 2 hrs. The annealed samples were allowed to cool naturally to room temperature.

Measurement

X-ray diffraction (XRD) of the prepared sample were recorded in a Phillips diffractometer equipped with a Cu$K\alpha$ monochromator. The identification of the crystalline phases present in the samples were achieved using the XRD profiles. Transmission Electron Microscope (TEM) JEOL JEM 1220 was used to explore the sample morphology and its particle size distribution. The room temperature infrared spectra of nanopowders were recorded using a Fourier Transform Infrared Spectrophotometer Perkin Elmer. The dispersing of the samples were observed in the range from 380 to 4000 cm^{-1}. The temperature and field dependence of magnetization were carried out in vibrating sample magnetometer (VSM). While dielectric measurement were carried out using open ended coaxial probe via Agilent HP 85072.

Results and discussion

XRD analysis

X- ray diffraction study of both samples confirmed the formation of single phase cubic spinel structure. The single phase spinel ferrite obtained by high temperature calcination at 900 ^{0}C is in agreement with the standard JCPDS data reference (JCPDS: 22-1086).

The micropgraph of the $CoFe_2O_4$ sintered sample at 600 ^{0}C and 900 ^{0}C are presented in Fig. 1. The average crystallite sizes were calculated by Scherer's equation (Eq.(1)) from the intensity of reflection of the spinel structure's of the (311) plane. The equation of Scherrer is given as [10];

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (1)$$

where k is a constant equal to 0.9, λ is the wavelength of the X-ray radiation (all diffraction patterns shown in this paper were performed with CuKa radiation), θ is the diffraction angle, and β is the full width half maximum (FWHM).

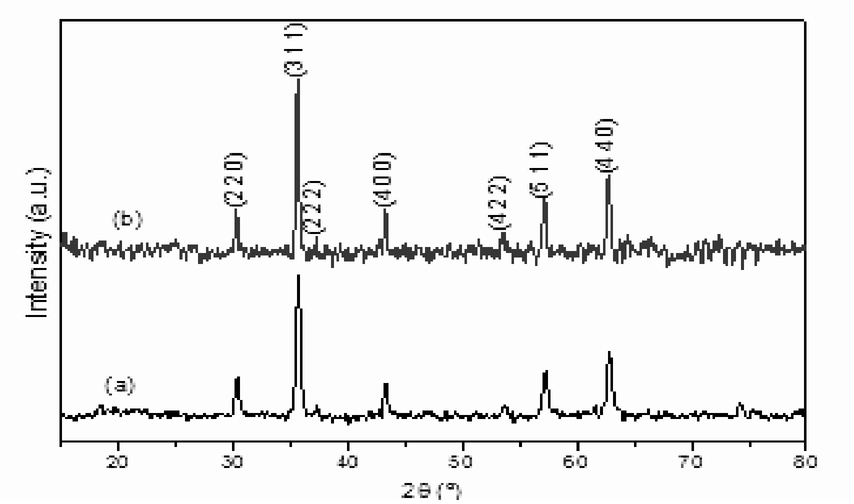

Figure 1: XRD pattern of cobalt ferrite nanoparticles calcined at (a) 600 ^{0}C and (b) 900 ^{0}C

The lattice parameters have been computed using the d-spacing values and the respective (hkl) parameters from the classical formula given in Eq.(2) [10].

$$a = \frac{\lambda[h^2 + k^2 + l^2]^{1/2}}{2sin\theta} \qquad (2)$$

Calculation showed that the crystallite size and lattice parameter of the powder were found to be 49.8nm and 8.343Å for 600 ^{0}C and 67.7 nm and 8.362Å for the 900 ^{0}C sintered sample. This finding indicated that the synthesized powders had nano size crystallites and that the sintering temperature caused the sample to increase in the crystallite size. In addition, the sintering temperature also led to a slight increase of 0.019Å in the lattice parameter. This is attributted to the heat coupling in the sample at higher temperature allowing the diffusion of metals into their octahedral sites [10].

The sharp increase in crystallinity of the sample is attributted to calcination temperature as observed for the 900 ^{0}C heating.

TEM measurement

Figure 2 shows the TEM images of the prepared cobalt ferrite nanoparticles after annealing with temperatures of 600 ^{0}C and 900 ^{0}C respectively. The particles in both cases are spherical and exhibit a homogeneous distribution, especially at lower temperature. The average sizes of the nanoparticles were found to be 43.5 nm and 62.5 nm for the 600 ^{0}C and 900 ^{0}C respectively. The result obtained for the average particle size distribution were in agreement with the values obtained using the XRD spectra. An increase of particle size with increasing annealing indicated that when temperature increases, more metal ions are produce which in turn increases the particle sizes. This increment in number of ions and particle size supports the enhancement of the intensity of absorption as shown in the FTIR spectra for the 900 ^{0}C annealed sample. It important to note that tiny amount of agglomeration is observed at higher temperature due to growing distribution of particle size. A summary of properties of the prepared sample is tabulated in Table 1.

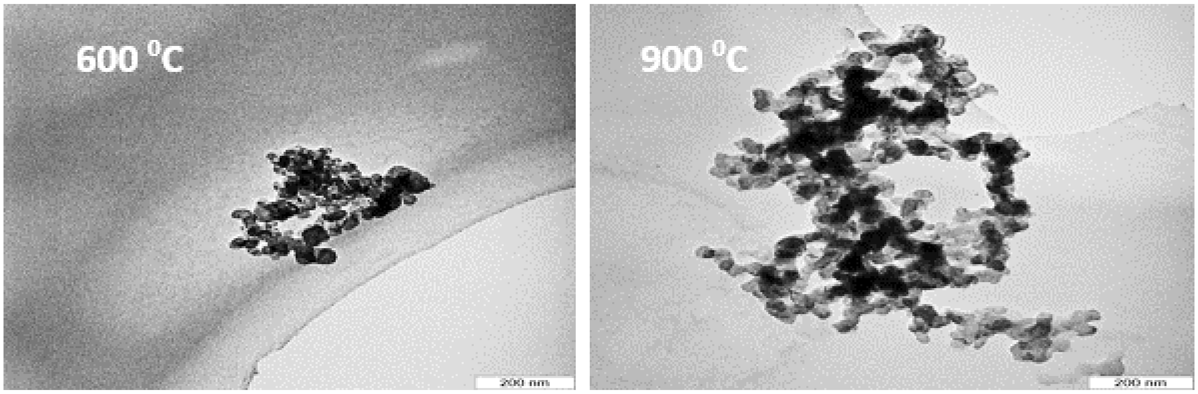

Figure 2: TEM images of cobalt ferrite nanoparticles calcined at 600 ^{0}C and 900 ^{0}C

Table 1. Magnetic parameters of cobalt ferrite

Compound	**T$_{calc}$ (^{0}C)**	***a* (Å)**	***d* (nm)**	**H$_C$ (Oe)**	**M$_r$ (μ_B/mol)**	**M$_S$ (μ_B/mol)**
$CoFe_2O_4$	600	8.343	43.5	12,405	2,819	3,349
				696	937	2,987
	900	8.362	62.5	10,640	3,080	3,569
				720	1,048	3,294

FTIR Spectroscopy

Careful observation on the FTIR spectra shown in figure 3 shows an absorption peak at 592cm^{-1} corresponding to intrinsic stretching vibrations of metal at the tetrahedral site, whereas the v2-lowest band, observed in the range of 400–300cm^{-1}, is due to the octahedral–metal stretching [11]. Co^{2+} ions usually occupy octahedral-site, while Fe^{3+} ions has the tendency to occupy both octahedral and tetrahedral sites [12]. Further observations shows strong absortions peaks at 3414 and 1617cm^{-1} wavelengths.

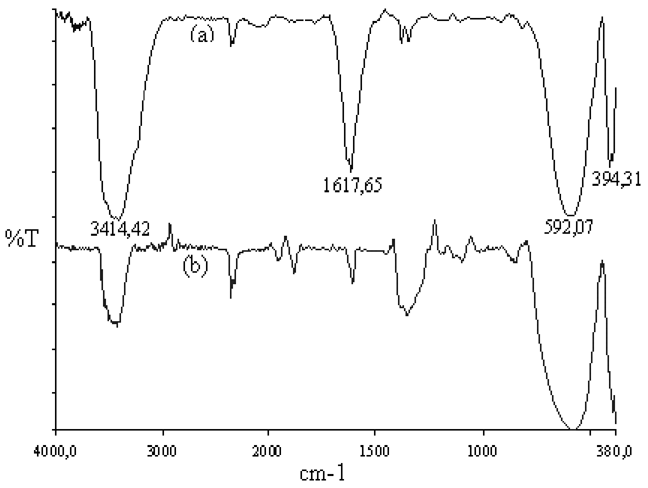

Figure 3: FTIR spectra of cobalt ferrite nanoparticles calcined at (a) 600 ^{0}C and (b) 900 ^{0}C

Magnetic measurement

Figure 4, represents the ZFC and FC curves of magnetization at both temperatures. Both ZFC and FC magnetization decreases by increasing the temperature. At low temperature in the presence of a magnetic field (FC), the magnetization direction of each particle is frozen in the field direction. While the ZFC magnetization is below the magnitude for FC. Both ZFC and FC magnetization are increased by increasing the annealing temperature. However, at higher calcination temperature, the magnetization in both cases is small compared to magnetization at lower temperature. In both cases, the ZFC and FC curves are distinguishable given an indication that there is a non-equilibrium magnetization below the separation temperature. For the ZFC case, the seperation represents the irreversibility temperature, (T_{irr}).

In general, T, represents the blocking–unblocking process of the particles magnetic moment when thermal energy is changed [13]. As the relaxation time of a magnetic particle decreases with increasing temperature, below a certain characteristic temperature called the blocking temperature (T_B) the particles moment remains blocked with respect to the time scale of the experiment. The difference between T_B and T_{irr} corresponds to the width of the blocking temperature distribution which gives an indication of the narrowness of the anisotropy energy barrier distribution of the particles [13,14].

Below the T_{irr}, the ZFC and FC curves significantly diverge and the sample is in the ferromagnetic state. The divergence in the ZFC–FC magnetization curves below T_B is attributed to the existence of magnetic anisotropy barriers [14]. In addition, figure 4 shows that there is a clear increase in the blocking temperature with size, and this increase is fast at smaller particles sizes. The larger particles seem to be blocked at high temperatures as compared to the smaller particles at the same field. For larger particles, the larger volume causes increased anisotropy energy which decreases the probability of a jump across the anisotropy barrier and hence the blocking is shifted to a higher temperature.

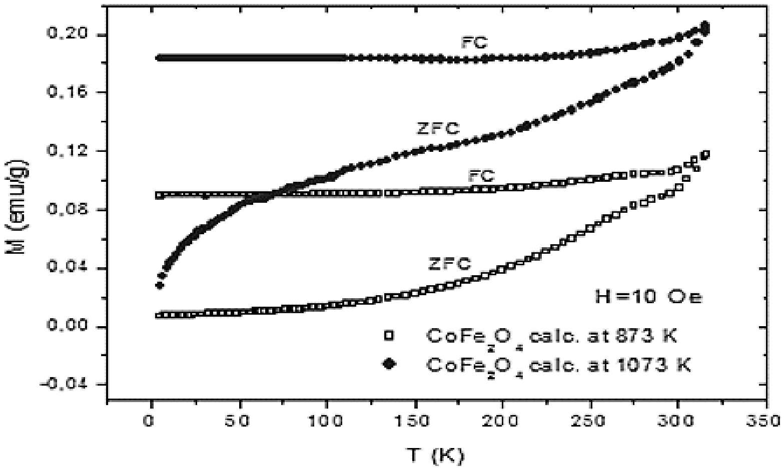

Figure 4: Temperature dependent magnetizations of sample

This behavior is confirmed by the isothermal magnetization curves obtained at 5 K and 320 K shown in Fig. 5. These results are in agreement with analysis obtained for the ZFC/FC discussed in Figure 4. The saturation temperature, coercivity was highest at 5 K for both annealing temperatures as shown in Table 1 whilst the magnetic hysteresis at 5K showed very large hysteresis with coercive fields of 12405 and 10640 Oe for 600 ^{0}C and 900 ^{0}C annealing respectively. This value is attributed to the size of the particles at 5K since particles tend to increase at 320K. The smaller the particles sizes the better the coercivity.

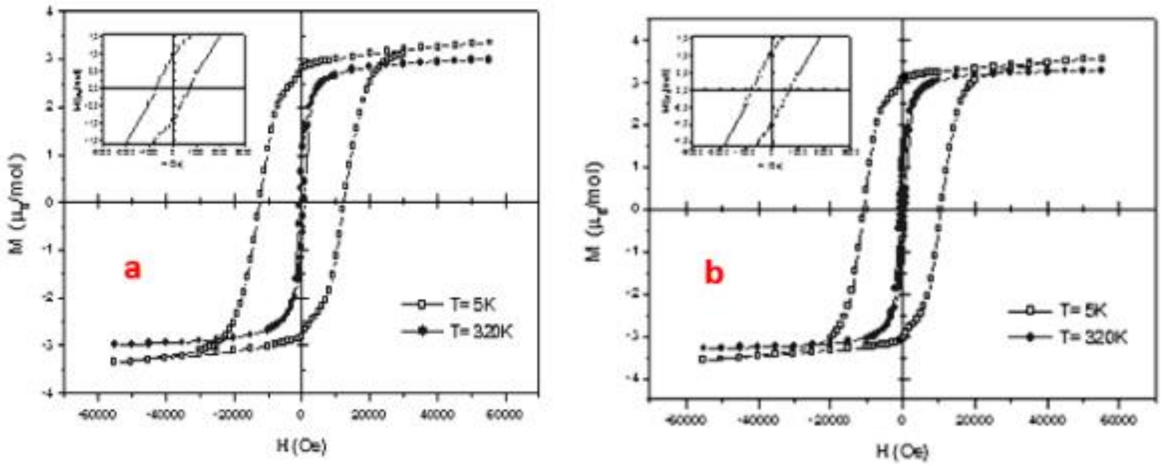

Figure 5: Hysteresis loops of the samples at (a) 600 ^{0}C and (b) 900 ^{0}C

Further observation showed that in Fig. 5 the coercitivity of the nanoparticles decreases as the temperature increases toward the blocking temperature. This is supported by the ascertion that, in the multidomain regime, the coercivity is inversely proportional to the grain size [3]. A larger grain size makes the motion of domain walls easier, and thereby decreases the coercivity [3]. The inserts in Fig. 5 shows part of the M(H) loops in the region of small applied field. The saturation magnetization is dependent on the thermal treatment where saturation magnetization obtained were, $M_S = 3.349\ \mu_B$/mol for sample calcined at 600 ^{0}C and $M_S = 3.569\ \mu_B$/mol for sample calcined at 900 ^{0}C at 5K. In order to verify the obtained inversion degree in the cobalt ferrite prepared in this work, the highest saturation magnetization: $M_S = 3.569\ \mu_B$/mol was used to verify inversion degree obtained. The inversion degree obtained was $\lambda = 0.85$.

Dielectric measurement

Open ended coaxial probe (Agilent 85702B) was used in the measurement of complex permittivity of both samples. The measurement was carried out at microwave frequency (8.2 GHz to 12.4 GHz). Careful observation on Figure 6(a) shows that dielectric constant decreases with the increase of frequency in both samples. The dependence of dielectric constant on frequency can be explained using interfacial polarization as predicted by Maxwell-Wagner [15]. It is expected that the dielectric structure of ferrite is made up of a conductive layer that consists of large ferrite grains and other grain boundaries that are poor conductors. Polarization is mainly due to electron exchange between Fe^{+2} and Fe^{+3} in the direction of applied field. Measurement result showed that the mean dielectric constant calculated were 4.46 and 5.05 for the 600 ^{0}C and 900 ^{0}C annealed samples respectively.

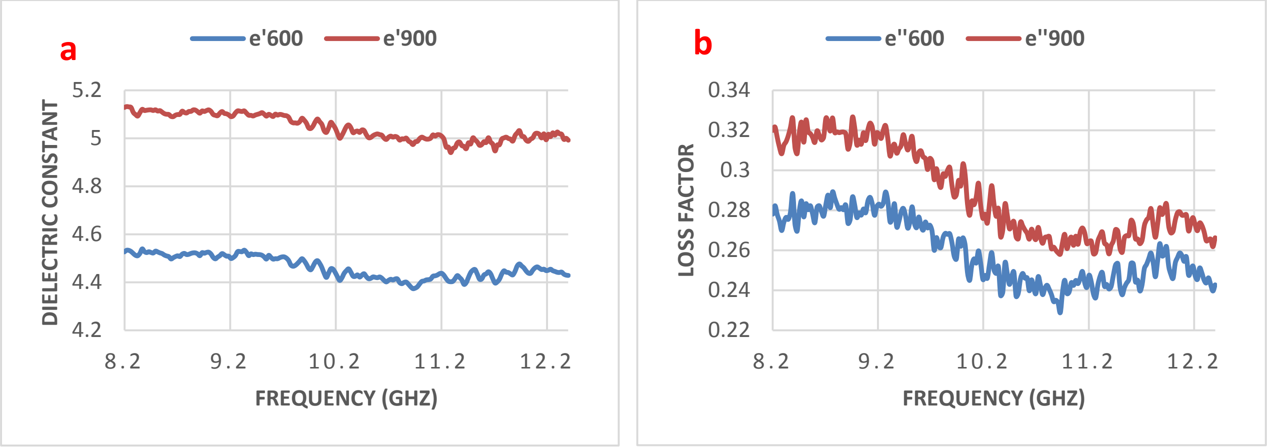

Figure 6: Complex permittivity of samples annealed at 600 ^{0}C and 900 ^{0}C

As shown in figure 6(b), the large value of loss factor at lower frequency might be attributted to the dominant species like Fe^{+2} ions, oxygen vacancies, grain boundary defects, etc. The loss factor at high frequency are due to particles which have low resistivity. The mean loss factor obtained for both samples are 0.26 and 0.29 for the 600 ^{0}C and 900 ^{0}C calcinations respectively.

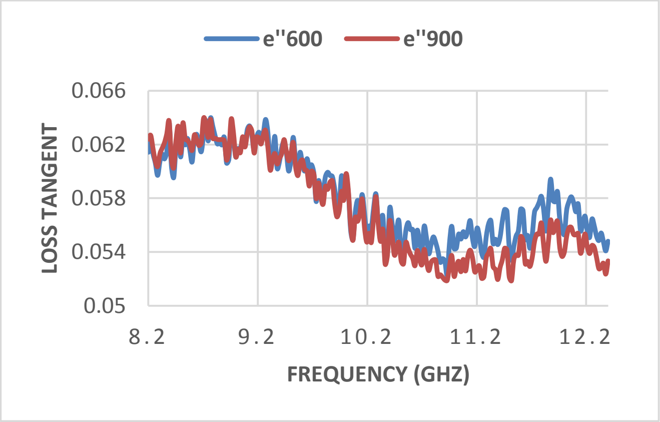

Figure 7: Loss tangent of samples at annealed at 600 ^{0}C and 900 ^{0}C

Figure 7 depicts the loss tangent of sample annealed at 600 and 900 ^{0}C. The value were obtained from the ratio of loss factor to the dielectric constant. The loss tangent (tanδ) is shown to decrease with the increase of frequency and then stagnate at higher frequencies for both samples. The mean magnitude of the loss tangent obtained are 0.058 and 0.057 for the 600 ^{0}C and 900 ^{0}C calcinations respectively. This results indicates that the 900 ^{0}C annealed sample would absorb higher than the 600 ^{0}C annealed sample which is in accordance with result obtained from the FTIR analysis. The loss (tanδ) depends on factors, such as material stoichiometry, Fe^{+2} content and material dispersion, which in turn depends on the composition and synthesis methods. The decrease in loss tangent with frequency may be attributed to the Maxwell-Wagner polarization and conduction mechanism in ferrites [16].

Conclusions

The thermal heat caused an increase in the average crystallite size, magnetization and the coercive field of the sample. Similarly, infrared spectroscopy studies confirms the presence of metal oxide in the prepared nanoparticles. The main characteristic of the field cooled (FC) and zero field cooled (ZFC) curves is its irreversibility below room temperature suggesting the presence of a superparamagnetic behavior. In addition, the magnetic properties exhibit some dependence on the calcination temperature. The M_S values increases with increase in calcination temperature whilst the maximun value of H_C is about 12405 Oe which is much higher than the coercitivity of bulk material (5400 Oe). The increase in the value of lattice parameter with increase in temperature suggests the expansion of the unit cell of the sample. Crystallinity and the crystallite size are observed to increase with increase in temperature.

References

[1] Köseoğlu, Y., Oleiwi, M. I. O., Yilgin, R., & Koçbay, A. N. (2012). Effect of chromium addition on the structural, morphological and magnetic properties of nano-crystalline cobalt ferrite system. *Ceramics International*, *38*(8), 6671-6676.

[2] Carta, D., Casula, M. F., Falqui, A., Loche, D., Mountjoy, G., Sangregorio, C., & Corrias, A. (2009). A structural and magnetic investigation of the inversion degree in ferrite nanocrystals MFe_2O_4 (M= Mn, Co, Ni). *The Journal of Physical Chemistry C*, *113*(20), 8606-8615.

[3] Xavier, S., Thankachan, S., Jacob, B. P., & Mohammed, E. M. (2013). Effect of Samarium Substitution on the Structural and Magnetic Properties of Nanocrystalline Cobalt Ferrite. *Journal of Nanoscience*, Vol. *2013*. http://dx.doi.org/10.1155/2013/524380

[4] Raj, K., Moskowitz, B., & Casciari, R. (1995). Advances in ferrofluid technology. *Journal of magnetism and magnetic materials*, *149*(1), 174-180.

[5] Kim, D. K., Zhang, Y., Kehr, J., Klason, T., Bjelke, B., & Muhammed, M. (2001). Characterization and MRI study of surfactant-coated superparamagnetic nanoparticles administered into the rat brain. *Journal of Magnetism and Magnetic Materials*, *225*(1), 256-261.

[6 Rashad, M. M., Mohamed, R. M., & El-Shall, H. (2008). Magnetic properties of nanocrystalline Sm-substituted $CoFe_2O_4$ synthesized by citrate precursor method. *journal of materials processing technology*, *198*(1), 139-146.

[7] Peng, J., Hojamberdiev, M., Xu, Y., Cao, B., Wang, J., & Wu, H. (2011). Hydrothermal synthesis and magnetic properties of gadolinium-doped $CoFe_2O_4$ nanoparticles. *Journal of Magnetism and Magnetic Materials*, *323*(1), 133-137.

[8] Guo, L., Shen, X., Meng, X., & Feng, Y. (2010). Effect of Sm 3+ ions doping on structure and magnetic properties of nanocrystalline $NiFe_2O_4$ fibers. *Journal of Alloys and Compounds*, *490*(1), 301-306.

[9] Tahar, L. B., Smiri, L. S., Artus, M., Joudrier, A. L., Herbst, F., Vaulay, M. J., ... & Fiévet, F. (2007). Characterization and magnetic properties of Sm-and Gd-substituted $CoFe_2O_4$ nanoparticles prepared by forced hydrolysis in polyol.*Materials Research Bulletin*, *42*(11), 1888-1896.

[10] Yakubu, A., Abbas, Z., Hashim, M. and Fahad, A. (2015). Effect of Sintering Temperature on

$Co_{0.5}Zn_{0.5}Fe_2O_4$ Nano-Particles Evolution and Particle Size Distribution. *Advances in Nanoparticles*, **4**, 37-44. http://dx.doi.org/10.4236/anp.2015.42005

[11] Hafner, S, (1961). The absorption of some metal oxides with spinel structure, *Zeitschrift Fur Kristallographie*, 115, 331–358.

[12] Yoon, S. J., Lee, S. H., Kim, K. H., & Ahn, K. S. (2002). Electrical and magnetic properties of spinel $ZnCr_{2-x}Fe_xO_4$ ($0\leq x\leq 1.0$). *Materials chemistry and physics*, *73*(2), 330-334.

[13] Sertkol, M., Köseoğlu, Y., Baykal, A., Kavas, H., & Başaran, A. C. (2009). Synthesis and magnetic characterization of $Zn_{0.6}Ni_{0.4}Fe_2O_4$ nanoparticles via a polyethylene glycol-assisted hydrothermal route. *Journal of Magnetism and Magnetic Materials*, *321*(3), 157-162

[14] Nathani, H., & Misra, R. D. K. (2004). Surface effects on the magnetic behavior of nanocrystalline nickel ferrites and nickel ferrite-polymer nanocomposites.*Materials Science and Engineering: B*, *113*(3), 228-235.

[15] Wagner, K. W. (1913). The theory of incomplete dielectricity. *Annals of Physics*, *40,* 817.

[16] Kumar, H., Srivastava, R. C., Negi, P., Agrawal, H. M., & Asokan, K. (2013). Dielectric Behaviour of Cobalt Ferrite Nanoparticles. *International Journal of Electrical and Electronics Engineering*, *2*, 59-66.