International Journal of Engineering, Science and Mathematics
Vol. 7 Issue 1, January 2018,
ISSN: 2320-0294 Impact Factor: 6.765
Journal Homepage: http://www.ijesm.co.in, Email: ijesmj@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

Analysis of structural and Magnetic properties of Cobalt Ferrite Nanoparticles prepared by Citrate Precursor method doped with 1% Cu, Ni and Zn

Nishit Kumar Pandey*, Amarendra Narayan and #Amresh Chandra Pandey*****

Abstract:
In the present study, cobalt ferrite has been doped with Ni, Zn and Cu in order to improve the electrical and magnetic properties maintaining a spinel structure and moderate saturation magnetization [1]. Samples of pure cobalt ferrite and cobalt ferrite doped with 1% Ni, Cu and Zn were prepared with citrate precursor route. The samples were annealed at high temperatures 450^0C and 650^0C to avoid any chances of possible superparamagnetism. These samples were analyzed by XRD and VSM. Analysis of purity of phases was also done to find out the possible impurities. The XRD pattern gave the value of lattice parameter which was analyzed to see the effect to ionic size on size of crystallites. With the help of Scherrer's formula, the sizes of nanoparticles were found and effect of temperature was studied. VSM Studies revealed the saturation magnetization, Coercivity and Retentivity of the samples and effect of temperature and dopant ion on these properties were studied. It is expected that present work will make it easier to quickly synthesize cobalt ferrite nanoparticles by a low cost route and analysis of its properties by taking into consideration the nature of dopant atoms, and annealing temperature.
Keywords: Spinel, Annealing, Scherrer's formula, Lattice parameter, Coercivity, Saturation Magnetization.

Introduction:

Spinel ferrite nanoparticles have been intensively investigated in recent years because of their remarkable electrical and magnetic properties and wide practical applications to information storage system, ferrofluid technology, magneto calorific refrigeration and magnetic diagnostics. Cobalt ferrite, having an inverse spinel structure and the inherent properties of high coercivity, moderate saturation magnetization and high electrical resistivity and high magnetocrystalline anisotropy is a potential candidate for magnetic storage devices and high frequency applications. Nanometer magnetic particles exhibit specific properties such as superparamagnetism [2] and spin glass behavior generally attributed to surface rather than volume disorder [3,4]. A better understanding of magnetism in such particles is crucial not only for basic physics but also because of the technological applications in information storage and medicine.

A lot of synthetic strategies for preparing nanosized cobalt ferrite have been undertaken. Pileni et al. utilized oil-in-water micelle to prepare size controlled Co-ferrite [5]. Zhang et. al. also reported the nanoparticles which were prepared in normal micelle similarly with same method[6]. Among the series of chemical route various other routes like organometallic precursor method, sol gel method, solution combustion method and hydrothermal method are popular [7]. The citrate precursor route is a chemical method [8], which we adopted and it provides low cost, highly controlled synthesis of nanoparticles with high purity.

PGT, ADS High School, Madhupur, Jharkhand, **Senior Lecturer, PG Dept. of Physics, Patna University, Patna,* *#Corresponding author****, ***Scientist (Agril. Engg.) Birsa Agricultural University, Ranchi, Jharkhand, email- acpandey10@hotmail.com*

We observed that the structural and magnetic property of cobalt ferrite depends mainly on properties of dopant atoms rather than slight variations in annealing temperature.

Material and Methods

The preparations were initiated by calculations of adequate amount of chemicals which may lead to desired pure or mixed ferrite. Generally we took nitrates, as their solubility is high in water. Cobalt nitrate Co $(NO_3)_2$ and Ferric Nitrate Fe $(NO_3)_3$ were taken in stoichiometric ratio and dissolved in distilled water. In case of mixed ferrite adequate amount of nitrates of the metal e.g. Ni $(NO_3)_2$, Cu $(NO_3)_2$, Zn $(NO_3)_2$ etc. were also taken as solution. Another solution of citric acid was also made and all these solutions were mixed and heated with stirring at 68^0C for two hours, giving a brown jelly. This jelly was placed in an oven for a day at 80^0C, which converted into a brittle material. This material was annealed at two temperatures 450^0C and 650^0C. The samples were analyzed with the help of XRD and VSM.

Observations:

These are the observations in a tabular form, shown in Table 1.

An inspection of the table reveals that in all the samples, when the temperature was increased, crystallite size increased except for $Ni_{0.1}Co_{0.99}Fe_2O_4$. This trend is in agreement with other works [9, 10, and 11]. During the annealing, the particles grow due to gain in energy, so higher the temperature, bigger the particles.

Another property is the lattice parameter, which depends on the choice of dopant atoms rather than temperature. As shown in Fig 2, At 450^0C, the lattice parameter of pure Cobalt ferrite is 2.52 Å, while it was 2.70, 2.52 and 2.70 Å, when Ni, Cu and Zn are doped respectively. The Cobalt ferrite is an inverse spinel, in which cobalt atom and half of the iron atoms are on **B** sites, while other half of the iron atoms are on **A** sites. Among all the dopants, only Zinc has the tendency to go to **A** sites [12]. On addition of Zn, the lattice parameter increases, it means Zn goes to **A** sites, and replaces Fe atoms, which are smaller than Zn atoms. Ni goes to **B** sites, with an option of replacing Fe or Co, but as the lattice parameter increases, we can say that it replaces Fe atoms. Likewise Cu atoms, having affinity for **B** sites seem to replace Fe atoms only but change is not very large. Our data strengthens earlier views and it can be checked later. The change in lattice parameter with temperature is not significant. The figure 2 is representing the variation of lattice parameter.

The magnetic properties of the samples were analyzed by the hysteresis loops shown as Figure 3 and Figure 4.

We can observe that in almost all the samples, the area has decreased with temperature, indicating it is better to use ferrites annealed at high temperature in memory elements. Additionally, at low temperature all samples behaved almost similarly, but at high temperature, Cobalt ferrite saturated earliest.

We observed that almost all the samples have shown increase in saturation magnetization (Figure5) with increasing annealing temperature [10, 13].

When the external magnetic field is applied over the sample, it tries to orient the magnetic dipoles either by domain rotation or by domain wall movement depending normally on the size of particle. At a particular field, maximum number of dipoles orient, the field is called saturation magnetization. The direction of net dipole moment of **A** sites and **B** sites are in opposite direction and their resultant decides the net field.

We know that Zn replaces Fe at **A** site [12]. The presence of Zn, which is non magnetic at **A** site and presence of Co and Fe at **B** site creates a large difference between the net fields of **A** and **B** sites and results in large saturation magnetization.

Ni and Cu can replace Fe or Co at B sites. It is possible that they have replaced Co atoms, because in this way, the dipole moments due to Fe atoms would cancel and net uncompensated moment due to Ni can create some difference. This assumption will be verified later.

The coercivity is very important factor in defining the magnetic characteristics of a material. It is the field strength necessary to reverse the spin orientation direction [9]. The Wohlfarth model assumes that there is a uniform magnetization throughout the particle and it remains so throughout the rotation process [14]. Generally the energies required to reverse the spin orientation within single domain are larger than those needed in bigger ones so coercivity is larger in small particles. In other word, when particle size decreases to single domain, the domain rotation is preferred, consuming more strength of external field making coercivity high. At the blocking temperature, when thermal energy is sufficient to break the anisotropy barrier, the coercivity gets zero. Below this temperature, the coercivity is the field which together with thermal energy can overcome the anisotropy. Therefore coercivity increases with size, below blocking temperature [14].

In all the samples shown, as shown in figure 6, the coercivity is more at lower annealing temperature. This trend of ours verifies the established theories about dependence of coercivity with temperature.

X-Ray diffraction data, which we had obtained, was matched with ICDD (International centre for Diffraction Data), which indicated that the phases are pure, but small amount of impurities were present at 450^0C, which were seen settled at high temperature. It may be due to their decomposition.

The $CoFe_2O_4$ sample had trace amounts of FeO, and Fe_2O_3, shown by lines at 33.162, 35.630, 49.465 degrees. At higher temperature these are negligible. $Cu_{0.1}Co_{0.99}Fe_2O_4$ sample was having oxides of iron in very little amount but at high high temperature the oxides are absent. In all the mixed ferrite we found that oxides of iron are more likely to be found as impurity at low temperature. At high temperature, the phases are more pure.

Conclusion:

It is clear that properties of Cobalt ferrite can be wisely tailored by addition of calculated amount of impurities in this. The atomic size and magnetic properties of mixed ferrite greatly depends on dopant atoms. At high temperature, the cobalt ferrite is more likely to be pure. In future, we shall dope high percentage of impurities to find out whether the trend continues or not.

References:

1. Mah Rukh Siddiquah, Electrical and Magnetic properties of cobalt ferrite, Quaid-I-Azam University, Islamabad.
2. C. P. Bean, J. Appln. Physics, 30, 120S, 1959
3. B. Martinez et.al. Phys. Review Letters. 80, 181, 1998
4. J. F. Hochepied et.al. Magnetic properties of mixed cobalt zinc Nanoparticles, Journal of applied physics, vol. 87, Number 5, 1.3.2000
5. N Moumen, M. Pileni, J. Magn. Magn. Materials, 149, 1995, 67
6. Z. J. Zhang, J. Am. Chem. Society, 122, 2000, 6263
7. R. K. Singh, study of magnetic behavior of some nanocrystalline ferrites, (PhD Thesis) Patna University, Patna, India

8. R. N. Panda et.al. “Magnetic properties of nanocrystalline Gd or Pr substituted $CoFe_2O_4$ synthesized by citrate precursor technique”, J. Magn. Magn. Magnetic materials, 257, 2003, 79-87
9. L. D. Tung, V. Kolesnichenko, G. Caruntu, D. Caruntu, Y. Remond, V. O. Golub, C.J. O’Connor, L. Spinu, Annealing effect on the magnetic properties of nanocrystalline zinc ferrite, physica B, 319(2002)116-121.
10. Adriana S. Albuquerque, Jose’ D. Ardisson, Waldemar, A.A. Macedo, Nanosized powders of NiZn ferrite, Synthesis, structure and magnetism, Jour. Appl. Phys. Vol. 87 p4352-4357 (2000)
11. Yuan Zhihao, Zhang Lide, synthesis and structural characterization of capped $ZnFe_2O_4$ nanoparticles, material research bulletin, Vol.33 p 1587-1592 (1998)
12. A. K. Bandopadhyay, Nanomaterials, New age international publishers
13. T. Sato, K. Haneda N. Seki, T. Iijima, Appl. Phys. A 50 (1990) 13
14. Georgia C. Papaefthymiou, Nanoparticle magnetism, Nano Today, 2009. 4, 438-447

Table 1. Table of Cumulative data

450^{0}C				
Sample names	Size nm	Sat. Mag. emu/g	Coercive field (G)	Rem. Magn.
$CoFe_2O_4$	43.4	36.7	1460.0	19.5
$Cu_{0.1}Co_{0.99}Fe_2O_4$	61.3	42.4	1768.1	24.0
$Ni_{0.1}Co_{0.99}Fe_2O_4$	89.7	39.9	1321.3	19.5
$Zn_{0.1}Co_{0.99}Fe_2O_4$	40.6	41.7	1070.3	18.6
650^{0}C				
Sample names	Size nm	Sat. Mag. emu/g	Coercive field (G)	Rem. Magn.
$CoFe_2O_4$	46.5	41.4	654.1	16.8
$Cu_{0.1}Co_{0.99}Fe_2O_4$	73.8	66.1	755.9	26.35
$Ni_{0.1}Co_{0.99}Fe_2O_4$	73.8	60.9	510.0	17.8
$Zn_{0.1}Co_{0.99}Fe_2O_4$	44.8	64.6	432.3	16.7

Figure 2. XRD patterns of samples

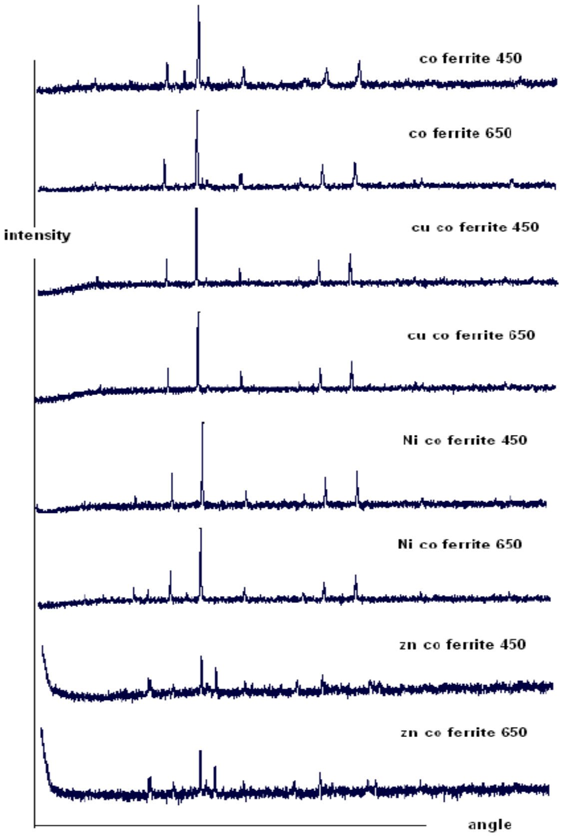

Figure 2 Variation of Lattice Parameter

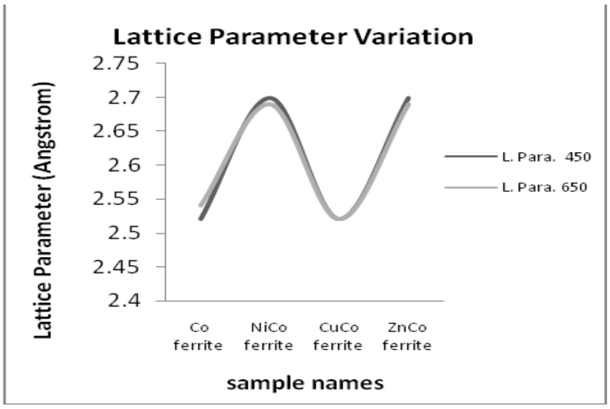

Figure 3 Hysteresis plots of samples annealed at 450^0 C

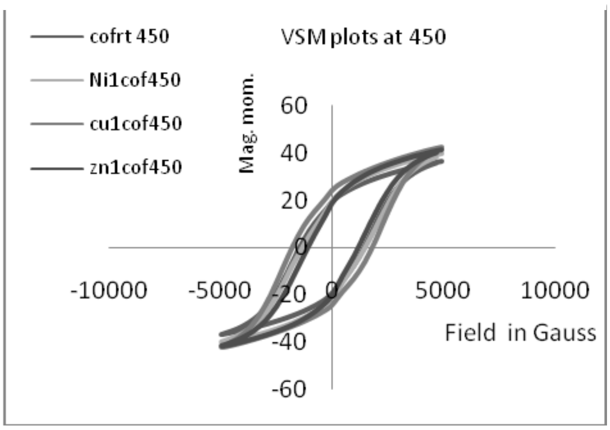

Figure 4 Hysteresis plots of samples annealed at 650^{0}C

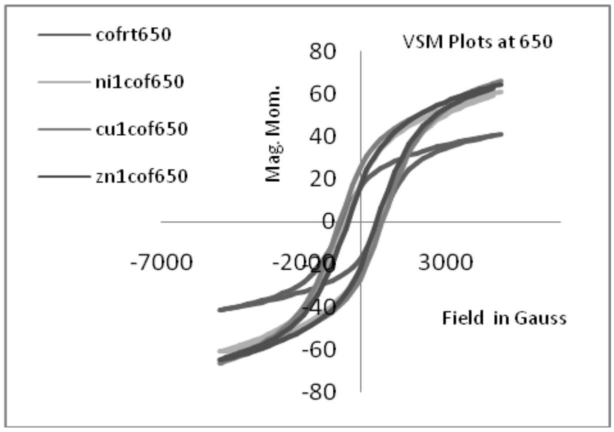

Figure 5. Variation of saturation magnetization

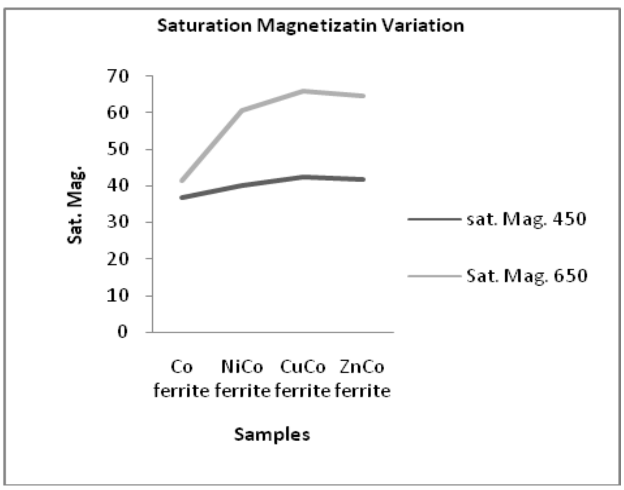

Figure 6 .Variation of Coercivity of samples