



Micro-Structural Studies of Gadolinium Doped Cobalt Ferrites

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ABSTRACT : $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$; $x = 0, 0.1, 0.15, \text{ and } 0.2$ were prepared using coprecipitation method. All the samples were sintered at 500°C. The structure has been studied using XRD, TEM and EDAX. Effect of Gd doping on crystal structure has also been studied and discussed. The particle size has been estimated using Scherrer equation. All the peaks in XRD patterns are narrow which means that particles are in nano range. The structure inferred from the XRD is cubic. Gd^{3+} being larger in size prefers octahedral site.

Keywords: Micro-structural; Ferrites; Coprecipitation.

I. INTRODUCTION

Control and understanding of matter at dimensions of roughly 1-100 nm has generated a lot of interest in recent years. These materials have many astonishing properties in contrast to their bulk counterparts. The different properties of these novel materials are ascribed to their characteristic structural features in between the isolated bulk macroscopic and atoms the materials. These typical properties of nano sized materials is due to quantum size effects and the large surface area of magnetic nanoparticles surprisingly change some of the magnetic properties and also exhibit superparamagnetism among other phenomena. It has been confirmed that the refinement of the grain size is an effective way of reducing the noise [1]. In general; spinels are classified as normal, inverse, and mixed. It has been reported that the presence of nonmagnetic ions reduces the magnetic interactions between the two interstitial sites, causes decrease in hyperfine magnetic fields, and hence changes the magnetic and electronic properties. These effects are particularly apparent in the Mossbauer studies. For all the magnetic nanoparticles there is a critical size dimension (D_{sp}) below which it will be superparamagnetic with no hysteresis and no remanence. So the useful particle size should be in the range $D_{sp} < D < D_{sd}$ where D_{sd} is single domain size [2].

Cobalt ferrite is a ferrimagnetic oxide which have large magneto crystalline anisotropy, high coercivity, moderate saturation magnetization, high chemical stability and high mechanical hardness. Nano scale cobalt ferrite fabrication has interested many researchers because of its physical properties such as magneto-optical and superparamagnetism. These interesting physical properties are result of strong quantum confinement effect which is not the case with bulk material [3, 4]. Synthesis of nanoparticles, especially spinel ferrites, characterized by a low size distribution is important due to their remarkable electrical and magnetic properties and wide practical applications in information storage systems, ferro-fluid technology, magneto-caloric refrigeration and magnetic diagnostics. They are also used in radio frequency circuits, high quality filters, rod antennas, transformer cores, high speed digital tapes. Cobalt ferrites

are among the most widely used magnetic materials having low cost, high performance for high frequency applications. Spinel ferrites are cubic close packed cage of oxygen ions occupying the tetrahedral (A) and octahedral (B) interstitial sites, which interact with each other through the superexchange interactions (J_{AB}) and the intra-exchange (J_{AA} , J_{BB}). All these interactions are negative and hence attractive. The order of magnitude of these interactions is $|J_{AB}| > |J_{AA}| > |J_{BB}|$, when A and B are totally magnetic. A selective magnetic dilution is very important in ferrites [5]. Small amounts of rare earths can be used for this purpose leading to control electrical, dielectric and magnetic properties of ferrites. The properties of ferrites are very sensitive to the processing techniques. The various processing techniques, which are used for the synthesis of spinel ferrite powders, include microwave refluxing, hydrothermal, sol gel, co-precipitation and spray pyrolysis. Cobalt ferrites prepared by different methods have different magnetic properties.

A molecule of spinel ferrite can be written as DT_2O_4 , where D is divalent ion and T is trivalent ion. The both the cations can occupy either tetrahedral (A) site or the octahedral [B] site. Hence the cation distribution can be expressed as $(D_{1-\delta}T_\delta)[D_\delta T_{1-\delta}]O_4$. Here δ is known as degree of inversion. If $\delta = 1$, the structure is called inverse spinel and if $\delta = 0$ it is normal spinel. For $0 < \delta < 1$ the spinel structure is referred to as mixed.

Many researchers have studied rare earth doped cobalt ferrites using different methods. Gadolinium-doped CoFe_2O_4 nanoparticles are discussed by Jianhong Peng *et al* [6] and R.P. Pant *et al* [7].

Jianhong Peng *et al* [6] showed that doping cobalt ferrites with gadolinium have a strong influence on saturation magnetization and coercivity. Ben Tahar *et al* [8] found a significant increase in saturation magnetization of cobalt ferrites by doping with Gd^{3+} and Sm^{3+} .

Jing Jiang *et al* showed that properties of ferrites are strongly affected by La^{3+} content [6]. The saturation magnetization decrease, while coercivity increases with increasing the La^{3+} content.

From above discussion it is clear that cobalt ferrites are very useful and it is of interest to investigate the effect of rare earth ions on the properties of cobalt ferrites. Our interest is to modulate the properties of cobalt ferrites. Our work is to produce lanthanum and gadolinium doped cobalt ferrites which have high resistivity and are single phase. Our work will be intended to synthesize nano particles with desired properties like magnetic moment, high permeability, resistivity, high dielectric constant, low dielectric loss.

II. MATERIAL AND METHODS

Gd-Co ferrite of composition $\text{CoGd}_{0.1}\text{Fe}_{1.9}\text{O}_4$ was prepared by the co-precipitation method. The materials used were cobalt nitrate (97% Merck, India), iron nitrate (98% Merck, India), gadolinium nitrate (Merck, Germany) and sodium hydroxide (96% Merck, India). One molar solution of these materials was made with distilled water. Sodium hydroxide (70 ml) was taken from one molar solution in approximately 1760 ml of distilled water to have the concentration of 0.37 mol/l and heated to boiling. Cobalt nitrate, gadolinium nitrate and iron (III) nitrate were taken from their molar solution in accurate stoichiometric proportions. These solutions were poured as quickly as possible into the boiling solution of NaOH under vigorous stirring produced by the glass mechanical stirrer (500 rpm). Mixing is very important; otherwise segregation of phases can take place. After co-precipitation, pH is set to 12.5–13. The beaker was covered to diminish the evaporation of the solution. Reaction was allowed to continue for 30–40 minute at temperature 95–100°C under vigorous stirring. The beaker was cooled to ambient temperature and particles precipitate. Total volume was reduced to 500 ml by the aspiration of supernatant. Precipitates were washed with distilled water (900 ml) and centrifuged at 7000 rpm for 10 minutes. The residue was dried and powdered. These samples were sintered in air at 500°C at a heating rate of 350°C/h for 3h and were subsequently cooled. These samples were then sintered in air at 500°C for 3h and were subsequently cooled. XRD was taken with XPERT-PRO system.

III. RESULT AND DISCUSSION

Fig. 1 shows the XRD patterns of nano-crystalline $\text{CoGd}_x\text{Fe}_{2-x}\text{O}_4$ for $x = 0, 0.10, 0.15$. Particle size as estimated from Scherrer equation [9] is listed in Table 1. Particle size decreases continuously with Gd^{3+} ions doping.

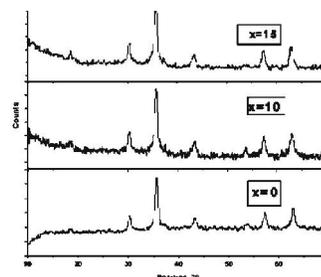


Fig. 1. XRD patterns of nano-crystalline $\text{CoGd}_x\text{Fe}_{2-x}\text{O}_4$ for $x = 0, 0.10, 0.15$.

Table 1. Particle size for $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$; for $x = 0, 0.1, 0.15$, and 0.2 nano particles.

Composition ($\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$)	Particle size(nm)
$X = 0$	49.84
$X = 0.05$	42.56
$X = 0.1$	35.01
$X = 0.15$	31.09

When some Fe^{3+} ions are substituted by Gd^{3+} ions, the lattice parameters are changed. The lattice parameters may increase or decrease (Table 2) depending upon the result of two effects. The large size of Gd^{3+} tries to increase the lattice parameter and the strain produced by its substitution in the cell, tries to decrease it. This has been investigated by many researchers [10, 11]. This explains the increase in lattice parameter up to $x = 0.15$ and decrease in lattice parameter thereafter for $x = 0.20$.

Table 2. Variation of lattice parameter with dopant concentration.

Composition	Lattice Parameter
$X = 0.05$	8.319 Å
$X = 0.10$	8.329 Å
$X = 0.15$	8.332 Å
$X = 0.20$	8.323 Å

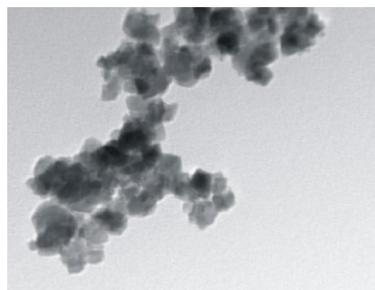


Fig. 2. TEM of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$; for $x = 0.1$

Fig. 2 shows TEM images of the samples for $x = 0.1$. There are no isolated particles and particles prefer to be in groups and agglomerates of many particles are clearly seen. This agglomeration shows that particles are attracted towards each other indicating their magnetic character.

Fig.3 shows the diffraction Tem image. Carefully seen the periodic arrangement of the constituents is visible. Crystal structure of the prepared ferrites is inferred from this figure.



Fig. 3. Diffraction TEM image for $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$; for $x = 0.1$

Fig. 4 and Table 3 show the EDAX analysis for $x = 0.1$. All the gadolinium added does not replace iron as is clear from the EDAX data. This is expected as some of the may be washed away and some of it may even be lying at the grain boundaries.

Table 3. Weight and Atomic percentage of different elements in the sample $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$; for $x = 0.1$ (from EDAX analysis).

Element %	Wt%	At
O	43.16	—
74.70	—	—
Gd	07.56	—
01.33	—	—
Fe	31.18	—
15.46	—	—
Co	18.10	—
08.51	—	—

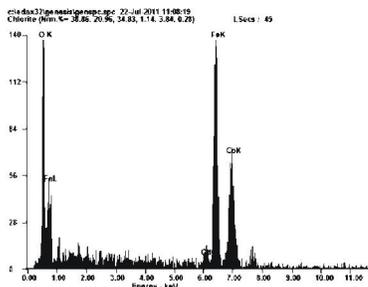


Fig. 4. EDAX-Energy Dispersive x-ray for $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$; $x = 0.1$

IV. CONCLUSIONS

The lattice parameter increases up to a concentration of $X = 0.15$ while after that the lattice parameter starts decreasing. All the gadolinium added does not replace iron as is clear from the EDAX data. Particle size goes on decreasing with gadolinium doping. All the particles are of uniform size. The magnetic character of the particles is clear from the agglomerates which are formed due to the attraction among themselves. The diffraction Tem image shows the periodic arrangements of the constituents. This clearly shows the crystal structure of the ferrite powder.

REFERENCES

- [1] Shun Hua Xiao, Kun Luo, Lin Zhang. *Materials Chemistry and Physics*, **123**: 385(2010) .
- [2] C.Yan,Fuxiang Cheng, Zuoyan Peng, Zhigang Xu, Chunsheng Liao, *J.Appl. Phys.*, **84**: 5703(1998).
- [3] F.Cheng, C.Liao, J. Kuang, Z. Xu, C. Yan, L. Chen, H. Zhao, Z. Liu, *J. Appl. Phys.*, **85**: 2782(1999).
- [4] D.I. Leisle-Pelecky, R.D. Rieke, *Chem. Mater.*, **8**: 1770 (1996).
- [5] M.A. Ahmed, N. Okasha and M.Gabal, *J. Materials Chemistry and Physics*, **83**: 107(2004).
- [6] Jianhong Peng, Mirabbos Hojamberdiev,Yunhua Xu, Baowei Cao, Juan Wang, Hong Wu *J. Magn. Magn. Mater.*, **323**: 133(2011) .
- [7] R.P. Pant , Manju Arora, Balwinder Kaur,Vinod Kumar, Ashok Kumar, *J. Magn. Magn. Mater.*, **322**: 3688 (2010).
- [8] L. Ben Tahar, M. Artus, S. Ammar, L.S. Smiri, F. Herbst, M.J. Vaulay, V. Richard,M. Greneche, F. Villain, F. Fievet, *J. Magn. Magn. Mater.*, **320**: 3242 (2008) .
- [9] B.D. Cullity, *Elements of x-ray diffraction* (Addison-Wesley, Reading, 1978).
- [10] B. Parvatheeswara and K.H.Rao, *J. Magn.Magn. Mater.*, **292**: 44(2005) .
- [11] R.K. Puri, M. Singh and S.P. Sud *J. Mater. Sci.* **29**: 2182(1994).