Dielectric and Magnetic Studies La\textsuperscript{3+} doped Cobalt Nano Ferrite

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Abstract. La\textsuperscript{3+} substituted cobalt ferrite nano-particles with the chemical composition La\textsubscript{x}CoFe\textsubscript{2-x}O\textsubscript{4} (here, x=0, 0.05, 0.1, 0.15 and 0.2) were synthesized using auto-combustion method. Structural and morphological studies were probed using X-ray diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM). Formation of rare-earth doped cobalt ferrite was confirmed using the X-ray diffraction studies. Average crystallite size (D) was found to be varying from 43.71nm to 55.37nm with the increase in La\textsuperscript{3+} concentration. Frequency dependent dielectric properties of synthesized samples were measured from 100 Hz to 1 MHz at room temperature using a precision HIOKI make LCR HI-TESTER. Dielectric dispersion was observed at lower frequencies for the synthesized samples. Magnetic properties were studies using Vibrating Sample Magnetometer (VSM), all the synthesized samples exhibited well defined magnetic hysteresis curves, there by confirming the magnetic behaviour of the sintered samples.

1. Introduction
Materials in the nano-scale regime exhibit remarkably new properties compared to materials at their bulk counterpart. Nanomaterials appear in every industry from agriculture to service sector. Numerous applications of nano-technology find in wide range of industries enlarges day to day and a few of applications are transformer inductors, humidity sensors, drug delivery systems, electronic components, multilayer chip inductors, in enhanced photo catalytic performance, magnetic resonance imaging etc. [1-5]. Among the ferrites, spinel ferrites with nano-structure are most important. Ferrites comes under magnetic materials family with the general spinel structure bearing the general chemical formula AB\textsubscript{2}O\textsubscript{4} (A\textsuperscript{2+} B\textsuperscript{3+} O\textsubscript{4}\textsuperscript{2-}) where A is divalent metal ion e.g. Fe, Mg, Zn, Ni, Mn, Cu, Co, etc., and B is trivalent cation e.g. Fe\textsuperscript{3+}, Al\textsuperscript{3+} etc., and O=oxyen anion e.g. O\textsuperscript{2-} Metal cations, A and B are fitted at A-site (tetrahedral site) and B-site (octahedral site) and oxygen has face centred cubic (FCC) close packing structure [6]. Spinel ferrites are familiar dielectric materials with high resistivity and low hysteresis loss. An account of their peculiar magnetic, dielectric and electrical properties of spinel ferrites, they are used in high density information storage system, medical diagnosis, transformer cores, inductor
coils, microwave devices, telecommunication, microwave absorbers, magnetic recording, biosensors, power transformers, radio electronics etc. [5,7-10].

Cobalt ferrites are a well-known fact that they are hard magnetic materials, which is studied in detail due to its high coercivity, high chemical stability, high saturation magnetization, mechanical hardness, high resistivity and good electrical insulator [11]. Various research studies explain the cobalt ferrites doped with divalent and trivalent metal ions such as Mn$^{2+}$, Mg$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, La$^{3+}$, Ga$^{3+}$ etc. are received increasingly attentiveness in many applications, especially for sensors and high frequency applications. Properties of cobalt ferrites can be altered such as by incorporating a dopant into its structure, sintering temperature and preparation methods. Consequently, based on their structural, optical, magnetic and electrical properties they can be used in many applications [12-14].

In this work, an in-expensive auto-combustion method is chosen as it provides good crystallinity, less power consumption, high purity, ease of sample preparation, stability etc. compared to other techniques like co-precipitation method, sol-gel, micro emulsion route, hydrothermal method [16-20]. Herein, La$^{3+}$ is elected as dopant and substituted it into cobalt ferrite system. Effect of lanthanum (La$^{3+}$) substitution in CoFe$_2$O$_4$ can be studied on its structural, morphological, dielectric, electrical and magnetic properties.

2. Experimental

Lanthanum (La$^{3+}$) doped nano cobalt ferrite powders were synthesized using auto-combustion method. This method is the simplest, reliable method for obtaining high purity nano-materials. To prepare La$_x$CoFe$_{2-x}$O$_4$ nano-powders, the precursors selected are, La(NO$_3$)$_3$.6H$_2$O (Lanthanum nitrate), Co(NO$_3$)$_2$.6H$_2$O (Cobalt nitrate), Fe(NO$_3$)$_3$.9H$_2$O (Ferric nitrate), C$_6$H$_8$O$_7$ (Citric Acid). All the chemicals were procured from Sigma Aldrich; all are of 99.8% purity. Calculated stoichiometry molar amounts of lanthanum, cobalt, and ferric nitrates are added with distilled water and mixed thoroughly using a magnetic stirrer until metallic nitrates are dissolved completely at RT. While aqueous solution of citric acid was prepared and added slowly to the aqueous solution of corresponding metallic nitrates. Redox mixture was taken in a silica crucible and allowed in to a muffle furnace, which was already pre-heated to a temperature of 500°C. Because of the auto-combustion reaction, aqueous mixture of metallic nitrates and organic fuel finally yields porous and fluffy voluminous powder. Obtained voluminous product was well grinded to get magnetic oxide nano powder. As obtained ash was sintered at 900°C for minimum 4 hours to achieve higher rate of crystallization and finally grinded so that La$^{3+}$ doped CoFe$_2$O$_4$ ferrite nano powders can be obtained.

3. Results and Discussion

3.1 Phase confirmation studies

Phase confirmation of the prepared samples is done using, Bruker AXE D8 Advanced diffractometer. Diffractogram of La$_x$CoFe$_{2-x}$O$_4$ (x=0, 0.05, 0.1, 0.15 and 0.20) powder nano-particles are shown in Fig 1. Obtained XRD data of La$^{3+}$ substituted CoFe$_2$O$_4$ are compared with standard data (JCPDS PDF card No.22-1086).

Average crystallite size(D) was calculated using the Scherer – Debye Eq. (1) [20].

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \] \hspace{1cm} (1)

Lattice parameter or lattice constant(a=b=c) is measured using Bragg’s equation for all LCF samples by the maximum intense peak (311) using Eq. (2) [20].

\[ a = d_{311} \sqrt{h^2+k^2+l^2} \] \hspace{1cm} (2)

Where $d_{311}$ is the inter-planar spacing for the (311) reflection plane and (h,k,l ) are the corresponding miller indices.
Average crystallite size was found to be varying from 43.71nm to 55.37nm along with the increase in the La\(^{3+}\) concentration from 0.05 to 0.2. This might be because of the distortion caused in the structure with the substitution of rare earth La\(^{3+}\) ions. Lattice constant increased from 8.37Å to 8.48Å with increase of the dopant La\(^{3+}\) concentration, this is due to that La\(^{3+}\) has larger ionic radii (1.031Å) replaces the Fe\(^{3+}\)(0.64Å) ions having lower ionic radii in La-doped CoFe\(_2\)O\(_4\) system. This kind of behaviour being caused by cation distribution between the two sites, which requires more energy so that La\(^{3+}\) ions to enter the spinel lattice to complete crystallization.

3.2 Morphological Studies

Surface morphology of the synthesized La\(^{3+}\) doped Cobalt ferrite (LCF) nano-particles were analysed using FESEM (FEG-Quanta-250), indicates that homogeneous nature for the obtained and samples of nano-powders are shown in Fig 2. Obtained micrographs shows that the morphology of the particles regular distribution of nano-particles. FESEM micrographs further suggests that the samples consist of cubical shaped nano-particles with agglomeration. As the doping concentration of La\(^{3+}\) increases, the grains become more and more dense.

3.3 Dielectric Studies

Variation of dielectric constant (\(\varepsilon'\)), and its imaginary counter-part (\(\varepsilon''\)) and ac conductivity (\(\sigma_{ac}\)) with frequency at room temperature for the pure cobalt ferrite and La\(^{3+}\) substituted cobalt ferrite is shown in Fig.3 (a) to Fig.3 (d), it is clear that \(\varepsilon'\) decreases steeply at lower frequencies and remains constant at higher frequencies. Variation of dielectric constant with applied frequency is due to charge transport relaxation. This dielectric dispersion is attributed to Maxwell and Wagner type of interfacial polarization which is in agreement with Koop’s theory, as the dielectric constant is a combined effect of dipolar, electronic, ionic and interfacial polarizations [20-24].

In order to understand the conduction mechanism and type of polaron responsible for conduction, ac conductivity, \(\sigma_{ac}\) were estimated as per \(\sigma_{ac} = \omega \varepsilon_0 \varepsilon''\), with \(\varepsilon_0\) is the permittivity of free space and \(\omega = 2\pi f\). Substitution of La\(^{3+}\) ions in place of Fe\(^{3+}\) ions, limits the degree of conduction by blocking as per Verwey’s hopping mechanism [24].
Variation of $\sigma_{ac}$ with frequency, $\omega$, is shown in Fig. 3(c) for the proposed samples. Obtained curves are linear except at very low frequencies, this indicates that the conduction occurs by the hopping of charge carriers between the localized states which confirms the small-polaron type of conduction [25-26].

Figure 2. Micrographs of the LCF samples with various doping concentrations.
4. Magnetic Studies

Magnetic hysteresis loops, at RT were recorded for the proposed samples. M-H loops for synthesized samples sintered at 900°C are shown in Fig.4. Synthesized and sintered samples exhibit magnetic hysteresis, which confirms the magnetic nature of the samples. Magnetic parameters extracted from M-H loops for pure as well as doped samples were mentioned in the Table.1. Compared to pure CoFe\textsubscript{2}O\textsubscript{4} sample, remanent magnetization, M\textsubscript{r}, decreases with the increase of La\textsuperscript{3+} concentration, it is because of the decrease in Fe\textsuperscript{3+}-Fe\textsuperscript{3+} (B-B) interactions resulting from doping with La\textsuperscript{3+} [29-30]. It is observed that for all sintered samples, coercive field, H\textsubscript{c}, remains almost same, except for La\textsubscript{0.15}CoFe\textsubscript{1.85}O\textsubscript{4}. It is because of the known fact that, coercivity depends on factors such as magneto-crystalline anisotropy, micro strain, size distribution and magnetic domain size [22-28].
Table 1. Magnetic Parameters extracted from M-H loops at Room temperature.

| Sample         | Ms (emu/g) | Mr (emu/g) | Hc (Oe) |
|----------------|------------|------------|---------|
| CoFe$_2$O$_4$  | 75.04      | 27.87      | 2548    |
| La$_{0.05}$CoFe$_{1.95}$O$_4$ | 30.64      | 11.29      | 2510    |
| La$_{0.1}$CoFe$_{1.9}$O$_4$  | 42.37      | 14.35      | 2580    |
| La$_{0.15}$CoFe$_{1.85}$O$_4$ | 33.58      | 10.53      | 2900    |
| La$_{0.2}$CoFe$_{1.8}$O$_4$  | 22.97      | 4.74       | 2600    |

5. Conclusions

All the synthesized samples have single phase spinel cubic structure, without any secondary phases indicating the absence of any impurities. From the dielectric measurements, it is observed that the synthesized samples exhibited dielectric dispersion. Linear nature of AC conductivity measurements, confirms the conduction mechanism in the proposed samples is because of small-polarons. Pure and rare-earth La$^{3+}$ doped samples show appreciable magnetic hysteresis with good value of saturation magnetization, remanence at room temperature.

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