Impact of doping on Structural, Electronic and Optical Properties of Cobalt Ferrite Prepared by Solid-state Reaction

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Abstract— Cobalt ferrite (CoFe$_2$O$_4$) is a promising material due to its exceptional ferroelectric, optical, electronic and magnetic properties that are most important for device applications. Partial substitution of iron with transition metals might play an important role to improve its different properties useful in various applications. Degree of crystallinity, particle size, electrical conductivity, optical absorption and low temperature magnetization of cobalt ferrite were measured before and after doping with transition metals Zr, Zn and Cd. The crystallinity improved for doping effect. The charge capacity and optical absorptivity also reported to be increase for doping effects.

Keywords— Calcinations, Characterization, Solid-State reaction, Ferroelectric materials, X-ray diffraction.

I. INTRODUCTION

Cobalt ferrite (CoFe$_2$O$_4$) are well-known ferroelectric materials. Ferroelectric magnets simultaneously show the properties of ferroelectrics and ferromagnets [1]. Ferroelectric materials possess two or more orientational states in the absence of an electric field and can be changed from one to another of these states by the application of an electric field. The combination of magnetic and electrical properties makes ferroelectric-magnet useful in many technological applications. It has covered a wide range of applications including electronic devices, high density information storage devices, high rate of change of strain with magnetic field, high coercivity, moderate saturation magnetization, high Curie temperature $T_C$, photo magnetism, good electrical insulation etc. [2]-[6]. Cobalt ferrites are suitable for magnetic recording applications such as audio and videotape and high-density digital recording disks etc. [7]. Cobalt ferrites are the subject of much interest due to their unusual optical, electronic and magnetic properties. Substitution of rare earth (Y$^{3+}$, Gd$^{3+}$, Ho$^{3+}$, Sm$^{3+}$, Nd$^{3+}$) ion into cobalt ferrites has been reported to lead to structural distortion that induces strains in the material which indicate improved crystallinity of the sample and to affect the electrical and magnetic properties significantly. The rare earth doped cobalt ferrites found an application in high frequency devices and power supply due to high resistivity and low dielectric losses [8], [9]. Cobalt ferrite has become an ingredient in the formation of metallic/magnetic nano-composites due to the observations of a wide range of magnetic, electric and other novel properties in its derivatives [10],[11]. Some transition metals were doped in iron site of the cobalt ferrite [CoFe$_2$M$_x$O$_{4+x}$, M=Zn, Zr, Cd] to enhance its structural, electronic, dielectric, optical and magnetic properties that might play important role in high efficiency device applications.

II. EXPERIMENT

High-purity (>99.9%) powders of CoO and Fe$_2$O$_3$ were used as the starting material for preparation of CoFe$_2$O$_4$. Initially we studied the phase formation employing a thermo balance (TG/DTA 630) in order to establish the procedure for synthesizing CoFe$_2$O$_4$. A stoichiometric mixture of CoO and Fe$_2$O$_3$ with molar ratio of Co:Fe = 1:1, was heated in a air atmosphere with a heating program as shown in the inset of Fig.1. A representative thermo gravimetric (TG) curve obtained for the raw material mixture is shown in Fig.1. From this TG analysis, it was found that the weight loss below 600$^\circ$C is too large.

![Fig.1 Thermo gravimetric curve for the phase formation process of CoFe$_2$O$_4$. The inset represents the heating program employed.](image-url)
At the first step of synthesis, the reactants were dried in air at 100 °C for 12 h. A powdered mixture of CoO and Fe₂O₃ with molar ratio of Co:Fe = 1:1, was mixed well in an agate mortar using ethanol, than dried and calcined at 800 °C for 24 h in an air atmosphere. Before the next heat treatment, the powder was reground thoroughly to ensure homogeneity. The powder was calcined again at 900°C for 12 h in an air atmosphere. After second heat treatment, the powder was ground and pelletized in 12 mm diameter under pressure of 60 KN using pressure gauze. The compressed pellets were sintered at 1000°C for 12 h in an air atmosphere. In all heat treatments, the temperature rising and cooling rates were 2°C/min. The transition metal doped cobalt ferrites [CoFe₂₋ₓMₓO₄, x=0.2; M =Zn, Zr & Cd] were prepared in the same way of stoichiometric CoFe₂O₄ sample. CoFe₁₋ₓZnₓO₄ were prepared using ZnO. CoFe₁₋ₓZrₓO₄ were prepared using ZrO₂ and CoFe₁₋ₓCdₓO₄ were prepared using CdCO₃.

The powder samples were analyzed by X-ray diffraction (XRD) using a CuKα (λ = 0.154 nm) radiation source using a Rigaku HYGD Multiflex X-ray diffractometer at room temperature in center for crystal science and technology, Japan. The diffraction angle (2θ) range between 5° and 85° was scanned. Fourier Transform Infrared Spectroscopy (FTIR) measurement of the samples was performed in the wave number range 400–4000 cm⁻¹ using the model Nicolet-6700 (Thermo electron Corporation). Before recording the FTIR spectrum of the studied samples, the instrument was calibrated using standard KBr pellet. The KBr powder was well ground using agate mortar and pestle to reduce the scattering of infrared beam. The grinding was continued until crystallites can no longer be seen and the powder became somewhat pasty and sticks to the mortar. Then, the fine powder was collected and a small amount of ferrite powdered sample (about 0.1 % of the KBr powder, or just enough to maintain the good transparency of the final pellet) mix with the KBr powder. Subsequently, the mixed powder (ferrite+ KBr) was ground for 5 minutes to make it homogeneous and the ferrite particles be dispersed properly in the mixture. A pellet of the powder with 3 mm diameter and thickness less than 0.5 mm was made using a Qwik Handi-Press. FTIR spectrophotometer (Spectrum 100, Perkin Elmer) was used for FTIR transmission spectrum of the powder samples. The Agilent Precision Impedance Analyzer (Agilent technologies, Model: 4294A Japan) was used for measurements of frequency dependences ac conductance, dielectric constant and capacitance. The samples were characterized by UV–Visible spectrophotometer (Shimazu: UV–1650 PC) for wavelength dependence absorption spectrum.

### III. RESULTS AND DISCUSSIONS

#### A. Structural properties

Crystalline CoFe₂O₄ powder was obtained by conventional solid-state reaction technique with a final firing at 900 °C. The powder samples of CoFe₂₋ₓMₓO₄ [M= Zn, Zr, Cd & x=0.2] were characterized at the room temperature by a Rigaku Mutiflex diffractometer range from 2θ = 5° to 85° with CuKα radiation ( = 1.5418 Å), at 40 KV and 30 mA. The unit cell refinement was accomplished using XRD data and CellCal software. Typical XRD patterns of CoFe₂₋ₓMₓO₄ crystalline powders shown in Fig. 2 reveal that all these materials are single phase with cubic crystal structure of space group Fd3m. The prepared samples were identified as highly crystalline and homogeneous by indexing these XRD patterns using JCPDS data No. 22-1086. The observed peaks at (220), (311), (222), (440), (422), (511), and (400) indicate that the CoFe₂O₄ material crystallizes in the inverse spinel phase. Here the sharp peaks indicate the good crystallinity and broad diffraction peaks represents the nanoscale crystallite size [9]. In principle, Co²⁺ ions will prefer to occupy the B sites by replacing Fe³⁺ ions in the Fe rich regime of cobalt ferrite [12].

No impurity phase such as alpha-Fe₂O₃ and CoO was detected from this pattern, so the pure phase solid is obtained, which indicates that CoFe₂₋ₓMₓO₄ can be synthesized fast by conventional solid-state reaction route.

No extra peaks were found with in case of Zn and Cd doping. Although two extra peaks were found on two sides of (220) peaks in case of Zr doping. The relative intensity of main peaks of CoFe₂O₄ increases with doping Zn & Zr but decreases with doping Cd. The larger value of intensity ratios of first and second largest peak reveals the better crystallinity [13]. It can be seen from the XRD patterns that crystallinity increases for doping Zn, Cd and Zr elements. The highest crystallinity is obtained with Zr doping as shown in table 1.

The table 1 lists the lattice parameters obtained from indexing of XRD pattern using CellCal program and corresponding intensity ratios of main peaks.

#### TABLE I

<table>
<thead>
<tr>
<th>Samples</th>
<th>I₁₁/I₄₀</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe₂O₄</td>
<td>1.868</td>
<td>8.38127</td>
</tr>
<tr>
<td>CoFe₁₋ₓZnₓO₄</td>
<td>2.319</td>
<td>8.35063</td>
</tr>
<tr>
<td>CoFe₁₋ₓCdₓO₄</td>
<td>2.425</td>
<td>9.36783</td>
</tr>
<tr>
<td>CoFe₁₋ₓZrₓO₄</td>
<td>2.823</td>
<td>8.33904</td>
</tr>
</tbody>
</table>
Fig. 2 X-ray diffraction patterns of the CoFe$_2$M$_x$O$_4$ [$x=0.2$; M = Zn, Zr & Cd] samples.

The calculated lattice parameters are approximately equal to the standard lattice constants obtained from the JCPDS card no. 22-1086. The lattice constants of the Zr and Zn-doped are seen to be smaller than those of the CoFe$_2$O$_4$. 
The variation of the lattice constant for the CoFe\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{4} and CoFe\textsubscript{1-x}Zn\textsubscript{x}O\textsubscript{4} can be understood by comparing the ionic radii of the high-spin Zr\textsuperscript{4+} (0.86 Å) ion and Zn\textsuperscript{2+} (0.88 Å) with that of the Co\textsuperscript{3+} (0.885 Å) ion in the octahedral site. Thus, the decreases in the lattice constant with Zr and Zn doping indicates that Zr\textsuperscript{4+} and Zn\textsuperscript{2+} substitutes at the tetrahedral Co\textsuperscript{3+} sites mostly [14].

However, the lattice constants of the Cd-doped are seen to be larger than those of the CoFe\textsubscript{2}O\textsubscript{4}. The variation of the lattice constant for the CoFe\textsubscript{1-x}Cd\textsubscript{x}O\textsubscript{4} can be understood by comparing the ionic radii of the high-spin Cd\textsuperscript{2+} (0.109 Å) ion with that of the Co\textsuperscript{3+} (0.885 Å) ion in the octahedral site [15]. Thus, the increase in the lattice constant with Cd doping in CoFe\textsubscript{2}O\textsubscript{4} indicates that Cd\textsuperscript{2+} substitutes at the octahedral Co\textsuperscript{3+} sites mostly. Good crystallinity enhances the performance of cobalt ferrite in various device applications.

The performance of the Cobalt Ferrite is affected by a numerous factors such as particle size (D), micro strain (ε) and dislocation density (δ). The average grain size of the CoFe\textsubscript{2-x}M\textsubscript{x}O\textsubscript{4} [x = 0.2; M = Zn, Zr & Cd] particles was calculated using Scherrer formula, 

$$D = \frac{0.94 \lambda}{\beta \cos \theta}$$

[16] and micro strain values calculated by 

$$\varepsilon = \frac{\beta}{4 \tan \theta}$$

where D is the grain size, λ is the X-ray wave length (1.5418 Å), 0.94 is the crystal shape constant, θ is the reflection angle of the highest peak and β is the full width at half maximum (FWHM) of the highest peak in radians. Micro-strain values are related to average particle size.

The dislocation density (δ) of the CoFe\textsubscript{2-x}M\textsubscript{x}O\textsubscript{4}CoFe\textsubscript{2-x}M\textsubscript{x}O\textsubscript{4} [x = 0.2; M = Zn, Zr & Cd] was estimated using the equation

$$\delta = \frac{1}{D^2}$$

(lines/m\textsuperscript{2}) [17]. The dislocation density (δ) indicates the length of dislocation lines per unit volume and measures the amount of defects in a crystal. The calculated D, δ and ε values are listed in Table 2.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>D (nm)</th>
<th>δ×10\textsuperscript{12} (lines/m\textsuperscript{2})</th>
<th>ε×10\textsuperscript{-3} (lines.m\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe\textsubscript{2}O\textsubscript{4}</td>
<td>71.42</td>
<td>1.96</td>
<td>1.649</td>
</tr>
<tr>
<td>CoFe\textsubscript{1}Zn\textsubscript{0.1}O\textsubscript{4}</td>
<td>89.97</td>
<td>1.24</td>
<td>1.307</td>
</tr>
<tr>
<td>CoFe\textsubscript{1}Zr\textsubscript{0.1}O\textsubscript{4}</td>
<td>116.24</td>
<td>7.40</td>
<td>1.012</td>
</tr>
<tr>
<td>CoFe\textsubscript{1}Cd\textsubscript{0.1}O\textsubscript{4}</td>
<td>83.85</td>
<td>1.42</td>
<td>1.406</td>
</tr>
</tbody>
</table>

The rare earth ions usually have empty, half filled or completely filled 4f orbital, which have a stable structure, giving the rare earth ions high thermal stability. So, a large amount of energy is required in order to form Re\textsuperscript{5+}. O\textsuperscript{2-} bond and the crystallization and growth of grains require higher temperatures as compared to the other doped cobalt ferrite samples [9]. Similarly the transition metal ions usually have empty, half filled or completely filled 3d orbital, which have a stable structure, giving the transition metal ions high thermal stability. Hence, a large amount of energy is required in order to form Tr\textsuperscript{3+}- O\textsuperscript{2-} bond and the crystallization and growth of grains require higher temperatures as compared to the other doped cobalt ferrite samples. The particle size, D increases with doping Cd(5s\textsuperscript{2} 4d\textsuperscript{10}), Zn(4s\textsuperscript{2} 3d\textsuperscript{10}) and Zr(5s\textsuperscript{2} 4d\textsuperscript{10}) respectively. The particle size, D for Zr-doped is very high because its d- orbital have only 2 electrons.

The values of dislocation density, δ decreases for Cd and Zn doped but increases for Zr doped. The values of micro strain, ε decreases for Zr, Zn and Cd doped respectively. Above all, the doping effects of Zr is very significant.

In order to get physical insight of the chemical bonding and phase formation, we also studied the structure by Fourier transform infra-red (FTIR) spectroscopy. FTIR spectroscopic technique is powerful for investigating the local structure and cation environment in oxides [18], [19]. Ferrite possesses the structure of mineral spinel MgAl\textsubscript{2}O\textsubscript{4}. It crystallizes in the cubic form with the space group Fd\textsubscript{3}m. Ferrite can be considered as a continuously bonded crystal with atoms bonded to all nearest neighbours by equivalent forces [20]. In the wave number range 300-1000 cm\textsuperscript{-1}, the infrared bands of solids are usually assigned to vibration of ions in the crystal lattice. The results of FTIR spectroscopic analysis are shown in the Fig. 3. The main spectrum of CoFe\textsubscript{2}O\textsubscript{4} contains the following main absorption bands: 258.63, 387.99, 587.83, 1112.41, 1384.49, 1633.81, and 3434.70 cm\textsuperscript{-1}. These results confirm the XRD observations showing that the vibration bands for precursors vanished and the vibration bands for the oxide network developed. In the far-infrared region, we observed the single well-resolved band at 258.63 cm\textsuperscript{-1}. Two main broad metal-oxygen bands are seen in the IR spectra of all spinels, and ferrites in particular. The highest one (v1) generally observed in the range 550-600 cm\textsuperscript{-1}, corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site, whereas the lowest band (v2), usually observed in the range 385-450 cm\textsuperscript{-1}, is assigned octahedral metal stretching [21]. The spectra showed prominent bands near 1600 and 3400 cm\textsuperscript{-1}, which were attributed to the stretching modes. Major change in transmission are found at the wavelength region 1500 cm\textsuperscript{-1} to 2000 cm\textsuperscript{-1} with doping Zr, Zn and Cd.
Fig. 3  FTIR spectrum of CoFe$_{2-x}$M$_x$O$_4$ [$x$=0.2; $M$ =Zn, Zr & Cd] crystalline sample.

B. Electronic properties

The ac conductance of the samples were measured by impedance analyzer, where the signal frequency was varied from 100 kHz to 10 M Hz and oscillating voltage 300 mV was applied. Fig. 4 shows the frequency dependence ac conductance of CoFe$_{2-x}$M$_x$O$_4$ [$x$=0.2; $M$ =Zn, Zr & Cd] samples. The frequency response ac conductance also depends on the doping with CoFe$_2$O$_4$. The ac conductance increases with frequency for Cd doping but decreases with frequency for Zr and Zn respectively. Good ac-conductivity enhances the performance of cobalt ferrite in various device applications.
C. Optical properties

The optical properties of a material are very important in some applications such as optical coatings, reflectors, absorbers and various optoelectronic devices. The dielectric property of a material is another important factor in electronic device applications.

Fig. 4 Frequency dependence ac conductance of CoFe$_{2-x}$M$_x$O$_4$ [$x$=0.2; $M$=Zn, Zr & Cd] sample.

![Fig. 4 Frequency dependence ac conductance of CoFe$_{2-x}$M$_x$O$_4$ [$x$=0.2; $M$=Zn, Zr & Cd] sample.]

Fig. 5 Frequency dependence capacitance of CoFe$_{2-x}$M$_x$O$_4$ [$x$=0.2; $M$=Zn, Zr & Cd] sample.

We evaluate the optical and dielectric properties of CoFe$_{2-x}$M$_x$O$_4$ [$x$=0.2; $M$=Zn, Zr & Cd] as a function of frequency. The frequency dependence capacitances of samples were measured at room temperature as shown in Fig. 5. The capacitance of CoFe$_{2-x}$M$_x$O$_4$ is high at low frequency region due to contribution of all kinds of polarization at low frequency, then decreases with increase of frequency up to approximately 0.06 MHz and then increases and finally approaches to all most constant value above 0.15 MHz. The capacitance is higher for Zr and Cd-doped than undoped CoFe$_2$O$_4$ because Zr and Cd are in O-shell region. As Zn is in N-shell region capacitance is lower than undoped CoFe$_2$O$_4$.

Dielectric properties of the CoFe$_{2-x}$M$_x$O$_4$ samples were measured by precision impedance analyzer. Dielectric constant is a measure of materials ability to store electric charge. This dependence upon frequency is because of the interfacial polarization as predicted by Maxwell-Wagner [22]. According to this model, the dielectric structure of a ferrite material is assumed to be made up of two layers; the first layer being a conductive layer that consists of large ferrite grains and the other being the grain boundaries that are poor conductors.
Rabinkin and Novikova [23] showed that the polarization in ferrites is through a mechanism similar to the conduction process. The large value of dielectric constant at lower frequency may be due to the predominance of species like Fe$^{2+}$ ions, oxygen vacancies, grain boundary defects, etc. The decrease of dielectric constant with frequency is obvious because of the fact that any effect contributing to polarization is found to show lagging behind the applied field at higher frequencies. By increasing the frequency within a certain frequency limit, the electron hopping cannot follow the electric field fluctuations causing a decrease in the dielectric constant. Koop [24] argued that the dielectric constant at low frequency comes from the grain boundaries which have a high dielectric constant due high resistivity at the grain boundary region. The dielectric constant at high frequency comes from the grains which have a small value of dielectric constant due to low resistivity. The higher value of dielectric constant at low frequency may be due to voids, dislocations and defects etc. Fig. 6 shows the frequency dependence dielectric constant of CoFe$_{2-x}$M$_x$O$_4$ samples that implies the same tendency of capacitance. Frequency response capacitance and dielectric constant strongly depends on doping of transition metal elements. The dielectric constants are higher for doped samples than undoped CoFe$_2$O$_4$ samples at low frequency. At high frequency dielectric constants are low and they remain constant. The results reveal that after doping the efficiency of cobalt ferrite improved in case of dielectric device applications.

![Dielectric Constant vs Frequency](image)

**Fig. 6** Frequency dependence dielectric constants of CoFe$_{2-x}$M$_x$O$_4$ [x=0.2; M =Zn, Zr & Cd] sample.

The UV-Visible absorption spectrum of the sample was recorded by using a UV-Vis spectrophotometer (Shimazu: UV–1650 PC) in the photon wavelength range between 200 – 800 nm. Fig.7 shows the absorption spectrum of CoFe$_{2-x}$M$_x$O$_4$ samples. The absorption slightly decreases with increase of wavelength in the visible. There are some absorption peaks in the ultraviolet region for all the samples. There are a strong absorption peaks at 204.2 nm in spectrum of the CoFe$_{1.997}$Zn$_{0.003}$O$_4$ sample. There are a medium peak at slightly above 200 nm for CoFe$_{1.99}$Zr$_{0.01}$O$_4$, CoFe$_{1.99}$Cd$_{0.01}$O$_4$ and CoFe$_2$O$_4$. There are also very weak peaks for all samples. This result reveals that cobalt ferrite is a strong absorber but in case of doping its absorptive power decreases. The absorptive power increases for Zn-doped and decreases for Zr and Cd-doped.

![Absorption vs Wavelength](image)

**Fig. 7** The UV–Visible absorption spectrum of CoFe$_{2-x}$M$_x$O$_4$ [x=0.2; M =Zn, Zr & Cd] sample.
D. Magnetic properties

We have studied on the freezing of magnetocrystalline of the cobalt ferrite at low temperature, i.e., down to 5 K. Fig. 8 shows the temperature variation in the magnetization of CoFe$_2$O$_4$ sample for field cooling (FC) measured at 1000 Oe. The FC data exhibit a decrease in the magnetization with the temperature due to magnetic anisotropy-induced loss of long-range ferrimagnetic ordering of the material. We have observed an anomaly (sudden fall of magnetization) in the FC curve at around 150 K. It could be due to a reentrant spin-glass behavior which is due to freezing of the spin. We have observed that the magnetization is constant below 150 K in the FC condition. The magnetic moments aligned during the field cooling condition to minimize the Helmholtz free energy ($H \sim 0$). Hence, bifurcation has been observed in the FC curves. However, it requires a very large magnetic field to overcome the surface effect in materials. Hence, we have not observed considerable bifurcation in the FC curves. The FC magnetization initially decreases with decreasing temperature and then saturates below 150 K, showing temperature independence. This may be a consequence of finite-size interaction effects which occur from dipolar interactions [25]. The FC curves reveal that the blocking temperature for the cobalt ferrite sample is well above room temperature (300 K). The relatively larger blocking temperature might be due to the large anisotropy in cobalt ferrite [26]. From the above discussion, it is clear that cobalt ferrite shows anomaly behavior at 150 K. The Zr-doped FC curve is similar to CoFe$_2$O$_4$. The Zn and Cd-doped sample has higher magnetization than CoFe$_2$O$_4$. Although the Cd-doped sample has large decrease in magnetization than CoFe$_2$O$_4$.

IV. CONCLUSION

The single phase polycrystalline powders of doped and transition metal doped cobalt ferrite have been successfully synthesized by solid state reaction technique. The phase formation condition in synthesize profile was demonstrated by thermal analysis and single crystalline phase was confirmed by X-ray diffraction study. In this study we reported that the crystallinity of cobalt ferrite increases for doping of transition metals in iron side. The dislocation density decreases for Cd and Zn-doped samples. The micro strain decreases for Zr, Zn and Cd-doped samples. The FTIR analysis corroborated the spinel structure of the samples. The absorptive power increases for Zn-doped. The ac conductivity increases with frequency for Cd-doped samples. The dielectric constants are higher for Zr and Zn-doped samples at low frequency. The dielectric constant decreases rapidly with increasing frequency and then reaches a constant value. Low dielectric constants materials are required for high–frequency application in electrical circuits to reduce dielectric losses. The Zn and Cd-doped sample has higher magnetization at low temperature.

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