EFFECT OF RARE EARTH SUSTITUENTS Pr\(^{3+}\) AND Ho\(^{3+}\) ON STRUCTURAL AND MAGNETIC PROPERTIES OF COBALT FERRITES

A. M. Pachpinde, M. M. Langade, U. M. Mandle, B. L. Shinde and K. S. Lohar

1Department of Chemistry, Jawahar College, Andur, Osmanabad, 413603, (MS), India
2Department of Chemistry, Sangmeshwar College, Solapur, 413001, (MS), India
3Department of Chemistry, Waghire College of Arts, Commerce and Science, Saswad, Pune, 412301, (MS), India
4Department of Chemistry, Shrikrishna Mahavidyalaya, Gunjoti, Osmanabad, 413606, (MS), India

Corresponding Author: kslohar@rediffmail.com

ABSTRACT

Rare earth doped cobalt ferrites with the chemical formula CoFe\(_2-x\)Pr\(_x\)O\(_4\) and CoFe\(_2-x\)Ho\(_x\)O\(_4\) (\(x = 0.00\) to 0.1 in the step of 0.025) successfully synthesized by sol-gel auto combustion method. The synthesised precursors calcinated at 600 \(^\circ\)C for 4 hours in an air atmosphere. XRD patterns of calcinated Pr\(^{3+}\) and Ho\(^{3+}\) substituted cobalt ferrite samples show the formation of cubic spinel structure. The Lattice constant, X-ray density, and hopping lengths increase with increasing Pr\(^{3+}\) and Ho\(^{3+}\) concentration. IR spectra of calcinated samples illustrate two distinguishable absorption bands in the range 700 – 755 cm\(^{-1}\) (\(\nu_1\)) and 452 – 495 (\(\nu_2\)) cm\(^{-1}\) and are the characteristics of spinel ferrites. SEM micrographs show spherical-shaped particles in the samples. The TEM micrograph shows a homogeneous and uniform distribution of the sample particles. Observed hysteresis loops illustrate the characteristic behavior of hard magnetic material. The remanence ratio was served from 0.317 to 0.347 for Pr\(^{3+}\) substituted cobalt ferrite and 0.451 to 0.467 for Pr\(^{3+}\) and Ho\(^{3+}\) substituted cobalt ferrite.

Keywords: Cobalt Ferrite, Cubic Spinel, Microstructure, Magnetic Properties, Magnetic Material.

INTRODUCTION

Nowadays various nanomaterials, including magnetic nanoparticles, are widely used, and have a lot of applications in different fields of engineering and biomedicine, to magnetic behaviors provide a huge range of applications from medicine for example magnetically activated drug delivery, D.N.A. isolation to electronics such as storage devices, optoelectronics, microwave, frequency devices, gas sensors, etc.\(^1,2\) Genially magnetic nanoparticle is a class of metallic, bimetallic and superparamagnetic iron oxide nanoparticle, for eg. transition metal oxides (MFe\(_2\)O\(_4\), M=Cu, Ni, Zn, Co, Mn, etc.) are mainly composed of about 70% iron oxide (Fe\(_2\)O\(_3\)) and a bought 30% other metal oxide including CuO, NiO, ZnO, MnO and or FeO.\(^3,4\) Among this ferrite, the spinel ferrites have cubic symmetry with spinel F.C.C. structure, with three types i.e. Normal, inverse, and random spinel. The cobalt ferrite nanoparticles having a mixed inverse spinel structure with divalent cobalt (Co\(^{2+}\)) cation and trivalent (Fe\(^{3+}\)) cation was scattered at tetrahedral (A) and octahedral (B) sites in its lattice structure\(^5\) have been attracted in scientific applicability because to its high saturations magnetization (~80 amu), coercivity (~5400 Oe), chemical stability, mechanical hardness etc.\(^6,7\) Number of chemical preparation methods have been carried out by many researchers to synthesize nano crystalline cobalt ferrites such as ceramic,\(^8\) wet chemical,\(^3\) thermal decomposition of organic precursors,\(^10\) microwave hydrothermal,\(^11,12\) sol-gel auto combustion,\(^13\) auto catalytic thermal decomposition of fumarato - hydrazinate ligands\(^14,15\) and micro emulsion method.\(^16,17\) The sol-gel auto combustion method is more convenient among these methods, because of the requirement of a very short time, no need for special apparatus or conditions nor any precipitating agent, as compared to other methods. From literature review concluded that introducing a slight amount of rare earth dopant into spinel lattice to alter the...
structure resulted in improved magneto-electric properties of cobalt ferrite because of magnetic moment of La 0.0 μB to 10.6 μB of Dy, and the 4f electron shells to Lu(14) from La (0) of the rare earth ion to spin–orbital coupling to the angular momentum, due to doping of rare earth element in cobalt ferrite spinel structure, there is 3d-4f orbital interaction, resulting increase in magnetic crystalline anisotropy and magnetic moment. In cobalt ferrite substitution of rare earth elements which have large ionic radii, it substitutes Fe3+ ions, changes crystallinity, grain size, and lattice parameters resulting in exploring magnetic properties. At present we report the effect of two rare earth dopant’s (Pr3+ and Ho3+) ions with different ionic radii and magnetic moments to modify structural parameters and magnetic properties of cobalt ferrites as a function of the concentration of Ho3+ and Pr3+ ions dopants, synthesized by sol-gel auto-combustion method. The advantages of this method over other methods of synthesis include, the mixing of cations of desired or excepted composition at the molecule level means synthesized products have good chemical homogeneity, fine and crystalline products with nanoparticle size distribution, the cation dopants can be easily introduced into the final product, simple equipment and synthesis process, low external energy required to carry synthesis process, multiple steps are not involved, as a result of sol-gel auto-combustion process final product which having high purity.

**EXPERIMENTAL**

**Material and Methods**

Due to more advantages of the sol-gel auto-combustion method, it was chosen to synthesize Pr3+ and Ho3+ substituted cobalt ferrite. Analytical grade praseodymium nitrate (Pr(NO3)3·6H2O), Holmium nitrate (Ho(NO3)3·H2O), Ferric nitrate ((Fe(NO3)3·6H2O), Citric acid (C6H8O7·H2O), were used to synthesized rare earth doped cobalt ferrite with a chemical formula CoFe2−xOxPr and CoFe2−xOxHo, with composition (x = 0.00 to 0.1 in step of 0.025). The stoichiometric amount of all metal salts aqueous solution was prepared in de-ionized water and stirred for half an hour to homogenize the solution to the homogeneous distribution of metal then citric acid was added to the solution with a 1:1 ratio of metal concentration to citric acid and the mixture was continuously stirred at 60 °C to get a clear solution. The pH was adjusted to ≈ 7 by using ammonia solution at the same temperature, then the heating at 80 °C, with continuous stirring using a magnetic stirrer, yielding a polymer precursor known as sol, at obtained sol was continued heated at 90 °C and the mixture was continuously stirred, then the sol was converted in to gel, with continuous heating the temperature of gel increase up to 300 °C, then gel undergo self-ignition process, with rapid evolution of large amount of gases accompanying by major mass loss leads to the formation of the precursors. The synthesized precursors then calcinated at 600 °C for 4h in an air atmosphere to obtain desired nano ferrites.

**Characterizations**

The structural parameters were studied by X-ray diffraction on a Phillips-3710 X-ray diffractometer with Cu-Kα radiation (λ=1.5405Å). The infrared spectra of all the samples were recorded in the range 300 cm−1 to 800 cm−1, at room temperature by Perkin Elmer infrared spectrophotometer. Microstructure of samples evaluated by JEOL-JSM-5600-N Scanning Electron Microscope (SEM) and on Philips-CM-200 Transmission Electron Microscope (TEM). Magnetic measurements were carried out at room temperature on a PARC EG&G vibrating sample magnetometer.

**RESULTS AND DISCUSSION**

The XRD patterns of Pr3+ and Ho3+ incorporated CoFe2O4 obtained by the sol-gel method are depicted in Fig.-1 are related to Braggs reflection from (220), (311), (400), (422), (511), and (440) planes to belong to inverse cubic spinel structure with space group fkd-M, which is in good agreement with JCPDS card No. 1007-0426, with no extra phases in Pr3+ (x = 0.000) and Ho3+ (x = 0.000). When Pr3+ ions doped in cobalt ferrite, Pr3+ ions successfully entered the lattice of spinel structure up to x ≥0.05 composition, after that some secondary PrFeO4 phases are observed, similarly in the case of Ho3+ ions doped Cobalt ferrite ortho-ferrite phases of HoFeO4 are observed above composition x ≥ 0.075. Similar types of observation are observed in the literature. The secondary phase formation is observed due to the structural alignment of ions and the larger ionic radius of substituted Pr3+ and Ho3+ ions of Re3+ ions. The Pr3+ and Ho3+ having ionic radii 1.13Å and 1.04Å respectively occupy tetrahedral (A) or octahedral (B) sites of Fe3+, therefore, when Re3+ (Pr3+ and Ho3+) substitution is more than expected, resulting the development of subordinate segments on grain boundaries.
The lattice constant ‘a’ of Pr$^{3+}$ and Ho$^{3+}$ doped in cobalt ferrite was calculated by using an equation discussed elsewhere and tabulated in Table-1. The lattice constants for Pr$^{3+}$ doped in cobalt ferrites are observed within the range of 8.373Å to 8.423 Å and Ho$^{3+}$ doped in cobalt ferrites are within the range of 8.353Å to 8.383Å, increases within Pr$^{3+}$ ion and Ho$^{3+}$ ion concentration in cobalt ferrite. The change in ‘a’ was mostly due to the dissimilarity between the ionic radius of iron and doped rare earth ions.

X-ray density ‘d$_x$’ of Pr$^{3+}$ and Ho$^{3+}$ doped cobalt ferrite calculated using the formula,

$$d_x = \frac{8M}{Na^3}$$ \hspace{1cm} (1)

Where ‘M’ and ‘N’ are the molecular weight and the Avogadro’s number, respectively. The values of X-ray density increased with Ho$^{3+}$ ion and Pr$^{3+}$ ion dopant concentration in cobalt ferrite (Table-1), due to the improved molecular weight of rare earth doped cobalt spinel ferrite. Debye Scherrer method based on XRD data was to evaluate the crystallite size (D$_{XRD}$) for Pr$^{3+}$ and Ho$^{3+}$ doped CoFe$_2$O$_4$. The calculated crystallite size values are within the range of 24 - 38 nm Pr$^{3+}$ doped cobalt ferrites and 32 - 40 nm Ho$^{3+}$ doped cobalt ferrites (Table-1).

Table-1: Lattice Constant (a), X-ray Density (d$_x$) and Hopping Lengths (L$_A$) and (L$_B$), Crystallite Size (D$_{XRD}$) and Porosity (P) of Pr$^{3+}$ and Ho$^{3+}$ Doped Cobalt Ferrite

<table>
<thead>
<tr>
<th>RE$^{3+}$</th>
<th>Comp. ‘x’</th>
<th>‘a’ (Å)</th>
<th>‘d$_x$’ (g/cm$^3$)</th>
<th>L$_A$ (Å)</th>
<th>L$_B$ (Å)</th>
<th>P (%)</th>
<th>D$_{XRD}$ (nm)</th>
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<tr>
<td>Pr$^{3+}$</td>
<td>0.000</td>
<td>8.371</td>
<td>5.307</td>
<td>3.624</td>
<td>2.958</td>
<td>18.408</td>
<td>24.513</td>
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<tr>
<td>Pr$^{3+}$</td>
<td>0.025</td>
<td>8.374</td>
<td>5.350</td>
<td>3.625</td>
<td>2.959</td>
<td>17.928</td>
<td>26.044</td>
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<tr>
<td>Pr$^{3+}$</td>
<td>0.050</td>
<td>8.382</td>
<td>5.384</td>
<td>3.628</td>
<td>2.962</td>
<td>17.598</td>
<td>37.881</td>
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<tr>
<td>Pr$^{3+}$</td>
<td>0.100</td>
<td>8.396</td>
<td>5.403</td>
<td>3.635</td>
<td>2.967</td>
<td>16.418</td>
<td>37.891</td>
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<tr>
<td>Ho$^{3+}$</td>
<td>0.000</td>
<td>8.353</td>
<td>5.343</td>
<td>3.615</td>
<td>2.951</td>
<td>18.578</td>
<td>32.098</td>
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<tr>
<td>Ho$^{3+}$</td>
<td>0.025</td>
<td>8.361</td>
<td>5.359</td>
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<td>2.954</td>
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<td>Ho$^{3+}$</td>
<td>0.050</td>
<td>8.377</td>
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<td>2.957</td>
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<td>Ho$^{3+}$</td>
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<td>37.898</td>
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<td>Ho$^{3+}$</td>
<td>0.100</td>
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<td>3.628</td>
<td>2.962</td>
<td>16.918</td>
<td>39.698</td>
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</table>

The porosity ‘P’ in percentage was calculated by following the equation discussed elsewhere. The porosity ‘P’ in Pr$^{3+}$ and Ho$^{3+}$ doped cobalt ferrite is decreased with Pr$^{3+}$ and Ho$^{3+}$ substitution.

By using the following equations, the hopping lengths L$_A$ and L$_B$ were obtained:

$$L_A = \frac{a\sqrt{3}}{4} \hspace{1cm} (2)$$

$$L_B = \frac{a\sqrt{2}}{4} \hspace{1cm} (3)$$

Fig.1: XRD Patterns of Pr$^{3+}$ and Ho$^{3+}$ Substituted Cobalt Ferrite

The porosity ‘P’ in Pr$^{3+}$ and Ho$^{3+}$ doped cobalt ferrite is decreased with Pr$^{3+}$ and Ho$^{3+}$ substitution.
The calculated hopping lengths are given in Table 1. The values of hopping lengths increased with the Pr$^{3+}$ and Ho$^{3+}$ concentration. The values of hopping lengths increased due to changes in the crystallographic structure of CoFe$_2$O$_4$ upon Pr$^{3+}$ and Ho$^{3+}$ substitution. Figure 2 represents the infrared (IR) spectra of the Pr$^{3+}$ and Ho$^{3+}$ doped cobalt ferrite. The two distinguishable bands observed at 700 – 755 cm$^{-1}$ ($\nu_1$) and 452 – 495 cm$^{-1}$ ($\nu_2$) (Table 2) are the characteristics of spinel ferrites. The $\nu_1$ and $\nu_2$ bands ascribed to the metal-oxygen vibrations at the A- and B-sites, respectively. Values of two bands $\nu_1$ and $\nu_2$ are different due to the difference in Fe$_B$-O$_2^-$ inter-ionic distance for the A- and B-sites. The vibrational frequency of bonds is dependent on the mass of the cation, bond length, and force constant of the bond.

Fig. 2: IR Spectra for the Pr$^{3+}$ and Ho$^{3+}$ Substituted Cobalt Ferrite

The microstructure of the Pr$^{3+}$ and Ho$^{3+}$ doped cobalt ferrite obtained by SEM. Figure 3 depicts typical SEM images of Pr$^{3+}$ and Ho$^{3+}$ doped cobalt ferrites. SEM micrographs illustrate the sphere-shaped nanoparticles of the samples. These images also indicate almost constant dispersal of grains, where distinct grain boundaries were evidenced at lower concentrations of Pr$^{3+}$ and Ho$^{3+}$ ions. Typical TEM images of the Pr$^{3+}$ and Ho$^{3+}$ doped cobalt ferrite are illustrated in Fig. 4. The TEM micrograph shows even and consistent spreading of the nano particulates in calcinated ferrite samples. The sample particulates were slightly agglomerate as the magnetic moment of the sample is relative to its volume. TEM images of calcinated samples illustrate that the particulates are combined and the crystalline particle formed in the nano size.

Fig. 3: Scanning Electron Micrograph of the (a) Pr$^{3+}$ (x = 0.025) and (b) Ho$^{3+}$ (x = 0.00) Substituted Cobalt Ferrites

Fig. 4: TEM Images of the (a) Pr$^{3+}$ (x = 0.025) and (b) Ho$^{3+}$ (x = 0.00) Substituted Cobalt Ferrites
Magnetic Properties

To modify the magnetic characteristics of the CoFe₂O₄ ferrites, Fe³⁺ ions were to some extent doped by Pr³⁺ and Ho³⁺ elements in cobalt ferrites. Magnetic measurements at room temperature were obtained for Pr³⁺ and Ho³⁺ substituted cobalt ferrites. The hysteresis loops given in Fig.-5 illustrate the typical behavior of hard magnetic material. The saturation magnetization (Ms), coercivity (Hc), remanence magnetization (Mr), and magneton number (n₀) are given in Table-2.

![Hysteresis Loops of Pr³⁺ and Ho³⁺ Substituted Cobalt Ferrite](image)

Magnetization is controlled by the super-exchange linkages of the cations between A- and B-sites. A-B interaction dominates the intra-sub lattice A-A and B-B interactions as per the molecular-field model proposed by Neel. The n₀ was obtained by the formula:

\[ n_{B}^{\text{cal.}} = M_{B} - M_{A} \]  

Where \( M_{B} \) and \( M_{A} \) are magnetic moments in \( \mu_{B} \) for the A and B sub-lattice, respectively. The change of \( n_{B}^{\text{cal.}} \) upon Pr³⁺ and Ho³⁺ incorporation is tabulated in Table-2. The content of Fe³⁺ decreased with the favored occupancy of Pr³⁺ and Ho³⁺ ions at the B-site in the cobalt ferrite increasing the overall \( n_{B}^{\text{cal.}} \).

The observed \( n_{B} \) in the Bohr magneton (\( \mu_{B} \)) was obtained by the expression:

\[ n_{B} = \frac{\text{Molecular weight (bzw) \times saturation magnetization (Ms)}}{5585} \]  

The observed and calculated \( n_{B} \) values are matching with each other.

Mr increased with Pr³⁺ and Ho³⁺ substitution (Table-2). Remanence ratio (R) = Mr/Ms is obtained for Pr³⁺ and Ho³⁺ incorporated cobalt ferrite. Table-2 shows that R ranges from 0.317 to 0.347 for Pr³⁺ substituted cobalt ferrite and 0.451 to 0.467 for Pr³⁺ and Ho³⁺ substituted cobalt ferrite indicating the single-domain name of magnetic particles.

Table-2: Band Position (\( v_{1} \) and \( v_{2} \)), Magnetization Saturation (Ms), Remanence Magnetization (Mr), Coercivity (Hc), Magneton Number (n₀), and Remanence Ratio of Pr³⁺ and Ho³⁺ Doped Cobalt Ferrite

<table>
<thead>
<tr>
<th>RE³⁺</th>
<th>Comp. 'x'</th>
<th>Band positions</th>
<th>Ms (emu/g)</th>
<th>Hc (Oe)</th>
<th>( n_{0} ) Obs. (( \mu_{B} ))</th>
<th>( n_{0} ) Cal. (( \mu_{B} ))</th>
<th>R</th>
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<tr>
<td>Pr³⁺</td>
<td>0.000</td>
<td>755.25 452.14</td>
<td>54.93</td>
<td>17.43</td>
<td>644 2.53 3.23 0.317</td>
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<td>Pr³⁺</td>
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<td>752.30 459.23</td>
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<td>19.63</td>
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<td>59.53</td>
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<td>712.75 475.61</td>
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<td>22.33</td>
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<td>32.27</td>
<td>1591 3.26 3.79 0.451</td>
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CONCLUSION
Rare earth-doped CoFe$_2$O$_4$ with a chemical stoichiometry: CoFe$_{2-x}$Pr$_x$O$_4$ and CoFe$_{2-x}$Ho$_x$O$_4$, were successfully synthesized by sol-gel technique. The synthesized precursors then calcinated at 600 $^\circ$C. X-ray analysis of calcinated Pr$^{3+}$ and Ho$^{3+}$ substituted cobalt ferrite indicates the development of cubic spinel crystalline nature. The $a'$, $dx'$, $L_A$, and $L_B$ increase with Pr$^{3+}$ ion and Ho$^{3+}$ ion concentration. The two bands in IR spectra were observed in the range 700–755 cm$^{-1}$ ($\nu_1$) and 452 – 495 ($\nu_2$) cm$^{-1}$ are the characteristics of spinel ferrites. SEM micrographs showed sphere-shaped grains. The TEM micrograph illustrates the consistent spreading of the sample particles. Magnetic MH loops illustrate the characteristic behavior of hard magnetic material. The remanence ratio was observed from 0.317 to 0.347 for Pr$^{3+}$ substituted cobalt ferrite and 0.451 to 0.467 for Pr$^{3+}$ and Ho$^{3+}$ substituted cobalt ferrite.

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CONFLICT OF INTERESTS
The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS
All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

A. M. Pachpine: https://orcid.org/0000-0003-4348-997X
M. M. Langade: https://orcid.org/0009-0000-0074-6898
U. M. Mandle: https://orcid.org/0000-0002-7308-7720
B. L. Shinde: https://orcid.org/0000-0003-1933-2542
K. S. Lohar: https://orcid.org/0000-0001-6568-5977

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REFERENCES