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Structural, Morphological, Optical and Dielectric Studies of RE^{3+} Doped $CoFe_2O_4$

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ABSTRACT

Cobalt ferrite nanoparticles, both undoped and Eu^{3+}-doped, with the formula CoEuxFe2-xO4 (where x = 0.00 and 0.10), were produced using the citrate gel auto-combustion technique. X-ray diffraction confirmed the successful formation of the phase and the purity of the synthesized nanoparticles. The morphological analysis was conducted using scanning electron microscopy (SEM). The optical properties of cobalt ferrite were analyzed using UV-Vis spectrometer. Dielectric properties, such as the real part of the dielectric constant and loss tangent, were evaluated using an LCR meter. Doping cobalt ferrite nanoparticles with europium resulted in a significant improvement in charge storage and transport characteristics.

Keywords- Europium (Eu^{3+}), Dielctric constant, Dielctric loss.

I. INTRODUCTION

RE^{3+}-doped cobalt ferrites have drawn significant attention because of their spinel structure, characterized by a face-centered cubic arrangement of oxygen ions, with metal cations located at tetrahedral (A) and octahedral (B) positions. The incorporation of RE^{3+} ions into these sites alters the material's electromagnetic properties, enhancing its potential for use in various applications, including magnetic sensors, energy storage, and spintronic devices.

Incorporating RE^{3+} ions into $CoFe_2O_4$ introduces significant changes to its magnetic, structural, and electrical characteristics. Due to their larger ionic radius and distinctive electronic configuration, RE^{3+} ions modify the distribution of cations within the spinel structure, impacting the magnetic interactions and often lowering the overall magnetic moment while increasing coercivity, which is useful in applications like magnetic storage and recording. Structurally, the larger RE^{3+} ions cause lattice expansion and introduce strain, enhancing the material's mechanical durability for use in spintronics and high-frequency devices [1],[2],[3],[4].

Electrically, RE^{3+} doping disrupts the electron transfer between Fe^{2+} and Fe^{3+} ions, increasing resistivity, which is advantageous in reducing energy losses in applications such as microwave devices and inductors. Additionally, RE^{3+} ions affect the material's dielectric behavior by influencing polarization, improving its performance in capacitors and sensors. RE^{3+}-doped $CoFe_2O_4$ also exhibits enhanced magnetocaloric properties[5,6,7], making it a promising material for energy-efficient cooling technologies. These combined effects make RE^{3+}-doped $CoFe_2O_4$ valuable for a variety of advanced applications in magnetic, electronic, and energy-efficient systems.

II. METHOD AND MATERIALS

Cobalt europium nano ferrites, represented as $CoEu_xFe_{2-x}O_4$ (with x = 0.0 and 0.1), were synthesized using the citrate gel auto-combustion method. The process involved mixing europium nitrate, cobalt nitrate, ferric nitrate, citric acid, and ammonia solution in carefully measured stoichiometric ratios. These materials were dissolved in distilled water, forming a uniform solution. Citric acid, chosen for its effectiveness as a fuel and homogenizing agent, was used at a metal nitrate to citric acid ratio of 1:3, creating a nitrate-citrate mixture. Ammonia was gradually added to adjust the pH to 7. The solution was then continuously stirred and heated at 100°C for 7–8 hours until it formed a thick gel. As the water evaporated, the gel dried and underwent internal combustion, leading to the formation of the desired ferrite powder, which was later calcined at 500°C for four hours.

III. CHARACTERIZATIONS

In the present research, the focus is on synthesizing and thoroughly investigating europium-doped cobalt ferrite. This study aims to explore its structural, morphological, optical, and dielectric properties. The structural analysis will be conducted using X-ray diffraction (XRD), providing insights into phase composition, crystallite size, and lattice parameters. Field emission scanning electron microscopy (FESEM) will be employed to examine the surface morphology and microstructural features of the doped ferrite samples, offering valuable information about particle size and distribution. Optical characteristics will be analyzed using UV-visible spectroscopy, helping to determine the material's optical bandgap and absorption behavior. Additionally, dielectric studies will be performed to evaluate the material's dielectric constant, loss tangent, and overall performance in electronic applications. Through this comprehensive characterization, the study aims to uncover the effects of europium doping on the properties of cobalt ferrite, contributing to a deeper understanding of its potential for advanced technological applications.

IV. RESULTS AND DISCUSSIONS

X-ray diffraction studies:

Figure 1 illustrates the X-ray diffraction pattern of $CoFe_2O_4$, synthesized using the citrate gel auto-combustion method. The diffraction peaks correspond to Bragg reflections from the (220), (311), (222), (400), (422), and (440) planes, which are consistent with the standard spinel cubic crystal structure of CoFe2O4, as indicated by JCPDS card no. 22-1086. This structure belongs to the Fd-3m space group, characteristic of spinel ferrites.

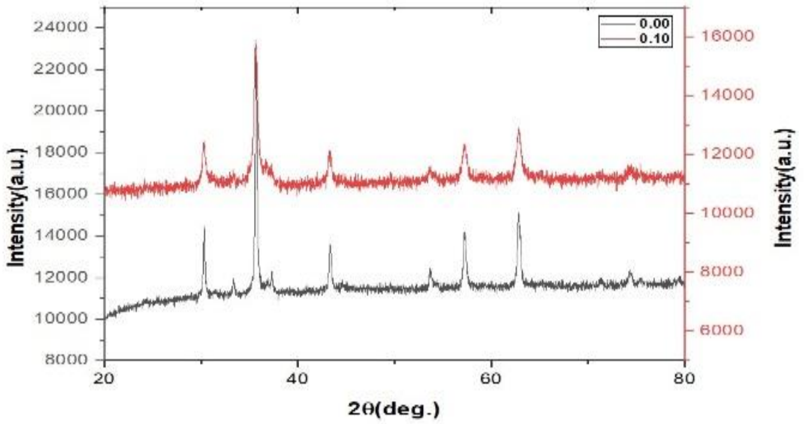

Figure 1: Shows the XRD patterns of Eu3+ doped cobalt Ferrites

The diffraction peaks confirm the successful formation of a pure spinel cubic phase in the synthesized pure and doped $CoFe_2O_4$, with no detectable impurity phases present. The peak positions and intensities closely match the reference data, validating the material's crystallinity and structural integrity. The sharp Bragg reflections indicate a well-ordered crystal structure typical of spinel ferrites, ensuring that the prepared $CoFe_2O_4$ nanoparticles possess the desired crystalline characteristics. This structural analysis via XRD provides a crucial basis for subsequent investigations into the material's physical and magnetic properties.

For all the samples, the lattice parameter "a" was calculated for the prominent peak by applying Bragg's equation.

$$a = d\sqrt{h^2 + k^2 + l^2} \text{ --------------- (1)}$$

The crystallite sizes of the ferrites were calculated from the broadening of the prominent diffraction peaks, specifically the (311) plane, by applying the Debye-Scherrer equation as follows.

$$D = {}^{K\lambda}/_{\beta cos\theta} \text{ -------------------- (2)}$$

Here, λ represents the wavelength of the X-rays, K is the Scherrer constant (approximately 1), θ is the Bragg angle, and D denotes the average size of the crystallites.

The theoretical density, based on X-ray diffraction data, was determined using the following equation:

$$\rho = {}^{8M}/_{Na^\wedge 3}$$

Where M represents the molecular weight of the sample in grams, N denotes Avogadro's number (per mole), and 'a' stands for the lattice parameter (A^0)

Table 1: XRD parameters of Europium doped $CoFe_2O_4$ nanoparticles.

Composition(x)	0.00	0.10
2θ	35.57	35.65
Lattice constant(a) A^0	8.37	8.34
Crystallite Size(D)	32.21	17.03
X-ray Density(ρx)	5.520×10^{-24}	5.582×10^{-24}

The decrease in the lattice constant from 8.37 Å to 8.34 Å with Eu^{3+} doping in cobalt ferrites can be explained by several factors. Despite Eu^{3+} having a larger ionic radius than Fe^{3+} and Co^{2+}, its incorporation into the lattice induces structural distortions and rearrangements [8,9,10]. These distortions may lead to localized strain and cause the lattice to contract slightly. Additionally, doping may alter bond strengths within the lattice, potentially forming shorter or stronger metal-oxygen bonds, further contributing to the reduction in lattice constant. Furthermore, a decrease in cation-cation repulsion due to Eu^{3+} substitution could also play a role in the observed contraction.

Morphological studies:

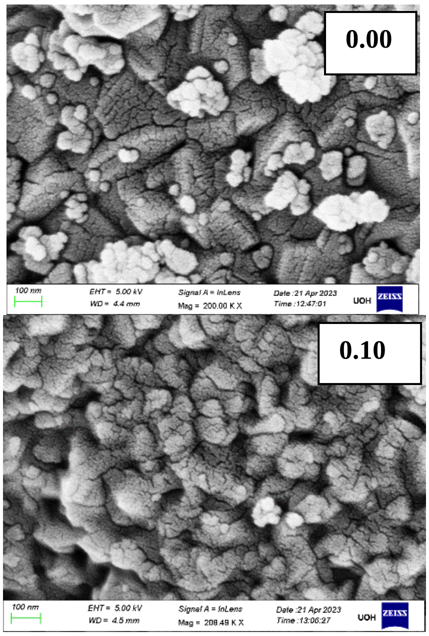

Figure 2: Shows the FESEM images of Eu^{3+} doped cobalt Ferrites.

The morphologies of $CoEu_xFe_{2-x}O_4$ nanoparticles (x = 0.00, and 0.10) were examined and are shown in Figure. 2. The images reveal that the particles exhibit spherical shapes and are uniformly distributed, though they appear to agglomerate due to magnetic interactions between the particles[11].

UV-Vis Studies:

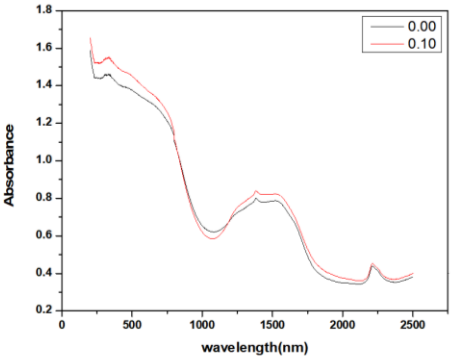

Figure 3 : UV-Vis spectra of Eu^{3+} doped cobalt Ferrites.

Figure.3 illustrates the UV-Vis spectra of Eu3+ doped cobalt Ferrites. UV-Vis spectra of Eu^{3+} doped cobalt Ferrites The UV-Vis spectra of Eu^{3+}-doped cobalt ferrites typically show absorption features related to the electronic transitions in both the cobalt ferrite matrix and the Eu^{3+} ions[12]. In cobalt ferrites, these transitions are usually associated with Fe^{3+} ions in tetrahedral and octahedral sites, along with Co^{2+}-oxygen interactions. When Eu^{3+} is introduced, additional absorption features due to f-f transitions within the Eu^{3+} ions may appear. Doping with Eu^{3+} can also cause a shift in the absorption edge, indicating changes in the band gap, which result from modifications to the material's electronic structure.

Dielectric studies:

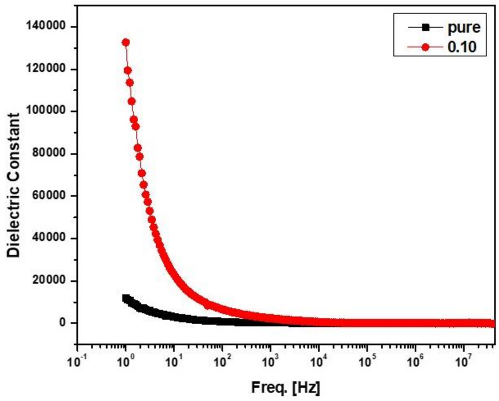

Figure 4: Dielectric constant vs Frequency graphs of Eu^{3+} doped $CoFe_2O_4$

Figure 4 illustrates the variation of frequency with the real part of permittivity (dielectric constant, ε′) for $CoEu_xFe_{2-x}O_4$ nanoparticles (where x = 0.00 and 0.10). The study, conducted over a frequency range of 1 1Hz to 10MHz at room temperature, reveals that as the frequency increases, the dielectric constant decreases. At lower frequencies, the dielectric constant exhibits higher values for all samples[13], but as the frequency rises, the dielectric constant steadily decreases.

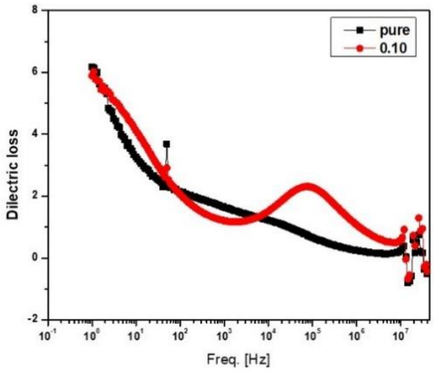

Figure 5: Dielectric constant vs Frequency graphs of Eu^{3+} doped $CoFe_2O_4$

Figure 5 presents the relationship between frequency and dielectric loss tangent for $CoFe_{2-x}Eu_xO_4$ (x=0.00, 0.10) nanoparticles, measured across a frequency range of 1 Hz to 10 MHz at room temperature. The presence of very low dielectric loss in the figure can be linked to the material's microstructure and the behavior of charge carriers in response to the applied electric field. Low dielectric loss indicates that the movement of charge carriers, such as electrons or ions, is restricted[14]. This limited mobility may result from charge carriers being strongly bound to localized states, which decreases the possibility of hopping or crossing grain boundaries.

V. CONCLUSIONS

The XRD analysis revealed the successful synthesis of $CoEu_xFe_{2-x}O_4$ nanoparticles with spinel cubic structures, confirming the incorporation of Europium and Neodymium ions into the crystal lattice. The lattice parameters were found to decrease (8.37 – 8.34A°) with the doping concentration of Eu ions, indicating cation redistribution in the octahedral and tetrahedral sites. The average crystallite size decreased with Eu^{3+} concentration in $CoFe_2O_4$ samples, showcasing a correlation between dopant concentration and crystal size. The dielectric loss factor and AC conductivity of the materials were influenced by the frequency, showing variations in the electrical properties of the Cobalt ferrites.

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