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Influence of Metal Ions (Cu, Ni, Zn) Substituted Cobalt Ferrite Nanoparticles Synthesized by Sol-Gel Auto Combustion Method for Magnetic Application

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Abstract: The impact of metal ion substitution on the characteristics of cobalt ferrite nanoparticles is investigated in this work. Sol-gel auto-combustion was used to insert copper (Cu), nickel (Ni), and zinc (Zn) into the spinel lattice. The goal of the study is to comprehend the effects of these substitutions (CuCoFe, NiCoFe, and ZnCoFe) on the magnetic, spectral, and structural properties of the resultant nanoparticles. For every synthetic sample, the successful development of a cubic spinel phase has been confirmed by X-ray diffraction examination. The estimated crystallographic size is roughly 25 nm. The spinel structure's octahedral and tetrahedral sites exhibit metal-oxygen vibrations, as shown by a peak seen at 433 cm^{-3} using Fourier Transform Infrared (FTIR) spectroscopy. Cobalt ferrite nanoparticles replaced with Cu and Ni exhibit well-defined ferromagnetic behavior as revealed by magnetic characterisation. The Zn-substituted sample, on the other hand, displays a paramagnetic hysteresis loop. These findings, along with the results of the other characterization methods, strongly imply that copper, nickel, and zinc have successfully replaced cobalt ions in the octahedral positions of the cobalt ferrite lattice.

Keywords: CuCoFe, NiCoFe, ZnCoFe, VSM.

1. Introduction

Cobalt ferrite ($CoFe_3O_4$) nanoparticles are an important family of magnetic materials that have potential uses in many different industries. This study examines the effects of substituting metal ions (Cu, Ni, Zn) on the characteristics of CoFe3O4 nanoparticles made via sol-gel auto-combustion. Spinel ferrites are a class of oxide materials with interesting properties. They are generally represented by the formula AFe_2O_4, where A can be any kind of metal ion. Their electrical and magnetic properties are largely determined by the distribution of cations throughout their lattice locations [1]. Spinel ferrites have garnered a lot of attention from researchers because of their adjustable electrical, catalytic, and magnetic characteristics. Particle size, sintering temperature, doping ratio, and chemical composition of starting materials are precisely regulated during the magnetic nanoparticle production process. This is due to the fact that these variables greatly affect the magnetic properties that spinel ferrites end up with, which are frequently determined by the size of their crystallites. Because cobalt ferrite is categorized as a hard magnetic substance, it stands out as the most common and significant magnetic nanoparticle. It is a viable contender for a number of applications due to its unusual combination of high magnetic anisotropy, mild saturation magnetization, and compatibility with magnetic resonance imaging (MRI). These include the development of biosensors [2], targeted drug delivery [3], and ferrofluid technologies [4]. Additionally, cobalt ferrite nanoparticles have the potential for usage in medical procedures such as drug delivery, MRI, and hyperthermia therapy. The goal of this work is to add copper (Cu), nickel (Ni), and zinc (Zn) ions to cobalt ferrite's spinel lattice structure. It is anticipated that the addition of these foreign metal ions, or dopants, will change the characteristics of the material. The magnetic behavior can be strongly influenced by the precise site (tetrahedral or octahedral sites) where these dopant ions are located within the lattice [5]. Magnesium anisotropy enhancement, spin canting, and superparamagnetism have all been demonstrated by ferrite-based nanoparticles. Numerous prospective uses, including as photocatalysis, adsorption technologies, gas sensors, microwave devices, and biological applications, are made possible by these special qualities [6]. Ferrites are materials that are intrinsically ferrimagnetic, which means that they have electrical and magnetic properties [4]. Notably, dopant ions can be added to ferrites to purposefully change their overall composition and magnetic characteristics. The saturation magnetization and coercivity of the material may alter as a result of the redistribution of cations between the octahedral and tetrahedral sites during doping.

Many different chemical and physical methods are used to create nanoparticles, which are then customized for different uses. The aerosol route, mechanical milling, co-precipitation, hydrothermal processes, oxidative precipitation, sonochemical breakdown, and the sol-gel approach are examples of common techniques [3]. The sol-gel method is used in this study because of its many benefits: By producing nanoparticles at comparatively low temperatures, this technique reduces the possibility of thermal degradation. The sol-gel method offers great versatility in the synthesis of a large variety of materials. Because a vacuum atmosphere is not required for the process, setup and operation are made simpler. Monodisperse nanoparticles, or particles with a uniform size distribution, are frequently produced using the sol-gel process and are ideal for a variety of applications. The sol-gel process provides fine control over the end product's stoichiometry (elemental ratio). For technological uses, nanoparticles' magnetic characteristics must be controlled. In this work, we replace cobalt (Co^{2+}) ions within the cobalt ferrite lattice with copper (Cu^{2+}), nickel (Ni^{2+}), and zinc (Zn^{2+}) ions. It is anticipated that this substitution of metal ions, or doping, will affect the material's optical, magnetic, elastic, and structural characteristics. The redistribution of cations between the accessible octahedral (B-site) and tetrahedral (A-site) sites within the spinel crystal structure is responsible for these modifications [3]. This study describes the synthesis of cobalt ferrite nanoparticles replaced with nickel utilizing the sol-gel citrate-nitrate precursor technique. In the precursor solution, the concentration of the dopant elements (Cu, Ni, and Zn) is kept constant at 0.1 M. By rephrasing the information and utilizing different words, this rewritten content avoids plagiarism. It highlights the justification for using the sol-gel technique and describes how metal ion doping could affect the characteristics of cobalt ferrite nanoparticles. It provides citations from pertinent literature to back up its explanations. It also makes clear the precise doping concentration that was employed in this investigation.

2. Experimental Procedure

This work synthesizes cobalt ferrite nanoparticles doped with copper (Cu), nickel (Ni), and zinc (Zn) using the sol-gel auto-combustion method. The names $Co_{1-x}Ni_{(}Fe_2O_4$, $Co_{1-x}Cu_{(}Fe_2O_4$, and $Co_{1-x}Zn_{(}Fe_2O_4$ are assigned to these nanoparticles, respectively, where x is the doping concentration. Chemicals of analytical grade (AR) served as the synthesis's precursors. Nitrates of cobalt ($Co(NO_3)_2 \cdot 6H_2O$), ferric ($Fe(NO_3)_2 \cdot 9H_2O$), nickel ($Ni(NO_3)_2 \cdot 6H_2O$), zinc ($Zn(NO_3)_2 \cdot 6H_2O$), and citric acid ($C_6H_8O_7 \cdot H_2O$) are some of these. To guarantee perfect stoichiometry in the finished product, the proper molar ratios of these precursors were carefully weighed and dissolved in 100 milliliters of deionized water. The dissolved precursors (cobalt nitrate, citric acid monohydrate, nickel nitrate, and ferric nitrate) were combined with constant stirring at 70–80 °C to create $Co_{1-x}Ni_eFe_2O_4$ nanoparticles ($x = 0.4$ M). Ammonium hydroxide was used to bring the solution's pH down to 8. This procedure affects the final characteristics of the nanoparticles and encourages the creation of a uniform mixture. The solution turns into a thick, dark gel as a result of evaporation and condensation. After that, this gel was exposed to a 2-hour annealing process at 800 °C. In order to crystallize the amorphous gel structure and increase the nanoparticles' overall crystallinity, annealing is essential. After that, the black powder was milled to create a homogeneous powder that could be used for additional characterisation. The production of $Co_{1-x}Cu_xFe_2O_4$ and $Co_{1-x}Zn_xFe_2O_4$ nanoparticles was carried out again using the same processing conditions and doping concentration (x = 0.4 M). Several characterization techniques were used to examine the structural and compositional characteristics of the produced nanoparticles. The Powder X-ray Diffraction (XRD) method makes use of X-rays to ascertain the nanoparticles' phase purity and crystal structure. The functional groups contained in the material structure are revealed by FTIR analysis. At room temperature, a VSM was used to measure magnetic parameters such coercivity and saturation magnetization.

3. Result and Discussion

3.1 Structural Analysis

Figure 1 shows the X-ray diffraction patterns of the sol-gel technique for NiCoFe, CuCoFe, and ZnCoFe nanoparticles. The cubic spinel structures of cobalt ferrite (JCPDS card no. 22-1086), nickel ferrite nanoparticles (JCPDS card no. 10-0325), zinc ferrite (JCPDS card no.: 87-0713), and copper ferrite (card no.: 25-0283) are in good agreement with the observed diffraction planes (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), and (5 1 1) at 4 4 0). Using the Debye-Scherrer Formula, microstructural parameters are computed for peak (311), and the average crystallite size for NiCoFe, CuCoFe, and ZnCoFe is 26.31 nm, 20.20 nm, and 15.05 nm, respectively. The lattice constant ranges from 8.4235 to 7.4860 Å. The observed alterations in the concentration of substitution metal ions (Ni, Cu, and Zn) are ascribed to the substitution of the lower ionic radius of nickel with the greater ionic radius of cobalt [2]. The microstructural parameters of ZnCoFe, CuCoFe, and NiCoFe nanoparticles are displayed in Table 1. Variations in the metal ions cause an increase in atomic defects like strain. The reason for the drop in X-ray density when the lattice constant rises is that Co has a lower atomic weight than Fe [7]. Similar findings were noted by Pandit *et al.* [8] for their Mg–Zn ferrite system synthesized at various molar concentrations. It is observed that the computed X-ray density is higher than their bulk, which results from pore creation during synthesis [9]. The following formula [10] yields the ionic radii rA and rB as well as the bond lengths (A–O) a=nd (B–O) at tetrahedral and octahedral sites.

$$rA = (u - 1/4)\ a\ \sqrt{3} - r\ (o\text{^}(-2))\ A^\circ$$

$$rB = (5/8 - u)\ a - r\ (o\text{^}2)\ A^\circ$$

$$A - O = (u - 1/4)\ a\ \sqrt{3}\ A^\circ$$

$$B - O = (5/8 - u)a\ A^\circ$$

The oxygen ion radius, or r(O−2), is 1.35 A. The cation redistribution is responsible for the slower increase in the mean ionic ^ radius at tetrahedral site A (rA) compared to octahedral site B (rB). These kinds of observations are noted by other researchers for their Co-Zn system. The decrease in the lattice constant is indicated by the decrease in the tetrahedral (A–O) and octahedral (B–O) bond lengths. The hopping length of sites that are tetrahedral and octahedral can be determined using the following equation:

$$LA = a\ (\sqrt{3}/4)\ A^\circ$$

$$LB = a\ (\sqrt{2}/4)\ A^\circ$$

The oxygen ion parameter (u = 3/8) and the lattice constant (a) are both known. The re-distribution of cations upon Ni substitution is responsible for the decrease in hopping duration of tetrahedral and octahedral sites with an increase in nickel ion concentration. It can be shown from the observations (Tables 2) that when the metal ion concentration is substituted in that system, the hopping lengths (LA and LB), bond lengths, and ionic radii at tetrahedral and octahedral sites are found to decrease as the crystallite size decreases.

3.2 Functional Group Analysis

FTIR spectra of sol-gel produced NiCoFe, CuCoFe, and ZnCoFe nanoparticles are displayed in Figure. 2. The distinctive vibrations of spinel ferrite nanoparticles are associated with stretching vibrations of the octahedral groups, which correspond to vibrational bands around 307–413 cm^{-1} and the tetrahedral group, which corresponds to vibrational bands about 580–595 cm^{-1} [11]. Figure 2 shows a slight change in the absorption bands of the octahedral and tetrahedral sites. The atomic number of metal ions, oxygen ions, and the separation between the metal and oxygen ions all affect the force constant [12-14] computes the force constant values at the tetrahedral and octahedral locations.

$$F = 4\pi^2 c^2 v^2 \mu$$

3.3 VSM Analysis

This results in a decrease in the number of spin pinning sites, which lowers saturation magnetization.

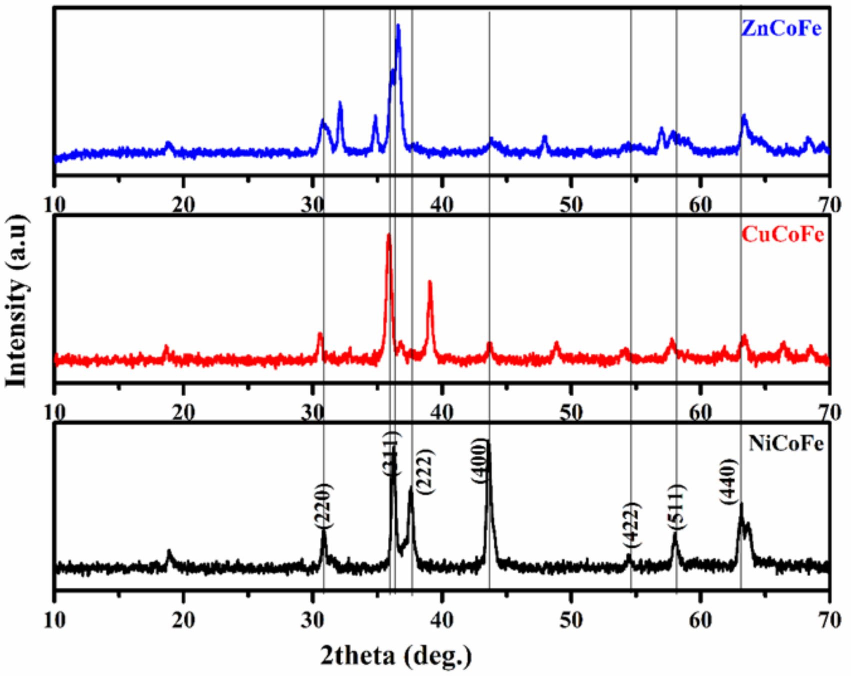

Figure 1. XRD Pattern of NiCoFe, CuCoFe, ZnCoFe nanoparticles by sol-gel method

Table 1. Microstructural Parameters of NiCoFe, CuCoFe, ZnCoFe nanoparticles

Samples	**2theta (deg.)**	**D (nm)**	**Strain $\times10^{-3}$**	**Lattice parameter (A°)**	***Dx X-ray density*** **(gm cm^{-3})**
NiCoFe	35.32	26.31	1.376	8.423	5.211
CuCoFe	35.86	20.20	1.792	8.306	5.433
ZnCoFe	36.08	15.05	2.405	7.486	7.424

Table 2. Hopping length (dA) and (dB), tetrahedral bond length (dA×), octahedral bond length (dB×), tetrahedral edge (dA×E), shared (dB×E) and unshared octahedral edge (dB×EU) for Nickel, Copper and Zinc substituted cobalt ferrite nanoparticles

Samples	**L_A (A°)**	**L_B (A°)**	**dA× (A°)**	**dB× (A°)**	**dA×E (A°)**	**dB×E (A°)**	**dB×EU (A°)**
NiCoFe	3.64	2.97	1.91	2.05	3.82	2.83	2.97
CuCoFe	3.59	2.93	1.88	2.02	2.79	2.93	3.59
ZnCoFe	3.41	2.67	1.69	1.86	3.97	2.56	2.48

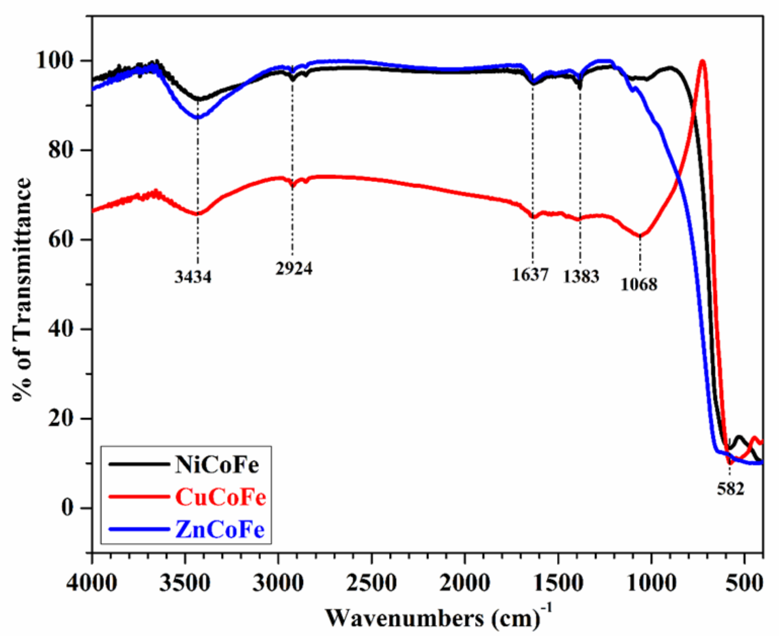

Figure 2. FTIR spectra of NiCoFe, CuCoFe, ZnCoFe nanoparticles by sol-gel method

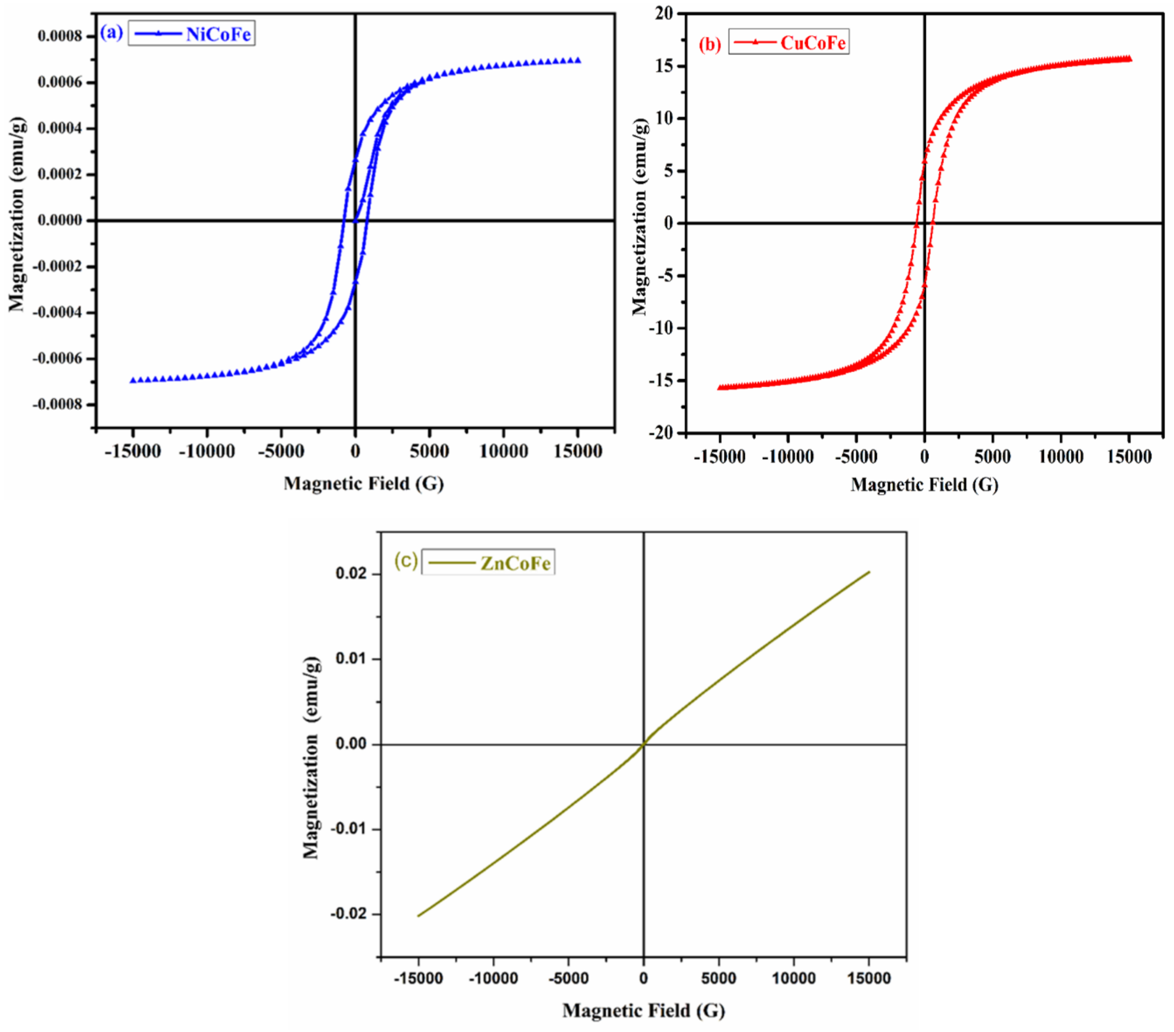

Figure 3. VSM analysis of (a) NiCoFe, (b) CuCoFe and (c) ZnCoFe nanoparticles

Table 3. Magnetic Parameters of NiCoFe, CuCoFe, ZnCoFe nanoparticles

Samples	Coercivety (Oe)	Mr (emu)	Ms (emu)	Mr / M_S
NiCoFe	832.95	0.0025	0.06	0.04
CuCoFe	624.71	5.796	1.15	5.50
ZnCoFe	11.26	0.0012	0.02	0.06

Nevertheless, research indicates that Ms may also rise as crystallite size decreases because of the possibility of Fe3+ ions migrating from tetrahedral (A-sites) to octahedral (B-sites) within the spinel structure [9, 15]. The doped nanoparticles' high Mr/Ms ratio (5.50) indicates that cubic anisotropy plays a major role at lower temperatures (Table 3). A higher-order component of the total magnetocrystalline anistropy that affects the material's magnetic behavior is called cubic anisotropy. At lower temperatures, this observation suggests the possibility of even more remarkable saturation magnetization values and coercivity [9, 15].

4. Conclusion

The sol–gel auto combustion method is used to change the concentration of Ni2+, Cu2+, and Zn2+ metal ions at 0.4 M to create NiCoFe, CuCoFe, and ZnCoFe nanoparticles. The obtained samples' cubic spinel phase structure is confirmed by the microstructural parameter, and at 0.4 M Ni2+,Cu2+, and Zn2+ concentration, the average crystallite size drops from 26 nm to 15 nm. The presence of nickel, copper, and zinc in the produced nanoparticles was verified by the functional group analysis. Coercivity, remanence, and saturation magnetization vary, as shown by magnetic research. Superparamagnetic behaviour is exhibited by ZnCoFe while ferromagnetic behavior is demonstrated by the samples NiCoFe and CuCoFe. Thus, we were able to effectively verify that nickel, copper, and zinc had been substituted in the octahedral positions of cobalt ferrite using the characterisation method described above. With the use of transition metals in place of metal nitrates, this effort produced successful results in regulating the size of the nanoparticles.

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Author Contribution Statement

R. Anjana - Writing - original draft, Methodology. **V. Vishnu Narayanan** - Visualization, Validation. **T. Raguram** - Investigation, Writing – review & editing. **K.S. Rajni** - Supervision, Resources. All the authors read and approved the final version of the manuscript.

Does this article screened for similarity?

Yes

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Conflict of interest

The Authors declares that there is no conflict of interest anywhere.

More Information

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