

Analysis of Bismuth-Doped Cobalt Ferrite (CoFe₂O₄) Nanomaterials on Structural and Morphological Changes

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Abstract - The inverse spinel ferrite cobalt ferrite (CoFe₂O₄) is well known for its superior mechanical hardness, chemical stability, and magnetic anisotropy. The structural, morphological, magnetic, and dielectric properties of CoFe₂O₄ can be effectively tuned by doping it with bismuth (Bi³⁺). Bi³⁺ breaks the spinel lattice, modifies grain formation mechanisms, introduces microstrain, and modifies particle shape due to its large ionic radius and non-magnetic 6s² configuration. This article offers a methodical examination of how Bi substitution affects the morphological and structural properties of CoFe₂O₄ nanomaterials. With a decreased lattice parameter and crystallite size with Bi doping, X-ray diffraction (XRD) consistently demonstrates the retention of the spinel phase. As the Bi content increases, SEM/TEM investigations show how the shape changes from compact grains to flake-like or spherical nanoparticles. We look closely at oxygen sublattice distortions, micro-strain development, and cation redistribution. Research gaps, possible device uses, and future directions are discussed in the review's conclusion.

Keywords – Bismuth-doped cobalt ferrite, CoFe₂O₄ nanoparticles, Spinel ferrites, Structural properties, Morphological properties.

1. Introduction

A versatile class of magnetic materials, spinel ferrites (MFe₂O₄) is utilized extensively in biomedical engineering, sensors, data storage, high-frequency devices, and catalysis [1]. Cobalt ferrite (CoFe₂O₄, CFO) is unique among them because of its considerable magnetocrystalline anisotropy, mild saturation magnetization, high coercivity, and outstanding chemical stability [2]. There are several potential for lattice engineering through doping because of its inverse spinel structure, in which Co²⁺ mainly occupies octahedral (B) sites while Fe³⁺ distributes over both tetrahedral (A) and octahedral sites [3]. Lattice distortions, cationic rearrangements, grain shape, and defect chemistry may all be considerably changed by substituting foreign cations at Fe³⁺ or Co²⁺ sites. Due to its enormous ionic radius (1.03 Å in eightfold coordination) and peculiar 6s² lone pair electronic configuration, which produce lattice strain and alter grain development dynamics, bismuth (Bi³⁺) has garnered significant interest among possible dopants [4][5][6]. For better dielectric tunability, magnetostrictive behavior, and usage in magnetoelectric composites, bi-doped cobalt ferrite (CoBi_xFe_{2-x}O₄) has been investigated [7][8][9][10]. Therefore, it is essential to device design to comprehend how Bi inclusion affects structural and morphological features. The structural and morphological impacts of Bi doping in CoFe₂O₄ nanoparticles are collected and sequentially analyzed in this study.

2. Structural Effects of Bi Doping

2.1 Phase Retention and Crystallinity

The majority of research indicates that at doping levels up to $x = 0.20$ – 0.30 , Bi-doped CoFe₂O₄ maintains the cubic spinel structure (Fd $\bar{3}m$) [1,4,5]. Phase purity of CoBi_xFe_{2-x}O₄ ($x \leq 0.20$) is

produced using sol–gel was proven by Gore et al. [1]. Up to $x = 0.15$, no secondary phases were seen by Kumar and Vijaya Kumar [5]. Spinel stability with Bi and rare-earth doping was previously verified by Kim et al. [6]. Depending on the circumstances of synthesis, several findings suggest the onset of Bi-rich secondary phases beyond $x > 0.25$ [7].

2.2 Lattice Parameter Modification

The lattice constant (a) of CoFe_2O_4 is often decreased by Bi^{3+} substitution [1,5,7]. Despite the fact that Bi^{3+} is bigger than Fe^{3+} , its actual incorporation—mainly into octahedral sites—causes lattice contraction because of local structural distortions, altered Fe–O–Fe bond angles, and changes in oxygen positioning characteristics. Typical findings from Gore et al. [1]: a dropped from 8.389 Å ($x = 0$) to 8.359 Å ($x = 0.20$). Similar linear decline up to $x = 0.15$, according to Kumar et al. [5]. Vegard's law is roughly followed by this.

2.3 Crystallite Size and Micro-strain

Crystallite size reduces with increasing Bi concentration, according to XRD peak broadening: 26 nm \rightarrow 17 nm for $x = 0 \rightarrow 0.25$ [5], and 35 nm \rightarrow 22 nm for sol–gel samples [7]. Ionic mismatch between Fe^{3+} and Bi^{3+} , local distortion caused by Bi's $6s^2$ lone pair, and stress buildup during crystallite formation are the reasons why microstrain, as determined by Williamson–Hall (W–H) plots, increases dramatically with Bi doping. Nearly doubled strain was observed at $x = 0.20$ by Gore et al. [1].

2.4 Cation Redistribution and Site Occupancy

Bi affects the distribution of Fe^{3+} between the A and B, according to Mössbauer spectroscopy. Fe–O bond lengths and exchange interactions are impacted by the migration of Fe^{3+} from A \rightarrow B sites with increasing Bi, while Bi^{3+} preferentially dwells on octahedral (B) sites. M–O bond alteration about 400–550 cm^{-1} is further confirmed by FTIR spectrum shifts [1][5][7].

3. Morphological Effects of Bi Doping

SEM Analysis: Grain Shape and Surface Evolution are in Table 1 illustrates how Bi doping significantly changes the shape of CoFe_2O_4 nanoparticles. This results from the disruption of grain development processes during combustion caused by Bi^{3+} .

Table: 1 - Basis of Bi level effect on morphology [1]

Bi Level	Morphology
$x = 0.00$	Compact grains, smooth texture
$x = 0.05$	Irregular grain boundaries
$x = 0.10$	Agglomerated clusters
$x = 0.15$	Flake-like structures
$x = 0.20$	Smaller, scattered spherical nanoparticles

High-resolution TEM investigations demonstrate Well-defined lattice fringes (thus retaining crystallinity), decreased particle sizes compatible with XRD, and Modified interplanar spacing with increasing Bi. SAED patterns resemble the spinel phase even at greater doping levels [5,7]. Porosity and Grain Density is analysis in which Bi doping results in lower bulk density, higher X-ray density, and more void formation, all of which enhance porosity. These are associated with lattice strain and deformation caused by Bi [5]. Successful Bi incorporation, uniform elemental substitution, and the absence of contaminants up to $x \approx 0.20$ are all confirmed by Chemical Composition (EDS) [1][5][7].

4. Effects of Structural/Morphological Changes on Functional Properties

- **Magnetic Properties:** Grain-size effects and cation redistribution are two ways that Bi doping influences magnetic properties. For $x = 0.10$ – 0.15 , saturation magnetization rose from 26.36 to 44.96 emu/g [1]. Because to increased microstrain, domain-wall pinning, and decreased particle size, coercivity first rises (little doping) and subsequently falls (greater doping).
- **Transport and Dielectric Properties:** Bi doping has an impact that demonstrates Lattice distortion causes slower electron hopping, a higher dielectric constant, and decreased AC conductivity [8].
- **Magnetostrictive and Magnetoelectric Uses:** Bi doping was shown to increase magnetostriction because of strain-induced anisotropy and modified B-site occupancy [9]. Bi-containing CoFe_2O_4 – BiFeO_3 composites show enhanced magnetoelectric coupling [10].

5. Synthesis Method

The most used method is sol-gel, however other approaches could provide more controlled morphology and less porosity [3][5]. Additionally, various synthesis methods are presented in Table 2.

Table: 2- Bi incorporation is highly dependent on the synthesis method

Method	Effect on Morphology
Sol-gel combustion	Finer particles, flake-like grains at high Bi
Hydrothermal	More uniform spherical nanoparticles
Auto-combustion	High strain, agglomerated structures

6. Futuristic research

- **High-doping studies** (>0.25 Bi) are limited.
- **Advanced site-specific analyses** (EXAFS, neutron diffraction) are rare.
- **In situ growth studies** of Bi diffusion are lacking.
- **Structure–property correlation** needs systematic multiscale modeling.
- **Application-driven studies** (EMI shielding, microwave absorption) require more exploration.

7. Conclusion

Bi doping in CoFe_2O_4 has a major impact on the nanoparticles' morphological and structural characteristics. Smaller crystallites and unique morphological changes emerge from the inclusion of Bi^{3+} , which also causes lattice contraction, increases microstrain, varies the cation distribution, and changes grain-growth behavior. Bi-doped cobalt ferrite is a viable option for magnetoelectric, sensing, and EMI shielding applications because of these structural modifications that directly control magnetic, dielectric, and magnetostrictive behavior. To fully realize this system's potential, more research utilizing sophisticated characterisation and high-doping regimens is necessary.

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