



WOLLEGA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
COLLEGE OF NATURAL AND COMPUTATIONAL
SCIENCE DEPARTMENT OF PHYSICS
INVESTIGATING THE INFLUENCE OF SILVER DOPING ON THE
STRUCTURAL AND OPTICAL CHARACTERISTICS OF COBALT
FERRITE NANO PARTICLES ($\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$)

MSc Thesis

BY:
TESFAYE BENTI TOLA

JANUARY, 2025
NEKEMTE, ETHIOPIA



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MSc. Thesis

This thesis is submitted to the School of Graduate Studies within the College of Natural and Computational Sciences at Wollega University. It fulfills a portion of the requirements for the degree of Master of Science (M.Sc.) in Physics, specializing in Condensed Matter Physics.

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APPROVAL SHEET FOR SUBMITTING THE FINAL THESIS

As member of the Board of the Final M.A thesis open defense, we certify that we have read and evaluated the thesis prepared by Tesfaye Benti Tola under the title **‘Investigating the Influence of Silver Doping on the Structural and Optical Characteristics of CoFe_2O_4 Nanoparticles($\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$)’** and recommended that the thesis is accepted as fulfilling the thesis requirement of the Degree of Master in physics.

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Certification of the final thesis

I hereby certify that all the correction and recommendation suggested by the board of examiners are incorporated in to the final thesis entitled title **“Investigating the Influence of Silver Doping on the Structural and Optical Characteristics of CoFe_2O_4 Nanoparticles($\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$)’** by Tesfaye Benti Tola.

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STATEMENT OF THE AUTHOR

I declare that this thesis entitled ‘**Investigating the Influence of Silver Doping on the Structural and Optical Characteristics of CoFe_2O_4 Nanoparticles($\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$)**’ is my work, and all sources of materials used for this thesis have been appropriately acknowledged. This thesis is submitted in partial fulfillment of the requirements for a master’s degree in physics at Wallaga University. I seriously declare that this thesis is not submitted to any other institution. For the sake of any degree or diploma. The thesis was deposited at the University library to be made available to borrowers under the rule of the Wallaga University library. Brief quotations from this thesis are allowable without special permission if an accurate acknowledgment of the source is made. However, requests for permission for extended quotations from or reproduction in part of this manuscript may be granted by Wallaga University, the School of graduate studies. In all other instances, permission must be obtained from the author.

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DECLARATION

This is to certify that this thesis, entitled “**Investigating the Influence of Silver Doping on the Structural and Optical Characteristics of CoFe₂O₄ Nano particles (Co_{1-x}Ag_xFe₂O₄)**” accepted in partial fulfillment of the requirements for the award of a masters in physics by the School of Graduate Studies at Wollega University through the collage of Natural and Computational Science done by **Tesfaye Benti Tola** is genuine work carried out by him under my guidance. The matter embodied in the thesis work has not been submitted earlier for the award of any degree or diploma. The assistance and help received during the course of this investigation have been duly acknowledged. Therefore, I recommend that it be accepted as full filling the research thesis requirements.

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ABBREVIATIONS AND ACRONYMS

A	:	Absorbance
AB ₂ O ₄	:	General formula of spinel ferrite
BSE	:	Back scattered electrons
CS	:	Count Shell
EBSD	:	Electron based scatter diffraction
E _g	:	Energy band gap
FCC	:	Face centered cubic
FTIR	:	Fourier- transform inferred
HRTEM	:	High resolution transmission electron microscope
FWHM	;	Full width at half maximum
JCPDS	:	Join Committee on Powder Diffraction Standards
MRI	:	Magnetic resonance imaging
N _A	:	Avogadro number
PVA	:	Polyvinyl alcohol
SEM	:	Scanning electron microscopy
SE	:	Secondary electron
TEM	:	Transmission electron microscopy
UV- Vis	:	UV- Visible spectroscopy
V	:	Volume of prepared unit cell
XRD	:	X-Ray Diffraction

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Abstract

The purpose of this work was to examine how silver doping affects the structural and optical properties of cobalt ferrite nanoparticles ($Co_{1-x}Ag_xFe_2O_4$, $x=0.0, 0.05, 0.1$), which were made using the sol-gel process. The prepared samples are in a single partially inverse cubic spinel ferrite structure with space group $Fd\bar{3}m$, according to the XRD data. According to the XRD analysis, the average crystal size dropped from 46.21 nm to 35.44 nm as the concentration of silver ions increased. Similarly, the lattice parameters dropped from 0.84nm to 0.83nm, suggesting that lattice strain caused by silver prevents grain formation. However, with doping with a 0.1 concentration of Ag ions for an x increase from 0.0 to 0.1, the theoretical density of the sample (x-ray density) increased from 5.27 g/cm³ for the undoped $CoFe_2O_4$ nanoparticles to 5.52 g/cm³. The granules are almost agglomerated, according to the SEM micrograph. Because of their narrow band gap and chemical stability, the UV-Vis spectroscopy measurements revealed a decrease in the energy band gap from 3.11 eV to 2.98 eV, potential applications in opto electronic and visible-light-based technologies may be includes : Magnetic Resonance Imaging(MRI) Ultrasound, CT scan, and X-ray devices.

Keywords: Crystal, doping, ferrite, band gap, XRD, SEM, UV-Vis spectroscopy, band gap

CHAPTER ONE

INTRODUCTION

The foundation for our investigation of silver-doped cobalt ferrite nanoparticles is established in this first chapter. We'll go into the details of cubic spinel ferrite structures and discuss the basic effects of silver doping on their optical characteristics. A general review of cobalt ferrites, their combined uses, and the rationale for this investigation are also included in this chapter. Lastly, we provide an overview of the research goals, problem statement, importance, constraints, and general structure of the thesis.

1.1. Background of the Study

Nanostructure ferrite (MFe_2O_4) materials have been used in a variety of fields, including magnetic fluids for information retrieval and storage of magnetic recording media, magnetic resonance imaging, enhanced magnetically guided drug delivery, catalysis, sensors, and pigments, among others (Sagmance et al., 2009; Trade et al., 2017; Zhang, 2006; Vasundhara et al., 2013). Because of their superior electrical and magnetic qualities, their use has increased significantly over the past ten years.

The chemical formula AB_2O_4 can be used to identify spinel ferrite materials, a class of metal oxides distinguished by their spinel structures. Metal ions occupy two different types of positions within this structure. Octahedral positions are represented by B and tetrahedral positions by A. Ferrite's physical and chemical characteristics are largely determined by the particular kinds, amounts, and configurations of these metal ions within the crystal lattice (Akbar et al., 2022). For a general chemical for (MFe_2O_4), where M is the divalent metal ion, such as Mn, Zn, Ni, etc.

One of the most intriguing ferrites (MFe_2O_4) is cobalt ferrite nanoparticles, which garner a lot of interest due to their exceptional optical characteristics, relatively large magnetic anisotropy, and mild saturation magnetization. Cobalt ferrite ($CoFe_2O_4$) has an inverse spinel structure, with half of the Fe^{3+} ions occupying tetrahedral sites and the other half occupying octahedral sites with Co^{2+} ions.

The magnetic moment in the tetrahedral site is oriented in the opposite direction to that of the inverse spinel structure. The net magnetic moment generated is from zero Fe^{3+} in the tetrahedral a sites. Therefore, the magnetism in the octahedral sites is responsible for the

magnetic moment of. Anisotropy is caused by the distribution of the unpaired magnetic moment in the magnet crystalline in the octahedral sites. Accordingly, cobalt ferrite is a ferromagnetic material (Goldman, 2006; Kahlenberg and Fisher, 2001). Its tetrahedral structure and three-dimensional framework structure make it an excellent core material for power transformers in the electronic, memory, and telecommunication industries.

Ferrite is a ceramic material made by burning large amounts of iron (III) oxide blend with CoFe_2O_4 and small amounts of one or more metallic elements, including zinc, cobalt, manganese, nickel, and magnesium (Minak et al., 2017). When B sites are occupied, ferrites are regarded as inverse spinels. A sites and divalent elements are completely divalent, and dependent on elements that are trivalent (Mathew et al., 2007). By altering the divalent elements in tetrahedral and octahedral sites, ferrite materials' characteristics can be adjusted (Nadir et al., 2015).

The most significant magnetic material that can be utilized in a variety of applications, including magnetic recordings, is the partially inverted structure with cobalt ferrite magnetic resonance imaging, biomedical drug delivery, and ferrofluid technology. This is due to the moderate saturation magnetization, high coercivity, high magneto-optical density, high chemical stability, and electrical insulation (Franco et al., 2007).

According to Jadhav et al. (2017), the distribution of metallic ions from the crystallographic crystal lattice location has a significant impact on the properties of ferrite material, which are also sensitive to very small sizes. This type of property is an extremely intriguing way to prepare those materials. We prepare nano-sized ferrites using a variety of techniques (Kim et al., 2003), such as sol-gel, citrate-gel, and co-precipitation. The sol-gel auto-combustion synthesis route is unique among these various techniques. Due to its many benefits, including the ability to control particle size, speed, simplicity, cost-effectiveness, and low temperature, it is a very appealing method for producing nano-sized material (Nasser et al., 2012).

It has an idea for tailor applications when we replace Fe with other different metals (Kumar et al., 2009). Due to its promising magneto astrictive properties, cobalt ferrite has recently attracted the attention of numerous researchers. For certain uses in the field of sensors and actuators, it has been suggested to be a suitable magneto astrictive material. The use of this material should result in lower energy loss and higher displacement

accuracy at high frequencies, which may offset this drawback in such applications where speed of response with precise displacements is crucial (Clarinda et al., 2013).

The synthesis of Ag metal, CoFe_2O_4 , and Ag-doped cobalt ferrite using the sol-gel auto combustion method through metal carboxyl ate as a precursor is reported in this study. The sol-gel combustion process uses PVA as fuel. Prepared samples are well-characterized using a variety of characterization methods including UV-Vis spectroscopy, SEM, and XRD.

1.2. Statement of the problem

Because of their intrinsic structural stability and promising optical properties, cobalt ferrite (CoFe_2O_3) nanoparticles hold great promise for cutting-edge technological applications. Although elemental doping is a tried-and-true method for altering and improving material performance, It is still unclear how particular concentrations of silver ions (Ag^+) as a dopant ($\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ for $x=0, 0.05, 0.1$) precisely affect the structural properties and, crucially, result in improved optical performance of these nanoparticles.

There is a clear lack of thorough research that systematically links controlled silver ion doping concentrations via this particular synthesis route with the ensuing improvements in both structural features and desired optical performance, despite the benefits of the sol-gel synthesis method for producing high-quality and homogeneous materials and the acknowledged advantages of silver in modifying properties. For this reasons many researchers did researches by doping silver with different materials to study the structural phase, and the coercivity of Ag cobalt ferrite. However, the specific influence of silver (Ag) ion doping in the cobalt ferrite nano particles remains insufficiently elucidated. Therefore, in this present work, we aimed to investigate the influence of silver ions doped in the place of cobalt ions with a chemical formula, $(\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4, x = 0.00, 0.05, 0.10)$ to investigate the influence of silver ions on its structural and optical characteristics of cobalt ferrite.

1.3 .Objectives of the study

1.3.1. General objective of the study

To attain the general objective, the following specific objectives have been being drawn;

- To investigate the structural and optical characteristics of silver ion-doped cobalt ferrite $\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ nanoparticles made using the sol-gel method with different silver concentrations of ($x=0, 0.05, 0.1$).

1.3.2. Specific Objectives

The following particular goals have been developed in order to achieve the overall goal:

- ❖ To investigate the effect of Ag doping on the structural and optical characteristics cobalt ferrite nano particles using sol-gel method.
- ❖ To characterize the crystal structure, phase purity, crystallite size, and lattice parameters of the synthesized $\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ nanoparticles using X-ray Diffraction (XRD).
- ❖ To analyze the morphology, particle size distribution of the nanoparticles using Scanning Electron Microscopy (SEM).
- ❖ To evaluate the optical absorption behavior and determine the band gap energy of the $\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ nanoparticles through UV-Visible Spectroscopy.

1.4. Significance of the Study

This study on silver ion-doped cobalt ferrite ($\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$) nanoparticles, which focuses on improving structural and optical properties using the sol-gel method, has important ramifications for a number of fields.

It will advance our basic knowledge of how the crystallographic structure is systematically affected by the incorporation of silver ions at different concentrations ($x=0, 0.05, 0.1$). The spinel ferrite lattice of CoFe_2O_4 morphological features and atomic site occupancy offer important insights into the precise mechanisms by which silver ion, resulting in observed changes and enhancement in the optical absorption and emission properties of cobalt ferrite. They also establish detailed structure-property correlations, clarifying how particular structural modifications induced by silver doping directly translate into improved optical performance.

Additionally, this work directly fills the knowledge gap about the precise effects of silver ion doping on the optical characteristics of cobalt ferrite nanoparticles, especially when the sol-gel method is used for synthesis. It offers a methodical examination of silver's dose-dependent effects, which is frequently absent from the literature.

1.5 .Thesis Organization

This thesis organized in to five chapters ;Chapter 1 contains Introduction ,Objective ,and significance of the study .Chapter 2 contains Review literature .Chapter 3 contains ; Material required for the research and methods of preparation of the sample.Chaoter 4; contains Experimental result discussion and Chapter 5; contains Conclusion of the thesis and investigation

CHAPTER TWO

REVIEW OF RELATED LITERATURE

2.1. Introduction

This chapter provides a thorough review of the existing literature relevant to the study of silver doping and its effects on the structural and optical properties of CoFe_2O_4 nanoparticles. It lays the groundwork for understanding spinel ferrites, particularly cobalt ferrite, by examining their distinctive magnetic, structural, and optical characteristics, along with their various applications. Additionally, this review investigates the impact of different doping methods on these properties, with a particular emphasis on the effects of noble metal doping, such as silver, on the physical attributes of semiconductor nano materials. The chapter will critically analyze pertinent theoretical frameworks and experimental results from prior research, highlighting the current state of knowledge and pinpointing the specific research gaps that this thesis intends to address through its experimental study.

2.2. Crystalline materials

Crystalline materials are formed when atoms are arranged in a regular, ordered pattern in three dimensions. This periodic arrangement is referred to as crystal structure (O'Keeffe et al., 2020). It encompasses much more than just the inter atomic distances (Shcherbakov et al., 2021). This ordered cubic structure occupies the entire volume of the material within a single crystal (Clark et al., 1979). There are seven crystal systems: cubic, tetragonal, trigonal, hexagonal, rhombohedral, monoclinic, and triclinic (Dannay et al., 1977). Various crystal structures are based on the framework of one of the 14 Bravais lattices. The directions and distances within the crystal are determined by parallel planes of atoms that intersect the unit cell. The distance between adjacent planes is referred to as "d spacing." The orientation and interlinear spacing (d) of these lattice planes are defined by three integers h, k, and l, known as Miller Indices (Liu et al., 2020). The crystal face or family of planes, in a crystal lattice is represented by the symbol (h k l). Polycrystalline materials are formed.

2.3. Ferrite

Ferrites represent a category of ceramic materials composed of iron oxide combined with various metallic elements. They display ferromagnetic properties and follow the general formula, where M_e signifies divalent metal ions such as Co^{2+} and Zn^{2+} . Ferrites crystallize

in a cubic spinel structure and are extensively utilized in electronic, magnetic, and optical devices due to their distinctive combination of magnetic and electrical insulating characteristics. Ferrites are magnetic ceramic materials primarily made of iron oxide recognized for their chemical stability, high frequency, and moderate saturation magnetization. The introduction of noble materials like silver alters lattice parameters and electronic structures, thereby affecting both magnetic and optical properties. Consequently, due to their potential applications in magnetic devices, numerous research groups have focused on the study of spinel oxides, particularly in microwave technology and high-density magnetic recording media. The three categories of commercial ferrites each possess unique crystal structures (Tatrachuk, 2017). These categories of ferrites are listed below: Soft ferrite with a garnet structure, such as microwave ferrites Soft ferrite with cubic spinel structure hard ferrites with a magnetoplumbite (hexagonal) structure. Ferrites are extensively employed in transformers and inductors for power conversion; dereference suppression, and telecommunications (Kumar et al., 2023). A significant amount of ferrite-related research has been conducted since the 1950s, driven by technological advancements across various fields.

2.4. Classifications and types of Ferrites

Ferrites consist of iron oxides as their primary component along with metal oxides. Based on their crystal structure, ferrites can be classified into the following types (Stojanovic et al., 2018):

- ❖ Spinel Ferrite
- ❖ Garnet Ferrite
- ❖ Ortho ferrite, and
- ❖ Hexagonal Ferrites

2.4.1. Spinel Ferrite

MeFe_2O_4 ($\text{Me}=\text{Co}, \text{Ni}, \text{Zn}$, or other metals) is the chemical formula for spinel ferrite. It is characterized by a cubic, densely packed arrangement of oxygen atoms, with Me^{2+} and Fe^{3+} ions occupying either tetrahedral (A) or octahedral (B) sites (Althubayti et al., 2020). Spinel ferrite nanoparticles have attracted a lot of attention because of their distinct electrical, magnetic, and catalytic properties when compared to their bulk counterparts

One of the spinel ferrites with the inverse spinel structure is cobalt ferrite, which in its ideal form has all Co^{2+} ions in B sites and all Fe^{3+} ions equally divided between A and B states (Naik et al., 2013).

Because of its strong electromagnetic performance, superior chemical stability, mechanical hardness, high coercivity, and moderate saturation magnetization, Cobalt ferrite has been extensively researched as a potential material for electronic components used in computers, recording devices, and magnetic cards. These characteristics rely on the chemical composition and microstructure characteristics, which can be changed during the steps of synthesis and manufacturing. Its reverse spinel structure makes it the most fundamental ferrite, and the production process makes it easy to spread weather resistance. Their composition and chemical substitution determine their magnetic characteristics

2.4.2. Garnet Ferrite

The chemical formula for ferromagnetic garnet ferrite ($\text{MeFe}_3\text{O}_{12}$) is where *Me* a trivalent ion is similar to yttrium of rare earth. Eight molecules, or 160 carbon atoms, make up the cubic unit cell (ELIZLABETHGEORGE et al., 2023) of $\text{MeFe}_3\text{O}_{12}$. Three different types of sites are covered by metal. According to Mondegarian et al (1976), the Fe^{3+} ions were distributed in 3: 2 ratios between the tetrahedral and octahedral sites.

2.4.3 .Ortho Ferrites

The general formula for ortho ferrites is (MeFeO_3), where According to Irfan Hassan et al. (2020), *Me* is a big trivalent metal ion, like a rare earth ion. They have a deformed perovskite structure and crystallize in an orthorhombic unit cell. The weak ferromagnetism seen in these ortho-ferrites has been attributed to a tiny canting in the alignment of two anti-Ferro magnetically coupled lattices (Ahmad et al., 2022). Although the tilted angle is only about 10^{-2} radians, it is enough to create a little net ferromagnetic moment that is perpendicular to the anti-ferromagnetic axis.

At ambient temperature, the spin orientation of the Fe ion in (HfFeO_3) and (ErFeO_3) was found to be parallel to the (100) axis. As the temperature drops the spin axis rotates, and at 1.25K the direction is (001) for (HfFeO_3), and (110) for (ErFeO_3). A significantly lower Neel temperature is used to calculate the spin moment of the rare ion [6.5 K for HfFeO_3 and 4.3 K for ErFeO_3].

2.4.4. Hexagonal Ferrite

The compounds exhibit the most basic structure. Barium ferrite, a well-known type of hard ferrite, falls within this category. These compounds are characterized by the general formula $\text{Me Fe}_{12}\text{O}_{19}$, where Me represents a divalent ion with a large ionic radius, such as Ba^{2+} , Sr^{2+} , and Pb^{2+} . Additionally, some compounds containing trivalent Me ions (e.g., La^{3+} , Al, Ga, Cr, Fe) are also recognized. In these instances, one iron atom per formula unit exists as Fe^{2+} to facilitate charge compensation. The crystal structure of barium ferrite is hexagonal, comprising a unit cell that consists of two unit formulas. This structure is analogous to the spinel structure, where the oxygen lattice is face-centered cubic (FCC) and consists of a series of hexagonal layers of oxygen. Numerous ferrites possess a hexagonal crystal structure, and several of these have gained significant technological importance in recent years (Pullar et al., 2012). These ferrites are categorized into compounds designated as M, W, Y, Z, V, and U (Kalyane and Puthan, 2021).

2.5. Cobalt ferrite

Due to its medium magnetization and extremely high coercivity, cobalt ferrite belongs in the strong magnet categories (Shahbahrami et al., 2020). They are useful for a variety of purposes due to their excellent physical qualities and chemical stability (Van Oort et al., 2003). There is an apparent inverse spinel structure in cobalt ferrite (CoFe_2O_4) (Hou et al., 2010).

2.6. Structural and Cat ion Distribution of Ferrites

The spinel structure of ferrites features a closed-packed oxygen lattice, with cat ions occupying tetrahedral (A) and octahedral (B) interstitial sites. The distribution of metal ions among these sites significantly influences the magnetic and electrical properties. In normal spinel, divalent ions occupy A sites while trivalent ions occupy B sites. Conversely, in inverse spinel, trivalent ions are distributed between both sites, and divalent ions occupy B sites (Good enough, 1958). For example, cobalt ferrite typically adopts an inverse spinel structure, where Co^{2+} is present. It consists primarily of iron oxides as its main component, with metallic oxides favoring octahedral sites, contributing to high coercivity and moderate magnetization. These inorganic compounds are electrical insulators and possess electronic and catalytic properties. Ferrites are essential for spinel ferrites.

2.7. Doping in Ferrites

Doping ferrites with rare earth elements or noble metals significantly modifies their structural, magnetic, and optical properties. For example:

- Zn^{2+} doping in cobalt ferrite enhances magnetic softness and reduces coercivity.
- Ag^+ or Cu doping introduces lattice grain changes and alters the band gap due to modified electron transitions.
- Doping with rare earth elements often increases magnetic anisotropy and affects dielectric behavior. Such modifications enable researchers to customize ferrite properties for specific applications, including spin electronics, magnetic fluids, gas sensing, and energy storage (Shirsath et al., 2013).

2.8. Application of Ferrites

Ferrites are ceramic compounds made up of iron oxide (Fe_2O_3) combined with various metallic elements such as manganese, zinc, or nickel. They exhibit high magnetic permeability, which makes them useful in a broad spectrum of electronic and magnetic applications, including:

- ❖ Magnetic materials for memory devices, transformers, and inductors.
- ❖ Catalysts for environmental remediation, such as water splitting.
- ❖ Biomedical applications, including magnetic hyperthermia and drug delivery.
- ❖ Sensors, particularly for humidity and gas detection, due to their semiconducting properties.
- ❖ Permanent magnets, which are utilized in motors, loudspeakers, magnetic locks, and magnetic holding devices.
- ❖ Microwave devices, used in isolators, circulators, and phase shifters.
- ❖ Environmental applications in photo catalysis.

2.9. Synthesis Methods

There are two primary approaches that are frequently employed in the synthesis of nanoparticles: the top-down and bottom-up methods.

The top-down synthesis entails the creation of nanoparticles by diminishing the size of a bulk material through mechanical or physical techniques. A prevalent top-down method is milling, where larger particles are reduced to nanoscale dimensions using mechanical forces. Another technique is lithography, which employs methods such as electron beam

lithography or photolithography to pattern and etch nanoscale features onto a substrate. While top-down methods provide control over the size, shape, and composition of nanoparticles, they may face challenges regarding scalability and the production of monodisperse nanoparticles.

Conversely, bottom-up synthesis involves the assembly or growth of nanoparticles from smaller building blocks or precursor materials. Chemical synthesis techniques, including chemical precipitation and sol-gel methods, are categorized under bottom-up approaches. In chemical precipitation, nanoparticles are generated through the controlled precipitation of precursor materials from a solution. Sol-gel methods consist of the hydrolysis and condensation of precursor compounds to create a gel, which is subsequently processed to yield nanoparticles. Bottom-up methods offer exceptional control over the size, shape, and composition of nanoparticles and can produce monodisperse particles. These methods are frequently utilized for synthesizing complex nanoparticles with customized properties. In the current study, the sample was prepared using the sol-gel synthesis method, which is preferred as the primary approach for preparing cobalt ferrite due to its numerous advantages.

2.10. Characterization of nano particles

Different characterization techniques have been practiced for the analysis of various physicochemical properties of NPs. These include techniques such as X-ray diffraction, X-ray photoelectron spectroscopy, infrared, SEM, TEM, and particle size Analysis (Mabena *et al.*, 2011)

2.10.1 .Morphological characterizations

Morphological properties of nano particles are always of great interest, because morphology always affects most NP properties techniques such as polarized optical microscopy, SEM and TEM are the most important. The SEM technique is based on the principle of scanning electrons and we provide all available information about NPs at the nano scale level. Wide literature is available, where people used this technique to study not only the morphology of their nano materials, but also the dispersion of NPs in the bulk or matrix. The dispersion of SWNTs in the polymer matrix poly butylenes terephthalate, and nylon-6 revealed through this technique (Saeed, 2016 and Khan, 2014). The same group also provides POM study of their materials, which showed star-like

spherules of the formed materials, whose size was decreased with the incremental filling of SWNTs.

2.10.2 .Structural characterizations

The structural characteristics are of the primary importance to study the composition and nature of bonding materials, XRD, IR, Raman, BET, and Zeita size analyzer are the common techniques used to study structural properties of nano particles XRD is one of the most important characterization techniques to reveal the structural properties of NPs. It gives enough information about the crystalline and phase of NPs .It also provides rough idea about the particle size through Debye Scherer formula (Khan *et al.*, 2017).

2.10.3. Characterization of particle size and surface area.

Different techniques can be used to estimate the size of NPs. These include SEM, TEM, XRD, and dynamic light scattering. SEM, TEM, XRD, and, AFM can provide a better understanding of particle size. But a power size analyzer. DLS can be used to size NPs at a very low level. In one study, used the DLS technique to study the size variation of silica NPs with protein absorption from serum. The results showed that the size increased with the acquisition of the protein layer. However in the case of agglomeration and hydrophobicity, DLS can be capable of accurate measurements, in which case we should use high-resolution differential centrifugal sedimentation. Along with DSC nano particle tracking analysis is a relatively newer and specialized technique that can be helpful in biological systems such as proteins and DNA. In the NPTA method, NPs are visualized and analyzed in a liquid medium, which relates the Brownian speed to the particle size. This method allows us to find the size distribution profile of NPs with a diameter of $1 \times 10^{-8} - 1 \times 10^{-6} m$ min a liquid medium.

2.10.4. Optical characterizations

Optical properties are of great concerned in photo catalytic applications and therefore, photo-chemists acquired good knowledge of this technique to reveal the mechanism of their photochemical processes. These techniques provide information about the absorption, reflectance, luminescence, and phosphorescence properties of NPs. It is widely known that NPs, especially metals and semiconductors, are of different colors and are best ranked for photo-related applications. So it is always interesting to know the absorption reflectance values of these photoluminescence

CHAPTER THREE

MATERIALS AND METHOD

3.1 Introduction

This chapter discusses the preparation of the necessary chemicals, equipment, synthesis methods, experimental procedures, and characterization techniques. These techniques, which include X-ray diffraction, scanning electron microscopy, and UV-Visible spectroscopy, are detailed for the synthesis of samples aimed at investigating the effects of silver doping on the structural and optical properties of CoFe_2O_4 nanoparticles.

3.2. Chemicals to be used

To synthesize silver-doped cobalt ferrite, the following chemicals have been utilized

- ❖ Cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
- ❖ Silver nitrate ($\text{AgNO}_3 \cdot 9\text{H}_2\text{O}$)
- ❖ Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)
- ❖ Citric acid ($\text{C}_6\text{H}_8\text{O}_7$)
- ❖ Raw ingredients for chemicals include ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$)
- ❖ Acetone ($\text{C}_2\text{H}_6\text{O}$)
- ❖ Doubly de-ionized water has been employed as raw materials.

3.3. Apparatuses

For the synthesis of Ag^+ doped cobalt ferrite nanoparticles, the following apparatus will be utilized:

Beaker, spoon, spatula, electronic balance (for mass measurement), magnetic stirrer, magnetic beads, evaporating dish, hot oven, agate mortar with pestle, alumina crucible, alumina plate, temperature-controlled electric furnace, filter paper, and funnels are the apparatuses required for this work

3.4. Methods to be used

To prepare nanoparticles, the following method may be utilized:

Sol-gel method: The sol-gel synthesis method is favored the primary approach for preparing cobalt ferrite due to its numerous advantages such as: control over particle size, homogeneous composition, purity and chemical homogeneity, tailoring of properties, versatility and scalability, low-temperature processing.

In this study, we aim to prepare our sample using the sol-gel auto-composition method. This method is particularly appealing as it is one of the most effective techniques for synthesizing nanoscale ferrite materials. The sol-gel method offers numerous advantages, including excellent stoichiometric control, the capability to produce ultrafine particles, operation at very low temperatures, and a short synthesis time, all while utilizing inexpensive materials. The sol-gel auto-composition method has the potential to significantly influence the crystalline phase purity, particle size, and magnetic properties of ferrites (Cerenea et al., 2020).

3.5. Experimental Procedure

This section offers a comprehensive account of the synthesis process for silver ion-doped cobalt ferrite ($\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$) nanoparticles, which are produced with varying concentrations of silver ($x=0, 0.05, 0.1$) through the sol-gel method. Additionally, the methods utilized for the thorough structural and optical characterization of the synthesized nanoparticles are meticulously detailed.

- ❖ A specific quantity of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{AgNO}_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{C}_6\text{H}_8\text{O}_7$, $\text{C}_2\text{H}_3\text{O}_2$, and $\text{NH}_3 \cdot \text{H}_2\text{O}$ was measured according to their stoichiometric ratios and combined in a beaker containing doubly de-ionized water.
- ❖ The combined chemicals were placed on a hot plate of a magnetic stirrer and stirred at high speed to achieve a homogeneous solution.
- ❖ Subsequently, a clear and colloidal suspended solution, referred to as ‘Sol’, was produced due to the acidic nature of the solution from the addition of citric acid, ammonia solution was incrementally added to neutralize the solution (pH - 7).
- ❖ Over time, the sol-gel transitioned into a structured network, known as gel.
- ❖ The gel was transferred into an evaporating dish and placed in a hot oven to eliminate moisture at 220°C .
- ❖ This process resulted in the formation of ignited ash.
- ❖ The ash was then finely ground multiple times using an agate mortar and pestle to produce a powder.
- ❖ The ground powder was placed in an alumina crucible and subjected to a temperature-programmed electric furnace at 700°C for 3 hours to eliminate organic materials and impurities, a process referred to as calcinations or pre-sintering.
- ❖ After the temperature returned to room temperature, the loaded powder was removed from the furnace and ground again several times using an agate mortar. The finely

ground powder was then placed in an alumina crucible and loaded into an electric furnace for 4 hours at 800°C for further densification, a process known as final sintering (Sundaram, 2017).

- ❖ The powder was subsequently removed from the furnace, ground again finely multiple times, and prepared for characterization of the crystal structure using XRD, surface morphology, SEM, and optical properties using UV-Vis spectroscopy.

The below figure 3.1 schematic representation of the silver doped cobalt nanoparticles synthesis procedure is differing from the experimental procedure of 3.5 because it is used as to gave a supportive ideas for silver doped cobalt ferrite nanoparticles .

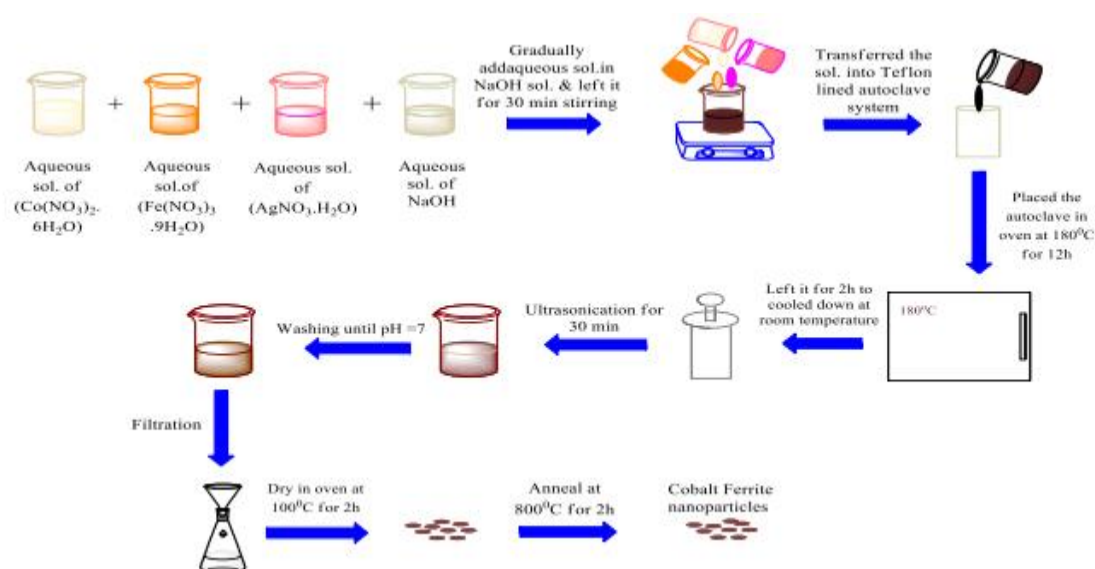
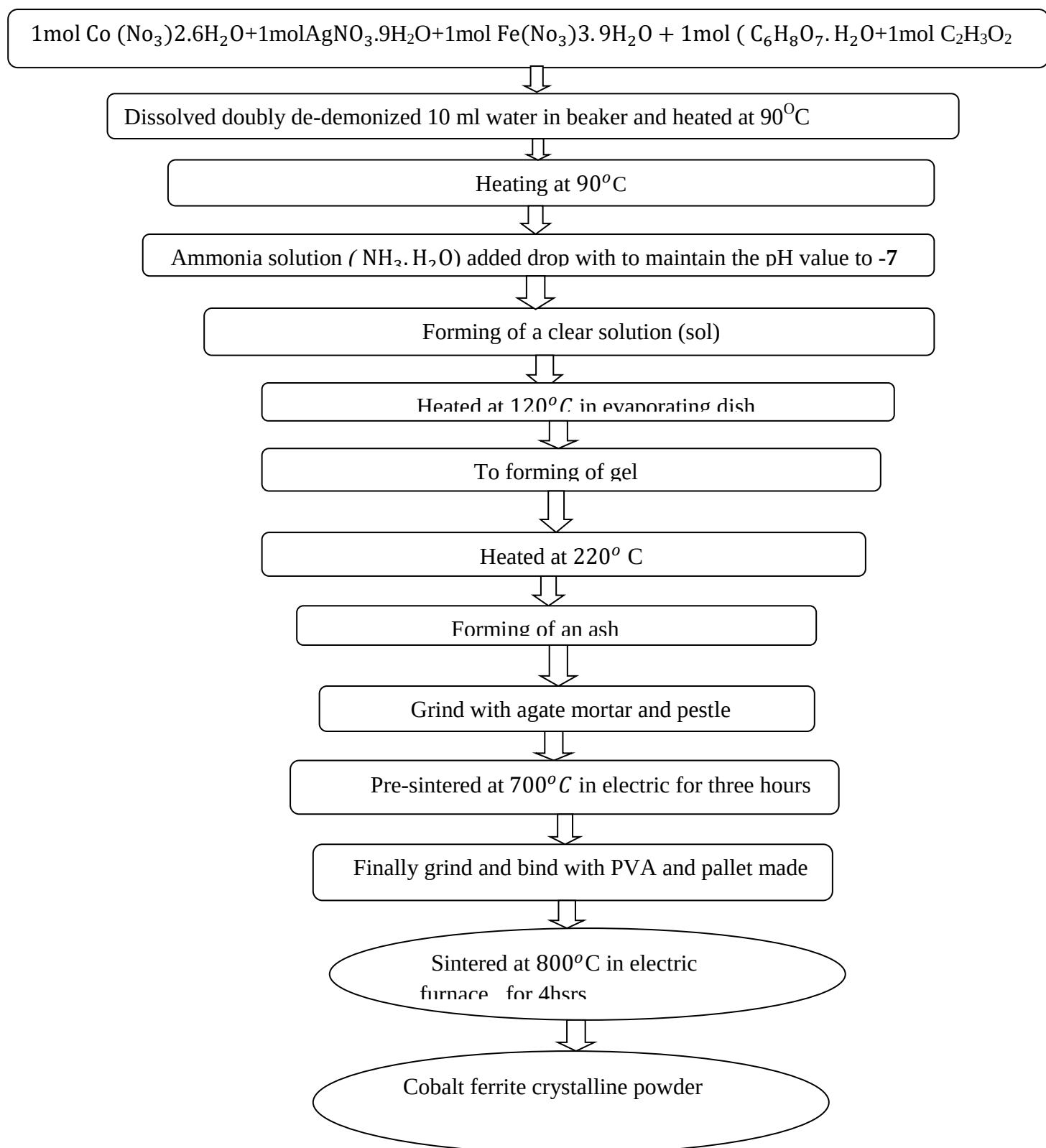


Figure 3.1; Schematic representation of silver doped cobalt ferrite nanoparticles synthesis procedure

3. 6.The flow charts of sol-gel powder preparation and procedures



3.7. Characterization Techniques

3.7.1. X-ray Diffraction

X-ray Diffraction (XRD) is a powerful method for examining the atomic and molecular structure of materials. It is based on the principle that when X-rays strike a crystalline substance, they interact with the atoms in its organized lattice, producing a unique diffraction pattern. This pattern acts as a distinctive fingerprint, encoding essential information regarding the arrangement of atoms within the crystal. The procedure entails directing a beam of X-rays onto the crystalline sample and carefully measuring the angles and intensities of the scattered (diffracted) X-rays. As the X-rays scatter, they interfere with one another, resulting in patterns of constructive and destructive interference. These interference patterns are recorded by a detector, and their subsequent analysis enables scientists to accurately ascertain the crystal structure, including the positions of individual atoms as well as the distances and angles between them. The knowledge obtained from analyzing these diffraction patterns is indispensable for understanding a material's properties and behavior, such as its chemical composition, crystal symmetry, and atomic arrangements. This comprehensive structural information is essential to the field of materials science (Cullity et al., 1978).

$$2 d \sin \theta = n \lambda \quad (3.1)$$

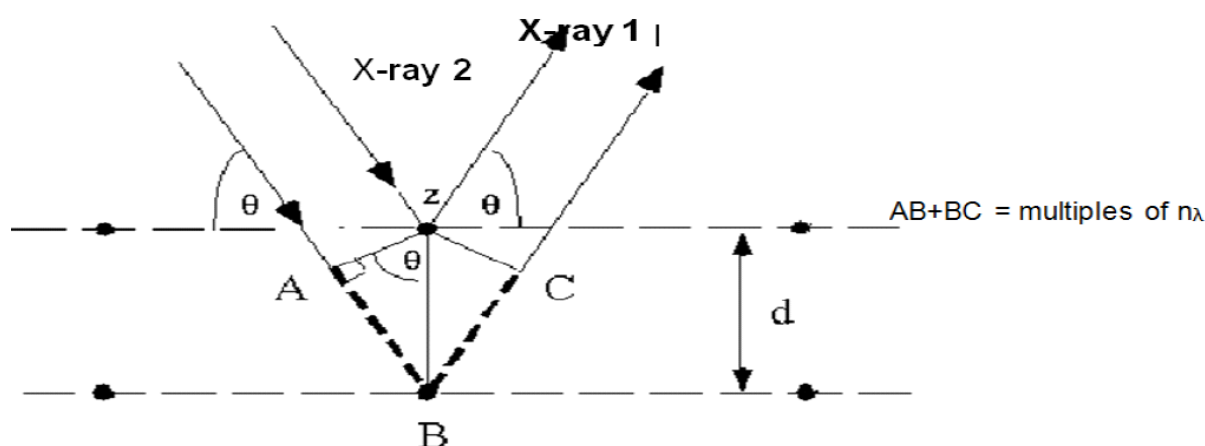


Figure 3.2. Representation of X-ray diffraction

The X-ray diffract meter can provide the following information

- ❖ Inter planar spacing (d of reflection)
- ❖ Sample quality and confirmation
- ❖ Unit cell dimensions and lattice type, including intensity reflections.

A practical method for determining the mean or average size of crystallites in bulk nano crystalline material is X-ray diffraction. In 1981, Paul Scherer, the pioneering scientist, published his findings in a paper that included the equation that would later be known as the Scherer equation. This is elucidated by the fact that, while X-ray diffraction is sensitive to the crystallite size within the particles, the crystallite size does not equate to the particle size. Furthermore, the crystallite size of these nanoparticles is calculated using Debye-Scherrer's formula:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3.2)$$

Where the diffraction angle is represented by " θ ". The full width at half maximum (FWHM) is denoted by " β ", the wavelength (1.5406Å) is represented by " λ ", and the FWHM of spherical crystals with cubic symmetry is indicated by " K ", a constant equal to 0.89. The X-ray of spherical crystals with cubic symmetry is represented by " K ", a constant equal to 0.89. The X-ray diffraction pattern of silver doped cobalt ferrite NPs produced by the sol-gel method and other techniques demonstrated that all ferrites possess a single-phase structure. The lattice parameter of silver-doped cobalt ferrite nanoparticles was calculated using the following equations.

For cubic crystal structures, the lattice spacing and the lattice constant can be related as follows (Zeeshan et al., 2015).

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (3.3)$$

Here h, k, and l are simply notations for the Miller indices of the crystal planes, and d represents the distance between them.

$$\text{One can compute the unit cell's volume; } V = a^3 \quad (3.4)$$

it is possible to determine the X-ray density, which is connected to the sample's theoretical density (Bretcan et al., 2006).

$$\rho_{\text{x-ray}} = \frac{8M}{N_A V} \quad (3.5)$$

According to Chandakar et al. (2020), N_A is the Avogadro number (6.023×10^{23}) and M is the molecular weight of the molecule present in the sample. 8 is the number of atoms in a unit cell of a cubic spinel structure, and V is the volume of the constructed unit cell.



Figure 3.3 .SEM instrument

3.7.2. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is an advanced imaging method that produces high-resolution, three-dimensional representations of a sample's surface. It provides in-depth insights into the topography, morphology, and composition of materials. The process operates as follows: A concentrated beam of electrons traverses the surface of the sample. As these electrons interact with the sample's atoms, they emit various signals. The two primary signals utilized are Secondary Electrons (SE) and Backscattered Electrons (BSE). Secondary electrons are low-energy electrons that are released from the very surface of the sample as a result of the interaction with the primary electron beam. These electrons are essential for uncovering the surface topography and generating clear, high-resolution images. Conversely, backscattered electrons are high-energy electrons that are reflected back from the atoms of the sample. The intensity of these backscattered electrons is directly related to the atomic number of the elements present. By detecting and analyzing these signals, researchers can obtain significant compositional information regarding the sample.

3.7. 3 .UV-Visible Spectroscopy

The wavelength range of UV radiation from 200 nm to 800 nm will be utilized. This spectroscopic method will be employed to determine the absorbance (A).

$$A = \text{Log}_{10} \left(\frac{I_0}{I} \right) \quad (3.6)$$

I_0 and I represent the incident intensity of photons on the sample and the transmitted intensity of the photons, respectively. L denotes the thickness of the sample holder (Cuvette in cm).

The absorption coefficient α of the sample can be derived from the recorded absorbance (A) data using the following equation:

$$\alpha = 2.302 \left(\frac{A}{L} \right) \quad (3.7)$$

L is the sample holder's thickness (Cuvette in cm), and I_0 and I are the photon's incidence and transmitted intensities, respectively.

The Tauc relation can be used to estimate the direct optical energy band gap from the absorbance spectrum data:

$$(\alpha h\nu)^2 = C(h\nu - E_g)^2 \quad (3.8)$$

Here, α is the absorption coefficient, $h\nu$ is the energy of the incident photon on the sample, C is the constant referred to as the band tailing parameter, and E_g is the band gap energy between the top of the valence band and the bottom of the conduction band. These apply to the wavelength range of 1200 nm to 400 nm, which is known as the near-ultraviolet region

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Structural Analysis

This section details the experimental outcomes derived from the study the effects of silver doping on the structural and optical properties of CoFe_2O_4 nanoparticles. The results from the synthesis and the subsequent characterization methods are organized in a systematic manner. After the results are presented, an in-depth discussion will follow, analyzing the observed alterations in structural parameters and optical characteristics in relation to the concentration of silver doping. This discussion will link the experimental findings with established theoretical models and pertinent literature, thus fulfilling the specific research aims set forth in the chapter.

4.1.1 .XRD Analysis

Figure 4.1 illustrates the X-ray Diffraction (XRD) patterns of CoFe_2O_4 nanoparticles, including both undoped and silver-doped variants $\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ which were synthesized through the sol-gel method at ambient temperature. The XRD analysis verifies that all samples produced display a pure cubic inverse spinel ferrite structure, as indicated by the successful indexing of all observed diffraction peaks to the characteristic reflections of CoFe_2O_4 . This structural classification aligns with JCPDS card No. 22-1086 confirming the space group as Fd-3m . Notable diffraction planes such as (111), (220), (311), (400), (422), (511), (440), and (533) were clearly identified at their corresponding 2θ angles (19° , 30.07° , 35.65° , 37.07° , 43.06° , 53.45° , 56.98° , and 62.38°). This substantiates the formation of the intended cubic spinel ferrite structure in all synthesized samples (Uzunoglu, 2019). Further structural analysis was performed utilizing the prominent (311) diffraction peak. The average crystallite size (D) was estimated using the Scherrer equation as outlined in Equation (3.2) of the methodology. Moreover, the interlinear spacing (d-spacing), lattice parameters, and X-ray density were computed using Equations (3.1), (3.3), and (3.5), respectively. As shown in Figure 4.1, the addition of silver ions affects the diffraction patterns. In particular, a greater clarity and intensity of the characteristic (311) peak is noted as the silver concentration increases. This finding indicates that the introduction of metal ions via doping results in changes to the crystal

structure and atomic configuration. The consolidated structural parameters are detailed in Table 4.1 and further depicted in Figure 4.

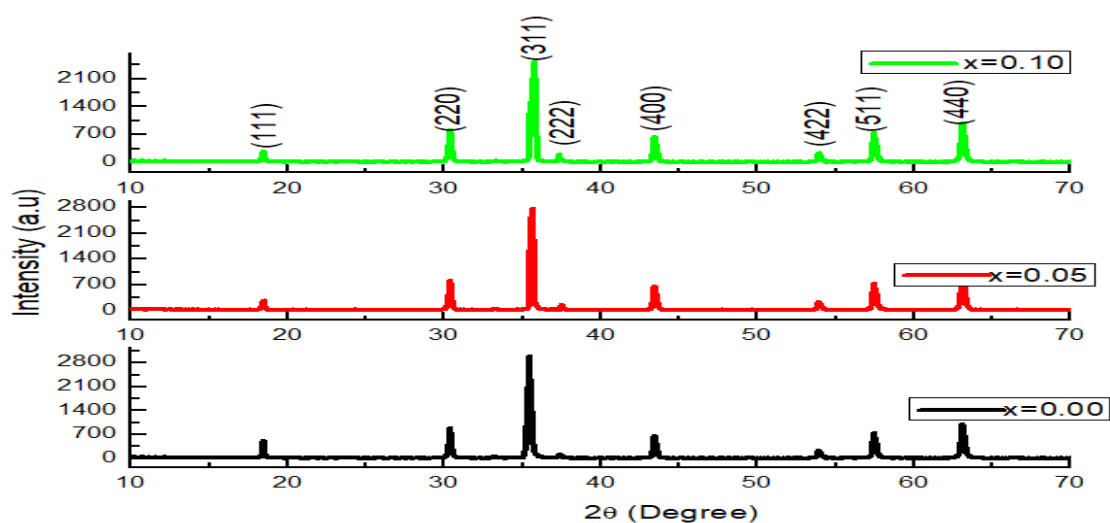


Figure 4.1.XRD pattern of $\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ nanoparticles

Table 4. 1. Values of various crystal parameters obtained from XRD data

<i>Sample</i>	<i>Crystallite size, D (nm)</i>	<i>d-spacing (nm)</i>	<i>a (nm)</i>	<i>x-ray (g/cm³)</i>	<i>density</i>
CoFe_2O_4	46.21003	0.25307	0.839338		5.2712
$\text{Co}_{0.95}\text{Ag}_{0.05}\text{Fe}_2\text{O}_4$	40.35998	0.25197	0.835689		5.3962
$\text{Co}_{0.9}\text{Ag}_{0.1}\text{Fe}_2\text{O}_4$	35.44	0.250879	0.832073		5.5219

As illustrated in table 4.1, the crystallite size of the synthesized sample diminished as the concentration of Ag in cobalt ferrite nanoparticles increased. This decrease in crystallite size can be mainly attributed to the grain growth inhibition effect caused by the silver dopant ions. During the sol-gel synthesis and subsequent calcinations processes the Ag^{1+} ions are likely to segregate at the grain boundaries of the developing CoFe_2O_4 crystallites, and thus are hindering their growth into larger particles. Moreover, the disparity in ionic radii between Ag^{1+} and Fe^{3+} , as well as the host $\text{Co}^{2+}/\text{Fe}^{3+}$ ions, may induce lattice strain, which is more easily accommodated by the formation of smaller crystallites. The findings also revealed it was observed that significant the lattice constant of CoFe_2O_4 nanoparticles decreased from 0.84 nm (undoped) to 0.83 nm when doped with 0.1 concentration of Ag. Although Ag^+ has a larger ionic radius compared to Co^{2+} and Fe^{3+} (which would typically

lead to lattice expansion), this contraction is primarily attributed to the formation of cation vacancies within the CoFe_2O_4 spinel lattice. The introduction of monovalent Ag^{1+} ions requires charge compensation, resulting in the creation of vacant cation sites. These vacancies effectively reduce the unit cell volume, thereby counteracting the size effect of the substituted silver ions

4.1.2. SEM Analysis

Figure 4.2 presents SEM micrographs of ($\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$, $x=0, 0.05, 0.1$) silver doped ferrite that was annealed at 800°C for 4 hours at room temperature. The prepared samples were analyzed using SEM. The SEM images indicate that all samples are composed of nearly spherical nanoparticles, exhibiting a slight tendency towards agglomeration, a common characteristic in ferrite nanoparticles due to magnetic dipole-dipole attractions and elevated surface energies (Shah et al., 2015; Ghodake et al., 2017). Consequently, for silver-doped CoFe_2O_4 nanoparticles, it can be observed that the material is highly crystalline, and the small sizes are nearly identical to one another, as shown in figure 4.2. This characteristic demonstrates that the produced materials contain nanoparticles.

The results depicted in figure 4.2 show the particle size distribution for the undoped sample ($x=0.00$, CoFe_2O_4), which is relatively larger, ranging around (46.21 nm) with smooth surfaces and uniform morphology. Upon the introduction of silver at ($x=0.05$, $\text{Co}_{0.95}\text{Ag}_{0.05}\text{Fe}_2\text{O}_4$) the mean particle size slightly decreased to approximately 40.36 nm, with some particles displaying rough surfaces, indicating lattice strain and defect generation due to Ag substitution in the CoFe_2O_4 spinel lattice. At the highest doping level ($x=0.1$, $\text{Co}_{0.9}\text{Ag}_{0.1}\text{Fe}_2\text{O}_4$) the particle sizes are slightly smaller, averaging (35.44 nm), and exhibit more irregular boundaries, attributed to increased defect density and crystallographic distortion caused by the higher Ag content (Shirsath, 2013). The morphological changes observed through SEM are consistent with XRD results, which indicate a reduction in crystallite size with Ag doping. These findings align with previous reports on noble-metal-doped ferrites, where dopant ions occupy octahedral sites, influencing grain growth and surface structure as illustrated in figure 4.2. The scale bar in all SEM micrographs represents 200 nm.

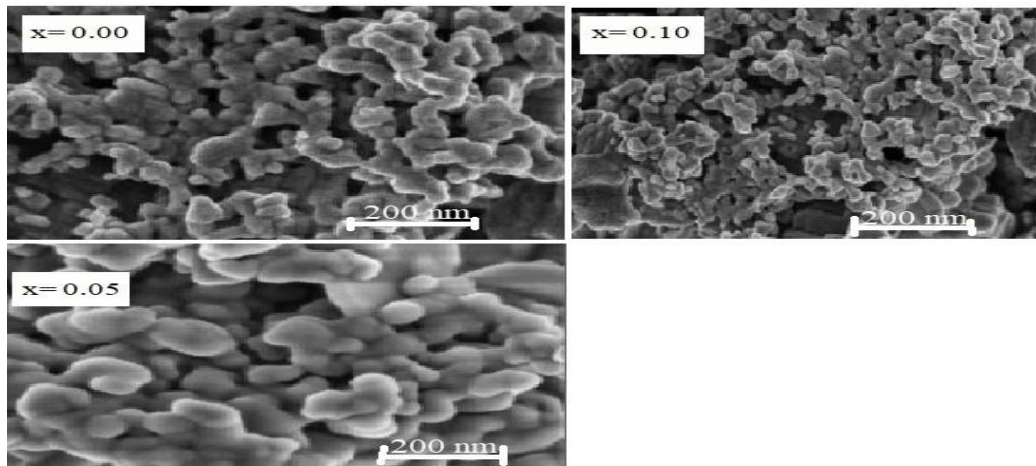


Figure 4. 2. SEM images of prepared silver -doping cobalt ferrite NPs samples

4.1.3. UV-Vis Analysis

This section has detailed the optical properties of silver ion-doped cobalt ferrite nanoparticles, emphasizing the effect of silver doping on their light absorption and emission characteristics. The optical absorption spectra of a substance, particularly in UV- visible spectroscopy, offer significant insights into its electronic structure, notably the energy band gap. The absorption spectra exhibited pronounced absorption in both the UV and visible regions, indicating semiconductor behavior, while the absorption edge shifted with increased silver doping, suggesting alterations in the electronic structure. The optical absorbance of $(\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4)$ where $x=0, 0.05, 0.1$) was measured at room temperature across the wavelength range from 350 nm to 700 nm, as illustrated in figure 4.3. Factors influencing the absorbance value of any material include grain size, surface roughness, and band gap impurities. The recorded absorbance and coefficient can be calculated using equations (3.6) and (3.7).

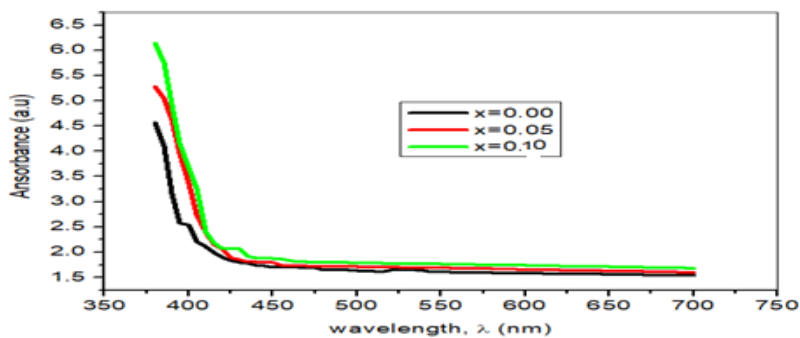


Figure 4. 3. Optical absorption spectra of band gap for $\text{Ag}^+(\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4)$

Figure 4.3 shows the UV-Visible absorption spectrum of silver doped cobalt ferrite nanoparticles recorded in the wave length the range of 350 nm. A strong absorption is observed in the UV region, with a characteristic absorption edge around 350nm, indicating electronic transitions from the valence band to conduction band. This is because of oxygen ions transfer to iron (III) ions charge, surface plasma resonance contribution from Ag doping and quantum size effects in nano particles.

From figure 4.3, the optical absorption spectra of the band gap can be estimated by transforming the absorption spectrum. The Tauc plot illustrates the relationship of $(\alpha h\nu)^2$ against $h\nu$ using the Tauc relation equation (3.8) for the direct band gap (Kiran Kumar and Sumathi, 2020). The results indicate that as the temperature rises, both the top of the valence band and the bottom of the conduction band increase, while the energy band gap decreases. The direct band gap, as shown in figure 4.3, illustrates the optical absorbance of $(\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4)$ where $(x=0, 0.05, \text{ and } 0.1)$.

The prepared samples were subjected to a temperature of 800°C for 4 hours at room temperature. The results were assessed by extrapolating the linear portion of the plot graph of the direct energy band gap against the energy gap. The UV-visible absorption spectra of undoped cobalt ferrite exhibit a strong absorption edge in the visible region, corresponding to its narrow band, due to Fe^{3+} charge transfer transitions and d-d transitions of $\text{Co}^{2+}/\text{Fe}^{3+}$ in the spinel lattice. This indicates semiconducting behavior, and the absorption edge shifts with increasing silver doping, suggesting alterations in the electronic structure.

As the result depicted from figure 4.3 the UV-Visible of $(\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4)$ NPs recorded in the mean of 350nm-700nm show in the UV region with a gradual decrease in the visible region. The absorption edge shifts toward longer wave lengths with increasing silver concentration, indicating band gap narrowing .Using the Tauc method, the optical band gap decreases. This characteristic is due to silver induced defect confirming that Ag beneficially improves the optical response of cobalt ferrite nano particles.

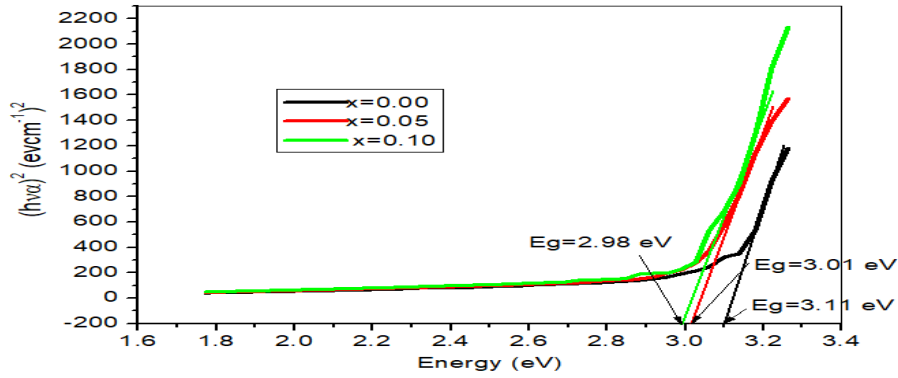


Figure 4.4. Determination of optical band gap energy for $(\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4)$ NPs

From the aforementioned figure 4.4, the optical band gap energy was determined from the plot of $(\alpha h\nu)^2$ against photon energy by extrapolating a straight line to its intersection on the horizontal energy axis at the point where $(\alpha h\nu)^2$ equals 0.

As illustrated in figure 4.4, the direct optical band gap energy of the optical absorption in the prepared samples of $\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$, where $x=0, 0.05$, and 0.1) decreased from 3.11 eV (for $x=0.0$) to 2.98 eV (for $x=0.1$) as the concentration of Ag^{1+} doping ions increased from 0.0 to 0.1. This reduction in the band gap is accompanied by an increase in absorption intensity within the visible range, indicating an enhanced capability for light harvesting due to Ag doping. This phenomenon occurs because Ag ions introduce impurity levels cause lattice distortions in the spinel structure, and the substitution of Co^{2+} (with an ionic radius of $0.74\text{\AA}$) by larger Ag^{1+} (with an ionic radius of $1.26\text{\AA}$) induces lattice strain and moderates the Fe-O-Co super exchange interactions, which alters the hybridization between the O 2p and Fe/Co 3d orbital's, thereby narrowing the band gap.

Furthermore, Ag doping generates oxygen vacancies, cat ion disorder and defect states near the conduction and valence bands, resulting in Urbach tail states that facilitate photon absorption at lower energies.

The greater the Ag content, the more pronounced these effects become, leading to a transition from 3.11 eV (for $x=0.0$) to 3.01 eV (for $x=0.05$) and finally to 2.98 eV (for $x=0.1$). This aligns with previous reports on noble-metal-doped ferrites, where doping-induced defects and strain contribute to band gap narrowing.

In general, the incorporation of silver doping decreases the optical band gap energy of cobalt ferrite, thereby improving its optical absorption within the visible spectrum. This enhancement is beneficial for applications such as photo catalysis, optoelectronics, solar energy utilization, and as a photo catalyst. Additionally, cobalt ferrite is employed in high magneto-optic recording devices due to its narrow band gap and chemical stability

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATION

5.1. Conclusions

In this study, samples of cobalt ferrite nanoparticles doped with silver ($\text{Co}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$), ($x=0, 0.05, 0.1$) showed notable structural and optical changes as a result of the addition of silver ions. The samples were made using the sol-gel method. The creation of a single phase with a cubic spinel structure (space group Fd-3m) was confirmed by XRD, indicating that the doping of silver ions into the CoFe_2O_4 matrix results in decreased particle size, altered lattice properties, and improved crystallites.

All of the samples had decreased crystal sizes from 46.21 nm to 35.44 nm, lattice parameters from 0.84 nm to 0.83 nm, and d-spacing from 0.253 nm to 0.251 nm, according to the XRD results. However, after doping with 0.1 concentrations of Ag ions, the x-ray density, which was connected to the theoretical density of the sample, increased from 5.2712 g/cm³ to 5.5219 g/cm³ because of its smaller ion radii when compared to the larger radii of Co^{2+} . In order to verify the creation of concentrations of silver ions, the SEM micrographs showed that the grains in the samples are homogeneous agglomerated spherical size; form irregular shapes, and have non-uniform surfaces

Because of the introduction of impurity energy levels and increased electron mobility, optical characterization usually shows gap energy with increasing silver concentration. Due to the introduction of impurity energy levels, electronic structure modification, lattice distortion brought on by the larger Ag ionic radius, quantum size effect, increased charge carrier density, and the formation of defect states like oxygen vacancies, the band gap energy dropped from 3.11 eV ($x=0$) to 2.98 eV ($x=0.1$).

Because of their narrow band gap and chemical stability, the results showed that controlled silver doping can effectively modify the structural and optical properties of cobalt ferrite Nps, increasing their potential for visible-light-driven applications like photo catalysis, optoelectronic solar light, and photo catalyst used in high magneto-optic recording devices.

5. 2. Recommendation

Based on the results of this study, some recommendations may be made that could help similar studies get the greatest outcomes:

- ❖ Update several methods to achieve the best outcome quickly.
- ❖ Examining the effects of additional transitional element dopant on the optical and structural properties of cobalt ferrite nanoparticles can shed light on the possibility of additional improvement.
- ❖ The XRD and UV images can be used to calculate average particle sizes.
- ❖ To determine their practical viability, application-oriented research such data storage or spin tonics should be investigated.
- ❖ The researcher ought to carry out more research of this kind in order to expand their understanding on how to prepare various samples
- ❖ Pull proof results can provide further details about structure, such as atom positions and molecular bonds.
- ❖ To make sure the doped NPs are suitable for long-term applications, their stability over time should be examined.

It is generally advised for future research that several reaction parameters, including temperature, pressure, duration, and pH, can be crucial in regulating the morphology and structure of nanoparticles materials. Therefore, it should be tuned to produce a particular characteristic product. In addition, unique characterization procedures must be employed to produce good results and characteristics

More importantly, before these materials are employed in any application, environmental issues must be taken into account. This is especially true for heavy metals, which can alter habitability and are prone to environmental problems.

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