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Synthesis and Studying the Structural, Electrical and Magnetic Properties of Substituted Cobalt Ferrite Nanoparticles

A Thesis
Submitted to the Council of the College of Science- University of Diyala in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy of Science in Physics

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا إِنَّكَ أَنتَ

الْعَلِيمُ الْحَكِيمُ

صدق الله العظيم

سورة البقرة

الاية ٣٢

Dedication

My PhD is dedicated to...

My merciful parents.

My supporters brother and sisters.

My lovely wife.

My beautiful children.....Ellen and Deleen.

Ali M. Mohammad

2019

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1- A. M. Mohammad, S. M. A. Ridha, and T. H. Mubarak, "Dielectric Properties of Cr-Substituted Cobalt Ferrite Nanoparticles Synthesis by Citrate-Gel Auto Combustion Method," *International Journal of Applied Engineering Research*, vol. 13, no. 8, pp. 6026-6035, 2018.

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List of Symbols

Symbol	*Definition*
θ	Bragg's angle
λ	Wavelength
M	Magnetization
H	Magnetic field
M_S	Saturation magnetization
H_c	Coercivity
M_r	Remanance magnetization
n_B	Magnetic moment
K	Magnetic anisotropy
T	Temperature
E_g	Energy band gap
'a'	Lattice parameters
ε'	Dielectric constant
ε''	Dielectric loss factor
$tan\ \delta$	Dielectric loss angle
σ_{ac}	ac conductivity
T_c	Curie temperature
T_N	Neel temperature,
μ_r	Relative permeability
μ_o	Vacuum permeability
μ	Permeability of specific medium
χ	Susceptibility
χ_m	Magnetic susceptibility
C	Curie constant.
P	Polarization

C	Capacitance
C_o	Capacitance of air
f	Frequency
d	Spacing between the atomic planes
D	Crystallite size
hkl	Miller indices
L	Hopping length
R	Reflectance intensity
ρ_x	X-ray density
M	Molecular weight

List of Abbreviations

Abbreviations	***Definition***
NPs	Nanoparticles
XRD	X-ray diffraction
TEM	Transmission electron microscopy
FT-IR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscopy
FE-SEM	Field emission-scanning electron microscopes
VSM	Vibrating sample magnetometer
DRS	Diffuse reflectance spectroscopy
MRI	Magnetic resonance imaging
FWHM	Full width at half-maximum
IR	Infrared radiation
COF	$CoFe_2O_4$
ICSD	Inorganic crystal structure database
RE	Rare earth
P_e	Electric polarization.
P_i	Ionic polarization
P_o	Orientation polarization
P_{Sc}	Space-charge polarization
R_s	Specular reflectance
R_d	Diffuse reflectance

Abstract

The objective of this thesis was to synthesis and studying the structural, electrical and magnetic properties of magnesium and chromium substituted cobalt ferrites nanoparticles with the stoichiometric formula $Co_{1-x}Mg_xFe_2O_4$ and $CoCr_xFe_{2-x}O_4$ (x=0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) respectively, were prepared using sol–gel auto-combustion method. The as-burnt powders were calcined at 600, 700, and 800 ˚C for 3h in order to study the structural and magnetic properties. The samples that calcined at 800 ˚C pressed into circular pellets and then sintered at 900 ˚C for 3h for studying the electrical properties.

The XRD diffraction analysis for Mg^{2+} substituted cobalt ferrite nanoparticles showed all the major peaks corresponding to the single spinel structure, while the absence of peaks in Cr^{3+} substituted cobalt ferrite of the as-burnt indicates the amorphous nature of the samples. The calcined samples at 600 and 700 ˚C confirm the formation of spinel structure. Moreover, calcined powder samples at 800 ˚C showed the formation of spinel cubic structure with single phased for all Cr^{3+} substituted cobalt ferrites. Generally, when the calcination temperature was elevated, the diffraction peaks became sharper, narrower and more intense. Fourier transform infrared (FT-IR) spectra of both series showed two principal absorption bands in the range of (600-400 cm^{-1}), that indicates formation of cubic spinel structure. In Mg^{2+} substituted cobalt ferrite nanoparticles a shifting in similar trend of the ν_1 and ν_2 bands towards the lower frequencies has observed with increasing the calcined temperature and Mg^{2+} substitutions. While, in Cr^{3+} substituted, the absence of any absorption peak of the as-burnt sample with increasing the Cr^{3+} substitution it also indicates the amorphous nature of the samples. However, the calcined samples at 600, 700 and 800 ˚C exhibited the characteristic FT-IR peaks of the ferrite. A slightly shifting of the ν_1 and

ν_2 bands towards higher frequencies has been observed with increase in Cr^{3+} substitution. The porous nature, nanosized and almost homogeneous distribution of particle size have been showed by field emission scanning electron microscopy (FE-SEM) images. The micrographs of Mg^{2+} and Cr^{3+} substituted cobalt ferrite revealed that the microstructure of the ferrites was affected by the substitutions and showed agglomeration with homogenous spherical and polyhedral particles. The optical energy band gap (E_g) of cobalt ferrite for as-burnt and those calcined at 600, 700 and 800 ˚C are equals to 1.610, 1.609, 1.605 and 1.598 eV respectively. These energies have been decreased with increasing calcination temperature and in turns increasing the particle size, while showed an increase with increasing the Mg^{2+} and Cr^{3+} substitution. The dielectric properties are measured by (LCR) meter in the frequency range of (50Hz-1MHz) at room temperature. The dielectric constant (ε'), dielectric loss angle ($tan\delta$) and dielectric loss factor (ε'') for Mg^{2+} and Cr^{3+} substituted cobalt ferrites are found to decrease with increasing frequency. This behavior is typical of ferrites as explained by Koop's model. The dielectric constant was found to increase with an increasing in Mg^{2+} and Cr^{3+} substitutions. While, the dielectric loss angle and dielectric loss factor of the cobalt ferrite have been reduced by Mg^{2+} and Cr^{3+} substitutions in the present work. The ac conductivity (σ_{ac}), gradually increased as the frequency increased, and decreased with increasing of Mg^{2+} and Cr^{3+} substitutions dependent on the partial substitution and the difference in the grain size. The weakened of magnetic interaction among cations are observed by means of vibrating sample magnetometer (VSM), due to replacement of Fe^{3+} and Co^{2+} at B-site (octahedral) by the Cr^{3+} and Mg^{2+} ions respectively, which caused decreasing in saturation magnetization (M_s) and remanance magnetization(M_r). The reduced magnetic anisotropy (K) and particle size was found responsible for

decrease in coercivity force (H_c). In general, the magnetization measurements show a gradual transformations from hard magnetic to softer magnetic characteristics, and that was witnessed with Mg and Cr substitutions as the magnetic parameters; M_s, M_r and H_c decreased with substitutions.

Chapter One

Concept of Nanoparticles and Literature

Review

1.1 Introduction

This chapter gives the background information about the concept of nanoparticles. Section 1.2 gives a brief introduction to the history of nanoscience and their applications. Section 1.3 gives a brief literature review of synthesis ferrite nanoparticles. Section 1.4 describes the aim of this research.

1.2 History of nanoscience and their applications

When the size of a material is reduced to the nanoscale, its chemical and physical properties will be changed completely, resulting in unique properties due to its large surface area or quantum size effect [1, 2]. Generally, nanoparticles (NPs) are tiny materials having size ranges from 1 to 100 nm [3, 4]. This class of materials is the bridge between atoms and the bulk-solids. For this reason, the properties of materials can be different at the nanoscale for two main reasons. First, nanomaterials have a relatively larger surface area when they are compared to the same mass of material produced in a larger form; this can make materials to be chemically reactive and affect their strength or electrical properties. Second, the quantum effects can begin to dominate the behavior of matter at the nanoscale, especially at the lower end, affecting the optical, electrical and magnetic behavior of materials. The area of nanoscience has seen clear annual growth due to emerging industrial methods as well as the availability of new tools for characterization. These nanomaterials have found several applications in many fields [5]. Magnetic properties are among those physical properties that change dramatically within the nanoscale. In fact, when the size of a ferromagnetic material is scaled down to create a nanoparticle (i.e. a 3D nanoscales object), a strange magnetic phenomena will emerge [6, 7].

Magnetic nanoparticles are the most developed and known materials for application in biomedicine and biotechnology. They are also used in technical ones such as magnetic data storage since last few years. Magnetic ferrites are kind of important magnetic materials with spinel structures for technological application and basic studies; it has received special attention by the scientists and researchers because of its excellent chemical stability, electrical properties, magneto-optical properties and reasonable cost that give a novel magnetic behavior. These special properties are affected by the method of preparation, chemical composition, sintering temperature, porosity and grain size. Spinel ferrite have large applications in many fields such as computer components, memory devices, magnetic recording media, satellite communication, ferrofluids, antenna rod transformers, magnetic resonance imaging etc. [8, 9].

Several chemical techniques have been developed to synthesize ferrite nanoparticle, which have a common feature that all reagents are mixed in atomic or molecular level; these include co-precipitation [10], sol–gel auto-combustion [11], microemulsion [12], hydrothermal [13], spray pyrolysis methods [14], etc.. Complex schedules and low production rate are common problems of these wet-chemical methods.

Sol-gel auto-combustion synthesis method (also called Citrate-gel auto combustion as well as sol-gel self-combustion), where the chemical sol-gel and combustion process, are combined and has demonstrated great potential in the preparation of spinel type of ferrite nanomaterials. In general, this method can be considered as a solution combustion technique. through the last decade, the application of the sol-gel combustion method for the synthesis of nanosized spinel ferrite powders has been used in an increasing intensity [15].

1.3 Literature review

Magnetic nanoparticles have captured attention in the past decades because of their essential applications. Spinel ferrite has gained considerable attention due to good magnetic properties, high packing density at low cost. They have been used regularly in studies from 1931. A lot of work has been undertaken to prepare substituted ferrite and cobalt ferrite nanoparticles from various methods, and outcome of various cationic substitutions on the fundamental, electrical and magnetic properties has been calculated. The few important works have been praised below:

B. G. Toksha et al., (2008) [16]**;** They studied the morphological and magnetic properties of $CoFe_2O_4$ nanoparticles synthesized by sol-gel auto combustion method using nitrates of respective metal. The size of the particle measured by both X-ray diffraction (XRD) and Transmission Electron Microscope (TEM) was good agreement with each other, indicating that there was no agglomeration and that the size distribution of the prepared nanoparticles was small. (TEM) tests confirmed the formation of single-phase $CoFe_2O_4$ nanoparticles in the range (11-40 nm) depending on the annealing temperature and time. It has been found that the particle size increases with the annealing temperature and time, while the coercivity goes through a maximum, peaking at around (25 nm).

K. Chandra et al., (2008) [17]**;** Prepared nano size $Mg_xCo_{1-x}Fe_2O_4$ ferrites (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) by sol gel method. The X-ray diffraction showed the crystallite size of as-obtained samples were obtained (~6 nm), which increases up to (~80 nm) after annealing at (1000 °C). The saturation magnetization of the samples annealed at (1000 °C) decreases from (80.0 –27.5 emu/g) with the increasing of Mg^{2+} ions, due to the diamagnetic behavior of the Mg^{2+} ions.

M. J. Iqbal and M. R. Siddiquah, (2008)[18]**;** Prepared a series of $CoCr_xFe_{2-x}O_4$ ($0.0 \leq x \geq 1.0$), by a micro-emulsion method using polyethylene glycol as surfactant at pH 9.5. The crystallite sizes of the materials were found in the range of (40–75 nm). The values of lattice parameters decreased but those of the X-ray density and bulk density increased with the addition of chromium cation. The DC electrical resistivity decreased with increasing temperature due to the decrease in the electron hopping by Cr-substitution. The activation energy of hopping increased from (0.34 eV) at x = 0.0 to (0.52 eV) at x = 1.0 because the Cr^{3+} ions entering the octahedral sites would reduce the electron exchange between Fe^{2+} and Fe^{3+}. The saturation magnetization (M_S) was found to be the maximum value of the sample with chromium x = 0.2, while the coercivity (H_c) decreases with increase in Cr^{3+} content in the samples indicating the loss of magneto crystalline anisotropy.

P. P. Hankare et al., (2009) [19]**;** synthesized spinel phase nanocrystalline of $CoCr_xFe_{2-x}O_4$ powders ($0.0 \leq x \leq 2.0$) by citrate-gel auto combustion method. The X-ray diffraction refers to the formation of single phase cubic spinel structure for all the compositions, and the lattice constant goes on decreasing with increase in chromium content. The (TEM) analysis confirmed that particle size decreases with the increasing of Cr content. The D.C. resistivity indicated semi-conducting nature of all the spinel ferrite materials. Magnetic measurements showed that the measured magnetic hysteresis loops become narrow and the saturation magnetization decreases with the increase of chromium content. The coercive field, saturation magnetization and remanent magnetization decreased with the increasing of chromium content because the Fe^{3+} ions replaced by Cr^{3+} ions weaken the sub lattice interaction and lower the magnetic moment of the unit cell.

P. P. Hankare et al., (2009) [20]**;** Prepared a series of Cr substituted magnesium ferrite $MgFe_{2-x}Cr_xO_4$ (x = 0.0, 0.5, 1.0, 1.5 and 2.0) by co-precipitation method using NaOH at a pH of 9.5. The X-ray results showed all the compounds exhibited cubic spinel symmetry and lattice constant varied between (8.40 and 8.33Å). FT-IR spectral studies indicated two strong bands one around 600 cm^{-1} which is attributed to the intrinsic vibrations of tetrahedral complexes, and other at (400 cm^{-1}) is due to octahedral one. They also discussed the hysteresis loop measurements which indicated a non-linear behavior in saturation magnetization and coercive field with the chromium content. However, electrical resistivity plot showed the semiconductor behavior of sample beyond (290 °C). At this temperature, there is a phase transition from metallic to the semiconductor phase.

M. G. Naseri et al., (2010) [21]**;** Synthesized the spinel cobalt ferrite $CoFe_2O_4$ nanoparticles by a thermal treatment method using cobalt nitrate, iron nitrate as precursors, (PVP) as an agglomeration capping agent and deionized water as a solvent. The particle sizes were obtained in the range of (12.5-39 nm) with calcination temperatures between (623 and 923 K), as confirmed by TEM and XRD analyzes. Calcination at (823 and 923 K) completely removed organic compounds and the nitrate ions. Magnetic studies showed that the saturation and remanent magnetization of the cobalt ferrite increased as temperature increased, while the coercivity field and remanence ratio increased until they achieved a maximum value and then decreased. This method is simple, cost-effective and environmentally friendly.

S. Abedini Khorrami et al., (2010) [22]**;** Prepared cobalt ferrite nano-crystalline powder by the combination of sol-gel auto-combustion and ultrasonic irradiation methods from metal nitrates and glycine. The X-ray diffraction confirmed the formation of spinel phase structure and

the crystallite size of as-burnt powders about (39.12 nm). The grains observed in the as-burnt powder proved to be $CoFe_2O_4$ nano-crystallites with high dispersibility and low agglomeration. The crystalline $CoFe_2O_4$ powders with magnetic properties having the maximum saturation magnetization (44.02 emu/g) were achieved for Fe^{3+}/Co^{2+} molar ratio 1:1 and calcination temperature 750°C for 4 h. The result suggested that this method might provide a wider space for further improving the magnetic properties of cobalt ferrite nanocrystalline. In addition to the feature of high-quality production, low cost and ease manipulation at low temperature

A. A. Thantet et al., (2010) [23]**;** Synthesized of soft ferrite $MgFe_2O_4$ with single phase magnetic particles by the auto-combustion assisted sol-gel method at a low temperature below 200 °C to improve their properties. The XRD analysis confirmed the formation of single-phase cubic spinel with a crystallite size (~ 7.4nm). The morphology of the powder was characterized by FE-SEM image and it represents a soft agglomerated structure composed of magnetically interacting ultrafine crystallites. These nanocrystallites synthesized at low temperature have improved the magnetic and electrical properties.

S. Singhal et al., (2010) [24]**;** Prepared $Zn_xCo_{1-x}Fe_2O_4$, (x = 0.0, 0.2, 0.4, 0.8 and 1.0) via sol-gel method, and studied the effect of Zn substituted cobalt ferrite on the saturation magnetization and lattice parameter. X ray diffraction showed the particle sizes of the as-obtained samples found to be (~10 nm) which increases up to (~92 nm) on annealing at 1000°C. The lattice parameter and X-ray density increased with increasing Zn concentration, due to larger ionic radii of Zn^{2+} ion. FT-IR spectra identified the frequency bands near (564-588 cm^{-1}) and (425-442 cm^{-1}) to the tetrahedral and octahedral clusters which confirm the presence of M-O stretching band in ferrites. The saturation

magnetization first increases from $CoFe_2O_4$ to $Co_{0.6}Zn_{0.4}Fe_2O_4$ and then shows a decreasing behavior till $ZnFe_2O_4$. The source of such behavior could be the exchange interaction variation between the tetrahedral and the octahedral sites.

B. G. Toksha et al., (2011) [25]**;** Synthesized $CoCr_xFe_{2-x}O_4$ ($0 \leq x \leq 1.0$) by sol-gel auto combustion method, using nitrates of respective elements and by keeping 1:3 ratio of metal nitrate to citrate. The XRD pattern revealed that the cubic spinel structure is maintained for all compositions, the lattice parameter, bulk density, and particle size are decreased, whereas the X-ray density, specific surface area, and porosity tend to increase with increasing Cr^{3+} substitution. Fourier transform infrared spectroscopy (FT-IR) spectra showed two prominent bands corresponding to spinel ferrite phase. The vibrating sample magnetometer (VSM) showed decrease in saturation magnetization with increasing Cr^{3+} content occurs because the replacement of Fe^{3+} by Cr^{3+} ions, suggesting that the superexchange interaction Fe(A)-O-Fe(B) link is stronger than that for the Fe(A)-O-Cr(B) link. Coercivity in the Cr-substituted cobalt ferrites was larger than that in pure $CoFe_2O_4$ compositions.

P.S. Aghav et al., (2011) [26]**;** They obtained a spinel ferrite system of $CoFe_{2-x}Al_xO_4$ powders (x=0.0 to 1.0 in the step of 0.2) by sol-gel auto combustion method using citric acid as a fuel. The X-ray diffraction analysis revealed that the prepared samples possess single phase cubic spinel structure. The crystallite size was obtained from (16–26 nm) using the Scherrer formula. SEM analysis showed formation of uniform grain growth and the grain size obtained from SEM results is of the order of (30nm). It has been observed that the maximum surface area to be of the order of (52 m^2/g). The highest value of saturation magnetization and coercivity was observed for pure cobalt ferrite sample and it decreased with increasing Al^{3+} content. The decrease in magnetic properties is due

to the substitution of Al^{3+} ions in place of Fe^{3+}. The substitution of Al^{3+} in $CoFe_2O_4$ affects the structural and magnetic properties, its shows improved structural and magnetic properties.

M. S. Khandekar et al., (2011) [27]**;** Reported the structural and electrical properties of $CoFe_2O_4$ synthesized by combustion route, with hexamine as a fuel. X-ray diffraction revealed that an increase in the particle size with the calcination temperature (i.e. 700, 800 and 900 °C). FTIR spectroscopy confirmed the presence of tetrahedral and octahedral group complexes within the spinel lattice. DC resistivity as a function of temperature indicated that all the samples obey the semiconducting behavior and it decreases with calcination temperature. The dielectric constant increased with the calcination temperature and all the samples exhibited usual dielectric dispersion which is due to the Maxwell–Wagner-type interfacial polarization. The ac conductivity measurement suggested that the conduction is due to small polaron hopping.

S. Singhal et al., (2011) [28]**;** synthesized the cobalt substituted nickel chromium ferrites $CrCo_xNi_{1-x}FeO_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) using sol-gel auto-combustion method and annealed at (400, 600, 800, and 1000 °C). The typical FT-IR spectra of the annealed samples at (400, 600, 800, and 1000 °C) showed two frequency bands in the range of (480 cm^{-1} and ∼590 cm^{-1}) corresponding to the formation of octahedral and tetrahedral clusters of metal oxide, respectively. The TEM images showed that crystallite size increases from (10 to 45nm) as the annealing temperature is increased from (400 to 1000 °C). The unit cell parameter "*a*" was found to increase on increasing the cobalt concentration due to the larger ionic radius of Co^{2+}. Also, with increased the cobalt concentration, the saturation magnetization increases from (4.32 to 19.85 emu/g). This is due to the fact that Co^{2+} ion replaces the less magnetic nickel ions. However, the coercivity decreases with increase in Co^{2+}

concentration due to the decrease in anisotropy field. The band gap was calculated using UV-VIS spectrophotometry and found its values in the range (~2.5 eV). However, the band gap increases up to (~3.0 eV) with the decrease of the particle size from (45 to 10 nm).

E. Pervaiz and I. H. Gul, (2012) [29]**;** Synthesized a series of $CoCr_xFe_{2-x}O_4$ (x=0.00, 0.25, 0.50) nanoparticles by sol–gel auto combustion and chemical co-precipitation techniques. Uniformly sized and homogeneous particles were observed by each synthesis techniques. X-ray diffractograms confirmed the single-phase cubic spinel structure for all investigated samples. Crystallite sizes of the series are within the range of 12–29 nm. The lattice parameters decreased from (8.395 to 8.364 Å) with increasing Cr^{3+} concentration (x) in both techniques. FTIR confirmed the presence of two lattice absorption bands. The values of DC electrical resistivity increase with addition of Cr^{3+} ions, but the most significant increase is in samples prepared by sol–gel combustion. This confirms the effect of the synthesis route on physical characteristics. The dielectric losses are reflected on the DC electrical resistivity measurements where the high resistivity materials show low losses and vice versa. The ac conductivity of nanosized Cr^{3+} substituted cobalt ferrites increases linearly with frequency. Magnetic behavior showed that increasing the concentration of Cr^{3+} reduces the magnetization and materials become soft magnetic material.

A. Franco et al., (2012) [30]**;** Synthesized and study the magnetic properties of $Co_{1-x}Mg_xFe_2O_4$ by forced hydrolysis method. The X-ray diffraction analysis showed that all samples exhibited sharp and intense peaks that correspond to the cubic inverse spinel structure and the crystallite size measured by Scherrer's formula was nearly the same for all samples, where it was (4.5 nm). Magnetization measurements show that all samples are superparamagnetic at room temperature, and the

saturation magnetization (M_s) revealed decreases with increasing the molar magnesium concentration, being (260 emu/cm^3) and (160 emu/cm^3) for x=0.0 and 0.6, respectively. Effective anisotropy constant, (K_{eff}) decreased with a replacement of Co^{2+} ion by non-magnetic Mg^{2+} ions in the spinel structure. These results are discussed in terms of interparticle interactions caused by the thermal fluctuations, distribution of cations and other imperfections that could increase with temperature increase.

Y. Koseoglu et al., (2012) [31]**;** Synthesized of nano-crystalline of $CoCr_xFe_{2-x}O_4$ (x=0.0, 0.3) by surfactant-assisted hydrothermal route. The crystallite size of the prepared samplers were found as (29.8 nm) for undoped sample and (27.7nm) for doped sample by using line profile fitting of XRD pattern. The SEM images showed that the surfaces of the samples showed well-defined crystalline nanoparticles of spherical shapes with small agglomeration. The substitution of Cr^{3+} ions resulted in a decrease in the average crystallite size, magnetization and the coercive field of the sample. The observed decreases in saturation magnetization and coercivity are explained on the bases of exchange interactions

M. Raghasudha et al., (2013) [32]**;** Synthesized a series of Co-Cr nanoferrites having the chemical formula $CoCr_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0) by citrate-gel auto combustion method. The X-ray diffraction analysis of as-obtained and sintered powders has confirmed the formation of single-phase cubic spinel structure. The average particle size was found to be (6-12 nm). Magnetic properties of Co-Cr nanoferrites were measured using a vibrating sample magnetometer (VSM) at room temperature, the result showed, that the saturation magnetization decreased from (33.84 to 13.83 emu/g) with increase in Cr^{3+} concentrations, indicating the fact that the lesser magnetic Cr^{3+} ions substitute Fe^{3+} ions in the octahedral sub lattice of the ferrite. With an

improvement in magnetic properties, the synthesized nanoferrites become soft magnetic materials. The coercivity of pure $CoFe_2O_4$ was larger than that of the Cr-doped cobalt ferrites.

R. Koferstein et al., (2013) [33]**;** Synthesized and characterized of nanosized $MgFe_2O_4$ by a starch-gel method. A phase-pure nanosized $MgFe_2O_4$ powder was obtained after calcining a (MgFe)-starch gel at 550 °C. The powder has a specific surface area of (60.6 m^2/g) and a crystallite size of (9 nm). TEM investigations revealed particles size within (7–15 nm). The activation energy of the crystallite growth process was calculated as (89 ± 14 kJ/mol). UV–Vis investigations of the nanosized powder (calcining at 550 °C /2 h) revealed an optical band gap of (2.38 eV), whereas calcination at (1100 °C) leads to a crystallite size of (129 nm) and a band gap of (2.16 eV). They found different saturation magnetizations (M_S) depending on the calcination temperature. The calcination at (550 °C) results in M_S = (20.0 emu/g) which increases with calcination temperature to a maximum of (37.7 emu/g), for powder calcined at (900 °C). Sintered ceramic bodies between (1450 and 1600 °C) exhibit (M_S) values of (25–28 emu/g). Magnetic investigations at (10 K) on powders (calcining at 550 °C /2 h- 1100 °C /2 h) show hysteresis loops with coercivities up to (950 Oe), remanences to (10 emu/g) and M_S values to (50.4 emu/g).

M. Raghasudha et al., (2013) [34]**;** Prepared nanoparticles of $CoCr_xFe_{2-x}O_4$ with stoichiometric proportion (x =0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) by the Citrate-gel auto combustion method. X-ray diffraction studies showed all the Cr-substituted cobalt ferrites a homogeneous and single-phased cubic spinel with a crystallite size of the particles in the range of 6-12nm. FTIR spectra revealed two significant absorption bands. The high frequency band (ν_1) around (600 cm^{-1}) is due to the intrinsic vibrations of tetrahedral complexes, and the low frequency band

(ν_2) around (400 cm^{-1}) is attributed to the octahedral complexes. The dielectric constant, loss tangent and AC conductivity shows a normal dielectric behavior with frequency which reveals that the dispersion is attributed to the Maxwell-Wagner type interfacial polarization and hopping of charge between Fe^{2+} and Fe^{3+}. The loss tangent was found to be decreased from (0.062 to 0.055) in higher frequency region. A qulitative explanation is given for composition and frequency dependence of the dielectric constnat, dielectric loss tangent and AC conductivity of the nano ferrite. A relaxation peak was observed in the loss tangent property of nano ferrite sample with composition $CoCr_{0.1}Fe_{1.9}O_4$.

T. H. Mubarak et al., (2013) [35]**;** They prepared nanoparticles of zinc substituted cobalt ferrite $Zn_xCo_{1-x}Fe_2O_4$, (x = 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5) via sol-gel route and investigated the effect of zinc concentration on lattice constant, particle size and powder density. X-ray diffraction analysis confirms the formation of ferrites in nano- phase, and the results showed that the particle size decreasing from (22 to 16 nm) with increasing the concentration of zinc to the (x= 0.5). The lattice constant increased from (8.36682 to 8.40943 Å) with increasing the concentration of zinc to (x = 0.5), while the theoretical powder density decreased from (5.3225 to 5.2237 g/cm^3) by increasing Zn ion concentration to value at (x=0.5).

M. G. Naseri et al., (2014) [36]**;** They synthesized of magnesium ferrite ($MgFe_2O_4$) nano-particles with cubic symmetry by a thermal-treatment method using a solution that contained poly (vinyl alcohol) (PVA) as a capping agent, Mg and Fe nitrates as alternative sources of metal. An increase in particle size was observed from (5 to 8 nm) when the calcination temperature increased from (673 to 973 K). The EDXA was used to characterize the composition of the samples, and it confirmed the presence of Mg, Fe, and O in the sample. The FT-IR spectra of all

prepared samples revealed two principle absorption bands in the range of (350–600 cm^{-1}), with the first band (ν_1)around (400 cm^{-1}) and the second band (ν_2) around (560cm^{-1}). All the samples calcined from (673 to 973 K) showed superparamagnetic behavior with unpaired electrons spins, which were confirmed using a vibrating sample magnetometer (VSM).

C. Singh et al., (2014) [37]**;** Synthesized the Nickel-doped cobalt ferrite nanoparticles $Ni_xCo_{1-x}Fe_2O_4$ (x= 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) using the reverse micelle method. Spherical particles with ordered cubic spinel structure were found that have the crystallite size of (4–6 nm). The FT-IR spectra of ferrites showed two peaks are observed, which is corresponding to the M–O bond in the octahedral and the tetrahedral sites of the ferrite sub-lattice. Diffused UV-visible reflectance spectroscopy was employed to investigate the optical properties of the prerpared ferrite nanoparticles. The estimated band gap values (E_g) were found to be (1.14, 1.27, 1.38, 1.62, 1.59 and 1.51 eV) for x= 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, respectively. The surface area calculated using the BET method was found to be highest for $Co_{0.4}Ni_{0.6}Fe_2O_4$ (154.02 m^2/g). $Co_{0.4}Ni_{0.6}Fe_2O_4$ showed the best catalytic activity for reduction of 4-nitrophenol to 4-aminophenol in the presence of $NaBH_4$ as reducing agent, whereas $CoFe_2O_4$ was found to be catalytically inactive.

A. C. Druc et al., (2014) [38]**;** Prepared $Mg_{1-x}Co_xFe_2O_4$ (***x*** = 0.00, 0.17, 0.34, 0.50, 0.67, 0.84 and 1.00) at (900°C) by sol-gel auto-combustion method, using glycine as chelating/fuel agent. Infrared microscopy confirmed the formation of spinel phase and disappearance of organic phases. X-ray diffraction analysis confirmed formation the spinel mono-phase formation for all samples. The crystallite size estimated by FullProf 2000 program was found in the range of (42−78 nm). The SEM micrographs confirmed the presence of nano-sized particles with uniform shape, and showed the formation of nanoparticle agglomerates. The

dielectric study showed normal dielectric behavior for all materials. The dielectric constant and dielectric loss decrease with increase in frequency and reaches a constant value at high frequencies.

A. Manikandan and S. A. Antony, (2015) [39]**;** They successfully synthesized pure $ZnFe_2O_4$ and Mn^{2+}-doped $ZnFe_2O_4$ nano-crystals by one-pot auto combustion method. Structural, morphological, optical and magnetic properties have been found to be sensitively dependent on the incorporation of Mn^{2+} ions in the Zn^{2+} lattice site. The observed diffraction peaks indicate the well-defined spinel phase, and it was observed that the crystal size is decreased from (23.25-17.53 nm) with increase in Mn content. From the FT-IR spectra, two of the strong absorption peaks observed at a lower frequency (825 and 430 cm^{-1}) which can be assigned to the M-O (Zn, Mn and Fe) bonds at A and B sites. This can be attributed to the high degree of crystalline nature. The HR-SEM images indicated that the as-prepared samples consist of well crystallized homogeneous spherical shaped particle-like nanocrystals. UV-Visible diffuse reflectance spectroscopy (DRS) measurement showed the estimated band gap (E_g) values of $Mn_xZn_{1-x}Fe_2O_4$ (x = 0.0, 0.1, 0.2, 0.3 0.4 and 0.5) nano-crystals are (1.95, 2.01, 2.18, 2.27, 2.31, and 2.40 eV), respectively. The VSM measurement showed a drastic change in magnetic properties, the value of M_s, M_r and H_c are increased with increasing the concentration of Mn^{2+}.

P. Laokul et al., (2015) [40]**;** Synthesized cobalt-ferrite ($CoFe_2O_4$) nanoparticles successfully by reverse micelle microemulsion method. The X-ray diffraction results showed that all samples have a spinel ferrite structure with calculated crystallite sizes in the range of (3.6–21.7 nm). The increasing calcination temperature from (650 to 900 °C) can lead to increase the crystallization of the powders. TEM images reveal the spherical shape of nanoparticles with serious agglomeration. Particle

sizes of calcined samples at (700, 800, and 900 °C) estimated from TEM images are (9.7±2.1, 10.6 ± 1.6 and 14.9 ± 0.4 nm), respectively. The estimated direct band gaps were evaluated using UV–visible spectroscopy and the results showed a decrease in the energy band gap (E_g) from (4.3 to 3.0 eV) with increasing crystallite size. Magnetic properties of the calcined $CoFe_2O_4$ nanoparticles at room temperature performed by vibrating sample magnetometry (VSM), the result indicate ferrimagnetic behavior in all samples. In addition, the specific magnetizations measured at the maximum field of ±30 kOe (M_{max}) and coercivity (H_c) are increased with increasing calcination temperature.

V. Vinayak., (2015) [41]**;** Synthesized nanocrystalline samples of $Co_{1-x}Mg_xFe_2O_4$ (x= 0.0, 0.25, 0.50, 0.75, and 1.0) by wet chemical sol-gel auto combustion method. The spinel cubic phase formation of ferrite samples was confirmed by X-ray diffraction (XRD) data analysis. The formation of nano-sized crystallites was confirmed through the microstructural studies were investigated through scanning electron microscopy (SEM) technique. The average grain size calculated from linear intercept method was found to be in the nanometer range of (45–66 nm). DC electrical resistivity decreased with increase in temperature while showing an increase with substitution of magnesium in cobalt ferrite increases. The dielectric behavior shows a strong frequency as well as composition dependence. The dielectric constant, dielectric loss, and dielectric loss tangent all decrease exponentially with increase in frequency. The decrease in loss tangent by increasing frequency may be ascribed to the Maxwell-Wagner polarization and conduction mechanism. At lower frequencies, it is observed that the dielectric properties are high.

R. Ahmad et al., (2016) [42]**;** Synthesized Cd substituted $CoFe_2O_4$ with formula $Cd_xCo_{1-x}Fe_2O_4$ (x=0.0, 0.2, 0.35 and 0.5), by wet chemical co-precipitation technique. X-Ray diffraction pattern confirmed the

formation of single face center cubic spinel. The average crystallite size obtained by Scherrer's formula within the range (15-19±2 nm). The lattice parameter '*a*' increased from (8.324 to 8.396 Å) with Cd^{2+} substitution has been observed due to difference in ionic radius. The electrical resistivity decreased with temperature suggests the semiconductor like nature of the ferrite samples. The activation energy of the samples increased with Cd^{2+} content, except at x=0.20. The dielectric properties variation has been studied at room temperature as a function of frequency. Variation of dielectric properties from 100 Hz to 5 MHz has been explained on the basis of Maxwell and Wagner's model and hopping of electrons on octahedral sites.

R. K. Panda et al., (2016) [43]**;** Prepared a series of $CoFe_{2-x}Cr_xO_4$ (x = 0, 0.15 and 0.3) by auto combustion method, and studied the effect of incorporation of Cr^{3+} into cobalt ferrite nanoparticles on its magnetic and electric properties. Average particle size was calculated from XRD and FE-SEM, and was observed significant reduction in particle size with Cr substitution. Mossbauer spectroscopy and magnetic characterization at room temperature were performed. The analysis of extracted parameters concluded that Cr^{3+} replaced the Fe^{3+} at B-site (octahedral). Magnetization reduction in B-site was found to be responsible for the decreased saturation magnetization and coercivity.

M. A. Ahmed et al., (2016) [44]**;** They obtained the nanoparticulate of cobalt ferrite $CoFe_2O_4$ (COF) at relatively low temperature by means of a facile chemical wet method, namely citrate auto-combustion. The XRD analysis results confirm the formation of single spinel phase structure of cobalt ferrite with an average lattice parameter of (8.38 nm). XRD analysis showed that the crystal size is about (43 nm), which is close to the particle sizes observed from TEM images (45.33 nm). FT-IR spectra measurements between (400 and 4000 cm^{-1}) confirmed the

intrinsic cation vibrations of the spinel structure of COF. The experimental results have been explained on the basis of size and surface effects of the nanodimensional crystal of COF. The high coercivity of the prepared nanodimensional COF is the figure of merit for permanent magnets. Dielectric parameters and AC conductivity were measured as a function of temperature (300 – 800 K) and frequency starting from 100 kHz up to 5 MHz. The conduction phenomenon was explained on the basis of the electron hopping model.

H. S. Mund and B. L. Ahuja, (2017) [45]**;** Prepared $Co_{1-x}Mg_xFe_2O_4$, by sol-gel auto-combustion method, and studied the effect of Mg doping on structural and magnetic properties of nanocobalt ferrites. The X-ray diffraction has confirmed the formation of single-phase cubic structure without impurity. Raman spectroscopy reveals a doublet like peak behavior in A_{1g} and E_g modes in all the ferrites arising due to different ionic radii of Co/Mg and Fe ions. The two prominent vibration frequencies in FTIR spectroscopy data confirm the cubic spinel structure in the prepared samples and the absorption band in the range (580-568 cm^{-1}) for the tetrahedral site and at (424-409 cm^{-1}) for octahedral sites. It is seen that the increase in magnesium substitution shifts high frequency bands ν_1 and low frequency ν_2 shift to lower values. Magnetization measurement shows that an increase in Mg^{2+} substitution reduces the saturation magnetization and magnetic moment. Moreover, substitution of Mg^{2+}into the cobalt ferrite alters its magnetic properties and transforms cobalt ferrite from hard to soft magnetic material.

N. Thomas et al., (2017) [46]**;** Prepared Mg substituted cobalt ferrite samples by a simple solution combustion method at a comparatively low temperature, using glycine as fuel. Structural characterization of the as-prepared samples obtained using the Rietveld refinement of PXRD pattern, show that the spinel phase with substitution of Co^{2+} by Mg^{2+} is

easily obtained using this method. The amount of heat released during the combustion reduces as substitution of magnesium increases that cause reduction in the crystallite size. Average crystallite size obtained shows an increase at first with magnesium substitution, i.e. a maximum at x=0.2 and then gradually decreases to (57 nm) at x=1.0. FTIR spectra showed two peaks, one corresponding to the tetrahedral sites and other corresponding to the octahedral sites. The peak at (~ 600 cm^{-1}) belongs to tetrahedral sites and that at (~ 400 cm^{-1}) belongs to octahedral sites. Variation of magnetic parameters at room temperature on substitution indicates hard to soft magnetic transition in these samples. Dielectric properties exhibit a behavior which is similar to what has been reported for spinel ferrite family. This behavior could be explained by a Maxwell–Wagner interfacial type polarization.

A. S. Khader et al., (2017) [47]**;** Synthesized of nickel substituted chromium ferrite nanoparticles $Ni_xCr_{1-x}Fe_2O_4$, (x=0, 0.25, 0.5, 0.75 and 1) by solution combustion method. The structural and dielectric properties of these samples, which are sintered at (800 °C) were studied. The peaks observed in the XRD patterns indicate single phase spinel cubic structure for the synthesized ferrite samples. The crystallite sizes for the sintered samples were calculated using Sherrer formula and are less than (100 nm). Surface morphology of the samples has been studied using FE-SEM. The results indicated that the nano-particles are nearly spherical in shape. The frequency dependence of dielectric constant (ε') and conductivity (σ_{ac}) can be understood through Maxwell-Wagner type interfacial polarization. The maximum value of (ε') and (σ_{ac}) observed for x=0.5 composition is because of excess formation of ferrous Fe^{+2} ions in the system.

M. Abdul Ammer Alsherefi et al., (2018) [48]**;** Prepared nanoparticles of magnesium-cobalt ferrites with the chemical formula

$Mg_{1-x}Co_xFe_2O_4$ by sol-gel auto combustion technique. The results showed change in the Co^{2+} content gives the significant effects in electrical and magnetic properties of the material. The X-ray patterns of prepared powder have confirmed the formation of single-phase cubic spinel structure. An average crystallite size was calculated using Scherrer relation is equal (53.12 nm). The lattice parameter showed an increase with increasing the Co^{2+} content. As well as porosity increase with increasing Co^{2+} content. The surface structure of the samples was investigated by Scanning Electron Microscope (SEM), and confirmed the formation of nano-size crystallites. The electromagnetic properties for prepared samples showed an increase in relative dielectric constant and permeability with cobalt content

H. Kiswanto et al., (2018) [49]**;** They investigated the effects of Zn^{2+} on the crystal structure and magnetic properties of $Co_{1-x}Zn_xFe_2O_4$ nanoparticles synthesized by co-precipitation method with synthesis temperature of (70 °C) and various of x from (0.2 to 0.8). The XRD patterns showed a single phase cubic spinel structure for all sample. The crystallite size of the samples was calculated by using Scherrer's formula, within the range of (9.3 to 11.2 nm). The increase in lattice parameter was observed (8.179 to 8.212 Å) by increasing zinc content as a result of the different ionic radii. FTIR spectra showed two peaks around (478 cm^{-1} and 586 cm^{-1}) were assigned to vibration of octahedral and tetrahedral sites which confirmed the presence of the metal-oxide stretching band. The decrease in saturation magnetization (M_s) from (34.3 - 20.3 $emu.g^{-1}$) and the decrease in coercivity (H_c) from (674 to 158 O_e) are significantly affected by the increase of Zn^{2+} content.

1.4 Aim of the work

1- Synthesis a series of $CoCr_xFe_{2-x}O_4$ and $Co_{1-x}Mg_xFe_2O_4$ ferrite nanoparticles with different compositions where, x takes values ($0.0 \leq x \leq 1.0$, step 0.2) using sol-gel auto-combustion method.

2- Studying the influence of substitution concentration of ions and the calcination temperature of synthesized ferrite nanoparticles on the structural properties (crystallite size, lattice constant, density and hopping length) and surface morphology.

3- Studying the electrical properties which is consist of diffuse reflectance spectroscopy (DRS) to study the band structure and home-made cell with an LCR meter to study the dielectric properties (dielectric constant (ε'), dielectric loss angle ($tan\ \delta$), dielectric loss factor (ε''), and ac conductivity (σ_{ac})) of synthesized ferrite nanoparticles as a function of frequency in the range 50 Hz – 1MHz at room temperature.

4- Studying the magnetic properties (saturation magnetization (M_s), remanance magnetization (M_r), coercivity (H_c), magnetic moment (n_B), squareness ratio (M_r/M_s), and magnetic anisotropy (K)) of synthesized ferrite nanoparticles in applied field ranging from −15 to +15 kOe using vibrating sample magnetometer (VSM) at room temperature.