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Magnetic and Electrical Properties of Substituted Cobalt Ferrite /TiO_2 Nanocomposites

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1.1 Introduction

This chapter provides basic information about the concept of nanoparticles. It includes a brief introduction to the history of nanoscience and its applications. It also includes a brief review of the literature on the synthesis of ferrite nanoparticles. It also describes the aim of this research.

1.2 History, Nanoscience and their applications.

Due to the immense hope it has inspired for imminent scientific revolutions that will alter the course of technology and lead to numerous new discoveries and advancements, nanotechnology is at the front of the most significant and interesting fields in the domains of physics and other sciences. Nanotechnology is the process of regulating and modifying matter at the atomic scale. This control technique is comparable to nanoscale engineering, and the procedure of nanofabrication is usually associated to [1,2].

Nanomaterials can be defined as advanced materials with dimensions ranging in dimensions from (1-100) nm[3-5]. Nanoparticles have unique properties due to their important mechanical and physical properties that may lead to new and exciting applications, due to their very precise size and high grain size limits [6].

Nanomaterials have a wide range of uses [5]. Among the physical qualities that vary substantially at the nanoscale are electrical and magnetic properties. In reality, a curious magnetic phenomena appears when a ferromagnetic material is decreased in size to generate a nanoparticle (i.e. a 3D nano-object) [6, 7].

Magnetic nanoparticles are the most advanced and widely used materials in biotechnology and medicine. Since a few years, they've been used in technical applications like magnetic data storage. Because of their excellent chemical stability, electrical properties, magneto-optical properties, low cost, and unique magnetic behavior, magnetic ferrites have attracted a lot of attention from scientists and researchers. They are important magnetic materials with spinel structures for technological applications and basic research. These distinctive features are influenced by the preparation method, chemical make-up, particle size, porosity, and sintering temperature. Magnetic resonance imaging, computer parts, memory devices, antenna rod transformers, ferrofluids, magnetic recording medium, and satellite communication, and other applications make extensive use of spinel ferrite, and other disciplines [8, 9].

Many chemical processes have been developed to synthesize ferrite nanoparticles, all with the common property of mixing all chemicals at co-precipitation[9], sol-gel auto-combustion[10], microemulsiond[9], hydrothermal[11], spray pyrolysis procedures, etc., are few examples. With these wet-chemical processes, complex scheduling and poor production rates are prevalent [10, 11].

The process of chemical sol-gel and combustion are combined in the sol gel auto combustion technique. This method has shown a lot of promise in the creation of nanomaterials of the ferrite type [12,13]. Generally, this technique falls under the category of solution combustion. Over the past ten years, the use of the sol-gel combustion technique to create nanosized spinel ferrite powders has become more widespread [14,15].

1.3 Literature review

M. G. Naseri et al., (2010) [16]**;** Cobalt nitrate and iron nitrate were used as precursors in the thermal treatment procedure used to create the spinel cobalt ferrite $CoFe_2O4$ nanoparticles. According to XRD analyses, the particle sizes were achieved at calcination temperatures between (623 to 923 K) and were in the range of (12.5-39 nm). The nitrate ions and organic components were entirely eliminated after calcination at (823 and 923 K). The coercivity field and remanence ratio dropped after peaking. Magnetic studies showed that cobalt ferrite saturation and remanent magnetization increased with temperature. This approach is straightforward, economical, and sustainable.

P.S. Aghav et al., (2011) [17]**;** Citric acid is used as fuel in the sol-gel auto combustion process, they were able to synthesized a spinel ferrite system out of $CoFe_{2-x}Al_xO_4$ powders (x=0.0 to 1.0 in the step of 0.2). The produced samples feature a cubic spinel structure in a single phase, according to the X-ray diffraction examination. The Scherrer formula was used to determine the crystallite size, which ranged from 16 to 26 nm. The findings of SEM investigation revealed consistent grain development and a grain size of the order of (30nm). The saturation magnetization and coercivity were found to be at their greatest values, and they progressively dropped as the Al^{3+} level rose. Al^{3+} ions are used in place of Fe^{3+} ions, which results in a loss in magnetic characteristics. The structural and magnetic characteristics of $CoFe_2O_4$ are improved when Al^{3+} is substituted, as seen by these improvements.

Franco et al., (2012) [18]**;** By using the forced hydrolysis method,

$Co_{1-x}Mg_xFe_2O_4$ was synthesized and its magnetic characteristics were studied. All samples displayed strong, intense peaks that are compatible with the cubic inverse spinel structure, according to the results of the X-ray diffraction analysis. Furthermore, Scherrer's calculation indicated that the average crystallite size for all samples was about the same (4.5 nm). All samples are superparamagnetic at room temperature, according to magnetization measurements, and the saturation magnetization (Ms), which is with increasing molar magnesium concentration, is disclosed, (260 $emu.cm^{-3}$) and (160 $emu.cm^{-3}$) for x=0 and 0.6 respectivly, with the substitution of non-magnetic Mg^{2+} ions for the Co^{2+} ion in the spinel structure, the effective anisotropy constant (Keff) dropped.

Koferstein et al., (2013) [19]**;** Using a starch-gel technique, nanoscale $MgFe_2O_4$ was synthesized and analyzed. The end product of 550 °C calcining a (MgFe)-starch gel was a phase-pure nanosized $MgFe_2O_4$ powder. In contrast, calcination at (1100 °C) results in crystallites that are 129 nm in size and have UV-Vis studies on the nanopowder revealed that it exhibits an optical gap of 2.38 eV. (2.16 eV). They discovered that, depending on the calcination temperature, there are956+/ several saturation magnetizations (M_S). When the powder is calcined at a temperature of 900 °C, the M_S value is (20.0 emu/g), reaching a maximum of 37.7 emu/g. This value increases with higher calcination temperatures.

C. Drug et al., (2014) [20]; Using glycine as a chelating/fuel agent, glycine was used to prepare at $Mg_{1-x}Co_xFe_2O_4$ (x = 0.00, 0.17, 0.34, 0.50, 0.67, 0.84, and 1.00) 900°C. The development of the spinel phase and the eradication of the organic phases were both verified by infrared microscopy. The creation of the spinel mono-phase was verified for all samples by X-ray diffraction analysis. The Full Prof 2000 program's predicted crystallite size of between (42 and 78 nm) was discovered. The SEM micrographs demonstrated the development of aggregates of nanoparticles and validated the existence of uniformly shaped nanoparticles. According to the dielectric analysis, all materials exhibited typical dielectric behavior. When the frequency is high enough, both the dielectric constant and the dielectric loss are constant.

A. Manikandan and S. A. Antony, (2015) [21]**;** used the one-pot auto-combustion approach to successfully produce both pure $ZnFe_2O_4$ and $ZnFe_2O_4$ nanocrystals doped with Mn^{2+}. The inclusion of Mn^{2+} ions in the Zn2+ lattice site has been discovered to be highly sensitively reliant on structural, morphological, optical, and magnetic characteristics. The well-defined spinel phase is indicated by the observed diffraction peaks, and it was shown that an increase in Mn concentration causes a drop in crystal size from (23.25-17.53 nm). The FESEM images showed that the as-prepared samples are made up of uniformly well-crystallized nanocrystals with a spherical shape. The magnetic characteristics as measured by the VSM saw a significant shift; Mn^{2+} concentration increases Ms, Mr, and Hc values.

R. K. Panda et al., (2016) [22]**;** $CoFe_{2-x}Cr_xO_4$ was made in a series with x equal to 0, 0.15, and 0.3 using the auto combustion technique. The effect of Cr replacement on the presence of Cr^{3+} was investigated to see how it affected the electric and magnetic characteristics of the cobalt ferrite particles. there was a significant decrease in particle size as shown by XRD and FE-SEM calculations. At room temperature, magnetic characterization and Mossbauer spectroscopy were carried out. According to the study of the collected data, Cr^{3+} took the place of Fe^{3+} at the B-site (octahedral). It was discovered that the lower saturation magnetization and coercively was caused by magnetization reduction in the B-site.

N. Thomas et al., (2017) [23]**;** Samples of Mg-substituted cobalt ferrite were created utilizing a straightforward solution combustion technique at a relatively low temperature with glycine as the fuel. The spinel phase with Co^{2+} substitution by Mg^{2+} is easily synthesized using this approach, according to the structural characterization of the as-prepared samples acquired using the Rietveld refinement of the XRD pattern. As the replacement of magnesium rises, less heat is produced during burning, which results in smaller crystallites. The average crystallite size generated with magnesium substitution first increases, peaking at x=0.2, and then steadily drops to (57 nm) at x=1.0. Two peaks in the FTIR spectrum were visible, one of which matched the octahedral sites and the other the tetrahedral sites. Tetrahedral sites account for the peak at (about 600 cm^{-1}) while octahedral sites account for the peak at (about 400 cm^{-1}). The change in magnetic characteristics at room temperature upon replacement in these materials indicates a hard-to-soft magnetic transition. Dielectric characteristics display a behavior that resembles that of the spinel ferrite family, as has been observed. A Maxwell-Wagner interfacial type polarization may be able to explain this phenomenon.

M. Abdul Ammer Alsherefi et al., (2018) [24]; Synthesis was carried out using sol-gel auto-combustion $Mg_{1-x}Co_xFe_2O_4$ nanoparticles. Changes in Co^{2+} concentration affect electrical and magnetic characteristics, as shown. X-rays of the powder indicate a cubic spinel single-phase structure. Using Scherrer, the average crystallite size was calculated (53.12 nm). Lattice parameter rose with Co^{2+} concentration. With more Co2+, porosity rises. SEM demonstrated nanoscale crystallite growth on sample surfaces.

H. Kiswanto et al., (2018) [25]; They investigated how Zn^{2+} affected the magnetic and crystal characteristics of $Co_{1-x}Zn_xFe_2O_4$ nanoparticles. produced at 70 °C (0.2 to 0.8). All samples had a single-phase cubic spinel XRD pattern. Scherrer's formula was used to compute crystallite size (9.3 to 11.2 nm). Due to differing ionic radii, increasing zinc concentration increased lattice parameter (8.179 to 8.212). FTIR spectra indicated two peaks ascribed to octahedral and tetrahedral vibrations, confirming the metal-oxide stretching band.

A. M. Mohammad., (2019)[26] ; $Co_{1-x}Mg_xFe_2O_4$ and $CoCr_xFe_{2-x}O_4$, were synthesized and their structural, electrical, and magnetic characteristics were examined. These nanoparticles were made utilizing the sol-gel auto-combustion process. The Mg^{2+} substituted cobalt ferrite showed all of the key peaks associated with a single spinel structure in the XRD diffraction analysis, but the absence of peaks in the Cr^{3+} substituted as-burnt cobalt ferrite indicated amorphous samples. Spinel development is confirmed by the 600 and 700 C samples. All Cr^{3+} substituted cobalt ferrites developed spinel cubic structures during the 800 °C calcination process. Pictures taken with a FE-SEM show a particle size distribution that is virtually homogeneous, porous, and nanosized. Dielectric properties are measured using the LCR meter at room temperature (50Hz-1MHz). Cobalt ferrites replaced with Mg^{2+} and Cr^{3+} exhibit a decreasing dielectric constant (ε'), loss angle ($tan\delta$), and loss factor (ε'').

A. Omelyanchik et al., (2019) [27]; Cobalt, nickel, and ferrite were combined using the sol-gel spontaneous combustion method. In order to investigate the structural and morphological properties of the particles, techniques such as (XRD) and (EDX) were utilized. The as-prepared particles exhibit crystalline nature, monotonic elemental distribution, and a 17–29 nm particle size distribution. The produced particles have good magnetic characteristics, including variable saturation magnetization and magnetic anisotropy, or coercivity that is dependent on chemical composition.

S. M. Ansari et al., (2019)[28] ; The investigation of the particle size distribution and CFO surface morphology, oleic acid-based solvothermal and FE-SEM, examinations of $CoFe_2O_4$ nanoparticles were utilized. The magnetic properties of CFO NPs with regulated particle size was efficiently regulated by the OA concentration, according to precise magnetic measurements. According to the direct relation between the anisotropy constant and nanoparticle size, the magneto crystalline component controls the magnetic anisotropy in OA coated CFO.

R. Jabbar et al., (2020) [29]**;** Sol-gel precipitation with manganese (Mn^{+2}) doping was used to create spinel cobalt ferrites nanoparticles (NPs). Research was conducted using XRD, FTIR and (VSM), increase in the Mn^{+2} doping ratio, the average crystallite size

(D) increased, and subsequently decreased. The VSM hysteresis loop demonstrates the production of soft magnetic material and a reduction in saturation magnetization.

T. W. Mammo., (2020) [30] ; $CoFe_2O_4$ nan crystalline material is produced using the sol gel, auto combustion process. Using powder X-ray diffraction at room temperature, structural characteristics and phase formation were investigated (XRD). With a lattice parameter of 8.4277, the sample formation results in a pure cubic spinel. (FESEM) microstructural investigation revealed the sample's nanocrystalline structure with non-homogeneous grain sizes and grain shapes. FTIR characterization showed the spinel structure evolution at the tetrahedral and octahedral sites. The high resistive character of the sample was confirmed by the DC resistivity test, which was completed using a two-probe approach. In the frequency ranges of 100 Hz to 5 MHz, the dielectric and AC characteristics at room temperature were examined. At lower frequencies, the dielectric dispersion has been seen. Using the VSM approach, higher magnetization values have been measured.

K. Chandramouli, (2020)[31] ; Sol gel combustion was used to produce nanoparticles of complex ferrite. X-ray diffraction (XRD) assisted characterization reveals a spinel structure in a single phase with the space group of Fd^{-3}, in the $Cu_{0.7}Co_{0.3}Fe_xCr_xO_4$ composite material. Furthermore, the samples' crystal widths, as estimated by XRD data, ranged from 19.28 to 32.92 nm. The spinel structure was still there, according to the FTIR measurements unaltered even after doping with Cr ions. Despite the presence of irregularly shaped gains with sporadic moderate aggregation, materials that form polygonal grains may be seen in FESEM images. The component elements are present in the sample, according to the EDX analysis. The ferrite under research is semiconducting, as shown by the declining DC resistance pattern that is seen as temperature rises. VSM was used to define and calculate the saturation of magnetic features and sample strength.

P. Sinuhaj et al., (2021) [32] ; Co-precipitation at 200°C was used to prepare $CoFe_2O_4$. Microstructures, and magnetic properties were assessed XRD, and FE-SEM. According to XRD research, the peak of $CoFe_2O_4$ crystals decreases as the cobalt content rises. FE-SEM EDS verified the ferrite spinel structure in samples 1, 2, and 3. According to FE-SEM, particle size was decreased when Co formulations were increased. Spinel ferrite yields, according to FE-SEM research, at lower calcination temperatures.

C. J. Prabagaetr al., (2021) [33] ; Sol-gel auto combustion was used to create $Co_{1-x}Mn_xFe_2O_4$ nanoparticles with x = 0, 0.2, 0.4, and 0.6. Up to x = 0.2, XRD tests showed cubic spinel. In order to determine the crystallite size and strain, Scherrer and (W-H) were utilized. In Mn doped cobalt ferrites, metal-oxygen stretching bands were seen in FTIR spectra. Cobalt ferrite is identified by four sharp and potent Raman modes. Ferrite grains are seen in FESEM images to be spherical and less aggregated. The Mn-doped Cobalt ferrite materials contained Co, Fe, Mn, and O, according to an EDX analysis. Cobalt ferrite may be adjusted for technological applications by replacing the cobalt magnetic ions with Mn^{2+}.

G. A. Lone and M. Ikram (2022) [34]; Structure and dielectric characteristics of prepared spinel $CoFe_2O_4$ doped with nickel was studies. The samples were made utilizing a solid-state reaction technique, and their structural and dielectric properties were examined to determine the effect of doping. It was determined by rietveld refinement that each of the produced materials had a single-phase FCC cubic spinel structure with space group (Fd3 m). In contrast to Ni_{2+} occupancy, which is rising, the cationic distribution reveals a decrease in Fe^{2+} occupancy. FESEM and energy EDS were used to examine the samples' microstructure and elemental composition. The dielectric constant is temperature independent up to a point of around 270 K, then it begins to increase with the increase in temperature. This temperature begins to decrease with the increase of the activation ratio.

L. E. Caldeira (2022) [35] ; Investigated how $CoFe_2O_4$ structural, optical, and magnetic characteristics were affected by temperature and annealing time. The sol-gel precursor was created and heat treated at 550, 650, and 750 °C for 2, 4, and 6 hours, respectively. XRD, SEM, and Raman were used to examine the microstructure. Over 6-hour treatments at temperatures over 650 °C resulted in a decrease of inverted nanoparticles and an increase in crystal size. The VSM was impacted by the initial annealing conditions, but not the iron band gap. The sample that was annealed at 550 °C for two hours had the maximum coercivity. The characteristics of $CoFe_2O_4$ were altered by both initial conditions, however the effects were not identical.

1.4 Aim of the study

1- Preparation of magnesium cobalt ferrite and grafted with titanium by sol-gel auto combustion method.
2- Preparation of pure nickel cobalt ferrite and doped with titanium by sol-gel method.
3- Studying the structural, electrical and magnetic properties of substituted cobalt ferrite /TiO_2 nanocomposites.