SYNTHESIS, MICROSTRUCTURAL PROPERTIES AND APPLICATIONS OF COBALT FERRITE : A REVIEW

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Abstract:

This review literature focuses on the synthesis and properties of divalent doped cobalt ferrite ($CoFe_2O_4$) using sol-gel autocombustion method. Doping cobalt ferrite with divalent ion such as Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+} etc. offers exciting possibilities for tailoring its magnetic properties. The review provides an easy to understand overview of synthesis process, emphasizing the key steps and parameters involved. The effect of different divalent dopant and their concentration on their structural and magnetic properties of the material are discussed. The magnetic properties such as saturation magnetization and coercivity can be finally tuned by adjusting dopant concentration. Additionally potential application of these materials in the field such as magnetic storage, catalysis, and biomedicine are highlighted. The review concludes by identifying future research directions and challenges in the field offering insights into future advancement in the synthesis and applications of divalent doped cobalt ferrites material.

Keywords: Spinel ferrites, Cobalt ferrite, Synthetic methods, Cation distribution, Applications.

Introduction:

Ferrites have attracted significant attention in various technical fields owing to their wide range of applications in electronic circuits, such as serving as inductors, enabling high-frequency systems, functioning as power delivery components, contributing to magnetic recording media, forming essential transformer cores, and even finding utility as microwave absorbers [1,2] leads to very low eddy current losses. In recent times, spinel ferrite nanoparticles have captured immense interest from the perspective of fundamental science due to their exceptional properties and the vast array of promising applications they offer. These uses cover a broad spectrum of areas, encompassing diverse fields such as dense data storage, catalyst utilization, gas sensing, the development of rechargeable lithium batteries, information retention systems, utilization in magnetic bulk cores, creation of magnetic fluids, production of microwave absorbers, as well as applications in medical diagnostics and therapeutic procedures. The unique characteristics of spinel ferrite nanomaterials make them highly versatile and sought-after for advancing various technological advancements and scientific breakthroughs across multiple industries [3-8].

Cobalt ferrite continues to be a subject of significant interest, primarily because of its distinctive and captivating properties, which hold great potential for various applications. The control over these characteristics is made possible through the management of factors like the chosen synthesis method, structural form, dopant selection and concentration, and the distribution of cations within the tetrahedral and octahedral sites. A multitude of research studies have extensively explored the chemical, physical, electrical, magnetic and optical characteristics of both undoped and doped Co ferrites. This wealth of knowledge provides valuable insights into the material's behavior and paves the way for exciting possibilities in diverse technological and scientific endeavors. The extensive study and investigation on nanocrystal cobalt ferrite and their derivatives have been observed from reported studies. Numerous research endeavors have been dedicated to the creation and exploration of $CoFe_2O_4$ nanoparticles and their magnetic characteristics. Cobalt ferrite, commonly recognized as a semi-hard magnetic material, exhibits a distinct crystal structure, known as an inverse spinel type. In this arrangement, all cobalt ions are situated within octahedral sites, while iron ions occupy both tetrahedral and octahedral positions.

Synthetic method and influence on properties of cobalt ferrite

Several techniques have been documented for synthesizing both pure and doped cobalt ferrite nanoparticles. These methodologies include sol-gel processes, co-precipitation, polymerized complex formation, hydrothermal synthesis, thermal plasma techniques, solvothermal methods, thermal decomposition, ultrasonic cavitation, mechanical alloying, ball milling, pulsed laser deposition, reverse micelle, micro-emulsion, microwave-assisted synthesis, electrochemical procedures, and auto-combustion [9–13]. Among various techniques for creating nanoparticles, the sol-gel method combined with post-annealing stands out as a straightforward, achievable, and highly efficient approach. This process yields nanoparticles of exceptional purity even when carried out at lower temperatures.

Sol-gel Method

Sol-gel auto combustion method is combinations of sol-gel and combustion method. The sol-gel technique stands out as a widely recognized approach for crafting innovative metal oxide nanoparticles and hybrid oxide composites. This method offers considerable influence over the textural and surface characteristics of the resultant materials. The sol-gel process typically involves a series of stages leading to the production of the final metal oxide, list the steps involved**.**

- Preparation of metal precursor solution: Dissolve the metal salts (e.g., cobalt nitrate, iron nitrate, and the divalent dopant salt) in an appropriate solvent, such as water or ethanol. The metal salts should be in stoichiometric amounts to obtain the desired composition of the final cobalt ferrite.
- Formation of the gel: Mix the metal precursor solution thoroughly until a homogeneous solution is obtained. Then, add a suitable gelation agent, such as urea or citric acid, to the solution. The gelation agent helps in the formation of a gel by increasing the viscosity of the solution.
- Evaporation: Heat the metal precursor solution with the gelation agent to evaporate the solvent and concentrate the solution. This step helps in the formation of a gel-like consistency.
- Auto-combustion: Place the gel in an oven or furnace and heat it. Due to the exothermic nature of the decomposition of the gelation agent (e.g., urea), it undergoes spontaneous combustion. This combustion reaction drives the formation of the cobalt ferrite and results in the release of gaseous products, such as CO_2 and H_2O.
- Calcination: After the auto-combustion process is complete, the resulting product will be a mixture of cobalt ferrite and other by-products. To remove the residual carbon and other impurities, the combustion residue is further heated at a higher temperature in a process called calcination.
- Final product collection: Once the calcination is complete, cool down the product, and collect the final divalent doped cobalt ferrite powder.

The benefits associated with this approach encompass cost-effectiveness, simplicity, the ability to operate at modest temperatures without necessitating specialized machinery, and the potential to achieve a uniform nanoparticle size distribution.

V. R. Bhagwat *et. al*. synthesized [14] $Cofe_2O_4$ via sol gel autocombustion method using 3 different fuel(Ethylene glycol, Glycine, Urea) .The ratio of metal nitrates to fuel was set at 1:2 for ethylene glycol, 1:3 for glycine, and 1:4 for urea. To maintain a neutral pH of 7 in the solution, ammonia solution was introduced. Notably, the synthesis of cobalt ferrite nanoparticles was achieved at a relatively low temperature of approximately 110 °C. Subsequently, the synthesized powder underwent a sintering process at 550 °C for duration of 4 hours. It's noteworthy that as the nanoparticle size increased, saturation magnetization, coercivity, and remanent magnetization also exhibited an upward trend.

Sharma *et. al*. prepared $Cofe_2O_4$ by sol–gel auto-combustion method, The study uncovered the promising antimicrobial properties of $CoFe_2O_4$ nanoparticles (NPs), suggesting their potential application in a wide range of antimicrobial treatments. These findings open up new possibilities for exploring other ferrites and composite structures in similar areas of research.

Influence of substituent on properties of cobalt ferrite:

Mg doped cobalt ferrite

H. S. Mund and B. L. Ahuja [15] synthesized Mg^{2+} doped, cobalt ferrite via sol gel auto combustion method. Analysis of magnetization data reveals that higher concentrations of Mg^{2+} lead to a decrease in saturation magnetization. The presence of a magnetic moment is observed in cobalt ferrite, and interestingly, when magnesium is introduced into the structure, it brings about changes in the material's magnetic characteristics. This substitution effectively shifts cobalt ferrite's behavior from being a hard magnetic material to becoming a soft magnetic material. The analysis via X-ray diffraction confirming the existence of a sole-phase cubic structure entirely free from any impurities. G. L. Jadhav *et. al*. [16] prepared thin films of cobalt ferrite doped with magnesium, represented as [$Co_{1-x}Mg_xFe_2O_4$], were fabricated on pristine glass substrates via the spray pyrolysis technique**.** TEM analysis provided clear evidence of the films' nanocrystalline nature, as indicated by the observed particle size. Interestingly, as the Mg content denoted as "x" increased, the band gap of the films showed a noticeable reduction, decreasing from 2.83 eV to 2.37 eV. Incorporating magnesium into cobalt ferrite thin films leads to significant alterations in their morphological, structural, optical, and wettability attributes.

Cu doped cobalt ferrite

S. Saleem *et. al***.** [17] synthesized Cu doped cobalt ferrite via sol-gel technique. The XRD analysis confirmed the presence of spinel-phased crystalline structures in the specimens, and importantly, no impurity phases were detected. Measurements were conducted across a spectrum, encompassing average grain sizes spanning from 4.55 to 7.07 nanometers, lattice constants ranging between 8.1770 and 8.1097 Å, cell volumes varying from 546.7414 to 533.3525 cubic Å, and porosity levels extending from 8.77percent down to 6.9 percent. The SEM analysis displayed noticeable alterations in the morphology of the specimens as the Cu^{2+} content increased. Furthermore, the electrical studies demonstrated that even a small amount of Cu^{2+} doping resulted in notable enhancements in the electrical properties. The incorporation of Cu^{2+} into cobalt ferrite nanoparticle led to significant improvements in their structural and electrical characteristics, rendering them extremely for a wide range of applications, including electrical devices, diodes, and sensor technology. M. P. Ghosh *et. al*. [18] Nanoparticles of cobalt ferrite with copper substitution, denoted as [$Cu_xCo_{1-x}Fe_2O_4$: x = 0.00, 0.15, 0.30, 0.45, 0.60], were synthesized using the chemical coprecipitation method. The X-ray diffraction patterns provided clear evidence of the production of cobalt ferrite nanoparticles in a single-phase structure, along with the presence of microstrain in the minute crystals. Magnetization measurements further indicated that the introduction of Cu^{2+} ions into cobalt ferrite had an observable impact. Ferrite results decreased in coercivity and saturation magnetization. The M-T curves demonstrated that all the samples had Curie temperatures above room temperature. Notably, as the Cu concentration increased, the Curie temperature decreased. J. Balavijayalaxmi *et. al*. [19] the impact of copper on the magnetic characteristics of nano-sized cobalt ferrite, synthesized via the co-precipitation method. The analysis revealed that the average dimensions of the Nano-crystalline particles fell within the 37 to 52 nm range. Notably, as copper content increased through substitution, a discernible reduction was observed in several magnetic properties, including saturation magnetization (Ms), remanent magnetization (Mr), and coercivity (Hc). The SEM micrographs provide visual evidence of sponge-

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like and plate-like structures becoming more prevalent as the copper content rises. A. Samavati, *et. al*. [20] Cobalt ferrite nanoparticles synthesized using the co-precipitation method. The study investigated the variations in crystal structure, optical properties, and antibacterial behavior of the samples concerning Cu-substituted content. As the Cu concentration increased, the Nano-particle size decreased from approximately 30 nm to around 20 nm. Cu^{2+} ion substitutions lead to a decrease in specific saturation magnetization (MS), remnant magnetization (Mr.), and coercivity (Ch.) in spinel ferrites. Additionally, the FTIR spectra reveal distinct absorption bands at approximately 595 cm−1 and 419 cm−1. We conducted room temperature measurements using a VSM to study the ferromagnetic properties of nanoparticles containing copper-substituted cobalt ferrite. Furthermore, our investigations unveiled that the replacement of cobalt with copper results in elevated levels of reactive oxygen species, subsequently amplifying the antibacterial efficacy.

Ni (Nickel) doped cobalt ferrite

N. B. Velhal *et. al*. [21] Nickel-doped cobalt ferrite nanoparticles, denoted as $Co_{1-x}Ni_xFe_2O_4$, were synthesized via auto-combustion technique at low temperatures. The X-ray diffraction pattern reveals the formation of cubic spinel phase with minor reflections of Fe_2O_3 phase. Incorporating 0.4 Ni into cobalt ferrite leads to a substantial increase in crystallite size 44 nm and a higher magnetic moment 92.86 emu/gm. The magnetic properties indicates that as Ni content increases the Ms(magnetic saturation), Mr (remanant magnetization), Hc (coercivity) and ratio of Mr/Ms decreases, this is due the lower magnetic moment of nickel. Also magnetic properties show the temperature dependent behavior, the values of magnetic saturation, remanant magnetization, coercivity and ratio of Mr/Ms decreases with temperature. A. Kumar *et. al*. [22] In this investigation, researchers focused on synthesizing Nickel-doped $CoFe_2O_4$ ferrite nanoparticles using the chemical co-precipitation method. They sought to explore the effects of Nickel doping on the properties of the ferrite nanoparticles. The X-ray diffraction (XRD) patterns and transmission electron microscopy (TEM) images revealed that the nanoparticles formed a single-phase structure of $Ni_xCo_{1-x}Fe_2O_4$. As the Ni content increased, the crystallite size increased, while the lattice parameters decreased. The average crystallite size ranged from 8.10 to 10.13 nm, while the particle size estimated from TEM images varied between 5-20 nm.

Zn (zinc doped cobalt ferrites)

Iqbal A *et. al*. [23] In the case of Zn-substituted Co ferrite nanoparticles synthesized through the sol-gel method, it was observed that the inhibition of bacterial growth rate was more pronounced against methicillin-resistant S. aureus strains compared to E. coli strains. Deepali D. Andhare *et. al*. [24] Using the chemical co-precipitation method, researchers synthesized Zn-doped $Co_{1-x}Zn_xFe_2O_4$ nanoparticles with varying Zn content (x=0.0, 0.3, 0.5, 0.7, and 1.0). After thermal studies X-ray diffraction (XRD) analysis confirmed the presence of a single-phase cubic structure in the Co-Zn ferrite nanoparticles. Scanning electron microscopy (SEM) images revealed that the grains exhibited a spherical nature, and the degree of agglomeration decreased as the concentration of zinc increased. To validate the stoichiometric proportions of elements in the samples, energy-dispersive X-ray spectroscopy (EDX) spectra were obtained. Moreover, the energy band gap of the prepared samples was calculated and found to increase from 2.258 eV to 2.8306 eV with the progressive addition of zinc. This study demonstrates the tunability of the material's band gap by adjusting the Zn concentration, opening up possibilities for potential applications in optoelectronic devices and other fields.

Cr (Chromium) Substituted cobalt ferrite

G. Raju *et. al*. [25] Cobalt ferrite materials doped with chromium ions (Cr^{2+}) have been effectively synthesized via the sol-gel auto-combustion method**.** XRD analysis confirmed a spinel structure with lattice parameters ranging from 8.328 to 8.412 Å. The powder samples exhibited an uneven distribution in both size and shape, at different concentration as observed in the FESEM (Field Emission Scanning Electron Microscope) images. The VSM measurements revealed a decrease in saturation magnetization with increasing Cr^{2+} content. However, the coercive force and remnant magnetization initially increased with Cr^{2+} content, then decreased. These findings provide important insights into the magnetic behavior, offering potential for improved magnetic materials in various applications.

Sr (Strontium doped cobalt ferrite)

M. K. Shobhana *et. al*. [26] Strontium-doped cobalt nanoferrites ($Co_{1-x}Sr_xFe_2O_4$) were prepared using a sol-gel combustion method. The study explored the phase, nanocrystalline properties, and optical characteristics of the as-prepared and annealed samples for two different strontium concentrations (x = 0.1 and 0.2). In this study, nanoferrites were examined, and their average crystallite sizes were found to be 36 nm, 40 nm, and 30 nm, respectively, for nanoparticles with lattice parameters measuring 8.25 Å, 8.30 Å, and 8.30 Å. The confirmation of the spinel structure of the ferrite crystals was accomplished using Raman spectroscopy. Additionally, the presence of cations at both the octahedral and tetrahedral sites in the nanoparticles was successfully confirmed through the utilization of X-ray photoelectron spectroscopy. A. Mir *et. al*. [27] investigated Strontium-doped Cobalt Ferrites using a sol-gel auto-combustion method and sintering at 900°C. XRD analysis confirmed a shift from a spinel to perovskite structure with strontium doping, accompanied by a decrease in crystallite size. At higher strontium levels, crystallite size increased due to ferric ion agglomeration. UV-Visible analysis confirmed that all samples were electrical insulators.

Applications of divalent doped cobalt ferrite

In this overview, we provide a concise summary of the latest notable advancements concerning the utilization of cobalt ferrite nanoparticles infused with divalent transition metals across various domains. These encompass their attributes in terms of coloration, magnetic responsiveness, catalytic behavior, antimicrobial potential, biological relevance, and dielectric characteristics.

Applications of coloristic properties

T. Dippong *et. al.* [28] Cobalt ferrite, a dark-hued compound, holds significant value as a black pigment in the ceramics sector due to its remarkable attributes such as robust chemical and thermal stability. Researchers explored the incorporation of $Zn_{0.6}Co_{0.4}Fe_2O_4$ nanoparticles to impart coloration to both translucent and opaque glazes for ceramic tiles. The process involved a sequential approach of sol-gel synthesis followed by post-annealing, resulting in the creation of Zn-doped cobalt ferrites (specifically, $Co_{0.3}Zn_{0.7}Fe_2O_4$ and $Co_{0.7}Zn_{0.3}Fe_2O_4$) nestled within a SiO_2 framework. These composite materials were then harnessed as ceramic pigments, offering shades ranging from deep gray to intense black.

Applications of magnetic properties**:** Co ferrite, a magnetic nanomaterial valued for its robust HC and MS, undergoes transformations when doped with nonmagnetic ions. This results in a reduction in MS, HC, TC, and the anisotropy constant (K), altering its magnetic properties from hard-magnetic to superparamagnetic behavior. This evolution opens doors to diverse applications. Researchers H. S. Mund and B. L. Ahuja embraced this concept, creating Mg^{2+}doped variants ($Co_{1-x}Mg_xFe_2O_4$, where x ranges from 0.0 to 1.0) using a sol-gel autocombustion technique.

Application of catalytic activity**:** Doped Cobalt Ferrites, containing elements like Chromium (Cr), Manganese (Mn), Cobalt (Co), and Zinc (Zn), hold promise as catalysts for breaking down stubborn organic compounds in wastewater and enhancing organic synthesis. A study by V. Maruthapandian et. al. [29] investigated CoxNi1−xFe2O4 nanoparticles (with varying Ni content from 0.0 to 1.0) synthesized through a citric acid-assisted sol-gel combustion method interestingly, these nanoparticles initially showed lower catalytic activity compared to bulk Nickel Ferrite. However, as the Ni content increased, their catalytic activity and electron transfer rates improved, suggesting that Nickel enhances their catalytic properties and electron transfer efficiency.

Applications of antimicrobial activity**:** Given the escalating bacterial resistance to traditional drugs, there's a growing interest in alternative antimicrobial solutions. One promising avenue involves the development of innovative multifunctional materials with antimicrobial properties that can be used in drug delivery systems. Such materials offer the potential to reduce the required antibiotic concentration. In a study by L. Zhang et al. [30], it was found that CuxCo1−xFe2O4 nanoparticles (with varying x values from 0.0 to 1.0) exhibited notable bactericidal effectiveness against gram-negative E. coli bacteria.

Conclusion:

Cobalt ferrite's distinctive and captivating properties pave the way for numerous promising avenues in terms of potential applications. Numerous studies have extensively investigated the characteristics of both undoped and doped Cobalt ferrites, encompassing their physical, chemical, magnetic, electrical, and optical properties. The incorporation of dopants and the advancement in synthesis methods have contributed to the significant improvement of ferrite nanoparticles' properties. Particularly, the introduction of divalent transition metal dopants into Co ferrites has resulted in excellent attributes, while the ability to customize their particle size, shape, purity, and chemical composition has made them highly promising for the next generation of nanomaterials. These tailored nanomaterials hold great potential for diverse applications in industries, environmental remediation, and medical fields. Provide a concise summery of the key finding from reviewed literature. Emphasize the significance of divalent doped cobalt ferrites as promising materials with tunable properties for various applications. Reiterate the potential impact of further research in this field and its contribution to advancing technology and scientific knowledge.

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