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A Review on Developments in Spinel Ferrite Nanomaterials: Synthesis, Characterization, and Diverse Applications

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Abstract
This paper explores a review on the synthesis, characterization, and wide range of uses of doped spinel ferrite nanoparticles, highlighting their important role in biosensors, industrial electronics, water treatment, transducers, transformers, cancer treatment, and magnetic resonance imaging. Substitution in the lattice sites of spinel ferrites with metals improves their electrical and magnetic characteristics, which makes them useful for a variety of applications, including microwave absorbers, magnetic fields, and biomedical devices. Spinel ferrites' physical characteristics can be altered to produce better performance by substitution of metallic atoms. Oxygen vacancies, crystal defects, and unsaturated metal cations exist on the surface of spinel ferrite magnetic nanomaterials. For this reason, hydroelectric cells that dissociate water molecules at room temperature have been fabricated using these materials. The dissociation of water molecules generates electricity in hydroelectric cells, which is revolutionary research of 21st century. The objective of this review is to assist researchers in maximizing the effectiveness of these adaptive materials by offering information on the selection of suitable magnetic ferrites according to anticipated applications.

Keywords: *Spinel Ferrite, Hydroelectric Cells, Magnetic, Metal Substitution.*

1. Introduction

Spinel ferrites are metallic oxides containing iron, with the chemical formula AB_2O_4. In this formula, A and B refer to different lattice sites, typically called tetrahedral and octahedral sites, respectively. The metal cations in spinel ferrites occupy these positions (A and B). The amount, kind, and substitution of the metals (cations) throughout the crystal structure have a a significant impression on the ferrites' physical and chemical characteristics [1-3]. [Das, S B et al., 2022]. Figure 1 shows a typical crystal structure of spinel ferrite. Polycrystalline magnetic materials have drawn interest from different sectors, including physical sciences, medicine, materials science, and engineering, because of their notable and distinguishing features.

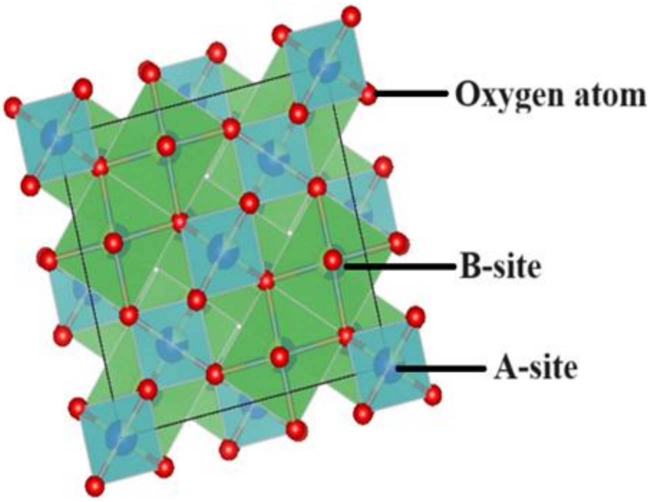

Figure 1 Crystal Structure of Spinel Ferrite

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[Shankar, U et al., 2022; Sarkar K et al, 2024]. Ferrites are fascinating both from practical and theoretical perspectives [4-7]. Nanoparticles of magnetic ferrites such as $CoFe_2O_4$, $MnFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$, and $NiFe_2O_4$ are particularly notable for their thermal and chemical stability, distinctive structural properties, and wide range of technological applications, such as drug delivery, biosensing, photocatalysis, humidity sensing, permanent magnets etc. [Salih, S.J. et al, 2023]. Because of its enhanced cubic anisotropy cobalt ferrite ($CoFe_2O_4$) is classified as a hard-magnetic material [8-10]. Its characteristics render it appropriate for use in magnetic storage as well as several other applications, such as drug delivery, MRI, and hyperthermia. One important ceramic material is zinc ferrite ($ZnFe_2O_4$) nanoparticles, which are known for their important features like enhanced electrical resistivity and low power loss. It also displays large curie temperature and permeability. Due of these characteristics, $ZnFe_2O_4$ can be used in diverse technological applications, including wave absorbers (electromagnetic), RF circuits, transformer cores, data storage, and biological therapeutic uses. [Kumar V et al., 2021]. The objective of this review is to provide an overview of the diverse applications of spinel ferrite nanoparticles along with some synthesis and characterization methods [11]. It aims to highlight their significant roles in various fields, including biosensors, industrial electronics, and biomedical applications. Additionally, it seeks to assist researchers in optimizing the use of these adaptive materials by offering detailed insights into their properties and potential uses [12].

2. Synthesis of Ferrite Nanomaterials

2.1. Sol-Gel Method

The sol-gel method, depicted schematically in Fig. 2, is widely employed to synthesize magnetic nanoparticles (NPs) with controlled nanostructures for engineering applications due to its ability to regulate shape and size. This method is straightforward and cost-effective; however, the primary limitation is the impurity of the final product, necessitating thermal treatment to achieve high-purity and crystalline nanomaterials [Das, S B et al., 2022; Shankar, U et al., 2022; Kumar V et al., 2021]. In the sol-gel process, the precursor solution undergoes polymerization or hydrolysis reactions to form a sol [13]. In order to produce a gel, polymers are added or sol condensation is used. This is accompanied by straightforward solvent evaporation to create ferrite nanomaterials. This technique's primary benefits are its low temperature requirements, highly regulated synthesis, and easy experimental setup. The sol-gel auto-combustion approach, which combines chemical sol-gel and combustion processes, can also be used to produce ferrite nanoparticles [14].

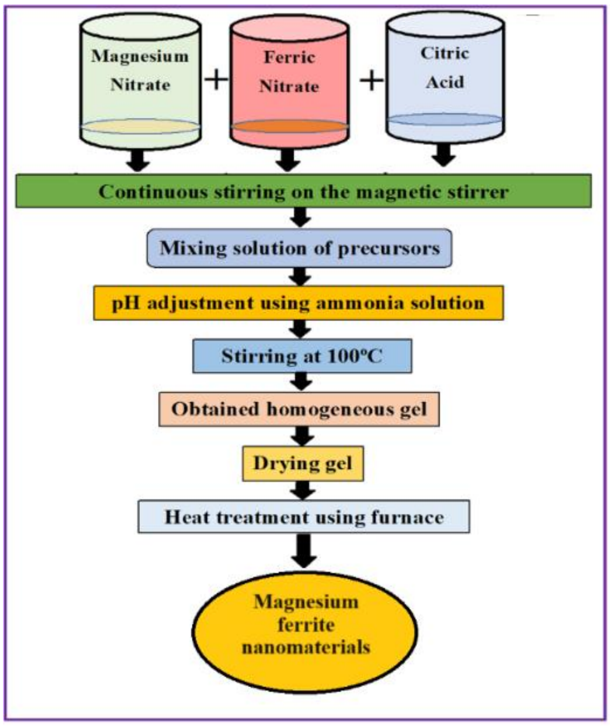

Figure 2 A Sol-Gel Process to Prepare Magnesium Ferrite Nanomaterials

2.2. Co-Precipitation Method

A simple and economical approach to producing magnetic NPs is co-precipitation. Spinel ferrites with a homogenous structure, excellent purity, and tunable size are produced by this technique. This process involves mixing a base—which serves as a precipitating agent—with a solution that contains stoichiometric concentrations of metal salts, such as nitrates, sulfates, or chlorides, at hot enough temperatures. It is significant to remember that the dimensions and shape of the nanomaterials can be

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controlled by variables that impact crystal development and particle aggregation, such as temperature, pH, and salt content [Salih, S.J. et al, 2023]. The precipitation-induced solid mass is gathered and cleaned. The hydroxides are then calcined to yield crystalline oxides. The spinel ferrites produced via this method are structurally homogeneous, highly pure, and size-controlled.

2.3. Hydrothermal Method

Hydrothermal method employs various wet-chemical processes to create crystalline magnetic NPs. These methods are simple and effective, capable of producing high-purity NPs with controllable morphology. Hydrothermal method, on the other hand, uses temperatures higher than the boiling point of water to initiate chemical processes in a solution of water. It uses autoclaves or high-pressure reactors to reach high temperatures and pressures. This method is also helpful for creating hollow and shaped spinel ferrites, like cubic structures and nanoflowers [Salih, S.J. et al, 2023]. Particle size, structure, and other physical characteristics can be efficiently modified by varying parameters such reaction temperature, duration, and doping agents.

3. Characterization of Spinel Ferrites

3.1. X-ray Diffraction

One of the most used methods for analyzing NPs is X-ray diffraction (XRD). The crystalline structure, phases, constants (lattice), and crystallite size are all important information that may be obtained by XRD [Sarkar, K et al., 2014, 2015, 2016, 2017, 2020, 2022, 2023]. The Scherrer equation, which examines the widening of the strongest peak in the XRD diffractogram of a specific specimen, is commonly used to assess crystallite size. Das et al have reported the crystallite size of yttrium substituted CoFe2O4 materials ranging from 17 to 32 nm [Das, S.B et al., 2022]. Shankar et al. found the variation of crystallite size from 10 to 22 nm of silver substituted magnesium ferrite nanomaterials [Shankar U et al., 2022]. Kumar et al. have reported the crystallite size ranging from 17 to 34 nm of Na-substituted $MgFe_2O_4$ nanomaterials [Kumar, V et al., 2023].

3.2. FTIR Analysis

A number of additional methods are also utilized to ascertain the size, content, structure, and various other essential characteristics of nanoparticles (NPs). One such method is Fourier transform infrared spectroscopy (FTIR), which analyzes electromagnetic radiation absorption in the mid-infrared range (4000–400 cm^{-1}). Various research studies indicate that for spinel ferrite the FTIR wavenumbers related to metal oxide bonds ranges from 415 cm^{-1} to 600 cm^{-1} [Das, S. B et. al., 2022; Shankar, U et al., 2022; Kumar, V et al., 2023]

3.3. Optical Characterization

Two types of optical characterizations are used to analyze spinel ferrites. These are Uv-Visible and photoluminescence (PL) spectroscopy. The Uv-Visible spectroscopy is helpful in determining the absorbance of the spinel ferrite between 200 to 800 nm wavelength. The absorbance data is helpful in determining the direct band gap of the spinel ferrite utilizing the Tauq equation. Research groups have utilized the Tauq equation and reported the direct band gap of spinel ferrites ranging from 1.7 to 4 eV [Das, S. B et. al., 2022; Shankar, U et al., 2022; Kumar, V et al., 2023]. The PL spectroscopy is basically used to observe the defects in the spinel ferrites. In PL spectroscopy, under a suitable excitation wavelength, an emission wavelength is noticed. This emission wavelength relates the crystallographic defects and the oxygen deficiencies present in the crystalline structure of the spinel ferrites. Some research groups have reported emission wavelengths ranging from 450 nm to 530 nm [Das, S. B et. al., 2022; Shankar, U et al., 2022; Kumar, V et al., 2023]

3.4. Vibrating Sample Magnetometer

To observe the M–H loops of magnetic nanomaterials and determine characteristics like saturation magnetization (M_s), coercivity and remanent magnetization (M_r), another method is vibrating sample magnetometry (VSM). This technique makes it possible to investigate how a nanoparticle's magnetic characteristics change with temperature, time, and magnetic field. Magnetic characteristics of materials are impacted by metal substitutions at lattice sites. Researchers have reported significant changes in magnetic properties with doping. Das et al have reported 42 to 70 emu/g of Y^{3+} substituted $CoFe_2O_4$ materials [Das, S.B et al., 2022] Kumar et al. have reported M_s ranging from 4 to 7 emu/g of $ZnFe_2O_4$ materials [Kumar, V et al., 2021]

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4. Application of Spinel Ferrites

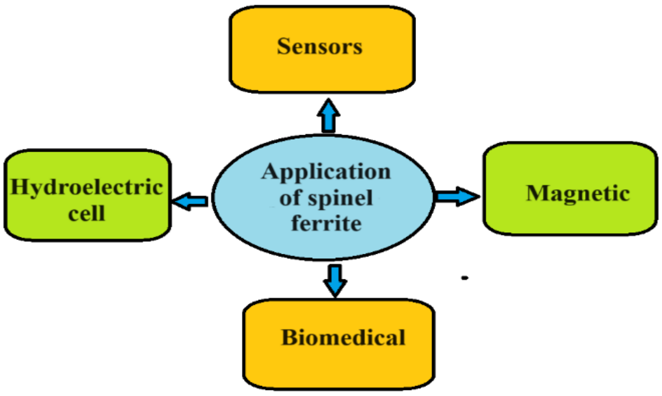

Figure 3 Applications of Spinel Ferrites

4.1. Sensors

Electronic equipment known as sensors are used to identify changes in the materials in an atmosphere. High signal-to-noise ratios, low detection limits, and remarkable sensitivity characterize ferrite nanoparticle-based sensors. Humidity monitoring represents one of the most popular uses for these sensors. Humidity control is crucial in both household and commercial settings because it promotes human convenience, controls storage conditions, and guarantees the best possible working conditions for a range of industrial processes and equipment. Because of their small size of grain, high surface area for adsorption of water vapor, and low barrier height, $ZnFe_2O_4$ nanoparticles are very susceptible to humidity [Salih, S.J. et al, 2023]. Effectiveness in identifying oxidizing gases, such chlorine, has also been shown for Co, Cu and Ni ferrite nanoparticles. Because of their stability and high coercivity (H_c) values, $CoFe_2O_4$ sensors and actuators are renowned for their dependability and extensive application. [Salih, S.J. et al, 2023].

4.2. Magnetic Application

Magnetization is dependent on grain size because of differences in exchange interactions between A and B sites. The magnetic particles should be nanoscale to restrict exchange contacts amongst adjacent grains and reduce media noise in magnetic recording (high-density). Furthermore, nanoparticles with large H_c are needed to achieve high storage density. Spinel ferrites' cationic arrangements among octahedral and tetrahedral sites, composition, particle size, and crystal structure all affect their magnetic characteristics, which include coercivity, saturation magnetization (M_s), and remanent magnetization (M_r) [Das, S.B et al, 2022]. As such, spinel ferrites can display paramagnetic, ferromagnetic, and antiferromagnetic properties. Hard materials are defined as having a high coercivity, whilst soft materials are defined as having a low coercivity. Permanent magnets require the materials which have high coercivity. Soft ferrites are perfect for electronic engineering uses including cores (transformer), inductors (high-frequency), and microwave equipments because they have low coercivity values and may have their magnetization altered. [Kumar, V et al., 2021; Shankar, U. et al., 2022]

4.3. Biomedical Applications

In order to be used in biomedical engineering spinel ferrite nanoparticles need to be biocompatible, have large Ms values, and be stable in aqueous solutions without aggregating. These nanoparticles can be used intracellularly to promote medication administration, induce magnetic fluid hyperthermia, and activate the metabolism via thermal excitation. For biological applications, the physical characteristics of $CoFe_2O_4$ have attracted a lot of attention, particularly its great stability. Drug delivery, imaging, and brain tumor treatments have all been applied to cobalt ferrites. Nevertheless, $CoFe_2O_4$ nanoparticles at elevated levels can discharge metal ions that penetrate cells and induce cytotoxicity [Salih, S.J. et al, 2023]. This may occur via blocking the production of proteins and cell the transcription process, which would change cellular functioning. To cure oncological disorders, hyperthermia is a therapeutic technique in which living tissues—including healthy and carcinoma cells—are continuously overheated (over 43°C), resulting in necrosis [Salih, S.J. et al, 2023]. A promising treatment is magnetic hyperthermia, which is brought on by magnetic nanoparticles through magnetic induction. It destroys and heats tumor tissue while causing the least amount of harm to tissue that is healthy. To help remove damaged tissues at a particular temperature range, this additional therapy for malignant tumors uses suitable magnetic nanoparticles in a magnetic field to produce heat. A pictorial view of some applications is presented in Fig. 3.

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4.4. Hydroelectric Cell Application

The hydroelectric cell (HEC), a novel green energy portable device that was recently developed, is an example of a device for splitting water molecules without the use of electrolytes. Figure 4 shows a schematic diagram of HEC

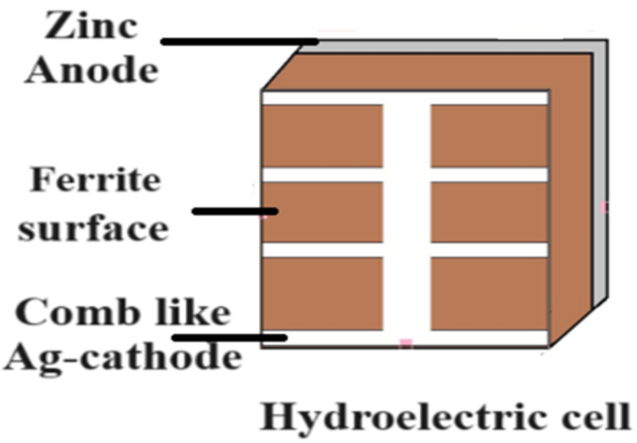

Figure 4 A Schematic Diagram of HEC

Previous research studies have shown that the hydroelectric cells have been fabricated using nanoporous and oxygen-deficient materials [Kumar, V et al., 2022]. This cell has an inert silver cathode arranged in a comb like pattern on one side and a zinc anode coupled with it on the other [Kumar, V et al., 2022]. Ionic conduction within the cell is facilitated by the carefully treated spinel ferrites, which breaks down H_2O into H_3O^+ and OH^- ions at room temperature. Hydroxide ions move in the direction of the zinc anode, where they undergo oxidation to produce zinc hydroxide and release two electrons. At the silver cathode, hydrogen gas and water are released when Ag electrode gathers hydronium ions and acquires electrons from the anode [Kumar, V et al., 2022]. Ag-$MgFe_2O_4$ nanocomposite was recently used to fabricate a hydroelectric cell (HEC) that produced a short circuit current mA and an open circuit voltage of 18 mA and 1.404 V, respectively [Kumar, V. et al., 2024].

Conclusion

This comprehensive review underscores the significant advancements and versatile applications of doped spinel ferrite nanoparticles. These materials exhibit unique electrical and magnetic properties enhanced through metal substitution in their lattice sites, making them highly suitable for various applications, including biosensors, industrial electronics, water treatment, transducers, transformers, cancer treatment, and magnetic resonance imaging. The adaptability of spinel ferrites, influenced by oxygen vacancies, crystal defects, and unsaturated metal cations, allows for optimization in different technological contexts. The synthesis methods, such as sol-gel, co-precipitation, and hydrothermal techniques, provide controlled nanostructures, essential for achieving desired properties in magnetic and biomedical applications. Characterization techniques like XRD, FTIR, UV-Visible spectroscopy, photoluminescence, and VSM are crucial in understanding the structural, optical, and magnetic attributes of these nanoparticles. The findings from these methods highlight the tailored physical properties achieved through precise synthesis and doping strategies. Spinel ferrite nanoparticles have demonstrated exceptional performance in sensor applications, particularly in humidity and gas detection, due to their small grain size and large surface area. Their magnetic properties, including high coercivity and magnetization values, make them ideal for high-density magnetic recording, advanced electronic engineering, and various biomedical applications. Notably, spinel ferrite nanoparticles have shown applications in drug delivery, hyperthermia, and imaging, although biocompatibility and cytotoxicity concerns necessitate further research. The innovative development of hydroelectric cells using spinel ferrites represents a groundbreaking advancement in green energy technology. These cells leverage the unique properties of spinel ferrites to dissociate water molecules at room temperature, generating electricity and showcasing the potential for sustainable energy solutions. This review aims to guide researchers in maximizing the effectiveness of spinel ferrite nanoparticles, facilitating advancements in diverse fields through informed material selection and application strategies.

Conflict of Interest

The authors do not have any conflict of interest.

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