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A Review on Spinel Ferrite Nanoparticles: Synthesis Methods and Applications

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Abstract: ***Spinel ferrites are among the most promising soft magnetic materials due to their superior coercivity, tailored band gap, high saturation magnetization, and other physical, thermal, and electrical characteristics. Spinel ferrite nanomaterialsare gaining importance due to their diverse applications in biomedical, water treatment, and industrial electronic devices. Ferrite nanoparticles are utilized in electronic domains to create sensors, biosensors, transducers, and transformers. In this review, attention has been paid to the synthesis and applications of spinel ferrites across various fields.***

Keywords: Spinel ferrites; Nanoparticles; Synthesis methods, Applications

1. Introduction

Spinel ferrite nanoparticles are in the spotlight of current nanoscience due to immense application potential. Very interesting aspects of the spinel ferrite nanoparticles are their excellent electrical and magnetic properties often accompanied with other functional properties, such as catalytic activity. Spinel ferrite materials are metal oxides with spinel structures that have the general chemical formula AB_2O_4, where A and B represent various metal cations that are located at tetrahedral (A site) and octahedral (B site) positions, respectively. The types, quantities, and placements of the metal cations in the crystalline structure have a significant impact on the physicochemical properties of ferrites [1, 2].

Due to their unique and remarkable properties, nanocrystalline magnetic materials have attracted attention from various fields. Nanomaterials have particle size up to 100 nm and high surface - to - volume ratio, which altered or enhanced reactivity, thermal, mechanical, optical, electrical, and magnetic properties as compared to their bulk counterparts [3 - 6]. While the chemical composition of bulk materials is the main determinant of their qualities, the particle size, and morphology of nanomaterials, in addition to the chemical composition, dictate the majority of their features. The size and shape of spinel ferrite nanomaterial can be controlled by manipulating reaction variables such as properties is manipulated by changing the synthesis method, processing temperature and also substitution [7 - 9].

Spinel ferrite nanoparticles can be fabricated by various methods such as hydrothermal method, sol - gel method, chemical co - precipitation method, citrate precursor method, combustion method, solid state high temperature reactions etc. Nanoparticles of spinel ferrites are of growing interest for a wide range of applications like high density magnetic information storage, magnetic resonance imaging, targeted drug delivery etc. They also offer immense possibilities of tailoring its various properties for applications [10, 11]. Magnetic $CoFe_2O_4$, $MnFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$, and $NiFe_2O_4$ nanoparticles have received a great deal of attention owing to their thermal and chemical stability, as well as their distinctive structural, magnetic, optical, electrical, and dielectric properties, and their broad range of technological applications including photo catalysis, photoluminescence, biosensors, humidity - sensors, catalysis, magnetic refrigeration, permanent magnets, magnetic drug delivery, magnetic (hyperthermia) [12, 13].

The purpose of this review gives some general processing methods and applications on spinel ferrite nanomaterial which is found to be useful due to their electronic, optical, electrical, magnetic and catalytic properties.

2. Synthesis methods

Different synthesis methods can be utilized simultaneously to produce nanoparticles of various sizes. It is known that the synthesis process affects the physical and chemical behavior of nanoparticles. The development of new preparation techniques and application scenarios has been a key area of research since the discovery of magnetic nanoparticles. Among the various methods available for the synthesis of spinel ferrite materials, the most popular include physical, chemical and biosynthesis methods. Chemical synthesis is the most common approach for preparing NPs since it has a high capacity for producing nanoparticles in a reasonable time and at a low cost. Some few synthesis method such as sol - gel method [14, 15], chemical co - precipitation [16], Hydrothermal and Solvo - thermal synthesis [17], Self - propagating high temperature synthesis (SHS) technique [18], Micro – emulsion technique [19], citrate precursor method [20] etc. have been discussed.

2.1 Sol - Gel Method

The sol - gel process involves the transition of a solution of metal compounds from a liquid sol into a solid gel. In liquid, sol is a diffusion of the solid particles where only the Brownian motions suspend the particles and this sol is heated and then to form a homogenous gel which can achieved by the addition of base or acidic solutions. A gel is intermediate where both liquid and solid are dispersed in each other, which presents a solid network containing liquid components. Usually inorganic metal salts or metal organic compounds such as metal alkoxides are used as starting precursors in the preparation of the sol. The purpose of this precursor is to a series of hydrolysis and polymerization reactions to form a colloidal suspension, or a sol. By elimination of water, the hydroxide molecules gets condensed and then formation of a metal hydroxide. When all metal hydroxides species are linked to one another in a network, and formation of dense porous gel is obtained. Further heating at higher temperature and then drying of the gel, the gel is converted into ultrafine powders of metal oxides.

2.2 Chemical Co - Precipitation

In the chemical co - precipitation method, an aqueous solution of suitable salts of iron, lithium, manganese and other desired, suitable materials is mixed under a fine control of pH by using a precipitating agent like NaOH or NH_4OH solutions which causes the precipitation of the other metals present in the solution. The precipitate represents a significantly uniform mixture of organic compounds of the ferrite metals on an atomic scale. In case of ferrite, it is important to prevent agglomeration; Ostwald ripening etc. Filtrated the precipitate and then dried. Then dried precipitate is heated at a high temperature to dehydrate the precipitate and to burn out carbonaceous matter leaving a residue of the oxides of the respective metals. After this, particles are sintered. The reaction and transport rates can be affected by the concentration of reactants, temperature, pH, the order in which the reagents are added to the solution and mixing. The particle structure and crystallinity can be influenced by reaction rates and impurities. This method doesn't work very well in cases where two reactants have very different solubilities in water and the reactants do not precipitate at the same rate. This method offers distinct advantages like simple, rapid preparation, easy control of particle size and composition.

2.3 Hydrothermal and solvothermal synthesis

To create crystalline nanoparticles, hydrothermal and solvothermal syntheses use a variety of wet - chemical processes. High purity and controllable morphology of nanoparticles can be produced by simple and effective hydrothermal and solvothermal procedures. A nonaqueous solution, such as methanol, ethanol, or ethylene glycol, is used in solvothermal synthesis to dissolve the metal precursors under high pressure and at a moderate temperature. Hydrothermal synthesis refers to the synthesis through chemical reactions in an aqueous solution above the boiling point of water.

2.4 Self - Propagating High Temperature Synthesis Technique

In this method, organic acid is taken as precursur in aqueous solution. This solution containing all necessary cations and combustible anions in the desired product. After dehydration, the precursor becomes dry gel and this dry gel is amorphous in nature. Moreover, when calcinating this dry gel directly yields the required materials in presence of air/oxygen. In case of this process, the starting materials are mixed in the atomic scale. The phase formation occurs at lower calcination temperature as compared to ceramic route and giving ultrafine powder. The overall process completes within 5 minutes.

2.5 Micro – emulsion Technique

Micro - emulsions are clear, isotropic mixtures of water, oil, and a surfactant that are stable and clear. This method uses surfactants to aid in the coexistence of two immiscible liquids in a single phase. One of the micro - emulsion solvents is water/oil, which is used to prepare the solution by dispersing immiscible solvents. The nanoparticles precursor is typically dispersed as 1–100 nm Nano droplets in the aqueous phase. Surfactant molecules encircle water droplets, forming "micelles" that act as nanoreactors. This results in the formation of magnetic nanoparticles inside the micelles, which confines the particles and limits particle nucleation, development, and agglomeration.

2.6 Citrate Precursor Method

In this method, the starting materials such as nitrates are complexed in an aqueous solution with α−carboxylic acids such as citric acid. By adding ammonium hydroxide to the solution, the pH is controlled at 7. The solution is refluxed with continuous stirring using magnetic bar agitator and then dried. By the evaporation of the solution, a highly viscous mass is formed and resulting from metal nitrates and citric acid making a redox reaction to occur and then this metal nitrates react with water. The chelating agent citric acid is used for deprotonating with ammonium hydroxide and the metal hydroxide by removing protons. Then the formation of metal ions having a positive valency and carboxylic ions with negative valency together with water molecules. This co - ordinate bonds are used to form the metal and acid complex which is the ash - synthesized powder obtained. At last point auto - combustion process takes place. The powder is pressed into pellets and then given final sintering for densification.

3. Applications of Spinel Ferrites

The properties of ferrite, including its structure, particle size, and shape, can vary depending on the cation type and synthesis method employed, resulting in diverse applications.

3.1 Sensors

Sensors are electronic devices that detect changes in a given material in a specific environment. Ferrite nanoparticle - based sensors possess exceptional sensitivity, low detection limits, and high signal - to - noise ratios. The detection of variations in humidity is one of the most common uses of sensors. The monitoring of humidity is a widespread practice in both industrial and residential settings, as it helps to maintain human comfort, regulate storage conditions for various items, and ensure optimal operating conditions for industrial processes and devices. Typically, humidity sensing is primarily attributed to the surface effects of the interaction between water vapor and solids.

3.2Photo luminescent applications

Mixed spinel nanostructures such as $CoFe_2O_4$, $NiFe_2O_4$, and $ZnFe_2O_4$ are known for their photoluminescence at room temperature, which is considered one of their most significant properties. The spectrum of photoluminescence offers insights into various characteristics such as surface oxygen vacancies, defects, charge carrier trapping, and transfer efficiency.

3.3 Magnetic applications

The variation of exchange contact between tetrahedral and octahedral sites causes the magnetization to be dependent on grain size. To minimize media noise in high - density magnetic recording, the magnetic particles utilized should have a nanoscale size to limit the exchange interactions occurring between adjacent grains. To achieve great storage density, the particles must also have high H_C values. The magnetic characteristics (M_R, M_S, and H_C) of spinel ferrites are affected by their composition, particle size, crystal structure, and cationic distribution between octahedral and tetrahedral sites.

3.4 Dielectric applications

The dielectric structure typically consists of grains that are good conductors separated by grain boundaries with low conductivity. The dielectric properties of spinel ferrites are influenced by factors such as structural homogeneity, cation distribution, particle size, density, and porosity.

Additionally, the dielectric properties can be significantly affected by synthesis techniques and thermal treatment parameters such as temperature, time, and heating/cooling rates.

3.5 Waste water treatment

Industrial wastewater management has become one of the most pressing issues in developed countries in recent years. Textile wastewaters contain a variety of non - biodegradable organic dyes, as well as other pollutants in varying concentrations. Untreated effluents harm not only humans and animals but also plants. RhB is a synthetic, highly poisonous, water - soluble organic dye that is commonly found in the wastewaters and is widely employed as a colorant in various industries. For the treatment of RhB - containing water, various procedures have been used, including ozonation, the electrochemical method, and the Fenton process. In recent years, magnetic NPs have attracted considerable attention due to their special magnetic properties, high adsorption capacities and surface area to volume ratio.

3.6 Catalytic applications

Spinel ferrites are commonly used as heterogeneous catalysts due to their ease of recovery from reaction mixtures by filtering or using an external magnetic field, making the process cost - effective and environmentally friendly through their multiple recyclings. To be economically valuable and ecologically friendly, heterogeneous catalytic nanoparticles play a key role in the selective protection of functional groups.

3.7Photo catalytic applications

Photo catalysts are important materials that facilitate the use of solar energy in oxidation and reduction reactions, with numerous applications including removing water and air pollution, managing odors, deactivating bacteria, splitting water to generate hydrogen, inactivating cancer cells, and other areas. Currently, photo catalysis is a preferred method for removing dyes, as irradiation of light on a semiconductor can generate electron - hole pairs that can be utilized for oxidation and reduction processes. Dye degradation is caused by the generation of active radicals during the photo catalytic reaction.

3.8 Biomedical applications

For use in biomedical applications, magnetic nanoparticles need to have high magnetic saturation values and be biocompatible, while also being stable and non - agglomerated when dispersed in water. These nanoparticles can be used within individual cells to facilitate magnetic fluid hyperthermia, drug delivery, and stimulation of metabolic pathways through thermal excitation. $MnFe_2O_4$ nanoparticles have attracted significant interest in the field of biomedicine due to their desirable properties, including simple synthesis, controllable size, high magnetization value, super paramagnetic nature, ability to be monitored by an external magnetic field, and high biocompatibility.

4. Conclusions

Recently nanostructured spinel ferrite materials have received a lot of attention due to its unique features, including stability under mechanical, chemical, and thermal conditions and can be modified suitably and promising technological applications in different fields of life. Among all the reviewed synthesis strategies, the usefulness of spinel ferrite in many applications depends largely on the synthesis processes; efficient synthesis processes yield spinel ferrite that can function better and endure the conditions under which they are synthesized. Nevertheless, the cost - effective synthesis of large amounts of spinel ferrite with monodisperse size and shape for a biomedical purposes, however, needs more study and it is important to take into account and thoroughly examine the toxicity of specific spinel ferrite nanoparticles.

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