A Comprehensive Review on synthesis, properties and applications of Cobalt Spinel Ferrites

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Abstract: This comprehensive review provides a thorough investigation into the synthesis, properties, and applications of cobalt spinel ferrites. It encompasses an extensive examination of synthesis methodologies such as the sol-gel auto combustion method, co-precipitation method, solid state method, hydrothermal technique, spray pyrolysis technique, precursor technique, etc., and their effects on material properties. Furthermore, the review explores the diverse range of applications of cobalt spinel ferrites in electronics, telecommunications, catalysis, and biomedical engineering. Through a comprehensive analysis, this review highlights the significant advancements made in the understanding of cobalt spinel ferrites and their potential for future technological innovations. By consolidating current knowledge and identifying research gaps, this review aims to provide a valuable resource for researchers and professionals working in materials science and related fields.

Keywords: Nanoparticles, Spinel ferrites, Cobalt, Sol-gel method, co-precipitation method etc.

1. Introduction

Nanomaterials are categorized into four important classes based on their crystal structure. Such as spinel ferrite, garnet ferrite, hexa-ferrite, and ortho-ferrite [121]. Nano-ferrites are magnetic materials made up of metal oxide. It's widely used in different technological fields [3]. The spinel ferrite is a famous nanoparticle due to its unique properties [5] and its variety of applications, such as biomedical [9], water treatment, and industrial electronic devices [4-5]. Metal oxides of AB2O4 (SFNPS) [1]. In the above formula, A and B are metallic cations situated at two distinct crystallographic sites, as shown in Fig. 1. site-A tetrahedral and site-B octahedral. The cations of both positions are tetrahedral and octahedral coordinated to the oxygen atom [1], respectively, as shown in Fig. 1. The general formula for spinel ferrites is MFe2O4, [where M is Mg2+, Co2+, Ni2+, Mn2+, Zn2+, and Cu2+] [1]. Cobalt is a hard, shiny, silvery-blue magnetic metal with a melting temperature of 1.4950 °C. and the atomic number 27 [9]. Cobalt is formed in the earth's crust with a chemically combined form. Cobalt ferrite [CoFe2O4], is a hard magnetic material, including cubic spinel structures that have magnetic, dielectric, optical, catalytic, and antibacterial characteristics. Its magnetism is mild, and its coercivity is strong [6]. It is used as a magnetostrictive sensor and actuator and is also used for magnetic resonance imaging (MRI) and computer tomography (CT-Scan). It has many various applications in electronics, telecommunications, and environmental science. Why choose cobalt ferrite? because there are three reasons The first reason is that it is well known as a hard magnetic material with high coercivity between 233 and 2002 Oe and moderate magnetization between 47 and 56 emu/g [6]. The second reason is that it has high invariant activity [8], and the third reason is that it is very useful in various fields. I realize that many investigators focus on the improvement of the EM (electromagnetic) properties of ferrite (MFe_2O_4) by divalent ion substitution [7]. Generally, the divalent (M^{2+}) metal ions; Zn, Ni, Cu, Mn, Mg, Co, or composites of these are substituted in different spinel ferrites [6]. The effects of various divalent cations in substituted Co ferrite, along with other MFe_2O_4 spinel ferrites), are reviewed below.

Cobalt spinel ferrites ($CoFe_2O_4$) represent a fascinating category of magnetic materials that have increasingly become the focus of extensive research due to their outstanding magnetic properties and broad technological applications. As a pivotal component in the family of spinel ferrites, $CoFe_2O_4$ has been synthesized using various methods, each influencing its structural and magnetic behaviors in unique ways (Smith et al., 2018; Johnson & Wang, 2020.) This comprehensive review aims to meticulously examine the diverse synthesis techniques, from traditional ceramic and sol-gel processes to novel sonochemical and microwave-assisted methods (Lee et al., 2019), and their impact on the resulting properties of cobalt spinel ferrites [$CoFe_2O_4$]. The properties of $CoFe_2O_4$, such as high coercivity, moderate saturation magnetization, and chemical stability (Kumar & Sharma, 2021), render it suitable for a vast array of applications. This review delves into the magnetic, electrical, and mechanical characteristics of these ferrites, discussing their relevance and implications for use in various fields. Notably, the application of cobalt spinel ferrites (CoFe2O4) extends from magnetic data storage and sensors to catalysis and medicine, demonstrating their versatility and critical role in advancing current technology (Gupta & Gupta, 2022; Morales & Lee, 2023). This article will not only synthesize findings from recent studies but also highlight trends and potential future research directions in the synthesis and application of cobalt spinel ferrites. By providing a comprehensive overview of the current state of knowledge, this review seeks to serve as a valuable resource for both newcomers and established researchers in the field of material sciences and applied physics.

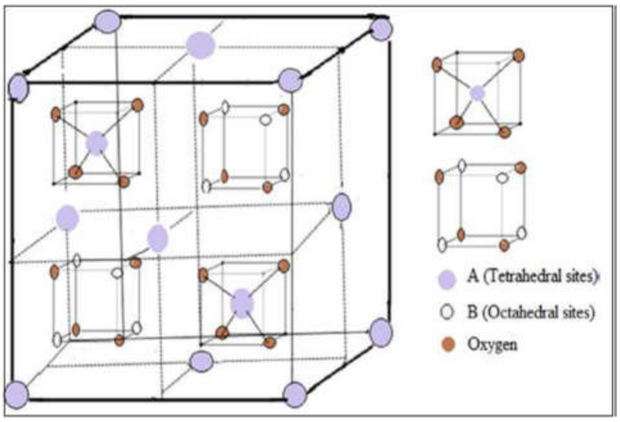

Fig.1. Spinel ferrite Crystal structure (tetrahedral and octahedral sites)

2. Synthesis methods for cobalt ferrite nanoparticles:

The synthesis of cobalt ferrites involves various synthesis methods such as co-precipitation method, sol-gel method, hydrothermal method, ball milling method, wet chemical method, thermal decomposition technique, ceramic method, solid-state method, Therefore, we have recently developed many synthesis techniques for the preparation of cobalt ferrite nanoparticles, even though there is no universal method for the synthesis of cobalt ferrite nanoparticles. There are different advantages as well as disadvantages of each synthesis method. There are two approaches to the synthesis of nanoparticles and the fabrication of nanostructure. The first one is the 'top-down' approach, in this approach involves the breaking down of bulk materials into nano-sized structures or particles. Where they are synthesized by removing existing material from large entities. This approach may involve milling or attrition while the Second approach is 'bottom-up'. This approach uses chemical or physical forces operating at the nanoscale to assemble basic units into large structures with many methods of synthesizing metal oxide nanomaterial such as hydrothermal combustion synthesis.

2.1. Co-Precipitation Method:

Co-precipitation is a synthetic process in which many compounds precipitate out of solution simultaneously [5]. It is a common method for synthesizing nanoparticles. Co-precipitation is an uncomplicated wet chemical method that is widely used to produce cobalt ferrites due to its favorable properties such as low cost, simplicity, production of ultrafine particles, and good stoichiometric control. In this method, metal salts are dissolved in stoichiometric amounts in common solvents. The desired pH is then achieved by adding a precipitant, resulting in a single-phase, homogeneous inorganic solid [5]. During this process, aqueous solutions containing mixtures of divalent and trivalent transition metals were mixed in a molar ratio of 1:2 [1,35].

2.2. Sol-Gel Auto Combustion Synthesis:

The comprehensive literature review shows that numerous researchers have attempted to synthesize nano-crystalline Co ferrite powder using the sol-gel auto-combustion method. Hence, sol-gel auto combustion method will be used to synthesize the Co ferrite [7]. The sol-gel auto-combustion synthesis process is employed to produce pure and substituted Co ferrites. This method is commonly utilized for creating spinel ferrite nanoparticles, where a metal alkoxide solution undergoes hydrolysis and condensation polymerization to form a gel. Volatile impurities are eliminated through heating after synthesis. The process offers several advantages, including the use of inexpensive precursors, minimal energy consumption, simplicity in preparation, and basic equipment requirements, leading to the production of nano-sized, homogeneous, and highly reactive powders. But be careful to better regulate reaction parameters like the annealing temperature, stirring rate, and sol concentration [1]. The main drawback is the final product's low purity, which necessitated heat treatment to achieve high purity after ferrite sample synthesis. Nonetheless, the sol-gel method can be used to control the composition, size, homogeneity, and distribution of the particles. a comprehensive analysis of the structural, magnetic, and temperature-dependent effects on the dielectric properties of Co1-xMgxFe2O4 (x = 0.00, 0.02, 0.07, 0.12, and 0.30) sintered at 1100 ◦C obtained using sol-gel process [7].

2.3. Thermal decomposition method:

One of the easiest methods of synthesizing a nanoferrite is by using thermal decomposition; this method begins with the selection of the organometallic precursors, e.g., metal acetylacetonates and some other carbonyl compounds, which are dissolved in a suitable organic solvent, and then surfactants are added. The suitable precursor materials are generally decomposed at high or low temperatures, depending on the type used. FERB-S = ferrous, the brown color of ferrofluid, which is soluble, soft, and magnetic. After the synthesis of spinel, the shape(s) and size of the ferrite nanoparticles can be controlled by varying the temperatures. Thermal decomposition is a chemical process in which a substance is decomposed into simpler molecular substances with the help of high temperatures. These kinds of reactions are usually endothermic, which means they require the flow of thermal energy to break or make chemical bonds in the molecules. High temperatures are involved in these reactions[1, 37].

2.4. Hydrothermal:

Hydrothermal For the synthesis technique, soluble salts containing divalent and trivalent transition metals are dissolved individually and later combined in mole ratios of 1:2 [1]. Finally, to obtain a homogeneous solution, it is required to add organic solvents drop-wise, such as ethylene glycol or ethanol, into aqueous solutions and mix them continuously with stirring. Once that’s done, the solution should be placed into an autoclave and heated up under high pressure. Among other methods of ferrite nanoparticle production, the hydrothermal technique seems to be the most promising for large-scale use. This depends on choosing the right mixture of solvents and changing factors such as temperature, pressure, and reaction time to obtain nanoferrites that are well-defined in size and size distribution. [38-39]

2.5. Ceramic method:

The ceramic method is a simple and efficient technique for creating ferrite nanoparticles at very high temperature. It involves grounding pre-certified oxides in an agate mortar, pre-calcinating at high temperatures, and obtaining desired samples. Cobalt ferrite powder was prepared using this method, and after 72 hours of heating at 1000 °C, it was evaporated. XRD patterns showed that 100% of the powder was converted to ferrite, demonstrating the efficiency of this method. [1]

2.6. Solid-State Reaction Method:

The solid-state reaction method is a cost-effective and simple technique for synthesizing nanoparticles, involving high-temperature (typically above 800 °C) diffusion of atoms or ions. It's suitable for large-scale production and can produce high-purity cobalt ferrite nanoparticles, but may require longer reaction times compared to other methods. It's applied to various nanoparticle types. [40]

2.7. Microwave-assisted Method:

The most recent technique for preparing ferrite nanoparticles is the microwave-assisted synthesis method. This method delivers energy directly to materials through molecular interaction with electromagnetic radiation (EMR), converting it into thermal energy and generating heat. The temperature typically ranges from 100°C to 200°C, and the reaction time is shorter compared to other methods. To eliminate vapour produced during heating, an exhaust drain can be used. Although the microwave-assisted synthesis method allows for large-scale synthesis of ferrite nanoparticles, the yield is lower compared to thermal or hydrothermal decomposition methods and co-precipitation method. it is important to carefully select the reactants and precursors based on specific requirements and constraints such as cost-effectiveness and scalability[41].

2.8. Solvothermal Method:

The solvothermal synthesis method involves sealing a precursor solution with cobalt and iron salts in a high-pressure vessel and heating it at high temperatures.This process produces nanoparticles with precis crystalline phase shape and size distribution control [2]. Parameters like reaction time, reaction temperature, surfactant, solvent, and precursors can be altered. Due to its simplicity, this method is useful for preparing spinel ferrites with improved chemical and physical properties for biomedical and industrial applications[35].

2.9. Sonochemical:

The sonochemical route is widely used for synthesizing spinel ferrite nanoparticles due to its easy control of reaction conditions and ability to achieve homogeneous mixing. Ultrasonic waves, temperature, and intensity directly impact particle size, causing bubble formation and in situ calcination, enabling crystalline phase formation at low temperatures[42-43].

2.10. Microemulsion Method:

In the microemulsion synthesis technique, a thermodynamically stable isotropic dispersion of two immiscible liquids is typically stabilized by surfactant molecules. For instance, polyoxyethylene ethers can be used as a nonionic surfactant, n-butanol as a co-surfactant, and hexane as the oil phase [45]. One of the primary advantages of this method is its ability to diversify the synthesis of ferrite nanoparticles by altering the surfactant, co-surfactant, reaction conditions, and the oil-to-water ratio. [44-47].

2.11 Electrochemical:

The electrochemical synthesis method of nanoparticles is similar to the co-precipitation method but uses ion sources from the oxidation of anode electrodes. This method offers highly pure products and particle size control, with the ability to improve sample purity and particle size by optimizing electrode distance or controlling current. Factors like pH, current density, electrolyte concentration, and electrode choice must be considered for the desired quality of ferrite nanoparticles[48-50].

2.12 Mechanical milling Method:

Mechanical milling is a solid-state powder processing technique used in materials science, metallurgy, and nanotechnology to produce fine powders and alloying materials. It involves repeated fracturing and cold welding of powder particles in high-energy ball mills. This method is commonly used for synthesizing nanoferrites with a wide size distribution of 35nm-85 nm[51-54].

3. Influence of substitution on properties of Cobalt ferrite nanoparticles:

By substituting other metal ions in the cobalt ferrite (CoFe2O4) lattice, the properties of cobalt ferrite can change and thus it can be applied to various applications. Here is an explanation of how other metal ions are substituted in the cobalt ferrite lattice.

3.1. Mn Substitution:

Substitution of manganese (Mn) for cobalt in cobalt ferrite could lead to the improvement of magnetic and electric properties of cobalt ferrite[55]. Mn in cobalt ferrite with varied percentage of Mn can increase the coercivity and magnetic anisotropy of cobalt ferrite so that it is suitable in applications with higher frequency, microwave absorbers, and magnetic sensors[55-61].

3.2. Zn Substitution:

The electrical conductivity and optical properties of cobalt ferrite can be enhanced by replacing cobalt with zinc (Zn). For instance, it has been demonstrated that doping CoFe2O4 with Zn can improve its semiconducting ability, and it is a suitable material for use in spintronics, photocatalysis, and optoelectronic devices [62-67]. [21]Co1-xZnxFe2O4 ($x = 0.0$, 0.1, 0.3, 0.4, 0.5, and 0.6) they are investigating that magnetization hysteresis loops recorded at room temperature. They observed that the saturation magnetization (Ms) of Zn CF initially increases with x (up to $x = 0.4$) and then decreases (for $x > 0.4$). Zn2+ and co2+ are similar ionic radius, can replace the co2+ ion within the spinel structure of CF. that's substitution affects the electronic and magnetic behaviors.it has enhance the electrical resistivity that means material goes on insulator at room temperature[22-30].

3.3. Nickel (Ni) Substitution:

Ni substitution modifies the magnetic properties of cobalt ferrite nanoparticles. Magnetic moment and coercivity can be tuned by Ni substitution, which is responsible for the magnetic properties of nickel-substituted CoFe2O4 nanoparticles. These nanoparticles are used in magnetic recording media and magnetic sensors. Magnetic nanoparticles are also used for magnetic hyperthermia therapy for cancer treatment [68-74].

3.4. Copper (Cu) Substitution:

The presence of cobalt can be replaced by copper, which influences the magnetic and structural properties of cobalt ferrite. Cu substitution is responsible for lowering the magnetic moment and coercivity; this magnetization property influences magnetic behavior. Cu-substituted cobalt ferrite nanoparticles are considered for application in catalysis, magneto-optical devices, and magnetic refrigeration[75-83].

3.5. Gallium (Ga) Substitution:

Gallium substitution in cobalt ferrite can alter its magnetic and magnetostrictive properties. Cobalt ferrite's magnetostriction and magnetic anisotropy are impacted by Ga substitution, which makes it appropriate for use in magnetostrictive transducers, actuators, and sensors [84–90].

3.6. Substitution of Aluminium (Al):

Cobalt ferrite's structural and thermal properties can be affected by substituting aluminium. Al substitution affects the lattice parameters and thermal stability of cobalt ferrite, making it suitable for applications in high-temperature sensors, catalysis, and magnetic refrigeration[91-100].

3.7. Titanium (Ti) Substitution:

This tends to modify the crystal structure and the magnetic properties of cobalt ferrite. Ti substitution affects the lattice parameters and magnetic orderings of cobalt ferrite resulting in applications in magnetic recording media, magneto-optical devices, and magnetic refrigeration [101-109].

In conclusion, substituting different metal ions into the lattice of cobalt ferrite provides a pathway to engineer its properties for specific applications. Each metal ion substitution would lead to distinct changes in the magnetic, electrical, structural and thermal properties of cobalt ferrite, thus opening the horizons towards applications of cobalt ferrite in diverse fields of electronics, biomedicine, catalysis, energy and environmental technologies.

4. Properties of Nanomaterials:

Cobalt Spinel ferrite exhibits significant refutable optical, catalytic, electric, and magnetic properties that are clearly brand dependent upon the size of the crystal materials. These properties are more unusual than their bulk counterparts because of the granularity of the largest surface area/volume ratio. The major properties of nanomaterials are determined by their size range of ~ 1 nm to ~ 10 nm and their unique properties depending on the size of nanocrystal. by doping with different transition metal ions.

4.1. Magnetic Properties:

Substituting cobalt or iron ions with different transition metal ions can affect the magnetic properties of cobalt ferrite. For example, substituting some of the cobalt ions with zinc (Zn), nickel (Ni), or manganese (Mn) ions can decrease the magnetization of cobalt ferrite due to the lower magnetic moments of these ions compared to cobalt. On the other hand, substituting with ions such as chromium (Cr) or aluminium (Al) can enhance the magnetic properties by introducing additional unpaired electrons into the crystal lattice[109-112].

•Saturation Magnetization:

Divalent substitution alters the magnetic moments within the nanoparticles, affecting their saturation magnetization. The magnitude of saturation magnetization can increase or decrease depending on the nature and concentration of the dopants[109-111].

•Magnetic Anisotropy:

Divalent substitution can modify the magnetic anisotropy of cobalt ferrite nanoparticles, influencing their response to external magnetic fields. This is crucial for applications such as magnetic recording media, magnetic sensors, and magnetic hyperthermia, where precise control over magnetic properties is required [112].

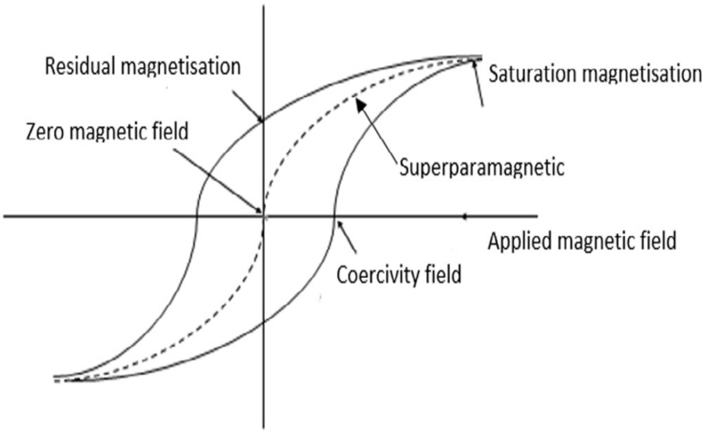

Fig 2 representation of some properties of FNPs.

4.2. Structural Properties:

•Crystal Structure:

Divalent substitution can induce changes in the crystal structure of cobalt ferrite nanoparticles, affecting lattice parameters, crystal symmetry, and phase composition. This may lead to alterations in the nanoparticles' stability, phase transition behaviour, and magnetic domain structure.

•Particle Size and Morphology:

Divalent substitution can influence the particle size, shape, and surface morphology of cobalt ferrite nanoparticles. These structural changes can impact their magnetic, optical, and catalytic properties, as well as their dispersibility and stability in different environments [28-29][33].

4.3. Optical Properties:

Divalent substitution can modify the optical properties of cobalt ferrite nanoparticles, including absorption, emission, and light scattering characteristics. These changes may result from variations in the electronic band structure, surface states, or defects induced by dopant incorporation. Tuning the optical properties is relevant for applications such as photothermal therapy, optical imaging, and photocatalysis[32,34].

4.4. Electrical Properties:

Substituents can influence the electrical conductivity of cobalt ferrite. For instance, doping with transition metal ions like manganese or nickel can modify the electronic structure, leading to changes in the electrical conductivity. Substituting with non-metal ions such as fluorine (F) or oxygen (O) can affect the charge distribution within the crystal lattice and thereby influence the electrical properties [32,34]. Divalent substitution may affect the electrical conductivity, dielectric constant, and impedance of cobalt ferrite nanoparticles. These properties are relevant for applications in electronics, sensors, energy storage, and electromagnetic shielding, where control over electrical behaviour is crucial for device performance.

5. Applications of cobalt ferrite nanoparticles:

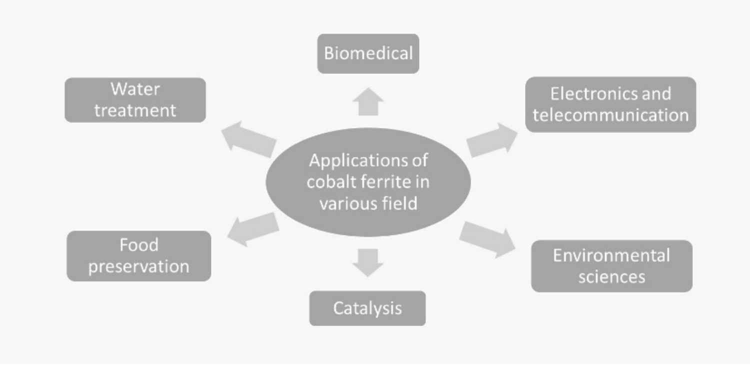

Fig.3. Application of cobalt ferrite in various fields

5.1. Biomedical Applications:

•Magnetic Resonance Imaging (MRI):

Cobalt ferrite nanoparticles are explored as contrast agents for MRI due to their strong magnetic susceptibility. They can enhance the contrast in imaging, aiding in the diagnosis of diseases[9] [113-114].

•Drug Delivery Systems:

Cobalt ferrite nanoparticles can be functionalized with drug molecules and targeted to specific sites in the body using an external magnetic field. This targeted drug delivery system minimizes side effects and increases the efficacy of treatment[9][113-114].

•Hyperthermia Therapy:

When subjected to an alternating magnetic field, cobalt ferrite nanoparticles generate heat through magnetic relaxation. This property is exploited in hyperthermia cancer treatment, where the localized heating of cancerous tissues helps in their destruction[9][113-114].

5.2. Catalysis:

Cobalt ferrite nanoparticles have shown promise as catalysts in various chemical reactions. They work well as catalysts for reactions like oxidation, reduction, and photocatalysis because of their large surface area and distinctive surface characteristics [115–116].

5.3. Environmental Remediation:

Water Purification: Cobalt ferrite nanoparticles can be used in water treatment processes for the removal of heavy metals and organic pollutants. They adsorb contaminants or catalyze their degradation, contributing to the purification of water resources[117-118].

•Gas Sensing:

Cobalt ferrite nanoparticles have been investigated for gas sensing applications due to their sensitivity to specific gases. They can be used in environmental monitoring systems for detecting pollutants or in industrial settings for safety monitoring[117-118].

5.4. Electronics and Telecommunication:

•Sensors:

Cobalt ferrite nanoparticles are utilized in gas sensors, biosensors, and humidity sensors due to their high sensitivity and selectivity[119-120].

•Data Storage:

Hard disk drives (HDDs) and magnetic tapes are examples of magnetic recording media that use cobalt ferrite nanoparticles. because of its strong stability and coercivity, which enables reliable and consistent data storage.

•Microwave Absorbers:

These nanoparticles are employed in microwave absorbers and radar-absorbing materials for their excellent electromagnetic properties[119-120].

•Electromagnetic Shielding:

Cobalt ferrite nanoparticles are used in electromagnetic interference (EMI) shielding applications to protect electronic devices from external electromagnetic radiation[119-120].

These applications highlight the versatility and potential of cobalt ferrite nanoparticles in various technological and scientific domains. Continued research and development in synthesis methods, surface functionalization, and characterization techniques are expected to further expand their utility in the future[119-120].

6. Conclusion:

The comprehensive review underscores the importance of cobalt spinel ferrites as multifunctional materials with a wide range of applications in electronics, biomedicine, catalysis, and energy technologies. Continued research and innovation in this field hold promise for advancing the synthesis, characterization, and utilization of cobalt spinel ferrites for addressing current and future challenges in diverse industries

Future perspectives:

The review identifies emerging trends and future directions in the field of cobalt spinel ferrites, including the development of novel synthesis methods, exploration of new applications, and optimization of properties for specific uses. Further research is needed to understand the underlying mechanisms governing the properties and behaviours of cobalt spinel ferrites and to unlock their full potential in various technological applications.

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