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Mixed Nanoferrites: Fabrication and Uses in Biomedical and Sensor Domains

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Abstract- For several novel applications, the synthesis and characterization of nanoferrites are crucial. Their synthesis techniques have a significant impact on their electrical and magnetic characteristics, which are important in many applications. The resultant ferrites can have different characteristics depending on the process used, including sol-gel (SG), SG auto-combustion, self-combustion, co-precipitation, reverse micelle, micro-emulsion, glass crystallization, precursor, and hydrothermal procedures. The synthesis, characterization, and applications of mixed nanoferrites with the formula MFe2O4 are reviewed in this study. M can represent a variety of elements, including Cu, Fe, Mg, Mn, Ni, and others. Excellent magnetic characteristics, such as strong coercivity, high anisotropy, high Curie temperature, and mild saturation magnetization, are displayed by nano-sized ferrites. They also possess noteworthy mechanical qualities including considerable hardness and desired electrical qualities like high electrical resistance and minimal eddy current losses. According to our investigation, mixed nanoferrites show better qualities than single-component ferrites, which make them attractive options for a range of cutting-edge applications. This paper tries to give a comprehensive overview of the characteristics, synthesis methods, and possible uses of mixed nanoferrites, highlighting the latter are potential for major practical effect. We concentrate on the effects of these materials' form, size, and cation dispersion on their electrical and magnetic characteristics. Furthermore, we investigate the possible uses of mixed nanoferrites in a number of domains, such as: Superior magnetic and dielectric materials for electronics and sensors High-performance magnetic resonance imaging (MRI) contrast agents Biomedical uses, such as medication administration and the management of hyperthermia.

Keywords: Mixed ferrites; Sensors; SG auto-combustion; Co-precipitation; Micro-emulsion; Precursor, and hydrothermal procedures; Magnetization and Coercivity, MRI, Biomedical applications.

I. INTRODUCTION

A ceramic substance composed of iron oxides plus one or more metals added chemically, ferrite has electrical and magnetic qualities that make it useful in a variety of electronic devices. These are a special class of chemicals that include fast-transition metals and lanthanides. Ferrites are often grey or black, brittle, hard, and contain iron. They are also polycrystalline. They don't conduct electricity. Their chemical mixture consists of iron oxide and one or more additional metals [1]. Oxygen anions and metal cations organise themselves into space lattices with various geometric configurations in ferrites, which are ferrimagnetic materials [2].

Ferrites' advantageous magnetic, electrical, and mechanical characteristics have led to their employment in a variety of applications, including medication delivery, radio frequency coils, transformer cores, high-density data storage, magnetocaloric cooling, magnetic resonance imaging, and rod antennas [3].

Ferrite's mechanical, electrical, and magnetic characteristics often undergo significant changes when the particle size is decreased from bulk to nanoscale. A particle is said to be in a single domain state when its size is smaller than the critical diameter of the domain formation.

Because of their superior morphology, magnetocrystalline anisotropy, small particle size, high resistivity, and low dielectric loss tangent at high frequencies, nanoferrites with super paramagnetic characteristics can have moderate permeability, low coercivity, high saturation magnetisation, and low loss factor at a wide range of frequencies [4]. Hexaferrites, garnets, orthoferrites, and spinel ferrites are the four categories into which nanoferrite materials are divided according to their structural makeup [5]. Of these four varieties, spinel ferrite has adjustable and adaptable magnetic and dielectric characteristics, including permeability, high electric resistivity, low coercivity, and Curie temperature. With the chemical formula MFe_2O_4, spinel ferrite has a cubic structure.

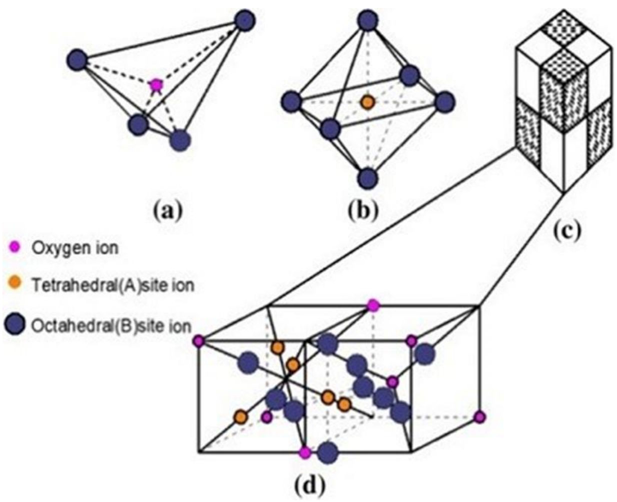

Fig 1: spinel ferrite's crystal structure.
a) The distribution of metal cations and oxygen ions; b) The octahedral B site; and c) The tetrahedral A site. [Image taken from La^{3+} ion doping's effects on Mg–Co ferrites' morphology and magnetic characteristics].

M is a divalent cation (Cu, Ni, Fe, Mg, Al, etc.) that occupies one eighth of the tetrahedral holes (M^{2+}), while Fe is a trivalent cation (Fe^{3+}) that occupies half of the octahedral lattice sites [1,2]. Figure 1 depicts the spinel ferrite crystal structure.

Mixed Nanoferrites

Doping the ferrites to enhance their structural, magnetic, and electromagnetic characteristics
Adding dopants to nanoferrite particles is essential for fulfilling technological demands.

Combination

It is possible to create ferrites with two distinct types of divalent ions, such as $MnZnFe_2O_4$.

The divalent cations in $NiZnFe_2O_4$ or MnZn, NiZn ferrites are Mn, Zn, and Ni, Zn.

[6] Doping dopants into nanoferrite particles is crucial to meeting technical criteria and improving the ferrites' structural, magnetic, and electromagnetic capabilities. It is possible to create mixed ferrites, such as $MnZnFe_2O_4$, that include two distinct types of divalentions.

The divalent cations in $NiZnFe_2O_4$ or MnZn, NiZn ferrites are Mn, Zn, and Ni, Zn [6]. Because multiple metal ions are combined, mixed nanoferrite materials have better magnetic characteristics, including stronger magnetisation and coercivity, compared to regular ferrite particles. Properties that may be tuned for certain purposes by altering the mixed ferrites' composition. Decreased toxicity: In comparison to individual metal oxides, several combined nanoferrites have demonstrated decreased toxicity, which makes them more appropriate for use in biomedical applications [7].

Techniques for the Synthesis of Mixed Nano-Ferrites

Nanoferrite particles can be produced in two methods.
1. Bottom-up synthesis
2. Top-down synthesis

Bottom-Up Method

When creating nanostructures, the bottom-up method starts with individual atoms and molecules that are put together by catalyst-controlled chemical processes. This method, which is frequently applied in domains including materials science and nanotechnology, enables the production of nanostructures with particular characteristics and capabilities.

Here are a few instances of bottom-up strategies:

Chemical synthesis is the process of combining atoms and molecules to create nanostructures through chemical processes.
Allowing atoms and molecules to self-assemble into nanostructures is known as
self-assembly.

These methods make it possible to create nanostructures with special qualities, such nanoparticles, nanotubes, and nanocrystals, which have uses in industries like electronics, energy, and medicine.

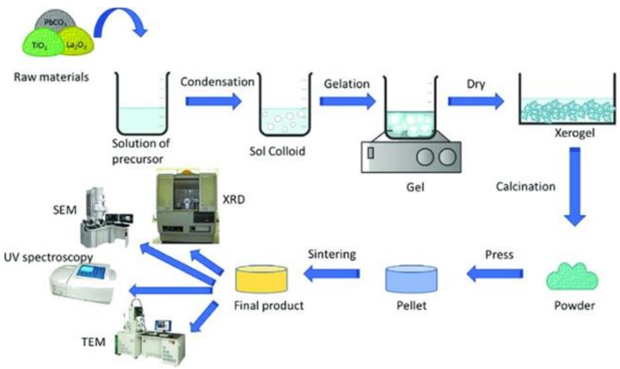

Fig 2: Block diagram representation of Sol-Gel synthesis

Sol-gel method

The bottom-up SG synthesis process is excellent at producing homogenous, very pure nanoferrites. The end product of this procedure is formed via a sequence of irreversible chemical reactions. Reactions involving hydrolysis or polymerisation produce the main molecules (sol). The combination can then develop and aggregate when the produced sol is transformed into a gel by condensation. A solid gel is then left behind when the solvent is eliminated by evaporation, drying, or extraction.

As seen in Fig. 2, calcination is subsequently carried out to eliminate organic residues and crystallise the particles. The SG approach has a number of benefits, such as: Minimal aggregation and consistent particle size Cost-efficiency Regulated morphology Coprecipitation method

The co-precipitation method is a straightforward and widely used technique for synthesizing nanosized particles, including ferrites. This method enables the production of ferrite particles with homogeneous structure, high purity, and controlled size. The process involves dissolving inorganic salts (chloride, nitrate, and sulphate) in a suitable medium, such as water, to form a homogeneous mixture. The pH of the solution is adjusted to between 7 and 9, and the solvent is evaporated to precipitate the nanoparticles. It is crucial to control temperature, salt concentration, pH and pH change rate, as these factors can impact particle growth and crystal formation. The resulting solid mass is washed, collected, and heated to its boiling point to dry the product and form hydroxides. Calcination is then used to convert the hydroxides into crystalline oxides.

For example, cobalt ferrites can be synthesized using cobalt chloride, iron (III) chloride, and sodium hydroxide as raw materials. A 3 M solution is prepared in 60 mL of distilled water, and its pH is maintained between 11 and 12. The solution is then added to a sodium hydroxide solution at 353-358 K, stirred for 60 min, and allowed to sediment. The precipitate is washed, dried, and crushed into a powder using a mortar and pestle. This method offers several advantages, including the use of an aqueous medium and simplicity of synthesis. Moreover, the morphology and size of the nanoparticles can be easily controlled. However, the resulting ferrite powder may have a weak crystalline nature, and the synthesis process can be time-consuming[9].

II. 1.4 CITRATE-GEL AUTO-COMBUSTION METHOD FOR METAL FERRITES

Starting Materials:

a. Metal nitrates ($M(NO_3)_x \cdot nH_2O$) (e.g., Co, Fe, Er)
b. Citric acid ($C_6H_8O_7 \cdot H_2O$)
c. Ammonia solution (NH_3) and
d. Distilled water

The citrate-gel auto-combustion method for metal ferrites involves four steps. First, a clear metal nitrate solution is prepared by dissolving metal nitrates in distilled water and stirring at 300 rpm for 1 h to ensure homogeneity. Next, citric acid is added to the metal nitrate solution in a 1:3 ratio, followed by the addition of ammonia solution drop wise to maintain a pH ~7. The solution is then heated at 100 ° C for 10-12 h, allowing the water to evaporate slowly and leading to internal combustion and the formation of a black-coloured product. Finally, the product is manually ground and calcined at 500 ° C for 4 h in a furnace to produce the final metal ferrite material [10].

Top-down approach

The top-down approach to preparing nanostructures starts with a larger scale material or pattern and reduces its size or dimensions to create a nanostructure.
This approach often involves lithography, etching, and other fabrication techniques to
gradually shrink the size of the material or pattern. Top-down approaches are commonly used in fields like microelectronics, where largescale patterns are reduced in size to create tiny electronic circuits.

Other examples include:

- **Photolithography:** using light to pattern and etch materials
- **Electron beam lithography:** using a focused beam of electrons to pattern and etch materials
- **Scanning probe microscopy:** using a physical probe to pattern and manipulate materials at the nanoscale

While top-down approaches can create nanostructures with high precision and control,
they can be limited by the difficulty of scaling down certain materials or patterns.

In contrast, bottom-up approaches can create nanostructures with unique properties, but may lack the precision and control of top-down methods.
Both approaches have their strengths and are used in different contexts to create a wide range of nanostructures [8].

Ball Milling Process

The ball milling method is a widely used mechanical technique for synthesizing nanoparticles by grinding and blending materials. This process involves placing a bulk material, along with milling balls, into a rotating cylindrical container, commonly referred to as a ball mill. As the container rotates, the balls are lifted and then dropped onto the material, causing repeated impact and shear forces that fracture the particles, reducing their size to the nanoscale.

Key parameters such as the size, material, and number of milling balls, the rotation speed of the mill, and the duration of milling are crucial in determining the final particle size, morphology, and phase of the nanoparticles. The impact energy from the collisions between the milling balls and the material leads to a reduction in particle size and can also induce phase transformations, enhancing material properties.

Ball milling offers several advantages, including simplicity, costeffectiveness, scalability, and environmental friendliness. It does not require hazardous chemicals or solvents, making it a greener alternative to chemical synthesis methods. The technique is versatile and can be applied to a wide range of materials, including metals, alloys, ceramics, and polymers, enabling the production of both single-component and composite nanoparticles.

Nanoparticles synthesized via ball milling are utilized in various applications such as catalysis, drug delivery, electronics, and energy storage due to their unique properties. This method provides a straightforward approach to creating advanced materials with specific functionalities, making it a valuable tool in nanotechnology research and development [11, 12].

Laser ablation

The synthesis of nanoparticles using laser ablation is a physical method that involves irradiating a solid target material with a high-energy laser beam in a liquid medium or vacuum. This process leads to the formation of nanoparticles directly from the bulk material without the need for chemical reagents.
The method is particularly favored for its simplicity, cleanliness, and ability to produce pure nanoparticles with minimal contamination. During laser ablation, a pulsed laser is focused on the surface of a solid target material submerged in a liquid, such as water, ethanol, or other solvents. The intense laser pulses generate a rapid, localized rise in temperature, causing the material at the surface to vaporize or melt.

As this vaporized material cools and condenses in the surrounding liquid, nanoparticles form. The characteristics of the produced nanoparticles, such as size, shape, and composition, can be controlled by adjusting laser parameters like wavelength, pulse duration, energy, and repetition rate, as well as the properties of the liquid medium.

One of the key advantages of laser ablation in liquids (LAL) is the ability to produce highly pure nanoparticles, free from chemical by-products that often accompany chemical synthesis methods. This purity is crucial for applications in fields such as biomedicine, where nanoparticles are used for drug delivery, imaging, and as therapeutic agents.

Additionally, LAL allows for the synthesis of a wide range of nanoparticle materials, including metals, semiconductors, and oxides, making it a versatile technique. Laser ablation also enables the production of nanoparticles with unique properties due to the rapid quenching rates, which can lead to amorphous or metastable phases not easily achievable by other methods.

Moreover, the size distribution of the nanoparticles can be tuned by varying the laser parameters or by post synthesis treatments, such as centrifugation or filtration. Overall, the synthesis of nanoparticles using laser ablation is a powerful technique that provides precise control over nanoparticle production, offers high purity, and is versatile across different materials and applications. It is widely used in research and industry for developing advanced materials with tailored properties for specific applications[13].

Green synthesis of Nanoferrites

The green synthesis method is a sustainable and eco-friendly approach to synthesizing nanoparticles, using natural materials and environmentally friendly processes.

This method involves selecting natural materials, such as plant extracts, microorganisms, or biomolecules, as reducing agents and stabilizers. The natural material is then mixed with a metal salt solution under suitable conditions, such as temperature, pH, and concentration, to form a reaction mixture.

The natural material reduces the metal ions, forming nanoparticles, which then grow and are stabilized by the natural material. Finally, the synthesized nanoparticles are purified and characterized using various techniques.

Green synthesis offers several advantages over physical and chemical methods, including non-toxicity, pollution-free, environmental friendliness, economical, and sustainability. However, challenges and limitations of this method include the availability of raw materials, reaction time, and quality of final products, such as particle size and homogeneity.

Overall, green synthesis is a promising approach for sustainable nanoparticle production, with potential for advancement in various fields. This method provides a viable alternative to traditional methods, reducing the environmental impact and improving the sustainability of nanoparticle synthesis[14].

III. APPLICATIONS

Bio-Medical Applications

Magnetic nanoparticles (NPs) have unique properties making them suitable for nanomedicine applications such as drug delivery, imaging, and hyperthermia.
Iron oxide and cobalt-ferrite (Co-Fe) NPs are commonly used, with Co-Fe NPs showing larger magnetic anisotropy.

However, their toxicity needs to be understood for successful application. Studies have shown that surface coating can reduce toxicity, and predictive toxicology approaches can help forecast toxic effects.

This study explores the toxicological effects of Co-Fe NPs on cell viability and oxidative stress, using data mining and knowledge discovery to develop a predictive model of NP toxicity.

The model predicts the relative hierarchy of variables such as concentration, cell type, and exposure duration, providing a multi-dimensional perspective on NP toxicity[15].

Magnetic thermotherapy

Magnetic hyperthermia, a cutting-edge cancer treatment, leverages magnetic nanoparticles (MFNPs) to generate heat and selectively target tumor cells when exposed to an alternating magnetic field (AMF). Despite its clinical approval and registration, the technique faces limitations, including inefficient heat transfer. Recent breakthroughs have focused on optimizing MFNP properties to enhance heating efficiency.

Researchers have explored various strategies, such as tailoring size, morphology, composition, and surface modification, as well as exchange-coupled and assembled MFNPs.

Notably, innovative designs like vortex-domain nanorings (FVIOs) and exchange-coupled coreshell MFNPs have demonstrated significantly improved heating performance. While these advancements hold promise, further research is crucial to overcome existing challenges and unlock the full potential of magnetic hyperthermia. Continued innovation in MFNP design and optimization is essential to enhance treatment efficacy and pave the way for future applications[16].

Magnetic resonance imaging (MRI)

Magnetic Resonance Imaging is a crucial diagnostic tool in hospitals, relying on contrast agents to enhance image quality. Superparamagnetic iron oxide nanoparticles (SPIONs) are commonly used as MRI contrast agents, but their tendency to aggregate in water or tissue fluid limits their application. To overcome this, coating SPIONs with polymers like polyethylenimine (PEI) or poly(ethylene glycol) (PEG) improves their stability, biocompatibility, and circulation time.PEI-coated SPIONs have shown promise as MRI contrast agents, but PEI's toxicity limits its use. PEG, on the other hand, is a biocompatible and non-toxic polymer widely used in pharmaceuticals.

Recent studies have combined PEG with PEI for gene delivery, but PEG modified PEI-coated SPIONs have not been explored for MRI contrast agents. This highlights the potential for developing PEG-modified PEI-coated SPIONs as safe and effective MRI contrast agents, combining the benefits of both polymers[17].

Drug delivery

The application of magnetic nanoparticles (MNPs) in targeted drug delivery has revolutionized the field of medicine. MNPs have shown great promise in delivering drugs to specific sites in the body, reducing side effects and improving therapeutic outcomes. Magnetic nanoferrite particles can be used as a delivery vehicle for drugs, entrapping them in their matrix and releasing them at the target site as shown in fig3.

Advantages of magnetic nanoferrites

1. **Targeted drug delivery**: Magnetic nanoferrite particles can be guided to specific sites in the body using external magnetic fields, ensuring that the drug is delivered directly to the affected area.
2. **Controlled release:** Magnetic nanoferrite particles can be designed to release drugs in response to specific stimuli, such as changes in pH or temperature.
3. **Biocompatibility:** Magnetic nanoferrite particles are generally non-toxic and biocompatible, making them suitable for use in the body[18,19,20].

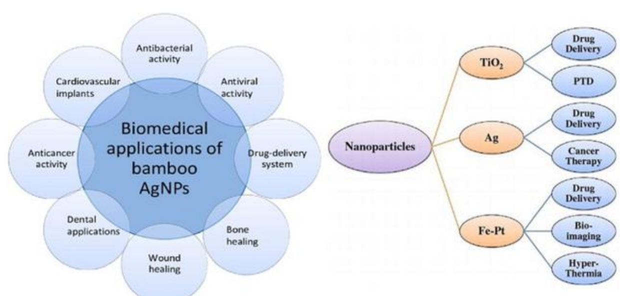

Fig 3 : Nanoparticles in biomedical applications

Sensor applications

Sensors are devices that convert physical or chemical phenomena into output signals, typically electrical signals.

There are various types of sensors available for wide-ranging applications, such as gas sensors, humidity sensors, light sensors, etc. Gas sensors, for instance, are designed to detect leaks of LPG gas or other harmful gases.Gas sensors have widely applications in chemical industries and laboratories.Researchers had reported that ferrite nanoparticles have great sensitivity property because of their morphology and surface state.

1D nanostructured materials have potential applications in sensor technology because of their high surface to volume ratio and surface area.

Chu Xiangfeng et.al.[31] have prepared nickel ferrite nanocubes and nanorods by hydrothermal method and showed that the sample is sensitive to triethylamine.et.al. A. El-Denglawey [32] prepared Manganese-Zinc Nanoferrite by Combustion synthesis and investigated the humidity sensing property of the prepared sample.et.al. E. Ranjith Kumar [33] have prepared Manganese doped copper nanocrystallineferrite by autocombustion method and studied the conductance property of the sample by exposing the sample to LPG a reducing gas.

Application Area	Specific Use Cases	Key Benefits
Biomedical	Drug delivery: Target specific cancer cells. Magnetic resonance imaging (MRI): Act as contrast agents to improve imaging sensitivity. Hyperthermia therapy: Heat and destroy cancerous tumors. Antimicrobial agents: Inhibit the growth of bacteria. Biosensors: Act as biosensing platforms for diagnostic purposes.	Enhanced efficiency for targeted therapies; improved diagnostic capabilities.
Environmental Remediation	Wastewater treatment: Adsorb and remove heavy metals, organic dyes, and other pollutants from water. Photocatalysis: Degrade harmful contaminants and dyes in water using photocatalytic properties.	Cost-effective and reusable materials for purification; efficient degradation of pollutants.
Electronics and Telecommunications	Microwave devices: Used in waveguides, antennas, and microwave absorbers. High-frequency devices: Low loss properties make them suitable for high-frequency applications. Magnetic core materials: Used in transformer cores and inductor cores. Electromagnetic shielding: Used to protect devices from electromagnetic interference.	High electrical resistivity and low eddy current losses, which improve performance.
Energy	Energy storage: Used in supercapacitors and lithium-ion batteries due to their redox activity and good ion storage capacity. Solar energy devices: Used for photocatalytic and photoelectrochemical applications, such as water splitting.	High power density and good electrochemical stability for energy storage; dual photochemical/ electrochemical activity for energy conversion.

Catalysis	Nanocatalysts: Used in various organic reactions, such as oxidation and alkylation, with a large surface area increasing efficiency and reducing reaction time. Recoverable catalysts: Magnetic properties allow for easy separation and reuse of catalysts.	High surface area for anchoring organic groups; increased reaction rates and cost-effectiveness.
Data Storage and Recording Media	Magnetic storage devices: Used in high-density storage devices and magnetic recordi media. Magnetic fluids (ferrofluids): Used for various applications, including sealing and heat transfer.	Tunable magnetic properties enable superior data storage performance.

IV. CONCLUSION

In summary, this review highlights [ref. 1 -33] the significant potential of mixed nanoferrites in various fields, including biomedicine and sensors.

The preparation and synthesis methods greatly influence the physical, electrical,m mechanical, and structural properties of these ferrite materials. As the size of the material decreases from bulk to the nanoscale, key characteristics such as surface-to-volume ratio, porosity, and other physical properties change, which directly impacts their potential applications. Current studies indicate that mixed nanoferrites offer more advantages compared to single-component ferrites.

Doping with transition or rare earth metals enhances their electrical and magnetic properties, resulting in features such as high saturation magnetization, very high coercivity, and high resistivity. These enhanced properties make mixed nanoferrites particularly suitable for a wide range of applications in medical and electronic fields. The ability to manipulate the composition and size of mixed nanoferrites allows for the development of materials with tailored properties, leading to numerous practical applications.

Their unique structure and properties, especially when enhanced by doping, provide a versatile platform for innovation in areas requiring advanced materials with specific performance characteristics.

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