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Research Article

Synthesis, characterization technique and effect of rare earth ion substitution on properties of soft substituted ferrite nano-particles – A bird's eye view

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ABSTRACT

Ferrites have been known since long times. They are a class of ceramic materials which are based on iron oxide. Rare earth ion substitution has emerged out as a promising strategy to tailor the properties of soft ferrite nanoparticles for various applications. This study investigates the impact of substituting rare earth ions (RE^{3+}) such as La^{3+}, Dy^{3+}, Gd^{3+} and Sc^{3+} on the structural, magnetic and electrical properties of soft ferrite nanoparticles by using different method. The results show that substitution of RE^{3+} significantly influences the particle size, lattice parameter, and magnetic anisotropy of the ferrite nanoparticles. The magnetic properties, including saturation magnetization and coercivity, are found to be enhanced with substitution of RE^{3+}. Additionally, the electrical properties, such as dielectric constant and loss tangent, are also modified with RE^{3+} substitution. In the review we observed that changes are attributed to the variation in the magnetic moment and the distortion of the crystal lattice due to substitution of RE^{3+}. This review provides valuable insights into the effects of rare earth ion substitution on the properties of soft ferrite nanoparticles, which can be useful for designing and developing advanced magnetic materials for various applications.

1 Introduction

In this review study we discussed about the synthesis techniques and applications of ferrites due to their large range of many new applications in great areas in our daily life. Ferrites have good-properties in electrical and magnetic areas including high value of permeability, resistivity, permittivity, low coercivity and saturation magnetization. Ferrites due to their use in various applications such as medical diagnostics, rechargeable lithium batteries, high frequency media, solar energy devices and magnetic fluids. Due to it's high resistivity and low eddy currents ferrites are better choice over metals. Ferrite nano particles are useful with better performance in magnetic recording, catalysis, ferro-fluids, and biomedical applications such as magnetic separation, drug delivery, hyperthermia [1-5]. The most important ferrite is magnetite (Fe_3O_4) which contains both Fe^{2+} ion and Fe^{3+} ion [6]. Because of high magnetic permeability and low magnetic losses, Spinel ferrites are widely used in many electronic and magnetic devices [7,8]. But these low-cost materials are easy to synthesize and gives advantages of greater shape formability than their metal as well as amorphous magnetic counterparts. Today almost every item of electronic equipment contains some ferrimagnetic spinel ferrite materials. Properties of ferrites are dependent upon several factors such as composition, method of preparation, substitution and doping of different cations, sintering temperature and time, sintered density, grain size and their distribution [9,10]. The main objective of this review paper is consisting of an overview on the ferrites, method of synthesis, properties and its potential applications in different fields of technology. Shinde et.al [18] investigated the effect of La^{3+} substitution on structural and magnetic parameters of $Ni_{0.7}Cu_{0.1}Zn_{0.2}La_xFe_{2-x}O_4$ nano-ferrites synthesized by oxalate co-precipitation method. Ahmed *et al.* [19] studied the effect of rare earth ions on the structural, magnetic and electrical properties of $(Mn_{0.5}Zn_{0.5})\,RE_{0.05}Fe_{1.95}O_4$ ferrites where RE = Tb, La, Ce and Th. Rezlescu et al. [20] observed the influence of rare earth ions like Yb, Er, Dy, Tb, Gd, Sm substitution on structural, magnetic and electrical properties of $(Li_{0.3}Zn_{0.4})\,Fe_{1.96}RE_{0.04}O_4$ ferrites. Zhao *et al.* [21] reported the effect of substitution of Fe^{3+} and Nd^{3+} ions on structural and magnetic properties of ($CoFe_{2-x}Nd_xO_4$) ferrites. Hsu *et al.* [22] obtained crystalline ferrite particles with particle size of about 30 nm. Rahman *et al.* [23] reported that the average crystallite size of dried ferrite powder was 10 nm and crystallite size influenced the coercivity. Modak *et al*. [24] reported that the coercive field for the ferrite with particle size 12 nm was interestingly low (87 Am^{-1}) and the saturation magnetization was moderately high (~ 50 Am^2kg^{-1}). Das and Singh [25] studied the structural, magnetic, and dielectric properties of Cu-substituted Ni–Zn ferrites. They reported that the coercivity and saturation magnetization of Ni–Zn ferrites improved by substituting Cu content. Avati et al. [26] illustrated that the poor densification and slow grain growth rate of Ni–Zn ferrites can be greatly improved by the substitution of Cu^{2+} ions. Shirsath et al. [27] investigated magnetic properties of Dy^{3+}substituted Ni–Cu–Zn ferrite nanoparticles. They reported that the saturation magnetization, initial permeability, and Curie temperature of the ferrites enhance by Dy^{3+} substitution. Chaudhari et al. [28] investigated the crystallographic, magnetic, and electrical properties of $Ni_{0.5}Cu_{0.25}Zn_{0.25}La_xFe_{2-x}O_4$ nano-ferrites. Zeshan Ali Sandhu, Muhammad Asam Raza et al. [29] investigated the tunability of the magnetic properties of cobalt ferrite through the strategic substitution of zinc ions within its lattice structure..

2 Experimental

In various electromagnetic devices Ni-Cu-Zn ferrite system is a widely used ferrite material system. The important properties of Ni-Cu-Zn ferrite like high resistivity, high permeability and comparatively low magnetic losses make this ferrite system very attractive [11]. In this paper we have represented a review of different synthesis techniques and influence of rare earth ion substitution on structural and magnetic properties of soft substituted ferrite nano-particles.

2.1 Synthesis of ferrite material

There are various methods which are used for the preparation of ferrites such as ceramic method, oxalate co-precipitation method [12], chemical route method, sol-gel auto combustion method, hydrothermal method, sono-chemical approach, etc. The magnetic, structural, electrical, optical and electromagnetic property of ferrites depends on the method of preparation, sintering temperature, sintering duration and sintering atmosphere [13-16].

2.1.1 Ceramic Method

The ceramic method called as the solid-state reaction method, is a widely used technique for synthesizing soft ferrites. In this method, required metal oxides (e.g., Fe2O3, MnO2, NiO, ZnO) are selected and weighed according to the desired composition. The metal oxides are mixed and ground together using a ball mill or mortar and pestle to ensure uniform distribution. The mixture is then calcined at a high temperature (around 1000°C) for several hours to decompose the metal oxides and form a homogeneous phase. The calcined powder is ground again and then pelletized using a hydraulic press or other forming techniques. The pellets are then sintered at an even higher temperature (around 1200°C) for several hours to densify the material and achieve the desired microstructure. The ceramic method involves high-temperature calcination and sintering steps, which can lead to grain growth and reduced magnetic properties. This method requires multiple processing steps, including calcination, grinding, and sintering, which can take several days or even weeks. The ceramic method is a relatively simple and cost-effective technique compared to other methods, such as sol-gel or hydrothermal synthesis. This method can produce high yields of soft ferrite materials. But this method involves high-temperature calcination and sintering steps, which can lead to grain growth and reduced magnetic properties.

2.1.2 Co-Precipitation Method

In this method, reactants are taken in the form of chlorides or nitrates and mixed in distilled water and then suitable precipitating agent such as hydroxides is added as to get precipitates. The precipitates are the uniform mixture of reactants in the form of ferrite metals on the atomic scale. The precipitates are washed so as to remove the impurities and separated from the mother liquor with the help of centrifuge. The obtained precipitates are dried in hot oven to burn the carbonaceous matter leaving a residue of the ferrite metals [16]. The residue is grinded to obtain powder. For the growth of suitable nanoparticles pre-sintering and sintering is done at suitable temperature [17]. Co-precipitation process was used to synthesis of Ni-Cu-Zn ferrites by many researchers [22-24].

2.1.3 Sol-gel Auto-combustion Method

The Sol-Gel Auto-Combustion method is a wet chemical technique used to synthesize ferrite nano particles. This method is simple and cost effective. In this method firstly a solution is prepared by dissolving metal salts (e.g., nitrates, chlorides) in a solvent (e.g., water, ethanol). A gelating agent (e.g., citric acid, ethylene glycol) is added to the solution to form a gel-like substance. The gel is then heated to a temperature (usually around 200-300°C) at which it undergoes a self-sustaining combustion reaction, resulting in the formation of a powder. The resulting powder is then calcined at a higher temperature (usually around 500-800°C) to remove any residual organic materials and to crystallize the powder. Nanocrystalline ferrites with the composition of $Zn_xCo_{1-x}Fe_2O_4$ were synthesized by the sol-gel auto combustion method [29]

2.1.4 Hydrothermal Method

In hydrothermal method, the reaction is carried out in aqueous media in stainless steel autoclave at autogenous pressure and constant temperature. The reaction in this technique is carried out through either hydrolysis or oxidation or neutralization of mixed metal hydroxides which results in ferrite formation. The size and shape of the nano-particles can be optimized by adjusting their reaction time, temperature, reactant concentration, ratio type of solvent and precursors.

2.2 Characterization Techniques

Different methos like X-Ray Diffraction (XRD), Transmission Electron Microscope (TEM), Vibrating Sample Magnetometer (VSM), Fourier Transform Infrared Spectroscopy (FTIR), Keithley electrometer were used for the characterization and evaluation of properties. Structural characterization was done using XRD analysis.

2.2.1 X-Ray Diffraction method (XRD)

X-ray Diffraction (XRD) is a technique which is used to determine the structural properties of materials, including their crystal structure, lattice parameters, and phase composition. Working of

XRD is based on the principle of diffraction, where X-rays are scattered by the atoms in a crystal lattice. The scattered X-rays produce a diffraction pattern, which is characteristic of the material's crystal structure A typical XRD instrument consists of X-ray source which produces X-rays, usually Cu Kα radiation, Sample holder which holds the sample in place, Goniometer which moves the sample and detector to scan the diffraction pattern and detector which measures the intensity of the scattered X-rays In this the sample is prepared by grinding or crushing it into a fine powder. Then the powder is loaded into the sample holder. The sample is then irradiated with X-rays. In this way the diffraction pattern is collected by scanning the sample and detector. The collected data is analyzed using specialized software.

2.2.2 Transmission Electron Microscope (TEM)

TEM is a powerful tool for characterizing the structure and morphology of materials at the nanoscale. TEM works by transmitting a beam of electrons through a thin sample, which interacts with the sample's internal structure. The transmitted electrons are then detected and used to form an image. It Produces a beam of electrons. Then it focuses the electron beam onto the sample. Sample holder holds the sample in place. Then objective lens Collects the transmitted electrons and forms an image. Image detector captures the image. TEM can operate in various imaging modes, including: Bright-field (BF) imaging. It Provides information on the sample's morphology and structure. Dark-field (DF) imaging. It highlights the sample's internal structure and defects. High-resolution (HR) imaging. It Provides atomic-resolution images of the sample's structure.

2.2.3 FTIR (Fourier Transform Infrared)

FTIR is a non-destructive analytical technique used to identify and characterize the molecular structure of materials. FTIR works by measuring the absorption of infrared radiation by molecules. The absorbed radiation causes the molecules to vibrate, and the resulting spectrum is used to identify the molecular structure. A typical FTIR instrument consists of IR source, Interferometer, Detector Sample compartment. FTIR can analyze various types of samples. FTIR has a wide range of applications such as material identification, Chemical analysis, pharmaceutical analysis, Forensic analysis and Environmental monitoring.

2.2.4 Vibrating Sample Magnetometry (VSM)

VSM is a laboratory technique which is used to measure the magnetic properties of materials. VSM works by vibrating a sample between a set of coils, which induces an electromotive force (EMF) proportional to the sample's magnetization. A typical VSM instrument have magnet which provides a controlled magnetic field, Vibrating sample holder which holds the sample and vibrates it at a fixed frequency, Pickup coils which are used to detect the EMF induced by the vibrating sample and lock-in amplifier which measures the EMF and calculates the sample's magnetizations can measure various magnetic properties such as magnetization, magnetic field (H) curves, hysteresis loops, Saturation magnetization, Coercivity etc. It has a wide range of applications, including: Materials research: Studying the magnetic properties of novel materials, Quality control: Verifying the magnetic properties of materials in industrial production, for research and development. VSM have several advantages like high sensitivity, wide dynamic range, ability to measure small samples and non-destructive testing etc.

2.2.5 Scanning Electron Microscopy (SEM)

SEM is a laboratory technique used to produce high-resolution images of the surface morphology of materials. SEM operates by scanning a focused beam of electrons across the surface of a sample, which interacts with the sample's atoms, producing various signals. A typical SEM instrument consists of electron gun which produces a beam of electrons, Column -which is used to focus the electron beam onto the sample. Sample chamber-which holds the sample in place and detectors to collect various signals produced by the interaction between the electron beam and the sample. SEM can detect various signals including Secondary electrons (SE) that provide topographic information. Backscattered electrons (BSE) which provide compositional information and X-rays provide elemental information.

3 Conclusion

The rare earth ion substitution has been found to significantly impact the properties of soft ferrite nanoparticles. The changes in structural, magnetic, and electrical properties have been attributed to variations in ionic radius, magnetic moment, and crystal structure. Further research is needed to fully understand the mechanisms1 governing these changes and to explore the potential applications of these nanoparticles. This review summarized the current state of knowledge on the influence of rare earth ions on the substitution of soft ferrites. The substitution of rare earth ions, such as La^{3+}, Nd^{3+}, Dy^{3+} and Sm^{3+}, has been shown significant impact the structural, magnetic, and electrical properties of soft ferrites. The findings of this review suggest that rare earth ion substitution can enhance the magnetic properties, such as saturation magnetization and coercivity of soft ferrites. Additionally, the substitution can also modify the electrical properties, such as dielectric constant and loss tangent. The underlying mechanisms governing these changes have been discussed, highlighting the importance of factors such as ionic radius, magnetic moment, and crystal structure. This review has also identified areas for future research, including the exploration of new rare earth ions and the development of novel synthesis methods. The substitution of rare earth ions in soft ferrites offers a promising strategy for tailoring their properties for various applications. Further research in this area is expected to lead to the development of advanced magnetic materials with enhanced performance characteristics.

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