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# Effect of Rare Earth Doping on Structural, Magnetic and Electrical Properties of Spinel Ferrite Nanoparticle: A review.

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## Abstract

Rare Earth (RE) ion doped spinel ferrite nanoparticles are very important due to their tunable structural, magnetic and electrical properties, which are crucial for advanced technological applications such as magnetic storage, electronic and microwave devices, sensors and energy systems. This review systematically analyses current literature to understand the structural changes and modifications in the magnetic and electrical properties of RE ion doped spinel ferrite nanoparticles. Investigations on the RE induced structural changes reveal unit cell expansion, increased lattice strain, cation redistribution and decreased grain size; thereby altering fundamental super exchange interactions. Magnetic properties such as saturation magnetization ($M_S$), coercivity ($H_C$) and blocking temperature (TB) are found to be very sensitive to dopant type and concentration. Low level doping sometimes enhances $M_S$, while high doping concentration leads to magnetic dilution and spin canting, thereby reduces $M_S$. RE doping induced grain size reduction sometimes produces single domain particles of super paramagnetic nature. Analysis of electrical properties discloses increased DC resistivity and activation energy, which make these doped ferrites suitable for high frequency applications. More studies are needed to optimize the concentrations of RE dopants and to establish the correlation between structural changes and electrical and magnetic properties of RE substituted spinel ferrite nanoparticles.

**Key Words**: Spinel ferrite nanoparticles, rare earth doping, structural properties, magnetic properties, electrical properties

## 1. Introduction

Spinel ferrite nanoparticles have gained significant attention in recent years because of their technological importance in high density magnetic storage, electronic and microwave devices, telecommunication

equipments, magnetic fluids, magnetic refrigeration, gas sensing, catalysis, waste water treatment and biomedical applications such as magnetically guided drug delivery, imaging techniques, magnetic hyperthermia and biosensing [1-6]

Spinel ferrites have the general formula $MFe_2O_4$, where M is a divalent metal ion such as $Mn^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Fe^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Cd^{2+}$ or more often a combination of these [7,8]. The presence of $Fe^{2+}$, $Ni^{2+}$, $Co^{2+}$ and $Mn^{2+}$ can provide unpaired electron spins and therefore contribute to the magnetic moment of spinel. Other divalent ions such as $Mg^{2+}$, $Zn^{2+}$ or $Cd^{2+}$ do not have unpaired electrons but them disproportionate the $Fe^{3+}$ ions on the crystal lattice sites to increase the magnetic moment. The distribution of metal ions among the tetrahedral (A) sites and octahedral (B) sites is very crucial which determine the properties of spinel ferrites. They possess very high electrical resistivity, thermal and chemical stability, distinctive magnetic, optical, and dielectric properties. Their unique and versatile properties make them suitable for a wide range of technological applications.

The properties of spinel ferrite nanoparticles are greatly influenced by the composition and microstructure, which are affected by the synthesis technique and sintering conditions. Ferrite nanoparticles are generally prepared by different physical and chemical techniques such as mechanical milling, inert gas condensation, hydrothermal reaction, ceramic method, solgel technique, coprecipitation method etc. [9]. Each method has its own advantages and disadvantages [9].

It is well known that the electrical and magnetic properties of soft ferrites can be tailored by the addition of suitable divalent, trivalent or tetravalent cations in to the spinel lattice. Among various modification strategies, doping with rare earth (RE) ions has proven to be an effective method for tuning the structural, magnetic, and electrical properties of spinel ferrites. Rare earth ions (e.g., $La^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$), have large ionic radii and high magnetic moments, which can induce changes in cation distribution among tetrahedral (A) and octahedral (B) sites, produce lattice strain, and alter super exchange interactions. These changes can significantly influence crystal structure, grain morphology, saturation magnetization, coercivity, magnetic anisotropy, dielectric constant, and electrical conductivity. The extent and nature of these changes are strongly dependent on factors such as type of dopant, concentration, and synthesis technique.

In recent years, a huge body of research has been devoted in understanding the impact of rare earth doping on the properties of spinel ferrite nanoparticles. A comprehensive analysis of the reported literature is

essential to identify consistent trends and to pave way for further research. This paper is an attempt to review the improvements made in the structural, electrical and magnetic properties of spinel ferrite nanoparticles by the substitution of trivalent rare earth (RE) metal ions.

## 2. Structural Changes in Spinel Ferrites due to RE Doping

Spinel ferrites have either normal spinel or inverse spinel structure. An arrangement in which the divalent ions are on B sites and trivalent ions are on the A sites within a cubic close-packed oxygen lattice is called normal spinel structure. $ZnFe_2O_4$ and $CdFe_2O_4$ are normal spinel in the micron regime. The structure in which divalent ions are in the B sites and trivalent ions are equally distributed on A and B sites, is called an inverse spinel structure. $CoFe_2O_4$ and $NiFe_2O_4$ ferrites have inverse structure and they are all ferrimagnetic [10]. Completely normal and completely inverse spinel structures represent extreme cases and in most of the spinel ferrites, cation distribution is in between them, especially in the nano regime. The exact cation distribution strongly influences the physical properties of the material.

Table.1. Structural Changes: Literature Summary.

| **Dopant** | **Base Ferrite** | **Synthesis Technique** | **Reported Structural Changes** | **References** |
|---|---|---|---|---|
| $Gd^{3+}$, $Dy^{3+}$, $Sm^{3+}$, $Eu^{3+}$ | $NiFe_2O_4$ | Co-precipitation, Sol-gel auto combustion, Hydrothermal | Lattice parameter and induced strain increased with RE concentration while reduction in crystallite size is reported. Migration of $Ni^{2+}$ from B site to A site is reported with increase in RE occupancy at B site. Reduction in crystallite size is prominent for $Gd^{3+}$ doping, while increase in the lattice parameter is maximum for $Dy^{3+}$ substitution. With higher RE concentration, secondary ortho ferrite phase formation is reported | [10, 11, 12, 13, 14, 15, 16] |
| $Sm^{3+}$ $La^{3+}$ | $CoFe_2O_4$ | Co-precipitatio | Crystallite size reduction and expansion of the unit cell is reported for most dopants with the smallest | [17, 18, |

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|---|---|---|---|---|
| $Ce^{3+}$ $Gd^{3+}$ $Dy^{3+}$ $Eu^{3+}$ $Nd^{3+}$ | | n, Sol-gel auto combustion | crystallite size 5 – 12nm achieved for $La^{3+}$ doping. Secondary phase formation is reported with $Ce^{3+}$ ($CeO_2$) and $Eu^{3+}$ ($Eu_2O_3$) doping. Reduction in the lattice parameter is reported in $Gd^{3+}$ doped cobalt ferrite due to $Nd^{3+}$ substitution. | 19, 20, 21, 22, 23, 24] |
| $Sm^{3+}$ $La^{3+}$ $Gd^{3+}$ $Eu^{3+}$ $Nd^{3+}$ | $ZnFe_2O_4$ | Co-precipitation, Sol-gel auto combustion | Due to RE doping, increase in lattice parameter and decrease in crystallite size is reported. Maximum reduction in crystallite size (5nm average) is reported for $Gd^{3+}$ and $Sm^{3+}$ co-doping. | [25, 26, 27, 28] |
| $Er^{3+}$ $Ce^{3+}$ $La^{3+}$ $Gd^{3+}$ | $CuFe_2O_4$ | Sol-gel auto combustion, Hydrothermal | M. Mustaqeem et al. [29] have reported increase in lattice parameter and average crystallite size of 50nm with $Er^{3+}$ substitution. Deviation from cubic spinel single phase when doping >0.12 is also reported. T. Roman et al. [30] have reported structural modification from typical cubic system to a tetrahedral spinel form, together with $Ce^{3+}$ cations exclusion and formation of secondary phases in $Ce^{3+}$ doped copper ferrite. Increase in the crystallite size is reported for sol-gel synthesized samples by $Ce^{3+}$ substitution [31]. | [29, 30, 31] |
| $Sm^{3+}$ $Gd^{3+}$ $La^{3+}$ $Dy^{3+}$ | $MgFe_2O_4$ | Sol-gel auto combustion, Co- | Usual behaviour of Increase in lattice parameter and reduction in crystallite size with RE substitution is reported. R.N. Kumbhar et al. [32] have reported the formation of secondary perovskite ortho ferrite phase in $Sm^{3+}$ and $Dy^{3+}$ co-doped Mg ferrite. S. Gaba et al. [33] have reported decrease in lattice strain when | [32, 33, 34, 35] |

| | | | | |
|---|---|---|---|---|
| | | precipitation | there is minor $La^{3+}$ doping and increase in lattice strain when there is higher $La^{3+}$ concentration. No change in the crystallite size with $Gd^{3+}$ substitution and the formation of secondary tetragonal phase is reported [34] | |

Rare earth substitution causes lattice expansion, as confirmed by X-ray diffraction (XRD) analyses. According to Bragg's law and Vegard's rule, the integration of larger RE ions in octahedral sites increases the lattice constant (*a*), leading to an overall increase in unit cell volume. This expansion reduces the crystallographic density and modifies interatomic distances, thereby affecting A–B and B–B super exchange interactions. The strong preference of RE ions for octahedral sites forces partial migration of $Fe^{3+}$ ions to tetrahedral sites, altering the cation distribution. This redistribution changes bond lengths and bond angles, which are directly related to magnetic and electrical properties. Largest expansions are typically observed for $La^{3+}$ and $Sm^{3+}$ doping due to their higher ionic radii (~1.032 Å and ~0.958 Å, respectively, in octahedral coordination). $Nd^{3+}$ and $Dy^{3+}$ substitutions result in moderate expansion, while $Gd^{3+}$ tends to produce steady but smaller increases.

At moderate doping concentrations, RE ions are usually fused into the spinel lattice without significant phase separation. However, at higher concentrations, the limited solubility of RE ions may lead to the formation of secondary phases such as $REFeO_3$ (orthoferrites), detectable in XRD patterns as minor peaks. These secondary phases alter the overall physical behavior by contributing additional magnetic or dielectric components. At low to moderate doping, the spinel structure remains phase-pure. Beyond these limits, secondary orthoferrite phases are often detected, especially in $Gd^{3+}$ doped systems, where solubility limits are lower. Phase purity at higher doping levels appears more achievable with controlled, low-temperature synthesis routes such as co-precipitation. RE ion doping introduces lattice strain in the spinel lattice, which inhibits grain growth, resulting in a reduction in average crystallite size. A smaller crystallite size can enhance surface-to-volume ratio, influencing surface-related phenomena and defect density. The effect is most pronounced for $Dy^{3+}$ and $Gd^{3+}$ dopants, possibly due to stronger strain fields in the lattice. Hydrothermal synthesis with $Sm^{3+}$ shows pronounced grain modification compared to sol–gel routes, indicating that synthesis temperature and precursor chemistry also play critical roles. While the cubic Fd-

3m symmetry is preserved for most doping ranges, higher RE concentrations—particularly with $Sm^{3+}$ can induce partial tetragonal distortion due to anisotropic lattice expansion and defect clustering.

## 3. RE Induced Modifications in the Magnetic Properties

Magnetic properties of spinel ferrite nanoparticles are strongly governed by cation distribution among tetrahedral (A) and octahedral (B) sites, particle size, and the strength of super exchange interactions. In spinel structure the net magnetization arises from the difference between magnetic moments of cations at the two sublattices, as described by Néel's two-sublattice model. In nanoscale systems, additional effects such as surface spin disorder, finite-size scaling, and interparticle interactions further influence the overall magnetic performance.

RE doping introduces remarkable modifications in the magnetic properties of spinel ferrite nanoparticles. The high magnetic moments of certain RE ions and their large ionic radii can enhance or reduce the net magnetization depending on the site occupancy and doping concentration. RE doping introduces remarkable modifications in the magnetic properties of spinel ferrite nanoparticles. The high magnetic moments of certain RE ions and their large ionic radii can enhance or reduce the net magnetization depending on the site occupancy and doping concentration.

### 3.1.Saturation magnetization ($M_S$)

RE ions preferably occupy octahedral (B) sites, causing $Fe^{3+}$ migration to tetrahedral (A) sites. As the A–B exchange interaction is antiferromagnetic, changes in $Fe^{3+}$ ion occupancy can strengthen or weaken net magnetization. If non-magnetic or weakly magnetic RE ions like $La^{3+}$ or $Sm^{3+}$ are used as the dopant, they replace magnetic $Fe^{3+}$ ions at B-sites, leading to a reduction in $M_s$ (magnetic dilution) at higher doping levels. $La^{3+}$ doped $NiFe_2O_4$ often exhibited a moderate increase in $M_S$ at low doping levels but a decrease at higher doping. Significant increase in $M_S$ is observed for $Ce^{3+}$ substituted $CuFe_2O_4$ at low concentrations because $Ce^{3+}$ carries a high magnetic moment, contributing directly to the total magnetization. Observed modification in $M_S$ of other base ferrite nanoparticles with RE ion substitution is illustrated in Table 2.

Table 2. Modification in magnetic properties: Literature summary.

| **Dopant** | **Base Ferrite** | **Synthesis Technique** | **Reported RE Induced Changes in Magnetic Properties** | **References** |
|---|---|---|---|---|
| $Gd^{3+}$, $Dy^{3+}$, $Sm^{3+}$, $Eu^{3+}$ | $NiFe_2O_4$ | Co-precipitation, Sol-gel auto combustion, Hydrothermal | Reduction in saturation magnetization ($M_S$), Curie Temperature and blocking temperature (TB) along with increase in coercivity ($H_C$) is the general behaviour observed due to RE doping with some exemptions. Decrease in $M_S$ from 36.51 emu/gm to 19.69 emu/gm and reduction in $H_C$ and remnant magnetization ($M_r$) were reported by $Gd^{3+}$ substitution [10]. Decrease in $H_C$ from 121 Oe to 48 Oe for x = 0.0 to 0.07 samples and again increases to 153 Oe for x = 0.10 is reported in $NiGd_xFe_{2-x}O_4$ [12]. Superparamagnetic behaviour is reported by $Dy^{3+}$ doping [13]. S. M. Rathod et al. [14] has reported slight increase in $M_S$ due to $Gd^{3+}$ substitution. Reduction in HC is reported due to the substitution of nonmagnetic $Sm^{3+}$ ions [15] | [10, 11, 12, 13, 14, 15] |
| $Sm^{3+}$ $La^{3+}$ $Ce^{3+}$ $Gd^{3+}$ $Dy^{3+}$ $Eu^{3+}$ $Nd^{3+}$ $Tb^{3+}$ | $CoFe_2O_4$ | Co-precipitation, Sol-gel auto combustion, Hydrothermal | $M_S$ decreases / slightly increases and then decreases as the RE doping concentration increases. However, the expected increase in $H_C$ due to the increase in RE ion induced anisotropy is observed only for $Ce^{3+}$ and $Dy^{3+}$ co-doping [24]. A. Sadaqat et al. [36] has reported decrease in $H_C$ due to $Tb^{3+}$ doping. Modification from the normal ferrimagnetic behaviour to superparamagnetic nature by $Eu^{3+}$ substitution is reported by many authors [21, 23]. | [17, 18, 19, 20, 21, 22, 23, 24, 36] |
| $Sm^{3+}$ | $ZnFe_2O_4$ | Co-precipitatio | Change from ferrimagnetic behaviour to weak ferrimagnetic or superparamagnetic nature is reported | [25, 27, |

| | | | | |
|---|---|---|---|---|
| $La^{3+}$ $Gd^{3+}$ $Eu^{3+}$ $Nd^{3+}$ | | n, Sol-gel auto combustion | for most of the studied RE dopants. Y. Belaiche et al. [27] has reported reduction in $M_S$ and increase in $H_C$ by $Gd^{3+}$ and $Sm^{3+}$ co-doping. Decrease in Neel temperature and magnetic moment is reported for La3+ substituted sol-gel synthesized zinc ferrite [37]. | 28, 37] |
| Gd3+ Nd3+ Ce3+ La3+ Gd3+ | $CuFe_2O_4$ | Co-precipitation, Sol-gel auto combustion | Substantial increase in $M_S$, $M_r$ and $H_C$ are reported by incorporating $Ce^{3+}$ ions in sol-gel synthesized Cu ferrite nanoparticles due to increase in magnetocrystalline anisotropy [31]. Reduction in $M_S$ and increase in $H_C$ is reported by the substitution of $Gd^{3+}$, $Nd^{3+}$ and $La^{3+}$ ions [38]. | [29, 30, 31, 38] |
| $Sm^{3+}$ $Gd^{3+}$ $La^{3+}$ $Dy^{3+}$ | $MgFe_2O_4$ | Co-precipitation, Sol-gel auto combustion, Hydrothermal | S. Gaba et al. [33] has reported superparamagnetic behaviour $La^{3+}$ doped Mg ferrite. $Gd^{3+}$ doping has reported to cause increase in MS, because of the high magnetic moment of $Gd^{3+}$, change of cubic/ tetragonal spinel ratio and increased particle size [34]. Decrease in $M_S$, $M_r$ and hyperfine magnetic field due to the doping of Sm3+ ions is reported [35]. Reduction in $M_r$ and $M_S$, but higher $H_C$ values are reported due to $Pr^{3+}$ substitution because of increased magnetocrystalline anisotropy [39]. | [33, 34, 35, 39] |

### 3.2.Coercivity ($H_C$)

RE doping induces lattice strain in spinel ferrite nanoparticles, which increases magneto crystalline anisotropy and thereby raises coercivity. However, reduction in particle size shifts the nanoparticles towards superparamagnetic behaviour reducing $H_C$, when crystallite size approaches single domain region. Certain RE dopants like $Dy^{3+}$ with strong spin orbit coupling substantially increases anisotropy

leading to high coercivity values. All these factors together determine the modification of coercivity in RE doped spinel ferrites. As demonstrated in Table.2, most of the studied ferrites exhibited slight or moderate increase in $H_C$ due to RE doping.

### 3.3. Superparamagnetism and Blocking Temperature

When RE doping causes remarkable reduction in particle size (below critical size), thermal energy randomizes magnetization direction, which results in superparamagnetism. Blocking temperature (TB) shifts reflect the interplay between particle size, anisotropy, and interparticle interactions. $Dy^{3+}$doped systems show significant TB elevation, consistent with their highest anisotropy values, whereas $Sm^{3+}$ or $Nd^{3+}$ doping in smaller-grain systems exhibited reduction in TB due to increased surface spin disorder.

RE doped ferrites show improved performance in high-frequency applications like microwave absorbers and EMI shielding due to changes in magnetic relaxation processes. Increased anisotropy in RE doped spinel ferrites shifts resonance frequency to higher values. Also, particle size reduction helps in achieving broad-band magnetic loss behavior.

## 4. Electrical Properties of RE Doped Spinel Ferrite Nanoparticles

Rare earth doping significantly alters electrical and dielectric behaviour of spinel ferrite nanoparticles by modifying crystal structure, defect chemistry, cation distribution, and microstructure. Understanding these changes is essential for tuning ferrites for electronic, microwave and sensor and applications. Electrical conduction in spinel ferrites is mainly by thermally activated hopping of charge carriers rather than band conduction. There are two important mechanisms. First is small-polaron hopping (SPH) between $Fe^{2+}$ and $Fe^{3+}$ at B (octahedral) sites. The resistivity follows an Arrhenius-type temperature dependence [7],

$$\rho(T) = \rho_0 \, exp\left(\Delta E / kT\right)$$

where $\rho$ is the resistivity and $\Delta E$ is the activation energy required for hopping of an electron from one lattice site to another. According to this relation, conductivity of ferrites increases with increase in temperature. Second is variable-range hopping (VRH) or other localized-hopping models in highly disordered systems. Key factors controlling these mechanisms are the $Fe^{2+}/Fe^{3+}$ ratio, B-site connectivity and presence of point defects and secondary phases.

Table 3. RE induced changes in electrical properties: Key literature summary.

| **RE Dopant** | **Base Ferrite** | **Synthesis Method** | **Reported Features** | **References** |
|---|---|---|---|---|
| $Gd^{3+}$ | $NiFe_2O_4$ | Coprecipitation, Sol-gel autocombustion | Many authors have reported reduction in dielectric constant and dielectric loss by $Gd^{3+}$ substitution due to reduced hopping rate of $Fe^{3+}$ at the octahedral sites. | 10, 12 |
| $Ce^{3+}$ $Dy^{3+}$ | $CoFe_2O_4$ | Coprecipitation | Decrease in dielectric constant, AC conductivity and dielectric loss is reported by the doping of $Ce^{3+}$. DC resistivity and activation energy are increased with $Ce^{3+}$ ion concentration. Hysteresis type behaviour exhibited by the current- voltage graph of $Ce^{3+}$ doped Co ferrites suggests its potential application in resistive random axes memory (ReRAM) devices. Similar behaviour is reported for $Dy^{3+}$ doped Co ferrites. | 18, 20 |
| $Er^{3+}$ | $ZnFe_2O_4$ | Coprecipitation | Forst increase in dielectric constant and dielectric loss up to x=0.4 and then reduction with further increase in $Er^{3+}$ concentration is reported for $ZnFe_{2-x}Er_xO_4$ nanoparticles | 26 |
| $Gd^{3+}$ $La^{3+}$ $Ce^{3+}$ | $CuFe_2O_4$ | Sonochemical, Coprecipitation | Significant reduction in dielectric loss and remarkable increase in resistivity is reported for $Gd^{3+}$, $Ce^{3+}$ and $La^{3+}$ doping. Change in electrical properties is maximum for $Gd^{3+}$ doping. | 38, 40 |
| $Pr^{3+}$ $Dy^{3+}$ | $MgFe_2O_4$ | Sol-gel autocombustion | M. T. Farid et al. [39] has reported enhancement in DC resistivity and activation energy by $Pr^{3+}$ substitution. | 39 |

In RE doped spinel ferrite, $RE^{3+}$ ions replaces $Fe^{3+}$ ions in the B-sites and causes charge imbalance, which is often compensated by the formation of $Fe^{2+}$ ions and oxygen vacancies. Increased $Fe^{2+}$ ion concentration enhances polaron hopping and there by conductivity, while oxygen vacancies diminish conductivity by reducing mobility. Lattice expansion caused by the addition of larger RE ions also reduces hopping rates and hence increases resistivity. Together with these factors, cation redistribution and the formation of secondary phases determine the electrical properties of RE ion doped ferrite nanoparticles. All the studied RE dopants induced similar modifications in the electrical properties of respective base spinel ferrite nanoparticles.

## 5. Conclusions

Addition of rare earth ions induces remarkable changes in spinel ferrite nanoparticles. At moderate doping concentrations, RE ions usually fuses into the spinel lattice without significant phase separation. However, at higher concentrations, the limited solubility of RE ions leads to the formation of secondary phases such as $REFeO_3$ (orthoferrites). Expansion of the unit cell is observed in all studied base ferrites by the doping of RE ions of larger radii. Most of the RE dopants inhibited grain growth and hence decrease in crystallite size is observed for RE doped ferrites. The effect is most pronounced for $Dy^{3+}$ and $Gd^{3+}$ dopants, possibly due to stronger strain fields in the lattice. The strong preference of RE ions for octahedral sites forces partial migration of $Fe^{3+}$ ions to tetrahedral sites, altering the cation distribution. This cation redistribution plays a major role in determining the properties of RE doped spinel ferrite nanoparticles. Reduction in saturation magnetization, Curie Temperature and blocking temperature (TB) along with increase in coercivity is observed due to RE doping, with some exemptions. In some cases, RE ion induced reduction in the particle size leads to the superparamagnetic behaviour of spinel ferrite nanoparticles. Decrease in dielectric constant, AC conductivity and dielectric loss along with significant increase in DC resistivity and activation energy is observed for RE doped ferrite nanoparticles. More studies are needed to establish the correlation between structural changes and modifications in the magnetic and electrical properties

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