Magnetic and structural properties of single-phase Gd$^{3+}$-substituted Co–Mg ferrite nanoparticles

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Nanocrystalline Gd$^{3+}$-doped Co–Mg ferrite nanoparticles with the chemical formula Co$_{0.7}$Mg$_{0.3}$Fe$_{2-x}$Gd$^{3+}$O$_4$ ($x = 0.02$) were prepared by coprecipitation for the first time. The properties of the nanoparticles were investigated by X-ray diffraction, confirming a single-phase, highly crystalline cubic spinel structure in the space group $Fd\bar{3}m$ and an average crystallite size of 54 nm. The Fourier-transform infrared spectrum showed two fundamental absorption bands in the wavenumber range of 437–748 cm$^{-1}$ attributed to the stretching vibration of tetrahedral and octahedral sites in the spinel structure. Scanning electron microscopy analysis showed that the nanoparticles are different in shape and slightly agglomerated. Energy-dispersive X-ray spectroscopy demonstrated the purity of the nano-ferrite powder. Magnetic measurements revealed ferrimagnetic behavior at room and low temperatures with high coercivity and a high saturation magnetization of 95.68 emu g$^{-1}$, larger than that of pure bulk cobalt ferrite (80.8 emu g$^{-1}$). Only ferrite cobalt synthesized sonochemically has been reported to have a higher saturation magnetization (92.5 emu g$^{-1}$).

In addition, many physical phenomena become more noticeable as the size of the system approaches the nanoscale. In recent years, a lot of work has been done on nanocrystalline materials because of their unusual and interesting properties compared to bulk materials. 4, 5 Several research groups are investigating spinel oxide nanoparticles and particularly nano-ferrites because of their potential applications in magnetic devices, microwave technology, high-density magnetic recording media, cancer treatment, drug delivery systems, magnetic resonance imaging, and other fields.

The composition and synthetic method play crucial roles in determining the physical and chemical properties of ferrites. Several researchers have synthesized substituted nanoscale ferrites using the standard ceramic technique, 6 solid-state methods, 7 coprecipitation, 8 sol–gel methods, 9 molten salt routes, 10 electrodeposition, 11 and mecanosynthesis. 12 Other studies have focused on improving the physical properties of these nanomaterials. For example, Li et al. have shown that at the nanoscale, the shape, particle size, and cationic distribution play crucial roles in determining the physical properties of spinel ferrite. 13, 14 They also demonstrated that the magnetoresistance of spinel ferrite decreases as the average grain size is reduced. 15, 16

Liu et al. 16 established a correlation between the coupling of the orbital angular momentum of electron spin in CoFe$_2$O$_4$ and the superparamagnetic properties of spinel ferrite nanoparticles (MgFe$_2$O$_4$) and deduced that due to the strong magnetic coupling of the Co$^{3+}$ lattice sites, the blocking temperature of the CoFe$_2$O$_4$ nanoparticles was at least 150 °C.
high than that of MgFe$_2$O$_4$ nanoparticles of the same size. On the other hand, rare earth (RE) elements possess high magnetic moments, high magneto-crystalline anisotropy, and very high magnetostriction at low temperature due to the localized nature of 4f electrons. Thus, doping with small quantities of REs can improve the magnetic properties of nano-ferrites, particularly the magnetic coercivity, making them suitable for different applications (e.g., the treatment of hyperthermia and other biomedical applications). Although numerous nanometric cobalt ferrites have been produced by coprecipitation, few studies have been compared the cationic distributions and magnetic properties of RE-substituted cobalt powders. To our knowledge, the cation distributions and microstructural distributions of RE-doped Co–Mg nano-ferrites have not been reported. Despite the different synthetic techniques, no reports are available on gadolinium-substituted Co–Mg nano-ferrites. In this study, a coprecipitation method was used to synthesize Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ nano-ferrites. This method was chosen for its simplicity, short reaction time, low cost, and ability to produce fine and homogeneous crystalline powders without any risk of contamination.

The objective of this work was to determine the effects of doping with Gd$^{3+}$ on the structural, magnetic, and morphological properties of Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ (x = 0.02) nanoparticles prepared via coprecipitation. To the best of our knowledge, no similar work has been reported to date.

Characterization

The synthesized powder was characterized by X-ray diffraction (XRD; PANalytical PW3050/60) to determine the crystalline phase. The lattice parameters and crystallite sizes were calculated using Rietveld refinement and the Debye–Scherrer formula, respectively. Fourier-transform infrared (FTIR) spectra were recorded on a VERTEX 70 FTIR spectrometer over the range of 400–4000 cm$^{-1}$. Scanning electron microscopy (SEM; Quanta 200) coupled with energy-dispersive X-ray spectrometry (EDS) was used to determine the particle morphology and the chemical composition of the sample. Magnetic measurements were conducted using a Magnetic Property Measurement System (Quantum Design MPMS-XL-7AC SQUID) to study the magnetic behavior.

Experimental details

Gd$^{3+}$-doped Co–Mg ferrite with the chemical formula Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ (x = 0.02) was synthesized by chemical coprecipitation. First, CoCl$_2$·6H$_2$O (≥98% pure, Sigma-Aldrich), FeCl$_3$ (≥99.0% pure, Sigma-Aldrich), Gd(NO$_3$)$_3$·6H$_2$O (≥99.0% pure, Sigma-Aldrich), and Mg(NO$_3$)$_2$ (≥99.0% pure, Sigma-Aldrich) were dissolved stoichiometrically in deionized water. The mixture was stirred with a magnetic stirrer until the solution became homogeneous. The pH of the solution was adjusted to 12 via the dropwise addition of sodium hydroxide under constant stirring. The coprecipitated products were washed several times with deionized water to remove unwanted residual salts. The precipitates were then filtered and dried overnight in an oven at 100 °C. The resulting powders were calcined at 800 °C and 900 °C.

Results and discussion

XRD analysis

The powder XRD patterns of Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ calcined at 800 °C and 900 °C are shown in Fig. 1. The patterns of both samples indicate a highly pure, single-phase spinel crystal structure. The spectrum of the powder calcined at 800 °C has a parasitic peak corresponding to GdFeO$_3$ impurity, which is attributed to incomplete crystallization. In the spectrum of the powder calcined at 900 °C, the diffraction peaks located at 2θ values of 18.41°, 30.24°, 35.65°, 37.25°, 43.22°, 53.60°, and 57.16° correspond to the (111), (220), (311), (222), (400), (422), and (511) planes, respectively, which match exactly with the ICDD data card no #01-080-6487 (for CoFe$_2$O$_4$). These results confirm the formation of single-phase products. Thus, all dopants simply replaced the Co$^{3+}$–Fe$^{3+}$ ions without distorting the cubic symmetry of the host cobalt ferrite, resulting in a single-phase cubic spinel structure (space group Fd$ar{3}$m); no other impurities were detected in the high-purity cobalt ferrite both with and without gadolinium doping.

The Rietveld refinement of the average intensity profiles of nanocrystalline CoFe$_2$O$_4$ and Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ calcined at 900 °C was carried out using the program FULLPROF to determine the structural properties. The fitted patterns are in good agreement with the respective experimental data with good fitting parameters; the obtained lattice parameters a are 8.3784 and 8.3805 Å for CoFe$_2$O$_4$ and Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$, respectively. All the peaks can be indexed to a spinel structure with space group Fd$ar{3}$m. Fig. 2 and 3 show the typical refinements for CoFe$_2$O$_4$ and Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ after the final cycle of Rietveld refinement.

The average crystallite size D of each sample was determined from the full width at half maximum (FWHM) using the Debye–Scherrer formula: 19

![Fig. 1 XRD patterns of Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ calcined at 800 and 900 °C.](image-url)
\[ D = \frac{0.90 \lambda}{\beta \cos(\theta)}, \]  
\[ \rho_{X-ray} = \frac{8M}{Na^2}, \]  
where \( \lambda \) is the wavelength of Cu(K\(a \)) radiation, \( \beta \) is the FWHM, \( \theta \) is the Bragg diffraction angle.

The theoretical density \( \rho_{X-ray} \) is determined by the following relation:\[ 20 \]

The values of \( D \) and \( \rho_{X-ray} \) determined from eqn (1) and (2) along with the \( a \) values calculated by Rietveld refinement are listed in Table 1.

The lattice parameter \( a = 8.3805 \) Å for \( \text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4 \) was larger than that of \( \text{CoFe}_2\text{O}_4 \) (\( a = 8.3784 \) Å). This can be attributed to the larger ionic radii of \( \text{Gd}^{3+} \) (0.094 nm) and \( \text{Co}^{2+} \) (0.074 nm) compared to the radii of \( \text{Fe}^{3+} \) (0.067 nm) and \( \text{Mg}^{2+} \) (0.072 nm), which resulted in an overall expansion of the lattice.

As shown in Table 1, the calculated value of the average crystallite size (\( D \)), of the doped sample \( \text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4 \) is smaller than that of the undoped cobalt ferrite \( \text{CoFe}_2\text{O}_4 \), a result that is similar to those reported for RE-doped ferrites. Indeed, by comparing our results with those found in the literature, we noticed that we observed similar structural behavior with that described in previous work, in terms of an increase in the lattice parameter and decrease in the average crystallite size, but totally different magnetic behavior.\[ 21-24 \]

Indeed, in the case of the two substitutions by magnesium and gadolinium, the saturation magnetization and coercivity decrease, whereas in our case the saturation magnetization and coercivity increase drastically despite having been doped with a low concentration of gadolinium. This phenomenon will be better elucidated later when discussing the magnetic properties.

From a structural point of view, this situation can result from the fact that the higher binding energy of \( \text{Gd}^{3+} - \text{O}^{2-} \) compared to \( \text{Fe}^{3+} - \text{O}^{2-} \). In fact, a large amount of energy is necessary to replace \( \text{Fe}^{3+} \) with \( \text{Gd}^{3+} \). As a result, \( \text{Gd}^{3+} \)-substituted ferrites have higher thermal stability than pure cobalt ferrites. The smaller crystallite size may also be related to the pressure created by the larger crystals of \( \text{Gd}^{3+} \) ions (large ionic rays) on the grain boundaries.\[ 25,26 \]

The calculated \( \rho_{X-ray} \) value of \( \text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4 \) is small compared to that of pure \( \text{CoFe}_2\text{O}_4 \). This can be explained by the decrease in molecular weight upon doping with \( \text{Gd}^{3+} \) and \( \text{Mg}^{2+} \). The relative molecular weight decreases as more \( \text{Co}^{2+} \) is replaced by \( \text{Mg}^{2+} \) since the atomic weight of \( \text{Co}^{2+} \) is greater than that of \( \text{Mg} \). In addition, the atomic percentage of \( \text{Gd}^{3+} \) in this compound is much smaller than that of \( \text{Mg}^{2+} \).

**Table 1**  
Crystallite size (\( D \)), lattice parameter (\( a \)), and X-ray density (\( \rho_{X-ray} \)) values for \( \text{CoFe}_2\text{O}_4 \) and \( \text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4 \)

| Sample                | Lattice parameter \( a \) (Å) | Average crystallite size \( D \) (nm) | Theoretical density \( \rho_{X-ray} \) (g cm\(^{-3}\)) | Reference |
|-----------------------|------------------------------|--------------------------------------|-------------------------------------------------|-----------|
| \( \text{CoFe}_2\text{O}_4 \)                       | 8.378                        | 81                                   | 5.299                                           | Present work |
| \( \text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4 \) | 8.380                        | 54                                   | 5.295                                           | 21         |
| \( \text{CoFe}_2\text{O}_4 \)                       | 8.355                        | 56                                   | 5.347                                           | 22         |
| \( \text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{2}\text{O}_4 \) | 8.387                        | 48                                   | 5.030                                           |           |
| \( \text{CoFe}_2\text{O}_4 \)                       | 8.354                        | 55                                   | 5.346                                           |           |
| \( \text{Co}_{0.7}\text{Gd}_{0.02}\text{O}_4 \)      | 8.397                        | 34                                   | 5.353                                           |           |
Bulk cobalt ferrite has an inverse spinel structure that shifts to a partially inverted structure in the case of nano-ferrites. In the inverse spinel, eight of the tetrahedral sites are occupied by Fe$^{3+}$, and half of the octahedral sites are occupied by Co$^{2+}$ and Fe$^{3+}$. When the size is reduced to the nanoscale, some of the Co$^{2+}$ ions at the octahedral site migrate to the tetrahedral site, leading to a partially inverted structure. Cobalt ferrite belongs to space group $Fd\bar{3}m$, and the lattice parameter is typically close to 8.39 Å.\(^{27}\)

In the literature, MgFe$_2$O$_4$ has been reported to have a partially inverted spinel ferrite structure.\(^{28}\) The distribution of metal ions in MgFe$_2$O$_4$ is given as $[\text{Mg}_1-x\text{Fe}_x]\text{Mg}_y\text{Fe}_z\text{O}_4$, where the parenthesis and square brackets denote cation sites of tetrahedral (A-sites) and octahedral [B-sites] coordination, respectively.\(^{29}\)

Studies have been conducted on the effects of the substitution of Co by Mg on the physicochemical properties of cobalt ferrite and vice versa. Several studies have been reported on the effect of metal ion substitution on the structure and magnetic properties of MgFe$_2$O$_4$. The main objective of these studies was to synthesize pure nanocrystalline powders with the general formula $\text{Mg}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4 (0.00 \leq x \leq 1.00)$.

The structural, morphological, electrical, dielectric, and magnetic properties of Co–Mg ferrite have been studied while continuing to verify and improve the quality of ferrite for various applications. Several experimental techniques have been used to evaluate the degree of inversion in these spinel systems, including X-ray absorption, neutron, and X-ray diffraction, and Raman and Mössbauer spectroscopy. However, these methods alone cannot determine the cation distribution in Co$_x$Mg$_{1-x}$Fe$_2$O$_4$ because they only target iron ions (reported results are summarized in Table 2). Therefore, it is interesting to study the properties of Co–Mg ferrite nanoparticles doped with gadolinium because the expected improvement in the structure can lead to the improvement of the magnetic properties.

According to the literature and in the light of the considerations mentioned above, the suggested cation distribution for the Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ samples in this study can be written as $[\text{Mg}_x\text{Fe}_1-x\text{Co}_y\text{Fe}_{0.98}\text{Gd}_{0.02}]^4\text{O}_4$,

where $\gamma$ is the concentration of Mg$^{2+}$ ions, and $\delta$ is the degree of inversion represented by the percentages of Mg$^{2+}$ and Fe$^{3+}$ at tetrahedral and octahedral sites.

The mean ionic radii of ions at the tetrahedral site $r_{\text{tet}}$ and octahedral site $r_{\text{oct}}$ can be described in terms of their concentrations as

$$r_{\text{tet}} = 12\delta r_{\text{Mg}^{2+}} + (1 - \delta)r_{\text{Fe}^{3+}},$$

and

$$r_{\text{oct}} = \frac{1}{2} \left[ (1 - \delta - \gamma)r_{\text{Co}^{2+}} + \gamma r_{\text{Mg}^{2+}} + (0.98 + \delta)r_{\text{Fe}^{3+}} + 0.02r_{\text{Gd}^{3+}} \right],$$

where $r_{\text{Fe}^{3+}}$, $r_{\text{Co}^{2+}}$, $r_{\text{Gd}^{3+}}$, and $r_{\text{Mg}^{2+}}$ are the radii of Fe$^{3+}$, Co$^{2+}$, Gd$^{3+}$, and Mg$^{2+}$ ions, respectively.

The lattice parameter can be calculated theoretically by the following equation:\(^{28}\)

$$a_0 = \frac{8}{3\sqrt{3}} \left[ (r_A + R_O) + \sqrt{3} (r_B + R_O) \right],$$

where $R_O$ is the radius of oxygen ion ($R_O = 1.32$ Å), and $r_A$ and $r_B$ are the radii of the tetrahedral and octahedral sites, respectively.

A mathematical model based on the formula proposed for cation distribution was constructed to search for the best match between the theoretical and experimental values of the lattice constant for the sample by optimizing the values of the parameters $\delta$ and $\gamma$ over the tetrahedral and octahedral sites; the obtained cation distribution is shown in Table 3.

The results obtained from the proposed model are in very good agreement with those obtained experimentally by Nakagomi et al.\(^{36}\) using Mössbauer and Raman spectroscopy.

From the results reported previously, it is clear that the tetrahedral site A is mainly occupied by Fe$^{3+}$ ions and a low percentage of Mg$^{2+}$ ions, while the octahedral site B is occupied by Fe$^{3+}$, Gd$^{3+}$, Co$^{2+}$, and Mg$^{2+}$ ions, in good agreement with other results obtained by different experimental methods (Table 2).

The spinel structure has a cubic arrangement of $\text{O}^{2-}$ ions (fcc); each unit cell contains eight $\text{AB}_2\text{O}_4$ units with the space group $Fd\bar{3}m$. The atom locations in the spinel depend on the choice of the origin in the spinel unit with the space group $Fd\bar{3}m$. The conventional choices for the origin in the cells of the spinel unit are either a cation site A with 43$m$ symmetry or an octahedral vacancy with 3$m$ symmetry.\(^{28}\)

If the cation site A with 43$m$ symmetry is taken as the origin, the oxygen position parameter or the anionic parameter $u$, which is the distance between the oxygen ion and the face of the

Table 2 Cation distributions found in the literature

| Site A | Site B | Method | Reference |
|--------|--------|--------|-----------|
| Coprecipitation | $[\text{Mg}_{0.5}\text{Fe}_{0.5}]$ | $[\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}]$ | Mathematical model | Present work |
| | $[\text{Mg}_{0.3}\text{Fe}_{0.7}]$ | $[\text{Mg}_{0.5}\text{Co}_{0.5}\text{Fe}_{1.1}]$ | XRD | 31 |
| | $[\text{Co}_{0.3}\text{Fe}_{0.7}]$ | $[\text{Co}_{0.5}\text{Gd}_{0.02}\text{Fe}_{1.2}]$ | Rietveld analysis | 32 |
| Sol-gel | $[\text{Co}_{0.1}\text{Mg}_{0.9}\text{Fe}_{0.85}]$ | $[\text{Mg}_{0.6}\text{Co}_{0.3}\text{Fe}_{1.2}]$ | Mössbauer spectroscopy | 33 |
| | | $[\text{Mg}_{0.6}\text{Co}_{0.4}\text{Fe}_{1.1}]$ | Mathematical model | 34 |
| | | $[\text{Mg}_{0.6}\text{Co}_{0.6}\text{Fe}_{1.1}]$ | Rietveld analysis | 35 |
| | $[\text{Mg}_{0.1}\text{Fe}_{0.9}]$ | $[\text{Mg}_{0.6}\text{Fe}_{1.1}]$ | Mössbauer spectroscopy | 36 |
| | $[\text{Mg}_{0.1}\text{Fe}_{0.9}]$ | $[\text{Mg}_{0.6}\text{Fe}_{1.1}]$ | Raman spectroscopy | 37 |
| Ceramic method | $[\text{Zn}_{0.3}\text{Mg}_{0.7}\text{Fe}_{0.6}]$ | $[\text{Mg}_{0.6}\text{Fe}_{1.1}]$ | Mössbauer spectroscopy | 37 |
edge along the cube diagonal of the spinel lattice, is calculated by:

$$u(\overline{3}m) = \frac{r_A + R_O}{a_{\text{exp}}} \sqrt[3]{1 + \frac{1}{4}},$$

(6)

where \(r_A\) is the ionic radius of the A-site, and \(R_O\) is the ionic radius of oxygen ion.

The calculated values of \(u(\overline{3}m)\) are 0.37886 and 0.3874 Å for the CoFe₂O₄ and Co₀.7Mg₀.3Fe₁.98Gd₀.02O₄ samples, respectively. The decrease in the oxygen positional parameter can be explained by the occupation of the Gd³⁺ only the octahedral sites but Mg²⁺ ions at the octahedral and tetrahedral sites. Consequently, the distance between the A and O²⁻ ions decreased, while that between B and O²⁻ increased.

FTIR spectra

FTIR spectroscopy makes it possible to predict the presence of the different bonds in a crystal. The FTIR spectra of the CoFe₂O₄ and Co₀.7Mg₀.3Fe₁.98Gd₀.02O₄ samples were recorded at room temperature in the wavenumber range of 400–4000 cm⁻¹ (Fig. 4).

The positions of the vibrational bands of CoFe₂O₄ and Co₀.7Mg₀.3Fe₁.98Gd₀.02O₄ are given in Table 4. For spinel ferrites, the vibrational band at around 750–850 cm⁻¹ corresponds to the stretching vibration of the tetrahedral site, while the vibrational band at around 400–500 cm⁻¹ corresponds to the stretching vibration of the octahedral site.

Table 4 indicates that the vibrational spectra consist of two main bands \((\nu_1 = 437.0807 \text{ cm}^{-1} \text{ and } \nu_2 = 779.7678 \text{ cm}^{-1})\) for CoFe₂O₄ and three bands \((\nu_1 = 445.28849 \text{ cm}^{-1}, \nu_2 = 812.0047 \text{ cm}^{-1}, \text{ and } \nu_3 = 1165.5477 \text{ cm}^{-1})\) for Co₀.7Mg₀.3Fe₁.98Gd₀.02O₄.

Table 3 Cation distribution of Co₀.7Mg₀.3Fe₁.98Gd₀.02O₄

| Cation distribution | A-site | B-site |
|-------------------|--------|--------|
| Co₀.7Mg₀.3Fe₁.98Gd₀.02 | Mg₀.1Fe₀.9 | Co₀.7Mg₀.3Fe₁.08Gd₀.02 |

Table 4 FTIR vibrational bands of CoFe₂O₄ and Co₀.7Mg₀.3Fe₁.98Gd₀.02O₄

| Sample | \(\nu_1 (\text{cm}^{-1})\) | \(\nu_2 (\text{cm}^{-1})\) | \(\nu_3 (\text{cm}^{-1})\) |
|--------|----------------|----------------|----------------|
| CoFe₂O₄ | 437.0807 | 779.7678 | — |
| Co₀.7Mg₀.3Fe₁.98Gd₀.02O₄ | 445.28849 | 812.0047 | 1165.5477 |

Fig. 4 FTIR spectra of samples Co₀.7Mg₀.3Fe₁.98Gd₀.02O₄ and CoFe₂O₄.

Fig. 5 SEM image of Co₀.7Mg₀.3Fe₁.98Gd₀.02O₄ nanoparticles and the corresponding particle size distribution.
Co₀.⁷Mg₀.₃Fe₁.⁹₈Gd₀.₀₂O₄. The absorption band ν₁ is assigned to the stretching vibration mode of metal–oxygen at tetrahedral sites, whereas ν₂ is attributed to octahedral sites. The positions of the two strong bands are clearly related to the difference in the Fe–O bond lengths at the A- and B-sites. The presence of the band ν₃ in Co₀.⁷Mg₀.₃Fe₁.⁹₈Gd₀.₀₂O₄ is related to the stretching vibration of the nitrate group (NO₃).⁴³

Compared to CoFe₂O₄, the FTIR bands of Co₀.⁷Mg₀.₃Fe₁.⁹₈Gd₀.₀₂O₄ are shifted toward higher frequency, as indicated in the inset of Fig. 4 (ν₁ = 437–445 cm⁻¹ and ν₂ = 749–812 cm⁻¹). These shifts are explained by the changes in the bond strength, bond length, and broadening of the tetrahedral and octahedral sites.⁴⁴

The changes in the octahedral site were greater than those in the tetrahedral site after doping with gadolinium. Thus, it can be concluded that the gadolinium ions have a greater effect on the octahedral sites. The doping ions can increase the absorption band length of the tetrahedral and octahedral site lattice.

### Table 5: Results of magnetic measurements

| T (K) | Mₛ (emu g⁻¹) | Mᵣ (emu g⁻¹) | Hᵣ (Oe) | Mᵣ/Mₛ | nₛ (μₛ) | K × 10⁵ (erg cm⁻³) |
|-------|--------------|--------------|---------|--------|----------|------------------|
| 300 K | 95.68        | 39.99        | 1702.28 | 0.41   | 3.87     | 1.69             |
| 10 K  | 109.53       | 82.58        | 11 959.53 | 0.75   | 4.43     | 13.64            |
In addition, Fe$^{3+}$, Co$^{2+}$, Mg$^{2+}$, and Gd$^{3+}$ mainly occupy the B-sites in the spinel structure, inducing stress at the octahedral and tetrahedral sites. This leads to an increase in the ionic rays at both sites, leading to a change in frequency.

**Morphological study**

The external morphology of Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ was visualized by SEM (Fig. 5). The nanoparticles agglomerated due to their mutual magnetic interactions and high surface energy. The shapes of the particles appeared to be non-spherical.

The particle size distribution was analyzed using ImageJ software. The particle size at the surface was roughly estimated to be in the range of 30–70 nm for the Gd-doped ferrite sample, close to the value of $D$ obtained by XRD analysis (Scherrer’s method) for the same sample.

The elemental composition of the Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ nanomaterial sample was investigated by EDS and the elemental mapping is shown in Fig. 6. The EDS spectrum and elemental mapping confirm the presence of Co, Mg, Gd, Fe, and O in the synthesized nanoparticles; no other traceable impurities were detected within the resolution limit of EDS. The theoretical elemental composition $x$ was calculated using the following formula:

$$x(\%) = \frac{M}{M_T} \times 100,$$

where $M$ is the molar mass of the element, $M_T$ is the total molar mass, and $z$ refers to the number of elements. The theoretical and experimental elemental compositions are presented in Table 6. The experimental elemental percentages agree with the theoretical values, and the crystal structure showed a homogeneous chemical composition.

**Magnetic properties**

The magnetic properties of Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ were investigated using a magnetic property measurement system. Fig. 6 shows the measured magnetic hysteresis loops at low and room temperature (10 and 300 K) under an applied external field of ±50 kOe. The loops indicate ferrimagnetic behavior.

The $M_S$ values of the two curves were determined by fitting the high-field ($1/H \rightarrow 0$) data using the following function:

$$M = M_S \left( 1 - \frac{\alpha}{H} \right),$$

where $\alpha$ is a fitting constant, and $H$ is the applied magnetic field. From the hysteresis loops, the magnetic parameters [$M_S$, $H_c$, remnant magnetization ($M_r$), squareness ($M_r/M_S$), anisotropy constant ($K$), and magnetic moment ($\mu_B$)] were calculated (Table 5).

The data in Table 5 show that $M_S$ and $M_r$ increased with decreasing temperature from 300 to 10 K for the doped sample, and these $M_S$ and $M_r$ values were higher than those of undoped cobalt ferrite. In contrast, the $M_S$ values of some RE-doped ferrites were reported to be lower compared to that of bulk cobalt ferrite. The $M_S$ determined at 10 K was higher than that determined at 300 K. This can be explained by the decrease in thermal energy at low temperature, which leads to the alignment of magnetic moments parallel to the direction of the applied magnetic field, resulting in an increase in saturation. The mechanism is exactly the opposite at high temperature, where the surface spins show some disordered states, weakening their response to the applied magnetic field and thus reducing magnetization. The higher values of $M_S$ at high and low temperature are attributed to the migration of some ferric ions from the octahedral site to the tetrahedral site. This observed variation in the $M_S$ and $M_r$ can be understood by considering the structure of the ferrimagnetic cubic spinel. The number of octahedral sites (B-sites) is twice the number of tetrahedral sites (A-sites), and the magnetic moments on the octahedral and tetrahedral sites are antiparallel to each other, leading to a net magnetization. In addition, the increase in size can be correlated with the transformation of the multi-domain structure into a monodomain structure upon doping the Co–Mg nano-ferrite with Gd$^{3+}$. At tetrahedral sites further from the proposed cation distribution, magnesium and ferric ions exhibit A–A exchange interactions; in contrast, at octahedral sites, cobalt, magnesium, ferric, and gadolinium ions exhibit B–B interactions. At tetrahedral and octahedral sites, bivalent (Co$^{2+}$ and Mg$^{2+}$) and trivalent (Fe$^{3+}$ and Gd$^{3+}$) metal ions exhibit superexchange A–B interactions. The superexchange A–B interactions are practically superior to the A–A and B–B interactions at the respective sites. The superexchange A–B interactions can increase upon the addition of Gd$^{3+}$ in spinel nano-ferrite Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$. This increase in A–B interaction implies an increase in $M_S$ and $\mu_B$. Based on the literature, the particle size of pure cobalt ferrite synthesized via coprecipitation is between 10 and 30 nm, while $M_S$ is in the range of 75–55 emu g$^{-1}$ (Table 6). In the case of Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$, as demonstrated by XRD analysis, the particle size is 54 nm, indicating that $M_S$ increases with particle size.

The distances along with the angles between the ions play a crucial role in determining the magnetic exchange interactions. In general, for spinel ferrites, these binding angles and

### Table 6 Magnetic properties of pure CoFe$_2$O$_4$ prepared via coprecipitation

| pH | Crystallite size (nm) | $M_s$ (emu g$^{-1}$) | $M_r$ (emu g$^{-1}$) | $H_c$ (Oe) | $K \times 10^3$ (erg cm$^{-3}$) | $\mu_B$ (μB) | Reference |
|----|----------------------|---------------------|---------------------|------------|-----------------------------|--------------|-----------|
| —  | 13                   | 59.74               | 12.68               | 306.90     | 19.10                       | 2.51         | 46        |
| <6 | 38.59                | 73.58               | 41.20               | 568        | —                           | 3.08         | 47        |
| —  | 16.84                | 61                  | 15.25               | 419.00     | —                           | —            | 48        |
| 12 | 15                   | 75                  | 19.3                | 400        | —                           | —            | 49        |

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Table 7  Expressions for determining the cation–cation (Me–Me) and cation–anion (Me–O) distances along with the bond angles

| Me–Me | Me–O | Bond angle |
|-------|------|------------|
| b = \sqrt{\frac{2}{3}} a | p = a\left(\frac{5}{6} - u^{(43m)}\right) | \theta_1 = \cos^{-1}\left(\frac{p^2 + q^2 - c^2}{2pq}\right) |
| c = \sqrt{\frac{11}{8}} a | q = a\sqrt{3}\left(u^{(43m)} - \frac{1}{4}\right) | \theta_1 = \cos^{-1}\left(\frac{p^2 + r^2 - c^2}{2pr}\right) |
| d = \sqrt{\frac{3}{4}} a | r = a\sqrt{11}\left(u^{(43m)} - \frac{1}{4}\right) | \theta_1 = \cos^{-1}\left(\frac{2p^2 - b^2}{2p^2}\right) |
| e = \frac{3\sqrt{3}}{8} a | s = a\sqrt{3}\left(u^{(43m)} + \frac{1}{3}\right) | \theta_1 = \cos^{-1}\left(\frac{p^2 + s^2 - f^2}{2ps}\right) |
| f = \frac{\sqrt{6}}{4} a | | \theta_1 = \cos^{-1}\left(\frac{r^2 + q^2 - d^2}{2rd}\right) |

Inter-ionic distances greatly affect the magnetic characteristics. Thus, the inter-ionic distances between the cation and anion (Me–O; p, q, r, and s) and between the cation and cation (Me–Me; b, c, d, e, and f) as well as the bond angles (θ₁, θ₂, θ₃, θ₄, and θ₅) between the cation and cation–anion were calculated using the equations presented in Table 7.¹⁰

Table 8  Calculated cation–anion (Me–O) and cation–cation (Me–Me) inter-ionic distances and bond angles in the Co₉Fe₂O₄ and CoFe₂O₄ samples

| Parameter | b (Å) | c (Å) | d (Å) | e (Å) | f (Å) | p (Å) | q (Å) | r (Å) | s (Å) |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| CoFe₂O₄   | 2.9622| 3.4735| 3.6279| 5.4419| 5.1307| 2.0622| 1.8699| 3.5807| 3.6466|
| Co₀.₇Mg₀.₃Fe₁.₉₈Gd₀.₀₂O₄ | 2.9629| 3.4743| 3.6288| 5.4432| 5.1319| 1.9912| 1.9944| 3.8190| 3.6888|

Table 9  Calculated bond angles of the Co₀.₇Mg₀.₃Fe₁.₉₈Gd₀.₀₂O₄ and CoFe₂O₄ samples

| Parameter | θ₁ (°) | θ₂ (°) | θ₃ (°) | θ₄ (°) | θ₅ (°) |
|-----------|--------|--------|--------|--------|--------|
| CoFe₂O₄   | 124.0221| 148.1105| 91.8114| 125.6836| 76.3662|
| Co₀.₇Mg₀.₃Fe₁.₉₈Gd₀.₀₂O₄ | 121.3193| 136.7599| 96.1482| 126.6282| 69.2622|

Tables 8, 9 and 11 show that doping with Mg²⁺ and Gd³⁺ caused the bond lengths between Me–O (r, q, and s) and Me–Me (b to f) to increase, while p decreased. An increase in site radius may be expected due to the replacement of smaller Fe³⁺ (0.067 nm) by larger Mg²⁺ (0.072 nm) and Gd³⁺ (0.094 nm) at octahedral sites. The ionic radius of a Gd³⁺ (0.094 nm) is large for the tetrahedral site; therefore, Gd³⁺ ions are forced to occupy octahedral sites. Similarly, Co²⁺ (0.074 nm) prefers to occupy octahedral sites because of its site preference binding energy. Fe³⁺ partially migrates from octahedral to tetrahedral sites, θ₁ and θ₂ are related to the A–B interaction, θ₃ and θ₄ are related to the B–B interaction, and θ₅ is related to the A–A interaction. The obtained inter-ionic angles are given in Table 11. Doping with Mg²⁺ and Gd³⁺ caused θ₁, θ₂, and θ₅ to decrease, while θ₃ and θ₄ increased. The increase in θ₅ indicates a strengthening of A–A interactions, while the increases in θ₁ and θ₄ suggest an increase in the strength of B–B exchange interactions. Thus, we can deduce that Fe³⁺, Mg²⁺, Gd³⁺, and Co²⁺ ions at B sites along with Fe³⁺ and a low concentration of Mg²⁺ at A sites reinforce the superexchange interaction A–B, leading to increased saturation magnetization. This enhancement in magnetic properties is also attributed to the higher magnetic moment (4f⁰ orbital, S = 7/2, L = 0, J = 7/2) and spin magnetic moment of Gd³⁺ compared to Fe³⁺ (3d⁵) and Co²⁺ (3d⁷, L = 3, S = 3/2, J = 9/2) due to strong L–S coupling. Recently, many studies have been devoted to the effects of various REE dopants on the physicochemical properties of ferrites, including Li–Ni, Ni–Zn, Mn–Zn, Mg–Cu, Cu–Zn.²⁶–₅₄ In most of these studies, M₅ decreased upon doping. Reports of increases in M₅ upon doping with REs are much rarer. Rare earth ions generally occupy octahedral sites and have limited solubility in the spinel lattice due to their large ionic radii. However, their precise solubility in the spinel network has not been determined. It should also be noted that doping with low concentrations of REs causes M₅ to increase, while high dopant concentrations cause M₅ to decrease.³⁵ Our results are in good agreement with the theoretical studies of Hou Y. H. et al.,¹⁸ who found that the net magnetic moment of CoFe₂O₄ increased upon doping with Gd³⁺. Yu-Hua et al. also showed that the rare earth ions prefer to substitute for Fe³⁺ located at octahedral
sites, and the lattice constant of CoFe$_{1.875}$RE$_{0.125}$O$_4$ (RE = La, Ce, Pr, Nd, Eu, and Gd) decreased due to the decreasing ionic radius of the RE with increasing atomic number. The saturation magnetization of CoFe$_2$O$_4$ increases upon doping only with Eu and Gd because there are more unpaired 4f electrons for Eu$^{3+}$ and Gd$^{3+}$. Similarly, Torkian et al.$^{28}$ reported that the magnetization of Gd$^{3+}$-doped Mn–Zn ferrite increased for Gd$^{3+}$ substitution of up to 15%. The most significant result of this work is the production of Gd-doped Co–Mg nano-ferrites with magnetization much higher than that of bulk cobalt ferrite. To the best of our knowledge, this result has not been previously reported. Similar findings have been reported for sonochemically produced CoFe$_2$O$_4$ and Zn$_{x}$Co$_{(1-x)}$Fe$_2$O$_4$ synthesized using complex precursors (Table 10).

The experimental magnetic moment per formula unit ($n_B$ of Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$) was measured using SQUID, and the magnetic moment can be interpreted based on the migration of rare earth ions to the grain boundaries, resulting in weak magnetic behavior. Moreover, the magnetic parameters of spinel ferrites depend upon various factors, including the synthetic technique, sintering temperature, crystallite size, grain size, and redistribution of cations among A and B sites.

The effective anisotropy constant $K$ can be calculated using the relationship

$$H_C = \frac{K_{\text{eff}} \times 0.96}{M_s},$$

where $H_C$ is the coercivity, and $M_s$ is the saturation magnetization. The coercivity value of the sample at 300 K is given in Table 5. It can be observed from Tables 5 and 6 that the coercivity of the sample at 300 K was higher than that of pure cobalt ferrite synthesized via coprecipitation. The observed variation in coercivity can be explained as follows. As discussed above, compared to other ions, Co$^{3+}$ exhibits stronger $L$–$S$ coupling and a weaker crystal field, resulting in stronger magneto-crystalline anisotropy related to the increase in the concentration of high-spin Co$^{3+}$ ions at octahedral sites.$^{65}$ Although Gd$^{3+}$ has zero orbital angular momentum, gadolinium has been reported to contribute to and strengthen anisotropy.$^{64}$

The coercivity of the sample increased from 1702.28 Oe at 300 K to 11 959.53 Oe at 10 K. The enhanced coercivity is attributed to the reduced thermal fluctuation energy at 10 K, which is less effective in reducing the effects of magneto-crystalline anisotropy energy. In addition, the enhanced coercivity could be interpreted as a result of the energy barriers in the nanoparticles becoming more apparent at low temperature. While these barriers always exist, they have been suggested to

Table 10 Magnetic properties of cobalt ferrite prepared by different synthetic methods

| Compound            | Method of synthesis | $M_s$ (emu g$^{-1}$ at 300 K) | $M_s$ (emu g$^{-1}$ at 5 K) | $H_C$ (Oe at 300 K) | $H_C$ (Oe at 5 K) | $M_s/M_a$ (300 K) | $M_s/M_a$ (5 K) | Reference          |
|---------------------|---------------------|------------------------------|------------------------------|---------------------|-------------------|-------------------|-------------------|-------------------|
| Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ | Coprecipitation     | 95.68                        | 109.5                        | 1702.28             | 11 959.53         | 0.4179            | 0.7539            | Present work       |
| CoFe$_2$O$_4$       | Classical ceramic method | 88                           | —                            | 141                 | —                 | —                 | —                 | 57                |
| Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ | Sonochemical method | 80.8                         | 93.9                         | —                   | 25 200            | —                 | —                 | 58                |
| CoFe$_2$O$_4$       | Chemical complexes  | 92.5                         | 109                          | 807                 | —                 | —                 | —                 | 59                |
| Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ | Sonocatalytic       | 92                           | 109                          | 12                  | —                 | —                 | —                 | 60                |
Table 11  Configurations of ion pairs in spinel ferrites with favorable distances and angles for effective magnetic interactions in samples Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ and CoFe$_2$O$_4$

|                | A-B interaction | B-B interaction | A-A interaction |
|----------------|-----------------|-----------------|-----------------|
| CoFe$_2$O$_4$  | ![Diagram](image1) | ![Diagram](image2) | ![Diagram](image3) |
| Co$_{0.7}$Mg$_{0.3}$Fe$_{1.98}$Gd$_{0.02}$O$_4$ | ![Diagram](image4) | ![Diagram](image5) | ![Diagram](image6) |
become more pronounced at low temperature; hence, these barriers might delay the alignment of magnetic moments in the direction of the applied magnetic field.

As indicated in Fig. 7, the hysteresis loops show “kink” behavior at 10 K. Various explanations have been suggested for these types of loops, including the magnetic coupling between two different magnetic phases with different coercivities. However, in this work, no secondary phase was observed. The kink behavior may also be explained by the oxidation of soft magnetic layers in the presence of atmospheric oxygen. Otherwise, this anomaly can only be attributed to the reordering of magnetic spins at 10 K under the influence of the applied field. These spin reorientations are responsible for constraining the M–H loop, which can be attributed to the reorientation of surface spins around particles and to the domain wall pinning of the potential wells formed by the directional order.65

The squareness ratio \( \frac{M_r}{M_s} \) at 300 K (0.4179) increased to 0.7539 at 10 K. At 300 K, \( \frac{M_r}{M_s} \) tends towards 0.5, corresponding to randomly oriented uniaxial anisotropic ferromagnetic particles. In contrast, at 10 K, \( \frac{M_r}{M_s} \) approaches 1, corresponding to typical isolated single-domain ferromagnetic particles. In the same vein, Stoner and Wohlfarth66 reported that the quadratic ratio of 0.5 indicates non-interactive, randomly oriented particles that undergo coherent rotation under the effect of the applied magnetic field. For quadratic ratios below 0.5, the particles interact only through magnetostatic interactions. Exchange coupling only manifests for a quadratic ratio of higher than 0.5.

The squareness ratio obtained at 10 K confirms that we synthesized nanosized materials with high surface area; the surface effects of the magnetic nanoparticles are responsible for their uniaxial anisotropy. Kodama67 effectively suggested that due to the high surface areas of nanomaterials, the spins at the surfaces are canted, and Néel’s model of two sublattices is no longer valid. This spin canting at the surface results in higher magneto-crystalline anisotropy in nanomaterials, in good agreement with the results of this study. Such effects may be approved by the contribution from the single-ion anisotropy of Gd\(^{3+}\) in the crystal lattice in conjunction with the surface effects resulting from the alteration of the magnetic structures on the surfaces of the nanoparticles.68

**Conclusion**

In the present work, coprecipitation was found to be an economical and efficient method for the synthesis of gadolinium-doped mixed Co–Mg ferrite nanoparticles. Structural analysis indicated a single-phase cubic spinel structure of ferrite after sintering at 900 °C, while GdFeO\(_3\) was observed as a secondary phase after sintering at 800 °C. The crystallite size calculated from the XRD data was in the order of 54 nm. Rietveld refinement of the XRD data suggested an increase in the lattice constant after doping with Gd\(^{3+}\), which enhanced the crystallinity and induced compression deformations. The spinel structure was further confirmed by FTIR spectroscopy. EDS spectroscopy confirmed the presence of Co, Mg, Fe, Gd, and O in the investigated sample, verifying its purity and the good reactivity of gadolinium at 900 °C. The proposed cation distribution suggests that Co\(^{3+}\) and Gd\(^{3+}\) have strong preferences for the octahedral B sites, whereas Mg\(^{2+}\) and Fe\(^{3+}\) prefer to occupy tetrahedral A sites and octahedral B sites. The experimental and theoretical lattice constants were comparable. The measured saturation magnetization values at 10 and 300 K indicated that Gd\(^{3+}\) substitution in the mixed Co–Mg ferrite enhanced the saturation magnetization, which was attributed to the higher spin magnetic moment and anisotropy of Gd\(^{3+}\) compared to Fe\(^{3+}\) along with the strong L–S coupling of Co\(^{2+}\). Coercivity increased upon Gd\(^{3+}\) doping, which can be explained by the strong L–S coupling and weak crystal field of Co\(^{2+}\), resulting in stronger magneto-crystalline anisotropy related to the increase in the concentration of high-spin Co\(^{2+}\) ions at octahedral sites. The enhancements in magnetic properties \( (M_r \text{ and } n_a) \) after doping with Gd\(^{3+}\) were correlated with the changes in bond angles. Finally, we note that the obtained saturation magnetization was much higher than that of bulk cobalt ferrite.

**Conflicts of interest**

There are no conflicts to declare.

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