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# Magnetic and structural properties of single-phase Gd<sup>3+</sup>-substituted Co–Mg ferrite nanoparticles

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Nanocrystalline Gd<sup>3+</sup>-doped Co–Mg ferrite nanoparticles with the chemical formula Co<sub>0.7</sub>Mg<sub>0.3</sub>Fe<sub>(2-x)</sub>Gd<sub>x</sub>O<sub>4</sub> (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 *Fd3̄m* 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<sup>-1</sup> 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<sup>-1</sup>, larger than that of pure bulk cobalt ferrite (80.8 emu g<sup>-1</sup>). Only ferrite cobalt synthesized sonochemically has been reported to have a higher saturation magnetization (92.5 emu g<sup>-1</sup>).

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## Introduction

Research in the past decades has suggested that nanotechnology will have crucial long-term effects on all industrial sectors. Compared to bulk materials, nanomaterials have increased reactivity due to their increased solubility and higher proportion of surface atoms. The magnetic, electrical, mechanical, and optical properties along with the specific electronic states of nanomaterials are also totally different from those of the equivalent bulk materials.

The specific properties of nanomaterials give them a variety of physical and chemical functionalities that are highly desirable for applications in numerous industrial sectors.<sup>1–3</sup> The unique structural characteristics, energetics, tailoring, and production strategies of nanostructures constitute the experimental and conceptual background for the field of nanoscience. The suitable control of nanostructure properties and activity can lead to new devices and technologies. The deviation of the properties of nanosized materials from those of the corresponding bulk materials is related to surface effects, which mainly depend upon the ratio of surface area to volume, the particle size, the chemical composition, and interactions between the particles. It should be noted that rapid developments in the field of nanotechnology have opened up vast possibilities for understanding and using magnetic materials.

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.<sup>4,5</sup> 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,<sup>6</sup> solid-state methods,<sup>7</sup> coprecipitation,<sup>8,9</sup> sol–gel methods,<sup>10</sup> molten salt routes,<sup>11</sup> electrodeposition,<sup>12</sup> and mecnosynthesis.<sup>13</sup> 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.<sup>14,15</sup> They also demonstrated that the magneto-resistance of spinel ferrite decreases as the average grain size is reduced.<sup>16,17</sup>

Liu *et al.*<sup>14</sup> established a correlation between the coupling of the orbital angular momentum of electron spin in CoFe<sub>2</sub>O<sub>4</sub> and the superparamagnetic properties of spinel ferrite nanoparticles (MgFe<sub>2</sub>O<sub>4</sub>) and deduced that due to the strong magnetic coupling of the Co<sup>2+</sup> lattice sites, the blocking temperature of the CoFe<sub>2</sub>O<sub>4</sub> nanoparticles was at least 150 °C

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higher than that of  $\text{MgFe}_2\text{O}_4$  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).<sup>17,18</sup> 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  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  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  $\text{Gd}^{3+}$  on the structural, magnetic, and morphological properties of  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{(2-x)}\text{Gd}_x\text{O}_4$  ( $x = 0.02$ ) 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  $\text{cm}^{-1}$ . 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

$\text{Gd}^{3+}$ -doped Co–Mg ferrite with the chemical formula  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{2-x}\text{Gd}_x\text{O}_4$  ( $x = 0.02$ ) was synthesized by chemical coprecipitation. First,  $\text{CoCl}_2 \cdot 5\text{H}_2\text{O}$  ( $\geq 98\%$  pure, Sigma-Aldrich),  $\text{FeCl}_3$  ( $\geq 99.0\%$  pure, Sigma-Aldrich),  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $\geq 99.0\%$  pure, Sigma-Aldrich), and  $\text{Mg}(\text{NO}_3)_2$  ( $\geq 99.0\%$  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  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  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  $\text{GdFeO}_3$  impurity, which is attributed to incomplete crystallization. In the spectrum of the powder calcined at 900 °C, the diffraction peaks located at  $2\theta$  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  $\text{CoFe}_2\text{O}_4$ ). These results confirm the formation of single-phase products. Thus, all dopants simply replaced the  $\text{Co}^{2+}\text{-Fe}^{3+}$  ions without distorting the cubic symmetry of the host cobalt ferrite, resulting in a single-phase cubic spinel structure (space group  $Fd\bar{3}m$ ); 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  $\text{CoFe}_2\text{O}_4$  and  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  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  $\text{CoFe}_2\text{O}_4$  and  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$ , respectively. All the peaks can be indexed to a spinel structure with space group  $Fd\bar{3}m$ . Fig. 2 and 3 show the typical refinements for  $\text{CoFe}_2\text{O}_4$  and  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  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:<sup>19</sup>



Fig. 1 XRD patterns of  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  calcined at 800 and 900 °C.





Fig. 2 Typical Rietveld-refined XRD pattern for the  $\text{CoFe}_2\text{O}_4$  sample.



Fig. 3 Typical Rietveld-refined XRD pattern for the  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  sample.

$$D = \frac{0.90\lambda}{\beta \cos(\theta)}, \quad (1)$$

where  $\lambda$  is the wavelength of  $\text{Cu}(\text{K}\alpha)$  radiation,  $\beta$  is the FWHM, and  $\theta$  is the Bragg diffraction angle.

The theoretical density  $\rho_{\text{X-ray}}$  is determined by the following relation:<sup>20</sup>

$$\rho_{\text{X-ray}} = \frac{8M}{Na^3}, \quad (2)$$

where  $M$  is the molecular weight of the sample,  $N$  is Avogadro's number, and  $a$  is the lattice parameter.

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

The lattice parameter  $a = 8.3805 \text{ \AA}$  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  $\text{CoFe}_2\text{O}_4$  ( $a = 8.3784 \text{ \AA}$ ). This can be attributed to the larger ionic radii of  $\text{Gd}^{3+}$  (0.094 nm) and  $\text{Co}^{2+}$  (0.074 nm) at the octahedral site 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.<sup>21–24</sup> 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.<sup>25,26</sup>

The calculated  $\rho_{\text{X-ray}}$  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 ( $\rho_{\text{X-ray}}$ ) 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 $\rho_{\text{X-ray}}$ ( $\text{g cm}^{-3}$ ) | 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  |              |
| $\text{CoFe}_2\text{O}_4$  | 8.355                     | 56                                | 5.347  | 21           |
| $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_2\text{O}_4$                      | 8.387                     | 48                                | 5.050  |              |
| $\text{CoFe}_2\text{O}_4$  | 8.354                     | 55                                | 5.346  | 22           |
| $\text{CoFe}_{1.96}\text{Gd}_{0.04}\text{O}_4$                             | 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  $\text{Fe}^{3+}$ , and half of the octahedral sites are occupied by  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$ . When the size is reduced to the nanoscale, some of the  $\text{Co}^{2+}$  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  $8.39 \text{ \AA}$ .<sup>27</sup>

In the literature,  $\text{MgFe}_2\text{O}_4$  has been reported to have a partially inverted spinel ferrite structure.<sup>28</sup> The distribution of metal ions in  $\text{MgFe}_2\text{O}_4$  is given as  $(\text{Mg}_{1-x}\text{Fe}_x)[\text{Mg}_x\text{Fe}_{2-x}]\text{O}_4$ , where the parenthesis and square brackets denote cation sites of tetrahedral (A-sites) and octahedral [B-sites] coordination, respectively.<sup>29</sup>

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  $\text{MgFe}_2\text{O}_4$ . The main objective of these studies was to synthesize pure nanocrystalline powders with the general formula  $\text{Mg}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.00 \leq x \leq 1.00$ ).

The structural, morphological, electrical, dielectric, and magnetic properties of Co–Mg ferrite have been studied<sup>30</sup> 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  $\text{Co}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$  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  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  samples in this study can be written as



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

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

and

$$r_{\text{oct}} = \frac{1}{2} [(1 - \delta - \gamma)r_{\text{Co}^{2+}} + \gamma r_{\text{Mg}^{2+}} + (0.98 + \delta)r_{\text{Fe}^{3+}} + 0.02r_{\text{Gd}^{3+}}], \quad (4)$$

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

The lattice parameter can be calculated theoretically by the following equation:<sup>38</sup>

$$a_{\text{th}} = \frac{8}{3\sqrt{3}} [(r_{\text{A}} + R_{\text{O}}) + \sqrt{3}(r_{\text{B}} + R_{\text{O}})], \quad (5)$$

where  $R_{\text{O}}$  is the radius of oxygen ion ( $R_{\text{O}} = 1.32 \text{ \AA}$ ), and  $r_{\text{A}}$  and  $r_{\text{B}}$  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.*<sup>36</sup> using Mössbauer and Raman spectroscopy.

From the results reported previously, it is clear that the tetrahedral site A is mainly occupied by  $\text{Fe}^{3+}$  ions and a low percentage of  $\text{Mg}^{2+}$  ions, while the octahedral site B is occupied by  $\text{Fe}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Co}^{2+}$ , and  $\text{Mg}^{2+}$  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 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  $\bar{4}3m$  symmetry or an octahedral vacancy with  $\bar{3}m$  symmetry.<sup>39</sup>

If the cation site A with  $\bar{4}3m$  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 | $[\text{Mg}_{0.1}\text{Fe}_{0.9}]$                     | $[\text{Co}_{0.7}\text{Mg}_{0.2}\text{Fe}_{1.08}\text{Gd}_{0.02}]$ | Mathematical model     | Present work |
|                 | $[\text{Mg}_{0.1}\text{Fe}_{0.9}]$                     | $[\text{Mg}_{0.4}\text{Co}_{0.5}\text{Fe}_{1.1}]$                  | XRD                    | 31           |
|                 | $[\text{Co}_{0.31}\text{Fe}_{0.69}]$                   | $[\text{Co}_{0.69}\text{Gd}_{0.03}\text{Fe}_{1.28}]$               | Rietveld analysis      | 32           |
| Sol-gel         | $[\text{Co}_{0.106}\text{Mg}_{0.049}\text{Fe}_{0.85}]$ | $[\text{Mg}_{0.007}\text{Co}_{0.85}\text{Fe}_{1.2}]$               | Mössbauer spectroscopy | 33           |
|                 | $[\text{Mg}_{0.51}\text{Fe}_{0.49}]$                   | $[\text{Mg}_{0.29}\text{Co}_{0.2}\text{Fe}_{1.51}]$                | Mathematical model     | 34           |
|                 | $[\text{Mg}_{0.159}\text{Fe}_{0.841}]$                 | $[\text{Mg}_{0.841}\text{Fe}_{1.159}]$                             | Rietveld analysis      | 35           |
|                 | $[\text{Mg}_{0.15}\text{Fe}_{0.85}]$                   | $[\text{Mg}_{0.86}\text{Fe}_{1.15}]$                               | Mössbauer spectroscopy | 36           |
|                 | $[\text{Mg}_{0.14}\text{Fe}_{0.86}]$                   | $[\text{Mg}_{0.87}\text{Fe}_{1.13}]$                               | Raman spectroscopy     |              |
| Ceramic method  | $[\text{Zn}_{0.5}\text{Mg}_{0.08}\text{Fe}_{0.62}]$    | $[\text{Mg}_{0.62}\text{Fe}_{1.38}]$                               | Mössbauer spectroscopy | 37           |



Table 3 Cation distribution of  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$ 

| $a_{\text{exp}}$ | $a_{\text{th}}$ | $r_{\text{A}}$ | $r_{\text{B}}$ | Cation distribution              |  |
|------------------|-----------------|----------------|----------------|----------------------------------|--|
|                  |                 |                |                | A-site                           | B-site   |
| 8.3805           | 8.38016         | 0.6750         | 0.7022         | $\text{Mg}_{0.1}\text{Fe}_{0.9}$ | $\text{Co}_{0.7}\text{Mg}_{0.2}\text{Fe}_{1.08}\text{Gd}_{0.02}$ |

edge along the cube diagonal of the spinel lattice, is calculated by<sup>40</sup>

$$u(\bar{4}3m) = \frac{(r_{\text{A}} + R_{\text{O}})}{a_{\text{exp}}\sqrt{3}} + \frac{1}{4}, \quad (6)$$

where  $r_{\text{A}}$  is the ionic radius of the A-site, and  $R_{\text{O}}$  is the ionic radius of oxygen ion.

The calculated values of  $u(\bar{4}3m)$  are 0.37886 and 0.3874 Å for the  $\text{CoFe}_2\text{O}_4$  and  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  samples, respectively. The decrease in the oxygen positional parameter can be explained by the occupation of the  $\text{Gd}^{3+}$  only the octahedral sites but  $\text{Mg}^{2+}$  ions at the octahedral and tetrahedral sites. Consequently, the distance between the A and  $\text{O}^{2-}$  ions decreased, while that between B and  $\text{O}^{2-}$  increased.<sup>41</sup>

### FTIR spectra

FTIR spectroscopy makes it possible to predict the presence of the different bonds in a crystal. The FTIR spectra of the  $\text{CoFe}_2\text{O}_4$  and  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  samples were recorded at room temperature in the wavenumber range of 400–4000  $\text{cm}^{-1}$  (Fig. 4).

The positions of the vibrational bands of  $\text{CoFe}_2\text{O}_4$  and  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  are given in Table 4. For spinel ferrites, the vibrational band at around 750–850  $\text{cm}^{-1}$  corresponds to the stretching vibration of the tetrahedral site, while the

Table 4 FTIR vibrational bands of  $\text{CoFe}_2\text{O}_4$  and  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$ 

|  | $\nu_1$ ( $\text{cm}^{-1}$ ) | $\nu_2$ ( $\text{cm}^{-1}$ ) | $\nu_3$ ( $\text{cm}^{-1}$ ) |
|--|------------------------------|------------------------------|------------------------------|
| $\text{CoFe}_2\text{O}_4$  | 437.0807                     | 779.7678                     | —                            |
| $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$ | 445.28849                    | 812.0047                     | 1165.5477                    |

vibrational band at around 400–500  $\text{cm}^{-1}$  corresponds to the stretching vibration of the octahedral site.<sup>33,42</sup>

Table 4 indicates that the vibrational spectra consist of two main bands ( $\nu_1 = 437.0807$   $\text{cm}^{-1}$  and  $\nu_2 = 779.7678$   $\text{cm}^{-1}$ ) for  $\text{CoFe}_2\text{O}_4$  and three bands ( $\nu_1 = 445.28849$   $\text{cm}^{-1}$ ,  $\nu_2 = 812.0047$   $\text{cm}^{-1}$ , and  $\nu_3 = 1165.5477$   $\text{cm}^{-1}$ ) for

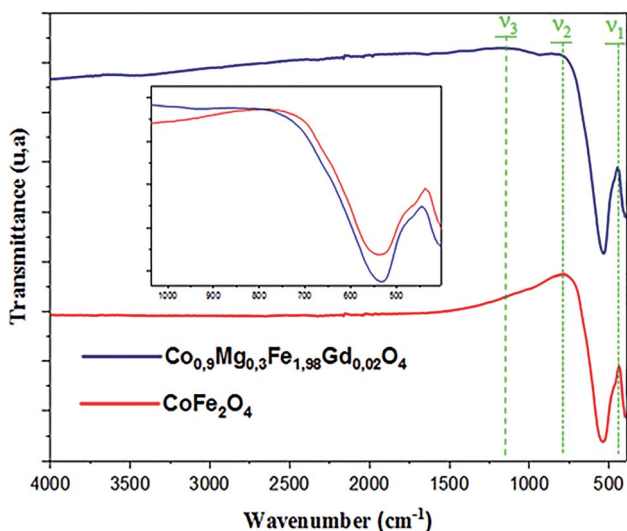


Fig. 4 FTIR spectra of samples  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$ .

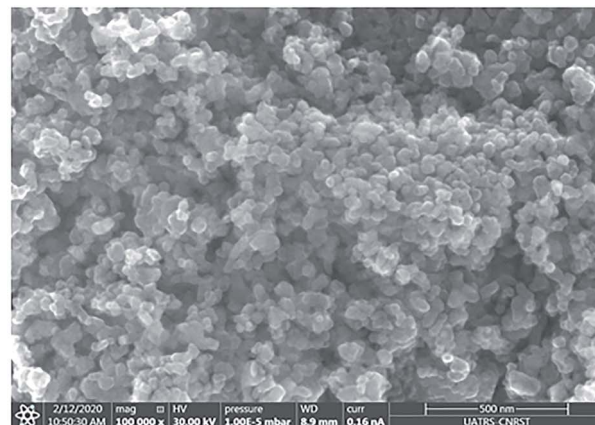


Fig. 5 SEM image of  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  nanoparticles and the corresponding particle size distribution.





Fig. 6 EDS spectrum and elemental maps of  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  and the corresponding elemental composition.

$\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$ . The absorption band  $\nu_1$  is assigned to the stretching vibration mode of metal–oxygen at tetrahedral sites, whereas  $\nu_2$  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  $\nu_3$  in  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  is related to the stretching vibration of the nitrate group ( $\text{NO}_3$ ).<sup>43</sup>

Compared to  $\text{CoFe}_2\text{O}_4$ , the FTIR bands of  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  are shifted toward higher frequency, as indicated in

the inset of Fig. 4 ( $\nu_1 = 437\text{--}445\text{ cm}^{-1}$  and  $\nu_2 = 749\text{--}812\text{ cm}^{-1}$ ). These shifts are explained by the changes in the bond strength, bond length, and broadening of the tetrahedral and octahedral sites.<sup>44</sup>

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

|       | $M_s$ (emu $\text{g}^{-1}$ ) | $M_r$ (emu $\text{g}^{-1}$ ) | $H_c$ (Oe) | $M_r/M_s$ | $n_B$ ( $\mu_B$ ) | $K \times 10^5$ (erg $\text{cm}^{-3}$ ) |
|-------|------------------------------|------------------------------|------------|-----------|-------------------|---|
| 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                                   |



Table 6 Magnetic properties of pure CoFe<sub>2</sub>O<sub>4</sub> prepared *via* coprecipitation

| pH | Crystallite size (nm) | $M_s$ (emu g <sup>-1</sup> ) | $M_r$ (emu g <sup>-1</sup> ) | $H_c$ (Oe) | $K \times 10^3$ (erg cm <sup>-3</sup> ) | $n_B$ ( $\mu_B$ ) | 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        |

In addition, Fe<sup>3+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>, and Gd<sup>3+</sup> 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 radii at both sites, leading to a change in frequency.

### Morphological study

The external morphology of Co<sub>0.7</sub>Mg<sub>0.3</sub>Fe<sub>1.98</sub>Gd<sub>0.02</sub>O<sub>4</sub> 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<sub>0.7</sub>Mg<sub>0.3</sub>Fe<sub>1.98</sub>Gd<sub>0.02</sub>O<sub>4</sub> 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:

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

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<sub>0.7</sub>Mg<sub>0.3</sub>Fe<sub>1.98</sub>Gd<sub>0.02</sub>O<sub>4</sub> 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  $\pm 50$  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:<sup>19</sup>

$$M = M_s \left( 1 - \frac{\alpha}{H} \right), \quad (7)$$

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 ( $n_B$ )] 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.<sup>22</sup> 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.<sup>45</sup> 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 magnetic moment  $M_{\text{cal}} = M_B - M_A$ . In addition, the increase in size can be correlated with the transformation of the multi-domain structure into a monodomain structure<sup>40,41</sup> upon doping the Co–Mg nano-ferrite with Gd<sup>3+</sup>. 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<sup>2+</sup> and Mg<sup>2+</sup>) and trivalent (Fe<sup>3+</sup> and Gd<sup>3+</sup>) 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 be increased upon the addition of Gd<sup>3+</sup> in spinel nano-ferrite Co<sub>0.7</sub>Mg<sub>0.3</sub>Fe<sub>1.98</sub>Gd<sub>0.02</sub>O<sub>4</sub>. This increase in A–B interaction implies an increase in  $M_s$  and  $n_B$ . 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 55–75 emu g<sup>-1</sup> (Table 6). In the case of Co<sub>0.7</sub>Mg<sub>0.3</sub>Fe<sub>1.98</sub>Gd<sub>0.02</sub>O<sub>4</sub>, 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 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   |
|----------------------------|---|--|
| $b = \frac{\sqrt{2}}{4}a$  | $p = a\left(\frac{5}{8} - u(\sqrt{43}m)\right)$                   | $\theta_1 = \cos^{-1}\left(\frac{p^2 + q^2 - c^2}{2pq}\right)$ |
| $c = \frac{\sqrt{11}}{8}a$ | $q = a\sqrt{3}\left(u(\sqrt{43}m) - \frac{1}{4}\right)$           | $\theta_1 = \cos^{-1}\left(\frac{p^2 + r^2 - e^2}{2pr}\right)$ |
| $d = \frac{\sqrt{3}}{4}a$  | $r = a\sqrt{11}\left(u(\sqrt{43}m) - \frac{1}{4}\right)$          | $\theta_1 = \cos^{-1}\left(\frac{2p^2 - b^2}{2p^2}\right)$     |
| $e = \frac{3\sqrt{3}}{8}a$ | $s = a\sqrt{3}\left(\frac{u(\sqrt{43}m)}{3} + \frac{1}{8}\right)$ | $\theta_1 = \cos^{-1}\left(\frac{p^2 + s^2 - f^2}{2ps}\right)$ |
| $f = \frac{\sqrt{6}}{4}a$  |   | $\theta_1 = \cos^{-1}\left(\frac{r^2 + q^2 - d^2}{2rq}\right)$ |

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 ( $\theta_1$ ,  $\theta_2$ ,  $\theta_3$ ,  $\theta_4$ , and  $\theta_5$ ) between the cation and cation–anion were calculated using the equations presented in Table 7.<sup>40</sup>

Tables 8, 9 and 11 show that doping with  $\text{Mg}^{2+}$  and  $\text{Gd}^{3+}$  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  $\text{Fe}^{3+}$  (0.067 nm) by larger  $\text{Mg}^{2+}$  (0.072 nm) and  $\text{Gd}^{3+}$  (0.094 nm) at octahedral sites. The ionic radius of a  $\text{Gd}^{3+}$  (0.094 nm) is large for the tetrahedral site; therefore,  $\text{Gd}^{3+}$  ions are forced to occupy octahedral sites. Similarly,  $\text{Co}^{2+}$  (0.074 nm) prefers to occupy octahedral sites because of its site preference binding energy.  $\text{Fe}^{3+}$  partially migrates from octahedral to tetrahedral sites.  $\theta_1$  and  $\theta_2$  are related to the A–B interaction,  $\theta_3$  and  $\theta_4$  are related to the B–B interaction, and  $\theta_5$  is related to the A–A interaction. The obtained inter-ionic binding angles are given in Table 11. Doping with  $\text{Mg}^{2+}$  and  $\text{Gd}^{3+}$  caused  $\theta_1$ ,  $\theta_2$ , and  $\theta_5$  to decrease, while  $\theta_3$  and  $\theta_4$  increased. The increase in  $\theta_5$  indicates a strengthening of A–A interactions, while the increases in  $\theta_3$  and  $\theta_4$  suggest an increase in the strength of B–B exchange interactions. Thus, we can deduce that  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Co}^{2+}$  ions at B sites along with  $\text{Fe}^{3+}$  and a low concentration of  $\text{Mg}^{2+}$  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 ( $4f^7$  orbital,  $S = 7/2$ ,  $L = 0$ ,  $J = 7/2$ ) and spin magnetic moment of  $\text{Gd}^{3+}$  compared to  $\text{Fe}^{3+}$  ( $3d^5$ ) and  $\text{Co}^{2+}$  ( $3d^7$ ,  $L = 3$ ,  $S = 3/2$ ,  $J = 9/2$ ) 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.<sup>50–54</sup> In most of these studies,  $M_s$  decreased upon doping. Reports of increases in  $M_s$  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 rays. 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  $M_s$  to increase, while high dopant concentrations cause  $M_s$  to decrease.<sup>55</sup> Our results are in good agreement with the theoretical studies of Hou Y. H. *et al.*,<sup>56</sup> who found that the net magnetic moment of  $\text{CoFe}_2\text{O}_4$  increased upon doping with  $\text{Gd}^{3+}$ . Yu-Hua *et al.* also showed that the rare earth ions prefer to substitute for  $\text{Fe}^{3+}$  located at octahedral

**Table 8** Calculated cation–anion (Me–O) and cation–cation (Me–Me) inter-ionic distances and bond angles in the  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  samples

| Parameter  | $b$ (Å) | $c$ (Å) | $d$ (Å) | $e$ (Å) | $f$ (Å) | $p$ (Å) | $q$ (Å) | $r$ (Å) | $s$ (Å) |
|--|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| $\text{CoFe}_2\text{O}_4$  | 2.9622  | 3.4735  | 3.6279  | 5.4419  | 5.1307  | 2.0622  | 1.8699  | 3.5807  | 3.6466  |
| $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$ | 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  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  samples

| Parameter  | $\theta_1$ (°) | $\theta_2$ (°) | $\theta_3$ (°) | $\theta_4$ (°) | $\theta_5$ (°) |
|--|----------------|----------------|----------------|----------------|----------------|
| $\text{CoFe}_2\text{O}_4$  | 124.0221       | 148.1105       | 91.8114        | 125.6836       | 76.3662        |
| $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$ | 121.3193       | 136.7599       | 96.1482        | 126.6282       | 69.2622        |



sites, and the lattice constant of  $\text{CoFe}_{1.875}\text{RE}_{0.125}\text{O}_4$  (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  $\text{CoFe}_2\text{O}_4$  increases upon doping only with Eu and Gd because there are more unpaired 4f electrons for  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$ . Similarly, Torkian *et al.*<sup>55</sup> reported that the magnetization of  $\text{Gd}^{3+}$ -doped Mn–Zn ferrite increased for  $\text{Gd}^{3+}$  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  $\text{CoFe}_2\text{O}_4$  and  $\text{Zn}_x\text{Co}_{(1-x)}\text{Fe}_2\text{O}_4$  synthesized using complex precursors (Table 10).

The experimental magnetic moment per formula unit ( $n_B$  of  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$ ) was calculated as follows:<sup>61</sup>

$$n_B = \frac{M \times M_s}{5585}, \quad (8)$$

where  $M$  is the molecular weight of the sample, and  $M_s$  is the measured saturation magnetization. The value of the magnetic moment varies from  $3.87 \mu_B$  at 300 K to  $4.43 \mu_B$  at 10 K, as shown in Table 7. This change in magnetic moment is in accordance with the variation in  $M_s$ .

According to the proposed cation distribution ( $\text{Mg}_{0.1}\text{Fe}_{0.9}$ )- $^A[\text{Co}_{0.7}\text{Mg}_{0.2}\text{Fe}_{1.08}\text{Gd}_{0.02}]^B\text{O}_4$  and using the magnetic moment values of  $\text{Mg}^{2+}$  ( $0 \mu_B$ ),  $\text{Fe}^{3+}$  ( $5 \mu_B$ ),  $\text{Gd}^{3+}$  ( $7 \mu_B$ ), and  $\text{Co}^{2+}$  ( $3 \mu_B$ ), the net magnetic moment  $M_{(\text{cal})}$  was calculated as  $M_{(\text{cal})} = M_B - M_A$ , where  $M_A$  and  $M_B$  represent the net magnetic moments of lattice sites A and B, respectively. The calculated value of  $M_{(\text{cal})}$  is  $3.14 \mu_B$ , comparable with the determined experimental value. Further from the proposed cation distribution, at tetrahedral locations, 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, the metal ions ( $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$ ) exhibit superexchange A–B interactions with  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Gd}^{3+}$ . Superexchange A–B interactions are practically superior to A–A and B–B interactions at the respective sites. There may be an increase in A–B superexchange interactions with the addition of  $\text{Gd}^{3+}$  to  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  spinel nano-ferrites. This increase in A–B interaction suggests an increase in the measured values of saturation magnetization and magnetic moment. In this work,  $M_s$  and  $n_B$  increased upon

the addition of  $\text{Gd}^{3+}$  in  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  ferrite spinels. This increase in magnetic parameters can be correlated with the bonding angles. The bonding angles  $\theta_1$ ,  $\theta_2$ , and  $\theta_5$  decreased upon doping, suggesting decreased A–A interactions. Meanwhile,  $\theta_3$  and  $\theta_4$  increased, indicating an increase in B–B and A–B interactions. The complete solubility of large  $\text{Gd}^{3+}$  ions at B sites could be responsible for the change in the magnetic behavior of the  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  nano-ferrites. This is probably why high  $M_s$  and  $n_B$  values have been obtained with low concentrations of gadolinium. For ferrites doped with high concentrations of other REs, the decrease in saturation magnetization and 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<sup>62</sup>

$$H_C = \frac{K_{\text{eff}} \times 0.96}{M_s}, \quad (9)$$

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 show 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,  $\text{Co}^{2+}$  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  $\text{Co}^{2+}$  ions at octahedral sites.<sup>63</sup> Although  $\text{Gd}^{3+}$  has zero orbital angular momentum, gadolinium has been reported to contribute to and strengthen anisotropy.<sup>64</sup>

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      | $M_s$<br>(emu g <sup>-1</sup> at 300 K) | $M_s$<br>(emu g <sup>-1</sup> at 5 K) | $H_C$<br>(Oe at 300 K) | $H_C$<br>(Oe at 5 K) | $M_r/M_s$<br>(300 K) | $M_r/M_s$<br>(5 K) | Reference    |
|--|--------------------------|---|---------------------------------------|------------------------|----------------------|----------------------|--------------------|--------------|
| $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$ | Coprecipitation          | 95.68                                   | 109.5                                 | 1702.28                | 11 959.53            | 0.4179               | 0.7539             | Present work |
| $\text{CoFe}_2\text{O}_4$  | Classical ceramic method | 88                                      | —                                     | 141                    | —                    | —                    | —                  | 57           |
| $\text{CoFe}_2\text{O}_4$  | —                        | 80.8                                    | 93.9                                  | —                      | 25 200               | —                    | —                  | 58           |
| $\text{CoFe}_2\text{O}_4$  | Sonochemical method      | 92.5                                    | —                                     | 807                    | —                    | —                    | —                  | 59           |
| $\text{CoFe}_2\text{O}_4$  | Chemical complexes       | 92                                      | 109                                   | —                      | 12                   | —                    | —                  | 60           |



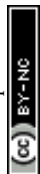
Table 11 Configurations of ion pairs in spinel ferrites with favorable distances and angles for effective magnetic interactions in samples  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$ 



Fig. 7 Hysteresis loops of sample  $\text{Co}_{0.7}\text{Mg}_{0.3}\text{Fe}_{1.98}\text{Gd}_{0.02}\text{O}_4$ .

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.<sup>65</sup>

The squareness ratio ( $M_r/M_s$ ) at 300 K (0.4179) increased to 0.7539 at 10 K. At 300 K,  $M_r/M_s$  tends towards 0.5, corresponding to randomly oriented uniaxial anisotropic ferromagnetic particles. In contrast, at 10 K,  $M_r/M_s$  approaches 1, corresponding to typical isolated single-domain ferromagnetic particles. In the same vein, Stoner and Wohlfarth<sup>66</sup> 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 magneto-static 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. Kodama<sup>67</sup> 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

$\text{Gd}^{3+}$  in the crystal lattice in conjunction with the surface effects resulting from the alteration of the magnetic structures on the surfaces of the nanoparticles.<sup>68</sup>

## 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  $\text{GdFeO}_3$  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 pattern indicated an increase in the lattice constant after doping with  $\text{Gd}^{3+}$ , 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  $\text{Co}^{2+}$  and  $\text{Gd}^{3+}$  have strong preferences for the octahedral B sites, whereas  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  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  $\text{Gd}^{3+}$  substitution in the mixed Co–Mg ferrite enhanced the saturation magnetization, which was attributed to the higher spin magnetic moment and anisotropy of  $\text{Gd}^{3+}$  compared  $\text{Fe}^{3+}$  along with the strong  $L$ - $S$  coupling of  $\text{Co}^{2+}$ . Coercivity increased upon  $\text{Gd}^{3+}$  doping, which can be explained by the strong  $L$ - $S$  coupling and weak crystal field of  $\text{Co}^{2+}$ , resulting in stronger magneto-crystalline anisotropy related to the increase in the concentration of high-spin  $\text{Co}^{2+}$  ions at octahedral sites. The enhancements in magnetic properties ( $M_s$  and  $n_B$ ) after doping with  $\text{Gd}^{3+}$  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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## References

- 1 P. M. Ajayan, M. Pulickel, L. S. Schadler, and P. V. Braun, *Nanocomposite science and technology*, John Wiley & Sons, 2006.
- 2 D. Astruc, E. Boisselier and C. Ornelas, *Chem. Rev.*, 2010, **110**, 1857–1959.
- 3 E. Boisselier and D. Astruc, *Chem. Soc. Rev.*, 2009, **38**, 1759.



- 4 C. D. Stanciu, A. V. Kimel, F. Hansteen, A. Tsukamoto, A. Itoh, A. Kirilyuk and Th. Rasing, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **73**, 220402.
- 5 R. K. Panda and D. Behera, *J. Alloys Compd.*, 2014, **587**, 481–486.
- 6 A. Lakshman, P. S. V. Subba Rao and K. H. Rao, *J. Magn. Magn. Mater.*, 2004, **284**, 352–357.
- 7 S. K. Sharma, R. Kumar, V. V. Siva Kumar, M. Knobel, V. R. Reddy, A. Gupta and M. Singh, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2006, **248**, 37–41.
- 8 M. Thomas and K. C. George, *Appl. Phys.*, 2009, **47**, 6.
- 9 L. Wang, J. Li, W. Ding, T. Zhou, B. Liu, W. Zhong, J. Wu and Y. Du, *J. Magn. Magn. Mater.*, 1999, **207**, 111–117.
- 10 P. Brown and L. J. Hope-Weeks, *J. Sol-Gel Sci. Technol.*, 2009, **51**, 238–243.
- 11 S. L. Darshane, R. G. Deshmukh, S. S. Suryavanshi and I. S. Mulla, *J. Am. Ceram. Soc.*, 2008, **91**, 2724–2726.
- 12 M. K. Roy and H. C. Verma, *J. Magn. Magn. Mater.*, 2006, **306**, 98–102.
- 13 T. M. Clark and B. J. Evans, *IEEE Trans. Magn.*, 1997, **33**, 3745.
- 14 C. Liu, B. Zou, A. J. Rondinone and Z. J. Zhang, *J. Am. Chem. Soc.*, 2000, **122**, 6263–6267.
- 15 J.-M. Li, X.-L. Zeng and Z.-A. Xu, *Appl. Phys. Lett.*, 2013, **103**, 232410.
- 16 J.-M. Li, A. C. H. Huan, L. Wang, Y.-W. Du and D. Feng, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **61**, 6876–6878.
- 17 I. Apostolova and J. M. Wesselinowa, *Solid State Commun.*, 2009, **149**, 986–990.
- 18 P. Kumar, J. Chand, S. Verma and M. Singh, *Int. J. Theor. Appl. Sci.*, 2011, **3**(2), 10–12.
- 19 Y. Mouhib, M. Belaiche and S. Briche, *Phys. Status Solidi A*, 2018, **215**, 1800469.
- 20 T. Prabhakaran, R. V. Mangalaraja, J. C. Denardin and J. A. Jiménez, *J. Alloys Compd.*, 2017, **716**, 171–183.
- 21 Q. Lin, Y. He, J. Lin, F. Yang, L. Wang and J. Dong, *J. Magn. Magn. Mater.*, 2019, **469**, 89–94.
- 22 Q. Lin, J. Lin, Y. He, R. Wang and J. Dong, *J. Nanomater.*, 2015, 1–6.
- 23 M. M. Rashad, R. M. Mohamed and H. El-Shall, *J. Mater. Process. Technol.*, 2008, **198**, 139–146.
- 24 L. Zhao, H. Yang, L. Yu, Y. Cui, X. Zhao, Y. Yan and S. Feng, *Phys. Lett. A*, 2004, **332**, 268–274.
- 25 L. Zhao, H. Yang, L. Yu, W. Sun, Y. Cui, Y. Yan and S. Feng, *Phys. Status Solidi A*, 2004, 3121–3128.
- 26 A. A. Sattar, A. M. Samy, R. S. El-Ezza and A. E. Eatah, *Phys. Status Solidi A*, 2002, **8**, 86–93.
- 27 A. Franco, F. L. A. Machado and V. S. Zapf, *J. Appl. Phys.*, 2011, **110**, 53913.
- 28 N. Aliyan, S. M. Mirkazemi, S. M. Masoudpanah and S. Akbari, *Appl. Phys. A*, 2017, **123**, 446.
- 29 S. K. Pradhan, S. Bid, M. Gateshki and V. Petkov, *Mater. Chem. Phys.*, 2005, **93**, 224–230.
- 30 L. Sun, R. Zhang, Q. Ni, E. Cao, W. Hao, Y. Zhang and L. Ju, *Phys. B*, 2018, **545**, 4–11.
- 31 D. Varshney, K. Verma and A. Kumar, *J. Mol. Struct.*, 2011, **1006**, 447–452.
- 32 S. Joshi, M. Kumar, S. Chhoker, A. Kumar and M. Singh, *J. Magn. Magn. Mater.*, 2017, **426**, 252–263.
- 33 G. P. Nethala, R. Tadi, A. V. Anupama, S. L. Shinde and V. Veeraiah, *Mater. Sci.*, 2018, **36**, 310–319.
- 34 N. Thomas, P. V. Jithin, V. D. Sudheesh and V. Sebastian, *Ceram. Int.*, 2017, **43**, 7305–7310.
- 35 N. K. Thanh, T. T. Loan, N. P. Duong, L. N. Anh, D. T. T. Nguyet, N. H. Nam, S. Soontaranon, W. Klysubun and T. D. Hien, *Phys. Status Solidi A*, 2018, **215**, 1700397.
- 36 F. Nakagomi, S. W. da Silva, V. K. Garg, A. C. Oliveira, P. C. Morais and A. Franco, *J. Solid State Chem.*, 2009, **182**, 2423–2429.
- 37 A. M. Gismelseed, K. A. Mohammed, H. M. Widatallah, A. D. Al-Rawas, M. E. Elzain and A. A. Yousif, *J. Phys.: Conf. Ser.*, 2010, **217**, 012138.
- 38 R. A. Pawar, S. M. Patange, A. R. Shitre, S. K. Gore, S. S. Jadhav and S. E. Shirsath, *RSC Adv.*, 2018, **8**, 25258–25267.
- 39 S. Panchal, S. Raghuvanshi, K. Gehlot, F. Mazaleyrat and S. N. Kane, *AIP Adv.*, 2016, **6**, 055930.
- 40 V. K. Lakhani, T. K. Pathak, N. H. Vasoya and K. B. Modi, *Solid State Sci.*, 2011, **13**, 539–547.
- 41 N. Najmoddin, A. Beitollahi, H. Kavas, S. Majid Mohseni, H. Rezaie, J. Åkerman and M. S. Toprak, *Ceram. Int.*, 2014, **40**, 3619–3625.
- 42 M. S. Khandekar, R. C. Kambale, J. Y. Patil, Y. D. Kolekar and S. S. Suryavanshi, *J. Alloys Compd.*, 2011, **509**, 1861–1865.
- 43 B. M. Ali, M. A. Siddig, Y. A. Alsabah, A. A. Elbadawi and A. I. Ahmed, *Adv. Nanoparticles*, 2018, **07**, 1.
- 44 H. S. Mund and B. L. Ahuja, *Mater. Res. Bull.*, 2017, **85**, 228–233.
- 45 S. R. Naik, A. V. Salker, S. M. Yusuf and S. S. Meena, *J. Alloys Compd.*, 2013, **566**, 54–61.
- 46 Z. Karimi, Y. Mohammadifar, H. Shokrollahi, Sh. K. Asl, Gh. Yousefi and L. Karimi, *J. Magn. Magn. Mater.*, 2014, **361**, 150–156.
- 47 A. K. Nikumbh, R. A. Pawar, D. V. Nighot, G. S. Gugale, M. D. Sangale, M. B. Khanvilkar and A. V. Nagawade, *J. Magn. Magn. Mater.*, 2014, **355**, 201–209.
- 48 S. Amiri and H. Shokrollahi, *J. Magn. Magn. Mater.*, 2013, **345**, 18–23.
- 49 R. Safi, A. Ghasemi, R. Shoja-Razavi and M. Tavousi, *J. Magn. Magn. Mater.*, 2015, **396**, 288–294.
- 50 M. F. Al-Hilli, S. Li and K. S. Kassim, *Mater. Sci. Eng., B*, 2009, **158**, 1–6.
- 51 A. C. F. M. Costa, A. P. A. Diniz, A. G. B. de Melo, R. H. G. A. Kiminami, D. R. Cornejo, A. A. Costa and L. Gama, *J. Magn. Magn. Mater.*, 2008, **320**, 742–749.
- 52 D. Ravinder and K. V. Kumar, *Bull. Mater. Sci.*, 2001, **24**, 505–509.
- 53 N. Rezlescu, E. Rezlescu, F. Tudorache and P. D. Popa, *J. Optoelectron. Adv. Mater.*, 2004, **6**, 695.
- 54 J. Jiang, L. Li, F. Xu and Y. Xie, *Mater. Sci. Eng., B*, 2007, **137**, 166–169.
- 55 S. Torkian, A. Ghasemi and R. S. Razavi, *J. Supercond. Nov. Magnetism*, 2016, **29**, 1617–1625.



- 56 Y. H. Hou, Y. L. Huang, S. J. Hou, S. C. Ma, Z. W. Liu and Y. F. Ouyang, *J. Magn. Magn. Mater.*, 2017, **421**, 300–305.
- 57 G. Dascalu, T. Popescu, M. Feder and O. F. Caltun, *J. Magn. Magn. Mater.*, 2013, **333**, 69–74.
- 58 M. Grigorova, H. J. Blythe, V. Blaskov, V. Rusanov, V. Petkov, V. Masheva, D. Nihtianova, Ll. M. Martinez, J. S. Muñoz and M. Mikhov, *J. Magn. Magn. Mater.*, 1998, **183**, 163–172.
- 59 M. Abbas, B. Parvatheeswara Rao, Md. Nazrul Islam, K. W. Kim, S. M. Naga, M. Takahashi and C. Kim, *Ceram. Int.*, 2014, **40**, 3269–3276.
- 60 V. Mameli, A. Musinu, A. Ardu, G. Ennas, D. Peddis, D. Niznansky, C. Sangregorio, C. Innocenti, N. T. K. Thanh and C. Cannas, *Nanoscale*, 2016, **8**, 10124–10137.
- 61 S. E. Shirsath, M. L. Mane, S. M. Patange, S. S. Jadhav and K. M. Jadhav, *J. Phys. Chem. C*, 2011, **115**, 20905–20912.
- 62 A. Nairan, M. Khan, U. Khan, M. Iqbal, S. Riaz and S. Naseem, *Nanomaterials*, 2016, **6**, 73.
- 63 *Modern magnetic materials: principles and applications*, ed. C. Oh. Robert and O. Handley, John Wiley Sons Inc, N. Y., 2000.
- 64 B. A. Calhoun and M. J. Freiser, *J. Appl. Phys.*, 1963, **34**, 1140–1145.
- 65 Q. Gao, G. Hong, J. Ni, W. Wang, J. Tang and J. He, *J. Appl. Phys.*, 2009, **105**, 07A516.
- 66 E. C. Stoner and E. P. Wohlfarth, *IEEE Trans. Magn.*, 1991, **27**, 3475–3518.
- 67 R. H. Kodama, *J. Magn. Magn. Mater.*, 1999, **200**, 359–372.
- 68 R. N. Panda, J. C. Shih and T. S. Chin, *J. Magn. Magn. Mater.*, 2003, **257**, 79–86.

