Effect of Gd-Doping on Structural, Optical, and Magnetic Properties of NiFe$_2$O$_4$ As-prepared Thin Films via Facile Sol–Gel Approach

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ABSTRACT: In the present research work, gadolinium-doped nickel ferrite (NiFe$_{2-x}$Gd$_x$O$_4$, $x = 0$–0.1) thin films have been synthesized by a facile sol–gel approach. The structural, optical, and magnetic performances of Gd-doping on nickel ferrite films have been investigated. The X-ray diffraction pattern indicated a cubic spinel ferrite structure and that the lattice parameter increased, while the crystalline size decreased with increasing the Gd concentration. Scanning electron microscopy analysis indicated that Gd-doped thin films were dense and smooth. The optical band gap value of the as-prepared thin films increased with increasing the Gd concentration. It showed that Gd-doping endowed nickel ferrite thin films with much better saturation magnetization (278.53 emu/cc) and remnant magnetization (67.83 emu/cc) at an appropriate 0.05 Gd-doping concentration. In addition, our results also revealed that the saturation magnetization remarkably increased, then sharply decreased with increasing of Gd doping content, which is attributed to effects of Gd-doping, exchange interaction, and redistribution of cations. Moreover, X-ray photoelectron spectroscopy analysis exhibited the effect of Gd-doping substitution on exchange interaction and redistribution of cations at the octahedral site and tetrahedral site.

INTRODUCTION

In ferrites system, spinel ferrites of extraordinary versatility are crucial materials and are widely applied in the electromagnetic devices field and for producing resonators, phase shifters, sensors, recording media, high-density data storage, and spintronics devices. The types of spinel ferrites have been classified into normal spinel ferrite, inverse spinel ferrite, and mixed spinel ferrite. For the above spinel ferrites types, nickel ferrite (NiFe$_2$O$_4$, NFO), as the classic inverse spinel structure, has gained much attention because of its peculiar physical and chemical properties (such as low-grade curie temperature, high electrical resistivity, high permeability, low magnetostriction, etc.). To further expand the technological application, much effort is being carried out to investigate microstructural, optical, electrical, and magnetic performances.

The doping of transition elements and rare-earth ions can significantly induce structural distortion and changes of optical and magnetic properties for NFO by partial substitution of Fe$^{3+}$ ions. Extensive studies of the impact of doping on magnetic properties of bulk, nanoparticles, and ceramics have been carried out. For example, Kamala Bharathi et al. investigated ferromagnetic properties and found that the substitution of Dy, Gd, and Nd for Fe lowered the saturation magnetization in NFO pellet samples. Singh et al. found that the doping of Gd$^{3+}$ ions reduced the magnetization and reflectance was dropped to 750 nm of the NiGd$_{0.04}$Fe$_{1.96}$O$_4$ nanoparticle system. Dixit et al. found that the magnetism and coercivity are dropped in Ce- and Gd-doped NFO nanoparticles. Recently, Heiba et al. reported that Gd concentration would lead to changes of magnetization and coercive field-dependent cation distributions linked with optic and magnetic performances in crystalline nickel ferrite.

Moreover, it is crucial to study these properties of NFO thin films for better prospects in magneto-electric and magneto-optical applications. Sun et al. revealed a hierarchy of optical band gaps by adopting first-principles calculations with optical spectroscopy to synthetically explore the electronic structure in epitaxial NFO thin films. Luiders et al. reported that magnetic moment enhanced about 250% in ultrathin NFO film resulting from Fe and Ni cations' abnormal distribution. Kamala Bharathi et al. revealed the influence of annealing on

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The doping of Gd concentration, which results from large ionic radii of Gd ions, plays a significant role in inducing changes in the optical and magnetic properties of the NiFe₂₋ₓGdₓO₄ nanoparticles. The X-ray diffraction (XRD) results reveal a single-phase inverse spinel structure. The lattice parameter (a) and crystallite size (D) of NiFe₂₋ₓGdₓO₄ films can be estimated using the Scherrer formula:

\[ a = \frac{d_{hkl} \sqrt{h^2 + k^2 + l^2}}{\cos \theta} \]

The value of the lattice parameter changes from 8.365 Å to 8.383 Å when Gd concentration increases as shown in Figure 1b. The lattice constants slightly increase resulting from increasing Gd³⁺ concentration and Gd³⁺ substituting Fe³⁺ site. The increasing trend in the lattice constant is ascribed to the larger Gd³⁺ ionic radii in comparison with Fe³⁺.

The grain size (D) of NiFe₂₋ₓGdₓO₄ samples is estimated from Scherrer formula:

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]

Herein, \( \lambda \) is wavelength, \( \beta \) is the measured half-width of the most intense diffraction peak (111), and \( \theta \) is the diffraction angles of diffraction peak (111) plane. Crystallite size shows a shrinking trend with the increasing doping content of Gd³⁺ ions. The values are shown in Table 1 and are consistent with the reported results. We try to clarify the reason for this decreasing trend. On the one hand, the large size mismatching between Gd³⁺ and Fe³⁺ can lead to grain anisotropy when the replacement of ions generates strain inside the crystal volume with an increase of Gd³⁺ doping content. Moreover, the balance of the crystal anisotropy and volume strain to each other can maintain in a stable equilibrium state. As a result, the grain size decreases with increasing Gd³⁺ concentration and Gd³⁺ substituting Fe³⁺ site. The increasing trend in the lattice constant is ascribed to the larger Gd³⁺ ionic radii in comparison with Fe³⁺.

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Herein, \( a \) represents the lattice constant value, \( r \) (O\(^{2-}\)) is oxygen ion radius (1.35 Å), \( \mu \) is oxygen ion parameter, in perfect spinel ferrite \( \mu = 3/8 \). \( r_A \) and \( r_B \) are the ionic radii of tetrahedral and octahedral site, respectively, whereas A–O and B–O are bond lengths. Jump lengths are expressed by \( L_A \) and \( L_B \). The calculated value is listed in Table 1. The results reveal that ionic radii values and magnetic ion and bond length distances change into larger values with the Gd\(^{3+}\) content increase resulting from lattice constant’s increase. The level of growth of \( r_A \) is less compared with that of \( r_B \) when the content of Gd\(^{3+}\) ions is increasing. The aforementioned results are similar to those of the other researchers.\(^{34}\)

The typical surface morphology images are displayed in Figure 2a–e, suggesting that the samples are uniform. Additionally, Gd doping induces a clear decrease in the crystalline size of NFO thin films with Gd concentration increase, which resulted from larger ionic radii Gd\(^{3+}\) into smaller Fe\(^{3+}\) in NFO lattice to suppress the growth of grains.\(^{24}\) This trend is consistent with our XRD results. Figure 2f presents the typical cross-sectional morphology image of the NiFe\(_{1.9}\)Gd\(_{0.1}\)O\(_4\) films on quartz substrate (inset shows optical band gap (\( E_g \)) vs Gd-doping concentration curves).

The optical transmittance spectra of Gd-doped NFO samples are presented in Figure 3a. The spectral features of NFO films are sensitive to Gd-doping concentration. A remarkable enhancement in the transmittance can be observed in NiFe\(_{1.925}\)Gd\(_{0.075}\)O\(_4\) thin films compared with that in pure NFO films. With increasing Gd-doping content, it is observed that Gd-doped NFO films show higher transparency, which suggests high quality and transparency.

To better understand the optical performance change owing to Gd substitution, a further investigation of the optical band gap is performed. Nickel ferrite is direct band gap materials and follows the form\(^{31}\)

\[
(\alpha h \nu)^2 = B(h \nu - E_g)
\]
\( h\nu \) presents incident photon energy, \( \alpha \) is absorption coefficient, \( B \) presents absorption edge width parameters, and \( E_g \) is the band gap.

The \((a\nu)^2\) versus \( \nu \) curves of NFO-doping films are shown in Figure 3b. The values in higher absorption regions are fitted to linear regression. The band gap values could be calculated and are listed in Table 2. It is evident that band gap increases with Gd content increase, changing from 2.58 to 2.75 eV on NFO also similar to the reported values of 2.5 eV of NFO.

Table 2. Optical Band Gap (\( E_g \)) and Magnetic Parameters (Saturation Magnetization (\( M_s \)), Remnant Magnetization (\( M_r \)), Coercive Field (\( H_c \)), and Squareness Ratio (\( R \)) vs Gd-Doping Concentration (\( x = 0, 0.025, 0.05, 0.075, \) and 0.1) of NiFe\(_{2}\)Gd\(_{0.1}\)O\(_4\) Thin Films at Room Temperature

| Gd content \( x \) | \( E_g \) (eV) | \( M_s \) (emu/cc) | \( M_r \) (emu/cc) | \( H_c \) (Oe) | \( R = M_r/M_s \) |
|---------------------|-------------|-----------------|-----------------|--------------|----------------|
| \( x = 0 \)         | 2.58        | 145.29          | 42.96           | 154.05       | 0.296          |
| \( x = 0.025 \)     | 2.60        | 164.47          | 40.02           | 138.26       | 0.244          |
| \( x = 0.05 \)      | 2.87        | 278.53          | 67.83           | 108.41       | 0.243          |
| \( x = 0.075 \)     | 2.73        | 72.38           | 15.36           | 116.04       | 0.226          |
| \( x = 0.1 \)       | 2.75        | 70.51           | 10.21           | 87.57        | 0.145          |

The magnetic hysteresis loops of Gd-doped NFO thin films are obtained by applying the magnetic field of 10 kOe. It can be seen from Figure 4a that all samples exhibit ferromagnetic behavior due to their narrow M–H loop and the shape of these loops vary with the increases in Gd concentration in the NFO films. Different magnetic parameters (saturation magnetization \( M_s \), remnant magnetization \( M_r \), coercivity \( H_c \), and squareness ratio \( R \)) were measured via these M–H loops, and the values are listed in Table 2. Magnetic moments and saturation magnetization are highly dependent on the Gd-doping concentration increase. The saturation magnetization first increases and then sharply decreases as shown in Figure 4b. It is noticed that the NiFe\(_{2}\)Gd\(_{0.05}\)O\(_4\) sample shows remarkable improvement for \( M_s \) and \( M_r \) values compared to those for the pure NFO film in Figure 4b. The above improvement in the magnetic performance can explain that the doping of the Gd\(_{3}^{+}\) ions in ferrite films leads to an increase of whole magnetic moments and redistribution of cations. \(^2\text{1,24,25,37–42}\)

The whole magnetization is given according to Neel’s model \(^3\text{9}\)

\[
M = M_A - M_B
\]

Here, \( M_A \) and \( M_B \) represent the A and B sublattice magnetic moments in \( \mu_B \), respectively. It is noted that the total magnetic moment value in the ferrimagnetic materials depends on the number of magnetic ions taking up the tetrahedral (A) and octahedral (B) sites. As a result, magnetization variation is dependent on the type and number of magnetic ions at different sites. \(^2\text{1,24,37–39}\)

In NFO material, \( \text{Fe}^{3+} \) ions are equally distributed between tetrahedral and octahedral sites, whereas the octahedral sites are occupied by \( \text{Ni}^{2+} \) ions. The net magnetic moment of NFO is 2 \( \mu_B \). Nevertheless, Gd doped into NFO lattice will result in the substitution of \( \text{Fe}^{3+} \) ions at the B site via \( \text{Gd}^{3+} \) ions. The \( \text{Gd}^{3+} \) ions possess a large spin magnetic moment of 7.9 \( \mu_B \) compared with that of \( \text{Fe}^{3+} \) ion of 5 \( \mu_B \). Therefore, a small part substitution of \( \text{Gd}^{3+} \) ions could lead to an increase in the total magnetic moment to enhance magnetization.

It is also noticed that the magnetization decreases above 0.05 Gd-doping concentration, which is attributed to weak...
exchange interaction and redistribution of cations at high Gd-doping concentration.\textsuperscript{24,37–41} The magnetic property of ferrites is largely dependent on the Fe\textsuperscript{3+}–Fe\textsuperscript{3+} interaction with 3d electrons spin coupling. The Gd\textsuperscript{3+} enters the Fe lattice, then Gd\textsuperscript{3+}–Fe\textsuperscript{3+} interaction occurs with 3d–4f electron coupling. Thus, the magnetic exchange interaction in A and B site cations is reduced, resulting in magnetization change. Furthermore, the Gd\textsuperscript{3+}–Fe\textsuperscript{3+} interactions are weak due to interactions mainly arising from the indirect 4f–5d–5d–4f mechanism.\textsuperscript{39} There are some reported research studies relating to magnetization decrease in NiFe\textsubscript{1+\alpha}Gd\textsubscript{\alpha}O\textsubscript{4} nanoparticles and Gd-doped CoFe\textsubscript{2}O\textsubscript{4}.\textsuperscript{25,41} It is also noticed that the coercivity decreases from 154.05 to 108.41 Oe, then increases to 116.04 Oe, and finally sharply decreases to 87.57 Oe with increasing of the Gd\textsuperscript{3+} concentration as shown in Figure 4d. Furthermore, the squareness ratio (R = M/M\textsubscript{s}) of Gd-doping NFO films is listed in Table 2. It is shown that the R value decreases with increasing Gd content. Coercivity has been regarded as a microstructure performance, and it is strongly related with defects and strains in the material. In our work, a remarkable decrease in the coercivity has been observed, which is linked with poorer crystallization, larger lattice distortion, and large strain in NFO thin films by Gd-doping.\textsuperscript{2,11,43}

To further investigate the chemical states and impact of Gd ion on magnetic properties considering that cation redistribution of tetrahedral and octahedral sites on NFO thin films, XPS was performed. The XPS spectra of representative samples were collected using high-resolution Ni, Fe, Gd, and O as shown in Figure 5. Figure 5a shows Ni 2p XPS spectra with satellite peaks appearing in 2p\textsubscript{1/2} and 2p\textsubscript{3/2} binding energy side regions. It shows that Ni presents an oxidation state. The deconvolution of 2p peak regions of samples shows two nonequivalent bonds because of tetrahedral and octahedral lattice sites. For NiFe\textsubscript{2−\alpha}Gd\textsubscript{\alpha}O\textsubscript{4} (x = 0.05) thin films, the contributions to the overall intensity of Ni ions at the O\textsubscript{h} and T\textsubscript{d} sites are 78 and 22\%, respectively. Nevertheless, for NiFe\textsubscript{2−\alpha}Gd\textsubscript{\alpha}O\textsubscript{4} (x = 0.1), the contributions to total intensity of Ni ions at the O\textsubscript{h} and T\textsubscript{d} sites are 78 and 22\%, respectively, as shown in Table 3.

### Table 3. Analysis Results of Ni 2p\textsubscript{1/2} and Fe 2p\textsubscript{3/2} XPS Spectra for NiFe\textsubscript{2−\alpha}Gd\textsubscript{\alpha}O\textsubscript{4} (x = 0.05 and 0.1) Thin Films

| Gd content | spectrum | BE (eV) | assignment | atomic percentage (%) |
|------------|----------|---------|------------|-----------------------|
| x = 0.05   | Ni 2p\textsubscript{3/2} | 855.0   | Ni\textsuperscript{2+} (O\textsubscript{h}) | 78                    |
|            | Ni 2p\textsubscript{3/2} | 856.7   | Ni\textsuperscript{2+} (T\textsubscript{d}) | 57                    |
|            | Fe 2p\textsubscript{3/2} | 710.9   | Fe\textsuperscript{3+} (O\textsubscript{h}) | 69                    |
|            | Fe 2p\textsubscript{3/2} | 712.8   | Fe\textsuperscript{3+} (T\textsubscript{d}) | 22                    |
| x = 0.1    | Ni 2p\textsubscript{3/2} | 855.0   | Ni\textsuperscript{2+} (O\textsubscript{h}) | 78                    |
|            | Ni 2p\textsubscript{3/2} | 856.7   | Ni\textsuperscript{2+} (T\textsubscript{d}) | 57                    |
|            | Fe 2p\textsubscript{3/2} | 711.2   | Fe\textsuperscript{3+} (O\textsubscript{h}) | 69                    |
|            | Fe 2p\textsubscript{3/2} | 713.0   | Fe\textsuperscript{3+} (T\textsubscript{d}) | 31                    |

Figure 5b presents the Fe 2p core-electron spectra of NiFe\textsubscript{2−\alpha}Gd\textsubscript{\alpha}O\textsubscript{4} (x = 0.05) and NiFe\textsubscript{2−\alpha}Gd\textsubscript{\alpha}O\textsubscript{4} (x = 0.1) samples. It contains Fe 2p\textsubscript{3/2} and Fe 2p\textsubscript{1/2} sections based on spin orbital splitting. The Fe 2p spectra are resolved into three peaks, the first peak is of Fe\textsuperscript{2+} and the rest of them are attributed to two lattice sites of Fe\textsuperscript{3+}.\textsuperscript{42–44} The doublets in films could be assigned to Fe 3p ions at O\textsubscript{h} sites and T\textsubscript{d} sites. The overall intensity contributions of Fe ions at O\textsubscript{h} sites and T\textsubscript{d} sites are 43 and 57\% of NiFe\textsubscript{2−\alpha}Gd\textsubscript{\alpha}O\textsubscript{4} (x = 0.05). However, the contributions to the overall intensity of Fe ions at O\textsubscript{h} sites and T\textsubscript{d} sites are 69 and 31\% of NiFe\textsubscript{2−\alpha}Gd\textsubscript{\alpha}O\textsubscript{4} (x = 0.1), respectively, as presented in Table 3. Therefore, Gd ion doping could induce changes of cation redistribution, which results in the change of magnetic property.\textsuperscript{38–41} Figure 5c shows 4d\textsubscript{3/2} and 4d\textsubscript{5/2} of Gd 4d, suggesting Gd\textsuperscript{3+} existence.\textsuperscript{45} Figure 5d exhibits the investigation of the O 1s peak. The low-fitting binding energy peak corresponds to the lattice oxygen, whereas the higher binding energy peak is ascribed to the non-lattice oxygen.\textsuperscript{2,11,45} This work would further stimulate much effort on the rare-earth-doped nickel ferrites thin film performances.
CONCLUSIONS

In summary, Gd-doped NiFe₂O₄ thin films were prepared via a facile sol–gel method. XRD revealed the formation of a cubic spinel ferrite structure. Additionally, Gd doping induced the increase of lattice parameter and decrease of crystalline size. With increasing the Gd concentration from 0 to 0.1, the value of optical band gap increased from 2.58 to 2.75 eV for Gd-doped NiFe₂O₄ thin films. Moreover, our results indicated that Gd-doping had important impacts on the magnetic property of NiFe₂O₄ thin films. The saturation of magnetization first increased, then decreased due to the effect of Gd-doping, exchange interaction, and redistribution of cations. However, the coercive field decreased with increasing Gd concentration. Our work suggests that Gd-doped NiFe₂O₄ thin films have potential applications in multifunctional materials.

EXPERIMENTAL SECTION

The NiFe₂₋ₓGdₓO₄ thin films (x = 0, 0.025, 0.05, 0.075, and 0.1) are synthesized using the facile sol–gel approach.⁹,¹⁰ The precursor solution is prepared using starting materials for Ni(CH₃COO)₂·4H₂O (AR, 99.90%, Aladdin), Fe(NO₃)₃·9H₂O (AR, 99.90%, Aladdin), and Gd(NO₃)₃·5H₂O (AR, 99.99%, Aladdin) with the stoichiometric molar ratio of 1:(2 – x):x. The thin films are synthesized on Pt and quartz substrates using spin-coating and annealed at 700 °C in 1 h. The crystalline phase has been investigated by XRD with Rigaku using spin-coating and annealed at 700 °C. The chemical states are analyzed via XPS performed using a 3150 UV double-beam spectrophotometer. Spectrophotometric measurements of samples have been performed using a 3150 UV double-beam spectrophotometer. The magnetism was measured via Quantum Design PPMS-9 at room temperature. The chemical states are analyzed via XPS (ESCALAB 250).

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Notes
The authors declare no competing financial interest.

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