IMPACT OF GD$^{3+}$/GRAPHENE SUBSTITUTION ON THE STRUCTURAL AND MAGNETIC PROPERTIES OF MAGNESIUM FERRITE

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Abstract:
Magnesium nano ferrite with composition MgFe$_2$O$_4$, MgGd$_{0.05}$Fe$_{1.95}$O$_4$ and MgFe$_2$O$_4$–5 wt % GO was synthesized using a citrate auto-combustion method. The crystal structure, morphology, and magnetic properties of the investigated samples were investigated. The direct effects of graphene on morphology, crystal structure as well as the enhanced magnetic properties reveal that the studied samples are suitable for turbidity color and removal. High Resolution Transmission Electron Microscopy (HRTEM) images show that the substitution of small amounts of Gd$^{3+}$/GO causes a considerable reduction of the grain size. Studies on the magnetic properties demonstrate that the coercivity of GO-substituted magnesium nano ferrites is enhanced from 71 Oe to 203 Oe and the magnetocrystalline anisotropy constant increases from 1170 to 3424 emu Oe/gm at 300 K. The magnetic entropy change is estimated from magnetization data using Maxwell relation. The calculated Curie temperature from the Curie–Weiss law and the maximum entropy change are in good agreement with each other.

Introduction:
Graphene nanoparticles an attractive carbon material, is promising for improving adsorption capacity, high chemical stability, good electrical properties, strong mechanical stability, and large specific surface area. Therefore it has attracted the attention of scientists and researchers due to its useful applications in various fields [1]. Recently, combining graphene with other nanoferrites were reported to develop novel nanocomposites. Graphene-based materials with low aggregation and high specific surface areas show high adsorption capacities for organic pollutants [2–4]. Therefore, it is important to prevent aggregation between the layers. For convenient separation, magnetic particles are introduced in the adsorbent to form magnetic graphene composites. The added magnetic particles also play an important role in preventing aggregation of the graphene sheets.

The rare earth ions are the promising substitute for the enhancement of the properties of nano ferrite samples. The addition of rare earth ions like Tb, Gd and La change the physical properties of the samples. [5]. Many workers [6-8] investigated the magnesium based ferrites for numerous applications. But the reports on rare earth substituted magnetic properties in Mg-Gd ferrite system are rather rare.

The aim of the present study is to synthesize and characterize MgFe$_2$O$_4$, MgGd$_{0.05}$Fe$_{1.95}$O$_4$, and graphene-based MgFe$_2$O$_4$ nano composites using citrate auto combustion method. We manufactured the graphene oxide (GO) sheets by adopting a modified Hummer’s method.

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Experimental:

Nanoparticles of doped magnesium ferrite was prepared using citrate auto combustion method [9]. In this method, the stoichiometric quantities of Fe(NO₃)₃.9H₂O, Mg(NO₃)₂.6H₂O and Gd(NO₃)₃.6H₂O were dissolved in double-distilled water and stirred well using a magnetic stirrer for about 1 h at 80 °C, followed by drying at 200 °C. The structure and crystallite sizes were tested by X-ray diffractometer (XRD) using Diano corporation of target Cu-Kα (k = 1.5418 Å). The average nanoparticle sizes were determined using Scherrer’s relationship [10]. The morphology of the samples was studied by High Resolution Transmission Electron Microscopy (HRTEM) attached with EDAX unit (energy dispersive X-ray analyses). The synthesized powder of Mg, Mg/Gd and Mg/Go samples was calcined at 600 for 4 h with heating rate of 4 °C/min. The magnetization M (emu/g) was measured at room temperature using a vibrating sample magnetometer (VSM) Model Lake Shore 7410.

Preparation of MgFe₂O₄/GO

A stoichiometric amount of magnesium (III) nitrate, [Mg (NO₃)₂.6H₂O] and iron (III) nitrate [Fe (NO₃)₃.9H₂O] were dissolved in 50 ml of double distilled water under magnetic stirring. Then 5 wt% of GO was added to above solution, followed by ultrasonic treatment for about 30 min until GO was well dispersed in the solution. The molar amount of citric acid added was equal to the total molar amount of metal nitrate in the solution. The solution was continuously stirred for 1 h at room temperature. Ammonia solution was slowly added to adjust the pH and also to stabilize the nitrate-citrate solution. The obtained precipitate was collected and followed by calcination at 600 °C for 4 h to obtain MgFe₂O₄/GO powder.

Results and discussion:

Figure (1: a-b) illustrate the x-ray diffraction pattern for MgFe₂O₄, MgGd₀.₀₅Fe₁.₉₅O₄ and MgFe₂O₄₋₅ wt% GO nano ferrite samples. The diffraction peaks correspond to spinel structure for the investigated samples. No extra reflection peaks are detected in the X-ray diffraction patterns corresponding to any impurity phase. Their structure fully matches with powder diffraction file JCPDS (01-088-1938).

Generally, the major peak in graphene oxide is due to the (001) reflection at 10.57°, which shows the complete oxidation and exfoliation of flake graphite precursor [11, 12]. However, there is no peak of graphene oxide in the synthesized composite samples (Fig.1: b). The absence of the characteristic peak (001) associated with graphene oxide in Mg/GO sample shows the complete reduction under condition mentioned in experimental synthesis. Actually, the absence of the characteristic peaks of graphene is also due to the intrinsic low crystalline structure of graphene. This ratifies that the substituted GO is completely dissolved in the magnesium nano-ferrite structure.

A slight increase in the peak broadens with the addition of Gd/GO is observed. This is identified with the crystallite refinement and lattice micro strain decrement. The theoretical lattice parameter for Mg and Gd substituted Mg is calculated as mentioned before [13]. The theoretical lattice parameter, experimental lattice parameter, crystallite size X-ray density, strain and tolerance factor are summarized in Table 1.

However the substitution of Gd ions induces structural distortion due to its larger size and yields micro-strain, utilizing the Williamson–Hall equation [14]. The tolerance factor, T, for pure Mg and Mg/Gd samples are calculated according to Roderick et al. [15]. It is found that for the studied samples, value of T is close to unity signifying defect-free formation of spinel structure.
Fig. (1: a-b): The X-ray diffraction patterns for (a) MgFe$_2$O$_4$, MgGd$_{0.05}$Fe$_{1.95}$O$_4$ and GO-MgFe$_2$O$_4$ and (b) graphene oxide and GO-MgFe$_2$O$_4$

As shown from the table the Gd$^{3+}$/ GO substitution decrease the lattice parameters. The decrease of the lattice constant supports the incorporation of Gd$^{3+}$/GO into the magnesium ferrite lattice.

The crystallite size is detected from XRD broadening of (311) peak using Scherrer’s formula [10]. The crystallite size of the pure magnesium nano ferrite decreases with the substitution of Gd$^{3+}$/GO oxide and the calculated data is shown in the Table. The growth of the MgFe$_2$O$_4$ is restricted by the substitution of Gd$^{3+}$/GO leading to a relatively small crystallite size compared with parent magnesium nano ferrite. The bond energy of Gd$^{3+}$–O$^{2-}$ is higher compared to Fe$^{3+}$–O$^{2-}$. This means that more energy is needed to incorporate Gd$^{3+}$ ions into the octahedral sites [16]. In this process the required energy is supplied at the expense of crystallization and therefore hinders the growth of the crystallites and a smaller crystallite size is obtained for the Gd$^{3+}$ doped samples.
Table 1: The experimental lattice parameter (a_{exp}), Theoretical lattice parameter (a_{theo}), Crystallite size (D), X-ray density, Strain, and Tolerance factor for the investigated samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exp. lattice parameter a (Å)</th>
<th>Theo. lattice parameter a (Å)</th>
<th>Crystallite size (nm)</th>
<th>x-ray density (gm/cm^3)</th>
<th>Strain</th>
<th>Tolerance factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg Fe_2O_4</td>
<td>8.397</td>
<td>8.381</td>
<td>27.6</td>
<td>4.488</td>
<td>0.0043</td>
<td>1.0</td>
</tr>
<tr>
<td>Mg Fe_{1.95}Gd_{0.05}O_4</td>
<td>8.394</td>
<td>8.400</td>
<td>15.4</td>
<td>5.077</td>
<td>0.0077</td>
<td>0.99</td>
</tr>
<tr>
<td>GO-MgFe_2O_4</td>
<td>8.373</td>
<td>------</td>
<td>12.7</td>
<td>-----------------------</td>
<td>0.0093</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure (2: a-e) shows the HRTEM images for the investigated samples. It is clear that the MgFe_2O_4 sample shows sphere-like morphology with uniform size distribution. The lattice fringes with interplanar distances of 2.519 nm correspond to the (311) crystal plane of MgFe_2O_4. Moreover, the doping of Gd^{3+} ions decreases the size of the grains. A clear difference is observed between the undoped and doped samples. This result is in good agreement with the size reduction detected by XRD analysis.

On the other hand, MgFe_2O_4 nanoparticles are adsorbed regularly on the paper-like GO, which can inhibit the stack of GO layers (Fig. 2d). Hence, there is no possibility of interaction between MgFe_2O_4 and GO. This reveals the same interlayer spacing, indicating that no change occurred in the lattice structure of MgFe_2O_4 after addition of GO. In addition, some wrinkles and folds are appeared on the graphene sheets which cause the intensification of the contact area with Mg nanoferrite phases [17].

The selected-area electron diffraction (SAED) pattern is shown in the inset of Fig. 2(b - d). It is clear that the image exhibits bright dots arrangement which ratify the feature of nano structure of the investigated samples. The size distribution of the studied samples is shown in Fig. (2: a, b and d) and the average particle sizes are in the range of 18 – 37 nm.
Fig. (2: a-e): (a, b and d) HRTEM micrographs with the histogram for MgFe$_2$O$_4$, MgGd$_{0.05}$Fe$_{1.95}$O$_4$ and MgFe$_2$O$_4$-graphene respectively and (c and e) the d-spacing for MgGd$_{0.05}$Fe$_{1.95}$O$_4$ and MgFe$_2$O$_4$-graphene.
Figure (3: a- d) shows the energy-dispersive X-ray spectroscopy (EDAX) analyses for the parent and Gd/GO doped samples. The characteristic peaks in the spectrum comprise Mg, Fe, Gd, C and O. The atomic percentage (at %) and weight percentage (wt %) of constituent elements, are calculated theoretically from the given formula MgFe\textsubscript{2}O\textsubscript{4}, Mg\textsubscript{0.05}Gd\textsubscript{1.95}Fe\textsubscript{4} and MgFe\textsubscript{2}O\textsubscript{4} – 5 wt% GO. The obtained data from EDAX elemental analysis is shown as inset of the figure.
Fig.(3a-d): EDAX for (a) MgFe₂O₄, (b) MgGd₀.₀₅Fe₁.₉₅O₄ (c) MgFe₂O₄-graphene and (d) graphene oxide. The inset table gives the quantitative estimation of elements obtained directly from the spectrum through its weight and atomic percentages.

As shown from Fig.3d carbon and oxygen are presented in the pure graphene oxide sample, which confirm the purity of the used material. Fascinatingly the EDAX data shows carbon peaks that are not noticeable in the XRD chart (Fig. 1).

Figure (4: a-b) shows the hysteresis loops of the investigated samples using a vibrating sample magnetometer (VSM) at 300K. From the figure, it is clear that the magnetization increases with the applied magnetic field until reaching saturation trend. From the hysteresis loops, the coercivity (Hₐ), saturation magnetization (Mₛ), remnant magnetization (Mᵣ), squareness (Mᵣ/Mₛ) and magnetic moment (nᵦ) are calculated and summarized in Table 2. Generally, the magnetic moment nᵦ is calculated from the saturation magnetization (Mₛ) value at room temperature as mentioned in the previous work [18]. The saturation magnetization is expressed by means of the following relation [19].

\[ nᵦ = Mᵦ \times Mₛ / 5585 \]  

(1)

where Mᵦ is the molecular weight of a particular ferrite composition.

![Graphene oxide EDAX spectrum](image)
Fig. (4: a-b): The hysteresis loops for (a) MgFe₂O₄ and (b) for Gd/GO doped MgFe₂O₄

It is clear from the table that the magnesium upon the addition of 5 wt% of graphene demonstrate an increase in magnetic saturation ($M_s$) as compared with the MgFe₂O₄ and MgGd₀.₀₅Fe₁.₉₅O₄ samples. The improvements in magnetic parameters in the presence of rare earth ions (Gd³⁺) and graphene (GO) can be influenced by numerous parameters (extrinsic and intrinsic). The extrinsic parameters depend on the crystallite size, morphology, and density of the nanoparticles [20]. While the intrinsic parameters, such as the relative distribution of metals cations at the tetrahedral and octahedral sites [21]. However, the incorporation of graphene in the MgFe₂O₄ nanocomposites increases the tetrahedral and octahedral distribution of the metal cations. Also it changes the surface morphology, and the crystal strains [22].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
<th>Energy loss (erg/g)</th>
<th>$M_r/M_s$</th>
<th>$K$ (emu. Oe /g)</th>
<th>$n_B$ (exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgFe₂O₄</td>
<td>15.71</td>
<td>1.67</td>
<td>72</td>
<td>4272</td>
<td>0.11</td>
<td>1171</td>
<td>0.562</td>
</tr>
<tr>
<td>MgGd₀.₀₅Fe₁.₉₅O₄</td>
<td>15.28</td>
<td>1.85</td>
<td>64</td>
<td>2846</td>
<td>0.12</td>
<td>1011</td>
<td>0.56</td>
</tr>
<tr>
<td>G-MgFe₂O₄</td>
<td>16.18</td>
<td>1.98</td>
<td>203</td>
<td>7184</td>
<td>0.12</td>
<td>3425</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 2: Saturation magnetization ($M_s$), Remnant magnetization ($M_r$), Coercive field ($H_c$), Energy loss, Squarness ($M_r/M_s$), Anisotropy constant ($K$), and Magnetic moment ($n_B$) for the investigated samples.

On the other side, the ionic radius of Gd³⁺ (0.938) ions is larger than that of Fe³⁺ (0.645) ions in B site. This leads to a reduction in the symmetry of the system and hence generates an internal stress inside the material [23, 24]. Moreover, the grain boundary between domains increases due to small crystallite size of MgGd³⁺ samples. Therefore, the area of disordered arrangement for ions on the grain boundaries may fix and hinder the domain walls motion, leading to an increase in the coercivity of the samples [24]. However the variation of the coercive field ($H_c$) is directly depends on the surface spin disorder [25]. The increase in $H_c$ for
the graphene-based magnesium nanocomposites confirms that GO increases the surface spin disorder.

Finally, in this study, the Mg/GO ferrite nanoparticles and the Mg Gd\textsubscript{0.05}Fe\textsubscript{1.95}O\textsubscript{4} nano ferrite samples have shown higher magnetic saturation levels as compared to the parent sample. This can be attributed to better morphology and the increase of the domain wall migration of the MgFe\textsubscript{2}O\textsubscript{4}/graphene nanocomposites and MgGd\textsubscript{0.05}Fe\textsubscript{1.95}O\textsubscript{4} [26, 27]. Furthermore, it is observed that the coercivity of the Mg/GO is enhanced by 2.8 times relative to the parent and Gd doped samples.

The variation of the molar magnetic susceptibility ($\chi_M$) with absolute temperature as a function of the magnetic field intensity ($H = 1010, 1340, \text{ and } 1660 \text{ Oe}$) for the studied samples is shown in Fig. 5(a-b). Reasonable decrease in ($\chi_M$) with increasing temperature is detected until a definite temperature ($T_c$) after which it reaches to its slightest value. Inset of the graph shows $dM/dT$ from which one can determine the Curie temperature of the investigated samples. In the high temperature region the inverse susceptibility $1/\chi$ ($=H/M$) follows the Curie–Weiss law [28]. The Curie temperature ($T_c$), Weiss constant ($\Theta$), and the effective magnetic moment are calculated from the relation between the reciprocal molar magnetic susceptibility $1/\chi$ and the absolute temperature (not present here). The obtained data is recorded in Table 3.

![Graph](image-url)

**Fig. (5: a-b):** Magnetic susceptibility versus temperature for (a) MgGd\textsubscript{0.05}Fe\textsubscript{1.95}O\textsubscript{4} and (b) MgFe\textsubscript{2}O\textsubscript{4}-graphene. The inset shows the 1st derivative of magnetic susceptibility with temperature.
The increase in the Curie temperature for Mg/GO nano ferrite sample can be explained on the basis of A-B exchange interactions. The decrease in the grain size and increase of A-B super exchange interaction causes spin arrangement that increases the magnetic characteristics of the present samples as shown in the table.

Table 3: The Curie temperature (Tc) from Curie Weiss law and from maximum entropy change, Weiss constant (Θ), and the effective magnetic moment μ_eff.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic field (Oe)</th>
<th>Tc (K) From Curie-Weiss</th>
<th>Tc (K) at maximum entropy</th>
<th>Θ(K)</th>
<th>μ_eff (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgFe₂O₄</td>
<td>H=5000 Oe</td>
<td>625</td>
<td>620</td>
<td>620</td>
<td>1.1</td>
</tr>
<tr>
<td>Mg/Gd</td>
<td>H=1340</td>
<td>642</td>
<td>644</td>
<td>633</td>
<td>2.854</td>
</tr>
<tr>
<td>Mg/GO</td>
<td>H=1340</td>
<td>720</td>
<td>725</td>
<td>710</td>
<td>3.239</td>
</tr>
</tbody>
</table>

Estimating the magnetic entropy change ΔS_M (T, H) from magnetization data is commonly done by the use of the following Maxwell relation [29]

\[
\Delta S_M(T, H) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH
\]  

(2)

which directly implies that the maximum disorder of the given system (max. ΔS) is obtained at the Curie temperature where the ferromagnetic–paramagnetic phase transition takes place. Figure 6(a-b) illustrates the magnetic entropy change as a function of temperature for the investigated sample. The calculated Tc from the Curie–Weiss law is agree well with Tc obtained from the maximum entropy change as shown in Table 3.
Fig. (6: a-b): The change of entropy with temperature at different magnetic fields for (a) MgGd$_{0.05}$Fe$_{1.95}$O$_4$ and (b) MgFe$_2$O$_4$-graphene.

**Conclusion**

1-Rare earth gadolinium doped magnesium ferrite nano-particles (MgGd$_{0.05}$Fe$_{1.95}$O$_4$) and MgFe$_2$O$_4$–5 wt% GO nanocomposites are successfully prepared by citrate auto combustion method.

2-The impact of the substitution of graphene and Gd$^{3+}$ ions on the structural and magnetic properties is systematically studied. The XRD chart reveals a mono-phasic cubic spinel structure and good crystalline nature of the prepared samples.

3-The HRTEM data indicates the distribution of the MgFe$_2$O$_4$ ferrite constituent elements across the graphene surface.

4-The graphene-based MgFe$_2$O$_4$ magnetic nanocomposites demonstrated an improvement in its structure and magnetic properties. These improvements of Mg/GO nano composites provide the basis for a broad range of applications.

5- The coercivity of GO-substituted magnesium nano ferrites is almost 2.8 times greater than coercivity of parent sample.

**References:**


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