Structural characterization of Mg substituted on A/B sites in NiFe$_2$O$_4$ nanoparticles using autocombustion method

MANOJIT DE and H S TEWARI$^*$

Department of Pure and Applied Physics, Guru Ghasidas Vishwavidyalaya, Bilaspur 495 009, India

$^*$Corresponding author. E-mail: tewari.hs@gmail.com

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Abstract. In the present paper, we are reporting the synthesis of pure nickel and magnesium ferrite [NiFe$_2$O$_4$, MgFe$_2$O$_4$] and magnesium-substituted nickel ferrite (Ni$_{1-x}$Mg$_x$/yFe$_{2-y}$O$_4$; $x = y = 0.60$) on A/B sites with particles size in nanometer range using autocombustion technique. In this study, it has been observed that with increase in sintering temperature, the estimated bulk density of the materials increases. The XRD patterns of the samples show the formation of single-phase materials and the lattice parameters are estimated from XRD patterns. From Raman spectra, the Raman shift of pure NiFe$_2$O$_4$ and MgFe$_2$O$_4$ are comparable with the experimental values reported in literature. The Raman spectra give five Raman active modes ($A_{1g} + E_g + 3F_{2g}$) which are expected in the spinel structure.

Keywords. Nickel ferrite; magnesium ferrite; nanoparticles; autocombustion method; X-ray powder diffraction; micro-Raman.

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1. Introduction

Ferrites with the spinel structure AB$_2$O$_4$ have been the subject of numerous investigations for many years due to their applications in spintronics, optoelectronics, magnetoelectronics, electrochemical science and technology and biotechnology [1–3]. The phase formations of nanocrystalline spinel ferrites play important roles in determining their physical properties in nano and subnanolevels [4]. Nickel ferrite is a soft ferrimagnetic material with spinel structure having the general chemical formula NiFe$_2$O$_4$ occupying octahedral and tetrahedral sites in the face-centred cubic (FCC) lattice formed by O$^{2-}$ anions. The tetrahedral A-sites (8A) are occupied by half of the Fe$^{3+}$ cations, whereas the rest of the Fe$^{3+}$ and Ni$^{2+}$ cations are distributed over the octahedral B-sites (16D) [5]. The cation distribution between A- and B-sites depends on the ionic radii, the type of bonding and the preparation method. NiFe$_2$O$_4$ has attracted considerable interest due to its remarkable optical, mechanical, thermal and magnetic properties that are exploited in many technological applications such as magnetic storage systems, magnetic resonance imaging, spintronics, LPG sensor [6] etc.

2. Experimental details

In the present work, spinel ferrite materials NiFe$_2$O$_4$, MgFe$_2$O$_4$ and their solid solutions were synthesized using autocombustion method. The calculation of molar ratio (stoichiometric fuel to oxidant ratio) has a significant role in redox-based combustion synthesis. In this method, nitrate salts (Ni(NO$_3$)$_2$·6H$_2$O (99%), Mg(NO$_3$)$_2$·6H$_2$O (99%) and Fe(NO$_3$)$_2$·9H$_2$O (99%)) were taken as reactants and citric acid (C$_6$H$_8$O$_7$) (99%) was taken as the fuel. The nickel, magnesium and ferric nitrate salts were taken in a stoichiometric amount in a beaker, then this mixture was heated above the melting point of the constituents (∼70°C) in the presence of citric acid. The mixture would melt to form a homogeneous solution. Then this solution was heated at a temperature range of 90—100°C (depending upon composition) for 15—20 min. As a result, combustion took place inside the beaker and the solution would be converted to a brownish powder. After grinding the powder, cylindrical pellets were formed by using KBr press pelletizer and sintered at 900°C for 6 h. The XRD analyses of sintered samples were performed using Rigaku Smart Lab (Japan).
X-ray diffractometer with CuKα1 (λ = 1.54056 Å) radiation. The data were collected with a scanning speed of 4° per minute with a step size of 0.06° over the angular range 2θ (10° ≤ 2θ ≤ 80°). Raman spectra were taken by STR-500 micro-Raman spectrometer (Japan) at room temperature for all compositions.

3. Results and discussions

3.1 X-ray diffraction (XRD) analysis

The X-ray powder diffraction pattern of Ni_{1-x}Mg_{x/2}Fe_{2-y}O_{4}; x = y = 0.60 sample prepared by auto-combustion method is shown in figure 1. The sharp crystalline peaks observed for samples sintered at 900°C are attributed to the face-centred cubic nature of NiFe$_2$O$_4$. The peaks appearing at 2θ values 18.50°, 30.27°, 35.55°, 37.39°, 43.39°, 53.80°, 57.30°, 62.98°, 71.39°, 74.56° and 75.68° may be assigned for X-ray reflections from the (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (4 2 2), (5 1 1), (4 4 0), (6 2 0), (5 3 3) and (6 2 2) planes of the spinel crystal lattice, respectively. The obtained values of lattice constant for NiFe$_2$O$_4$ is in good agreement with the standard JCPDS (74-2081) (space group: Fd-3m) data file as well as the values reported in literature. Inset of figure 1 shows the shifting of peak around 2θ = 30° due to doping of Mg in NiFe$_2$O$_4$. The increase in crystallite size may be due to higher sintering temperatures.

The average crystalline size (D in nm) of pure (undoped) as well as doped samples was calculated from the XRD peak broadening of (3 1 1) peak by using the Debye–Scherer relation [7,8]

\[ D_{hkl} \text{(nm)} = \frac{k\lambda}{\beta \cos \theta}, \]

where \( k = 0.9 \) is the Scherrer’s constant, \( \lambda = 1.540562 \) Å and \( \beta \) (in radian) is the full-width at half-maxima (FWHM) of the diffraction peak at an angle \( \theta \). Based on the obtained results, it has been observed that the single phase ferrite was achieved immediately after combustion. When similar attempts were made to prepare the same system with the aid of oleic acid and aloe-vera, the ferrite phase along with hematite phase was obtained as an impurity in the final state [9,10]. Hence, it is concluded that citric acid is the best fuel for the synthesis of NiFe$_2$O$_4$. Table 1 shows the crystallite size and lattice parameter of different compositions.

3.2 Raman analysis

Raman spectroscopy is a powerful probe to reveal the vibrational and structural properties of materials. NiFe$_2$O$_4$ has a cubic inverse spinel structure of type

![Figure 1. XRD patterns for pure and doped compositions sintered at 900°C. Inset figure shows peak shifting around 30°.](image)
Table 1. Table for peak position of (3 1 1) plane and the corresponding crystallite size, lattice parameter and unit cell volume.

<table>
<thead>
<tr>
<th>Name of the sample</th>
<th>Crystal structure</th>
<th>Crystallite size (nm)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgFe₂O₄</td>
<td>Cubic</td>
<td>34.42</td>
<td>8.42</td>
</tr>
<tr>
<td>Ni₀.₄Mg₀.₆Fe₂O₄</td>
<td>Cubic</td>
<td>35.39</td>
<td>8.42</td>
</tr>
<tr>
<td>NiMg₀.₆Fe₁.₆O₄</td>
<td>Cubic</td>
<td>60.15</td>
<td>8.41</td>
</tr>
<tr>
<td>NiFe₂O₄</td>
<td>Cubic</td>
<td>44.17</td>
<td>8.35</td>
</tr>
</tbody>
</table>

Figure 2. Room-temperature Raman spectra of pure and doped compositions.

AB₂O₄ that belongs to Fd-3m space group with eight formula units per unit cell. The full unit cell of cubic symmetry contains 56 atoms but the smallest Bravis cell contains only 14 atoms. Therefore, 42 vibrational modes are possible. Group theory predicts the following optical phonon distribution: 5T₁u + A₁g + E₉ + 3T₂g; the 5T₁u modes are IR active [11], whereas the other five (A₁g + E₉ + 3T₂g) are Raman active modes composed of the motion of O ions and both the A-site and B-site ions [12,13]. It may be noted that, in ferrites, the modes above 600 cm⁻¹ belong to the motion of the oxygen atoms in tetrahedral AO₄ group and modes below 600 cm⁻¹ belong to the motion of the oxygen atoms in octahedral BO₆ [14].

Room-temperature Raman spectra of the as-synthesized Ni₁₋ₓMgₓ/₀.₆Fe₂₋ₙO₄; x = y = 0.60 ferrite samples are plotted in the frequency range of 100–800 cm⁻¹ (figure 2). The spectra of NiFe₂O₄ consist of broadband nearly at 213, 334, 486, 574 cm⁻¹ and a strong band at 701 cm⁻¹. It has been observed that Raman band at 701 cm⁻¹ shows a shoulder-like feature at lower wave number side (670 cm⁻¹) against the reported single band to that of Fe₃O₄ in the range of 650–750 cm⁻¹. These bands are assigned to T₁g(1) and T₁g(2) modes reflecting the stretching vibration of

Table 2. Assignment for Raman modes in the spinel structure.

<table>
<thead>
<tr>
<th>Raman modes</th>
<th>Origin of mode [16–18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₉</td>
<td>The symmetric bending of oxygen atom with respect to the metal ion in AO₄ unit</td>
</tr>
<tr>
<td>T₂̃(3)</td>
<td>Due to the asymmetric bending of oxygen</td>
</tr>
<tr>
<td>T₂̃(2)</td>
<td>Due to asymmetric stretching of (Fe/Ni)–O bond</td>
</tr>
<tr>
<td>T₁g(1)</td>
<td>Attributed to the translational movement of the tetrahedron (metal ion at tetrahedral site together with four oxygen atoms)</td>
</tr>
<tr>
<td>A₁g</td>
<td>Assigned as the symmetric breathing mode of the AO₄ unit with spinel lattice (highest frequency)</td>
</tr>
</tbody>
</table>

Table 3. The variation of different Raman modes with doping at different sites.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>MgFe₂O₄</th>
<th>Ni₀.₄Mg₀.₆Fe₂O₄</th>
<th>NiMg₀.₆Fe₁.₆O₄</th>
<th>NiFe₂O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁g(1)</td>
<td>216.38</td>
<td>213.01</td>
<td>243.13</td>
<td>213.78</td>
</tr>
<tr>
<td>E₉</td>
<td>329.80</td>
<td>323.83</td>
<td>362.51</td>
<td>334.99</td>
</tr>
<tr>
<td>T₂̃(2)</td>
<td>482.50</td>
<td>474.56</td>
<td>513.69</td>
<td>486.33</td>
</tr>
<tr>
<td>T₂̃(3)</td>
<td>546.80</td>
<td>551.60</td>
<td>590.73</td>
<td>574.78</td>
</tr>
<tr>
<td>A₁g</td>
<td>706.75</td>
<td>701.55</td>
<td>731.51</td>
<td>704.15</td>
</tr>
</tbody>
</table>
Fe$^{3+}$ and O$^{2-}$ ions in the tetrahedral site. The other low-frequency modes are assigned to $T_{2g}$ and $E_g$ modes reflecting the vibration of that site [12].

The doublet-like feature in Ni$_{1-x}$Mg$_x$/yFe$_{2-y}$O$_4$; $x = y = 0.60$ is attributed to the local cation distribution. In Fe$_3$O$_4$, the tetrahedral and octahedral sites are completely occupied by Fe ions, while in NiFe$_2$O$_4$ most of the octahedral site is occupied by Ni and Fe ions and tetrahedral site is occupied by only Fe ion. Due to difference in ionic radii of Ni and Fe ions in NiFe$_2$O$_4$, the Fe–O, Ni–O bond distances redistribute between both the sites resulting in doublet-like structure [15] (tables 2, 3).

4. Conclusions

NiFe$_2$O$_4$, MgFe$_2$O$_4$ and the solid solution of both the samples are synthesized by auto-combustion method using citric acid as the fuel. XRD patterns confirm the phase purity of the synthesized samples. Synthesized materials are of cubic structure having lattice parameters of the range 8.35–8.42 Å. Evolution of Raman spectra confirms the five active phonon modes (as per the group theory analysis) for NiFe$_2$O$_4$, MgFe$_2$O$_4$ and solid solution of both the samples. Due to the cation distribution at both the sites, a doublet-like feature has been observed for the $A_{1g}$ mode. The Raman active modes are also in good agreement with the reported literature confirming the spinel structure of the synthesized samples.

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