X-ray Diffraction and Saturation Magnetization Studies of Mg$_{1-x}$Zn$_x$Gd$_{0.02}$Fe$_{1.98}$O$_4$ Ferrites

Mansour Al-Haj *

ABSTRACT

Mg$_{1-x}$Zn$_x$Gd$_{0.02}$Fe$_{1.98}$O$_4$ ferrites were prepared by the solid state reaction method and were characterized by X-ray diffraction and magnetization measurements. A single spinel phase was obtained in all prepared samples. It was found that the lattice parameter increases as the Mg$^{2+}$ ions are replaced by the Zn$^{2+}$ ions. The magnetization measurements indicate the increased effect of spin canting of Fe$^{3+}$ ions in the octahedral sites at $x > 0.3$.

KEYWORDS: Ferrites; X-ray diffraction; lattice parameter; saturation magnetization.

1. INTRODUCTION

Ferrites are an important class of magnetic materials which are used widely as cores for high-frequency transformers and inductors, and in making antennas for radio receivers. The spinel ferrites can be described by the formula $(M_{1-x}Fe_x)[M_{x/2}Fe_{1-x/2}]_2O_4$, where $M$ is a divalent element, the round and square brackets denote tetrahedral and octahedral sites of co-ordination, respectively, and $\gamma$ is the inversion parameter whose value is in the range $0 \leq \gamma \leq 1$. For example, the ferrite ZnFe$_2$O$_4$ has $\gamma = 0$ and is a normal spinel at room temperature (the Zn$^{2+}$ ions occupy tetrahedral sites), while the ferrite MgFe$_2$O$_4$ has a $\gamma$ value between 0.9 and 1.0 and is a mostly inverse spinel (the Mg$^{2+}$ ions prefer to occupy octahedral sites).

Research in the field of ferrites is very active, and various techniques can be used to investigate their properties. Structural studies on Cu$_{1-x}$Zn$_x$Ga$_{0.5}$Fe$_{1.5}$O$_4$ ferrites showed that the Zn$^{2+}$ ions occupy the tetrahedral sites, while the ferrite MgFe$_2$O$_4$ has a $\gamma$ value between 0.9 and 1.0 and is a mostly inverse spinel (the Mg$^{2+}$ ions prefer to occupy octahedral sites).

Mössbauer spectra of Mg$_{0.9}$Cu$_{0.1}$Mn$_{0.05}$Cr$_{0.95}$Fe$_{1.95}$O$_4$ ferrites showed two characteristic ferrimagnetic Zeeman sextets for lower concentration of Cr$^{3+}$ followed by relaxation phenomenon (Lakshman et al., 2006). Magnetic studies on CoFe$_2$O$_4$ ferrites was found to be less than that of CoFe$_2$O$_4$ ferrites (Zhao et al., 2006). The behavior of the initial magnetic permeability with temperature exhibited multidomain structure for Li$_{0.5}$Fe$_{2.4}$Gd$_{0.1}$O$_4$ ferrite (Ahmed et al., 2005). The dc electrical conductivity was found to increase with temperature for Li$_{0.5}$Co$_{0.5}$Fe$_{2.5}$O$_4$ ferrites, ensuring the semiconducting nature (Abo El Ata et al., 2005). The ac electrical conductivity and the dielectric constant were found to increase for Ni$_{1-x}$Zn$_x$La$_{0.05}$Fe$_{1.95}$O$_4$ ferrites, where $x \geq 0.6$ (Ahmed et al., 2005). The magnetic studies on Ni$_{0.7}$Mn$_{0.3}$Gd$_x$Fe$_{2-x}$O$_4$ ferrites revealed that the maximum Gd$^{3+}$ content doped into the ferrite lattice is $x = 0.06$ (Zhao et al., 2006). The behavior of the initial magnetic permeability with temperature exhibited multidomain structure for Li$_{0.5}$Fe$_{2.4}$Gd$_{0.1}$O$_4$ ferrite (Abo El Ata et al., 2006). The ac electrical conductivity and the dielectric constant were found to increase for Ni$_{1-x}$Zn$_x$La$_{0.05}$Fe$_{1.95}$O$_4$ ferrites, where $x \geq 0.6$ (Ahmed et al., 2005). The dc electrical conductivity was found to increase with temperature for Li$_{0.5}$Co$_{0.5}$Fe$_{2.5}$O$_4$ ferrites, ensuring the semiconducting nature (Abo El Ata et al., 2005).

The main aim of the present work is to study the influence of replacing Mg$^{2+}$ ions by Zn$^{2+}$ ions on the structural and magnetic properties of Mg$_{1-x}$Zn$_x$Gd$_{0.02}$Fe$_{1.98}$O$_4$ ferrites, where $x = 0.1, 0.2, 0.3, 0.4, and 0.5$. Only a small amount of Gd$^{3+}$ ions was added to the system in order to guarantee the formation of a single spinel phase, since these ions have a relatively large radius.

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2. EXPERIMENTAL PROCEDURE

The ferrite powders were prepared by the usual ceramic method. Analytical grade oxides (MgO, ZnO, Fe$_2$O$_3$, Gd$_2$O$_3$) were mixed, ground, and sintered at 1100 °C in a Carbolite furnace for 10 h. Each sample was then slowly cooled to room temperature, ground, and sintered again at 1100 °C for 10 h. The X-Ray Diffraction (XRD) patterns were taken using a Seifert 3003 TT diffractometer operating at 40 kV and 40 mA. A 0.2-mm slit was placed in front of the secondary monochromator. The diffractometer was calibrated using a standard Si powder. Each sample was scanned in steps of 0.02° with a counting time of 1 s. The magnetization measurements were made on samples of equal mass at room temperature using a 9600 LDJ vibrating sample magnetometer, which was calibrated using an Ni standard. The saturation magnetization of each sample is the measured saturated magnetic moment divided by the mass of the sample.

3. RESULTS AND DISCUSSION

The XRD patterns confirmed the formation of the single spinel phase in all samples. For example, Fig. 1 shows the XRD patterns for $x = 0.3$ and 0.5. The cationic distributions can be obtained from stoichiometry and the radii of the constituting ions (Table 1). The deduced cationic distributions for all samples are listed in Table (2). We see from the table that as $x$ is increased, the content of the Zn$^{2+}$ ions in the tetrahedral sites increases, while that of the Fe$^{3+}$ ions in the tetrahedral sites decreases. The radius of the Zn$^{2+}$ ion in a tetrahedral site, which is surrounded by four other ions, is 0.60 Å, while that of the Fe$^{3+}$ ion in a tetrahedral site is 0.49 Å. Therefore, the lattice parameter increases as $x$ is increased.

It was reported that the ratios $I_{220}/I_{222}$ and $I_{422}/I_{222}$ are sensitive to the residence of Cd$^{2+}$ cations in the tetrahedral sites for Co$_{1-x}$Cd$_x$Fe$_2$O$_4$ ferrites (Gabal et al., 2004). A similar analysis can be done to Zn$^{2+}$ ions in the tetrahedral sites. In Fig. 3, the values of $I_{220}/I_{222}$ and $I_{422}/I_{222}$, together with their fitting curves, are plotted as a function of $x$. As $x$ is increased, these ratios decrease, suggesting a continuous change in the occupation of the tetrahedral sites by the Zn$^{2+}$ ions, in agreement with the cationic distributions listed in Table (2).

The magnetic measurements indicate that all samples are soft ferrimagnetic materials at room temperature. The magnetic hysteresis loops for $x = 0.1$ and 0.5 are shown in Fig. 4a. The saturation magnetization $M_s$ as a function of $x$ is shown in Fig. 4b. It is known that the net magnetization of the ferrite lattice is given by the difference of the magnetizations of the tetrahedral and octahedral sublattices, i.e. $M = M_{\text{tet}} - M_{\text{oct}}$. From Fig. 4b, we see that $M_s$ increases as $x$ is increased up to a critical value around 0.3 and then decreases. A similar behavior of saturation magnetization was reported for Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ (Yadoji et al., 2003), for Ni$_{0.5}$Mn$_{0.5}$Zn$_{0.7-x}$

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius of ion in a tetrahedral site (Å)</th>
<th>Radius of ion in an octahedral site (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>0.57</td>
<td>0.72</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0.60</td>
<td>0.74</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.49</td>
<td>0.64</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>–</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table 2: The deduced cationic distributions for Mg$_{1-x}$Zn$_x$Gd$_{0.02}$Fe$_{1.98}$O$_4$ ferrites.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Cationic distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>(Fe$^{3+}<em>{0.68}$Zn$^{2+}</em>{0.32}$)[Mg$^{2+}<em>{0.48}$Fe$^{3+}</em>{0.52}$Gd$^{3+}_{0.01}$]O$_4$</td>
</tr>
<tr>
<td>0.2</td>
<td>(Fe$^{3+}<em>{0.7}$Zn$^{2+}</em>{0.3}$)[Mg$^{2+}<em>{0.05}$Fe$^{3+}</em>{0.95}$Gd$^{3+}_{0.01}$]O$_4$</td>
</tr>
<tr>
<td>0.3</td>
<td>(Fe$^{3+}<em>{0.7}$Zn$^{2+}</em>{0.3}$)[Mg$^{2+}<em>{0.05}$Fe$^{3+}</em>{0.95}$Gd$^{3+}_{0.01}$]O$_4$</td>
</tr>
<tr>
<td>0.4</td>
<td>(Fe$^{3+}<em>{0.68}$Zn$^{2+}</em>{0.32}$)[Mg$^{2+}<em>{0.3}$Fe$^{3+}</em>{0.7}$Gd$^{3+}_{0.01}$]O$_4$</td>
</tr>
<tr>
<td>0.5</td>
<td>(Fe$^{3+}<em>{0.5}$Zn$^{2+}</em>{0.5}$)[Mg$^{2+}<em>{0.25}$Fe$^{3+}</em>{0.74}$Gd$^{3+}_{0.01}$]O$_4$</td>
</tr>
</tbody>
</table>

where $d$ is the lattice plane separation and $(hkl)$ is the index of the XRD reflection peak. For an accurate calculation of the lattice parameter, we calculated the lattice parameter for each of the seven most intense peaks and took their average of them. The calculated values and the fitting curve as a function of $x$ are shown in Fig. 2. It is seen that the lattice parameter increases as $x$ is increased. This behavior can be explained using the cationic distributions listed in Table (2). We see from the table that as $x$ is increased, the content of the Zn$^{2+}$ ions in the tetrahedral sites increases, while that of the Fe$^{3+}$ ions in the tetrahedral sites decreases. The radius of the Zn$^{2+}$ ion in a tetrahedral site, which is surrounded by four other ions, is 0.60 Å, while that of the Fe$^{3+}$ ion in a tetrahedral site is 0.49 Å. Therefore, the lattice parameter increases as $x$ is increased.

The lattice parameter $a$ was calculated using the equation

$$a = d \sqrt{h^2 + k^2 + l^2},$$

where $d$ is the lattice plane separation and $(hkl)$ is the index of the XRD reflection peak. For an accurate calculation of the lattice parameter, we calculated the lattice parameter for each of the seven most intense peaks and took their average of them. The calculated values and the fitting curve as a function of $x$ are shown in Fig. 2. It is seen that the lattice parameter increases as $x$ is increased. This behavior can be explained using the cationic distributions listed in Table (2). We see from the table that as $x$ is increased, the content of the Zn$^{2+}$ ions in the tetrahedral sites increases, while that of the Fe$^{3+}$ ions in the tetrahedral sites decreases. The radius of the Zn$^{2+}$ ion in a tetrahedral site, which is surrounded by four other ions, is 0.60 Å, while that of the Fe$^{3+}$ ion in a tetrahedral site is 0.49 Å. Therefore, the lattice parameter increases as $x$ is increased.

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Fe$_2$O$_4$ (Singh et al., 2003), and for Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$
(Mazen et al., 2003) ferrites. From the cationic
distributions listed in Table (2), we see that as $x$ is
increased, the Fe$^{3+}$ content in the tetrahedral sites
decreases and that in the octahedral sites increases.
Therefore, the magnetization of the octahedral sublattice
increases, that of the tetrahedral sublattice decreases, and
the saturation magnetization of the sample increases until
the critical value around 0.3 is reached. At $x > 0.3$, the
content of Fe$^{3+}$ ions in the tetrahedral sites is low, and the
exchange interaction experienced by the Fe$^{3+}$ ions in the
cuboctahedral sites is not sufficient to align them in one
direction; this results in ‘spin canting’ of the Fe$^{3+}$ ions in
the octahedral sites. Therefore, $M_{sat}$ decreases and the
saturation magnetization of the sample decreases as well.

It should be mentioned that there is no change in the
crystal structure of samples at $x > 0.3$. Just the spin
magnetic moments of the Fe$^{3+}$ ions in the octahedral sites
are no longer parallel to each other.

4. CONCLUSIONS

(1) A single spinel phase was obtained in all Mg$_{1-}$
$\cdot Zn_xGd_{0.02}$Fe$_{1.98}$O$_4$ samples.

(2) The lattice parameter increases as the content of the
Zn$^{2+}$ ions is increased.

(3) The behavior of saturation magnetization indicates the
increased effect of spin canting of Fe$^{3+}$ ions in the
octahedral sites at $x > 0.3$.

![XRD patterns](image-url)

**Fig. 1** The XRD patterns for (a) $x = 0.3$ and (b) $x = 0.5$. 

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Fig. 2 Dependence of the lattice parameter on $x$.

Fig. 3 Dependence of the ratios $I_{220}/I_{222}$ and $I_{422}/I_{222}$ on $x$. 
Fig. 4 (a) The magnetic hysteresis loops for $x = 0.1$ and $x = 0.5$ and (b) dependence of saturation magnetization on $x$.

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