Structure, magnetic and transmission characteristics of the Co substituted Mg ferrites synthesized via a standard ceramic route

Mahtab Pourzaki, Roya Kavkhani, Abbas Kianvash⁎, Abdollah Hajalilou

Department of Materials Eng., University of Tabriz, Tabriz 51666-16471, Iran

ARTICLE INFO

Keywords:
A. Sintering
C. Magnetic properties
D. Ferrites
E. Soft magnets

ABSTRACT

Co-Mg ferrites, CoₓMg₁₋ₓFe₂₋yO₄ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, 0 < y < 0.34 and 0 < z < 0.67), were synthesized via a standard ceramic route, and the structural, morphological, magnetic properties and transmission parameter of the samples were studied. The thermal behavior of the ground powder was characterized using a differential thermal analysis technique (DTA). The XRD patterns proved the formation of single phase Mg-ferrite in the samples with “x” contents varying from 0.0 to 0.8. The sample with x = 1.0 showed two phases: a spinel Mg-ferrite and a secondary (Co,Mg)O phase. The lattice parameter and crystallite size of the samples increased remarkably by increasing the x content. The SEM images revealed that Co substitution in Mg ferrite at x = 0.2 causes the particle growth, but their growth was not significant until x = 0.8. For x = 1.0, a remarkable particle growth was again observed. A maximum bulk density of 4.94 g/cm³ was obtained for x = 0.8. Magnetic properties of the sintered samples showed an increase in coercive force up to 113 Oe by increasing Co substitution up to x = 1.0. Saturation magnetization reached a maximum value of ~45.40 emu/g at x = 0.8. Studying the microwave transmission behavior of the samples, using a vector network analyzer (VNA), indicated that by increasing Co, the transmission loss was reduced from ~15 dB for x = 0.0 to less than ~10 dB for x = 0.8 in the frequency range of 8–12 GHz.

1. Introduction

Spinel ferrites with a general chemical formula of MFe₂O₄, in which M is one or two of divalent metals, such as Co, Mg, Zn, Ni, etc. [1], have been used in various applications such as microwave based devices, telecommunication and switching circuits [2]. Magnesium ferrite with a chemical formula of MgFe₂O₄ has an inverse spinel structure, in which half of the trivalent cations occupy the tetrahedral (A) sites and the other half of the trivalent cations and all of the divalent cations fill the octahedral (B) sites [3]. It may also exhibit normal or random spinel structure. Normal spinel structures are usually cubic close-packed oxides with two tetrahedral and four octahedral sites per formula unit. Fe³⁺ ions occupy half of the octahedral sites, while M²⁺ ions occupy one-eighth of the tetrahedral sites [4]. In a completely random distribution, a statistically averaged occupation occurs in each site [5]. This indicates that the cation distribution is strongly dependent on the preparation route [6]. Thus, the processing technique used to synthesize ferrites, affect their properties [4,7]. There are various methods such as standard ceramic technique [8–10], mechanical alloying [6], co-precipitation [7,11] and sol-gel [1,12] to synthesize spinel ferrites. Standard ceramic technique is the most conventional and economical method to synthesize Mg-ferrites. In this technique, the reactions between the raw materials such as oxides, hydroxides or carbonates, which occur at relatively high temperatures, result in synthesizing the spinel [13]. The Mg-ferrites have the extensive range of applications from low frequencies to microwave frequencies because of their easy fabrications, high efficiencies, thermal stabilities, and low costs [14,15]. They are widely used in microwave devices as circulators, insulators and phase shifters [16,17] due to their excellent magnetic and electrical properties such as high permeability, high electrical resistivity and low dielectric and magnetic losses [12,15]. To achieve low dielectric losses, it is necessary to reduce the transmission loss [18]. On the other hand, the structure and morphology of the material has influence on the wave transmission performance; i.e., different morphologies have a complex influence on the electromagnetic parameters [19].

In the field of ferrites, in addition to concentrate on resistivity, the aim is to improve their saturation magnetization as much as possible, and at the same time to keep the coercivity in reasonable orders [20]. Since Co ferrites have shown excellent chemical stability, high coercivity, mechanical hardness and moderate saturation magnetization [1,2,8,9] and Co ions are strongly magnetic with large anisotropy [21],...
thus Co was used to improve the magnetic behavior of Mg ferrite and to broaden its microwave applications. Previous studies have shown that doping Mg ferrite by Co results in variation in saturation magnetization and coercivity, depending on the magnetic behavior of the samples on the Co concentration [8,10].

The present work is aimed to study the influence of Co-doping using Co3O4 on the magnetic and microwave properties of Co0.95Mg0.05Fe2.05O4 compounds with x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, 0 < y < 0.34 and 0 < z < 0.67, prepared using a ceramic technique.

2. Experimental

The Mg-Co ferrites with a general chemical formula Co0.95Mg1-yFe2-zO4 (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, 0 < y < 0.34 and 0 < z < 0.67, where x = y + z and y + z = 0.53) were prepared using a ceramic technique. It is worth to mention that cobalt oxide in the form of Co3O4 is more accessible and thermodynamically stable compared with CoO [22]. Therefore, in the present work, instead of using CoO as a raw material, Co3O4 was used and the replacement of Mg2+ and Fe3+ by Co2+ and Co3+ was taken into account in the computations as follows:

\[
\begin{align*}
(CO_3)O_2 & \rightarrow (CO)_{x/2},(CO_2O_3)_{1-x/2} \rightarrow x = y + z \\
(MgO)_{1-y} & \\
(FE_2O_3)_{1-z} & \\
\text{and as } O=4, \text{ so:} \\
(4x/3) + (1-y) + (3-3z/2) & = 4 \rightarrow y + 3z/2 = 0.53
\end{align*}
\]

High-purity oxides of Co3O4, MgO and Fe2O3 (all from Merck company with purities > 99%), in stoichiometric molar ratios, were thoroughly mixed by wet blending in distilled water using a planetary ball mill with AISI 52100 Cr-steel balls. The ball-to-powder ratio was 10:1. The samples were mixed for 3 h, and then dried in an oven at 80°C for 24 h. The powder was pressed into pellets of ϕ ~ 1 mm with ~5 mm height. The compacts were heated at 1000°C for 4 h, with a heating rate of 4°C/min and then furnace cooled to room temperature. The pellets were ground and pressed into cubes of dimensions 25 × 11 × 3.80 mm3 by adding 1.5% of polyvinyl alcohol (PVA) as a binder. The samples were finally sintered at 1300°C for 5 h, in air under the same conditions mentioned above. Sintered samples were then ground to dimensions of 21.86 × 10.11 × 3.50 mm3 required for the transmission measurement, using emery paper of grades ranging from 200 to 1000, respectively. The flowchart of the experimental procedure is shown in Fig. 1. To find out the decomposition temperature of Co3O4, differential thermal analysis (DTA-STA 504) was used in the range of 50–900°C with a heating rate of 10°C/min in argon atmosphere. The XRD analyses of the synthesized powders were undertaken using a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å) in the range of 2θ = 20°–80° at a step size of 0.02°. The morphology of the powders was evaluated using a scanning electron microscope (SEM-LEO 440i). The magnetic properties and transmission parameters of the electromagnetic waves were measured using a Magnet Physik C-300 permagraph and a HP 8510C vector network analyzer (VNA), respectively.

It should be mentioned that an appropriate microwave transmission material must present a wide frequency bandwidth and low absorption and reflection losses [7]. NRW (Nicolson-Ross, 1970; Weir, 1974) method is one of the most common methods to measurement electromagnetic waves properties that introduced transmission and reflection technique [23–25]. In this method, the complex scattering parameters, called S parameters, which correspond to the reflection loss (S11 or S22) and transmission loss (S21 or S12) in samples, are generally evaluated by a VNA [23,26]. If a sample was homogeneous, then there should not be any differences in the scattering characteristics between two ports i.e. (S21 = S12 and S11 = S22) [27]. S11 and S21 are used to calculate reflection loss and transmission loss respectively through the following formulas [23]:

\[
\begin{align*}
\text{Reflection loss} & = 20\log(|S_{11}|) \\
\text{Transmission loss} & = 20\log(|S_{21}|)
\end{align*}
\]

therefore, S21 measurement is adequate to estimate the transmission loss.

To determine S parameters, a two-port transmission approach is usually used, with a sample-under-test of smooth flat faces, filling completely the fixture cross section, and being placed inside a rectangular waveguide [24]. Samples are placed between two waveguide ports at the left and right of X-axis. The wave is excited from positive X-axis (Port 1) toward negative X-axis (Port 2) to calculate complex S11 (reflection of port 1 at 1) and complex S21 (transmission at port 2 due to 1) parameters (Fig. 2) [28]. Full two ports calibration are initially done on the test setup in order to remove the errors due to the directivity, source match, load match, isolation, etc., in both the forward and reverse direction [26].

In the current work, it was attempted to study the transmission

\[
\begin{align*}
\text{Reflection loss} & = 20\log(|S_{11}|) \\
\text{Transmission loss} & = 20\log(|S_{21}|)
\end{align*}
\]

\[
S_{11} = S_{22} \text{ and } S_{12} = S_{21}
\]

\[
\begin{align*}
\text{Reflection loss} & = 20\log(|S_{11}|) \\
\text{Transmission loss} & = 20\log(|S_{21}|)
\end{align*}
\]
parameter $S_{21}$ which was evaluated by a VNA. The electromagnetic wave transmission properties were investigated in X-band frequency range (8–12 GHz).

### 3. Results and discussion

#### 3.1. DTA results evaluation

Almost similar DTA curves were obtained for $\text{Co}_{x}\text{Mg}_{1-y}\text{Fe}_{2-z}\text{O}_4$ compounds with $x=0.0$–$1.0$. A typical DTA curve for a $\text{Co}_{0.4}\text{Mg}_{0.86}\text{Fe}_{1.74}\text{O}_4$ powder with $x=0.4$ is shown in Fig. 3. An endothermic peak which is observed in almost all the samples at around 400 °C is attributed to decomposition of $\text{Co}_3\text{O}_4$ [29].

#### 3.2. XRD analysis

Fig. 4 shows XRD patterns for the $\text{Co}_{x}\text{Mg}_{1-y}\text{Fe}_{2-z}\text{O}_4$ ferrites with $x=0.0$–$1.0$. XRD patterns were analyzed by X′Pert High Score software. The samples up to $x=0.8$ exhibit MgFe$_2$O$_4$ single phase spinel structure, which is in accordance with ICDD card Nos. 00-001-1120 and no extra peak was observed. All the reflection peaks at 2θ = 30.42, 35.79, 43.43, 53.77, 57.28, 62.90, 71.42 and 74.40 correspond to diffraction planes of (220), (311), (400), (422), (511), (440), (620) and (533), respectively. It can be seen that the diffraction peaks are either all even or all odd, which suggests a spinel phase for all the samples [30].

In the sample with $x=1.0$, additional peaks in the planes (111), (200), (220), (311) and (222), marked by “*”, are related to (Co,Mg)O according to ICDD card nos. 01-073-1720. This suggests that higher Co content of $\geq 1$ results in secondary phase formation. It should be noted that the peak emerged in plane (311) of (Co,Mg)O overlaps with peak (533) of MgFe$_2$O$_4$.

The lattice parameter of the samples, $a$, was calculated from the XRD patterns via the following formula [8,31]:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$  

(7)

where $(hkl)$ and $d$ are Miller indices and interplanar distance of each plane, respectively.

The crystallite size and lattice strain were also extracted from the XRD data using Williamson-Hall formula through the following equation [32]:

$$b \cos \theta = \frac{0.9\lambda}{d} + 2\eta \sin \theta$$  

(8)

where $b$ is the full width of peak at half maximum (FWHM), $\theta$ is the Bragg angle, $d$ is the average crystallite size, $\lambda$ is the wavelength of X-ray and $\eta$ is the lattice strain.

The theoretical density was calculated according to the equation suggested by Smit and Wijn as follows [30,31]:

$$\rho_{\text{theo}} = \frac{8M}{N_a a^3}$$  

(9)

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

The porosity ($P$) of the samples was estimated by using the following formula [7]:

$$P = \left[1 - \frac{\rho_{\text{exp}}}{\rho_{\text{theo}}}\right] \times 100$$  

(10)

### Table 1

Calculated structural parameters, saturation magnetization ($M_s$) and coercivity ($H_c$) of $\text{Co}_{x}\text{Mg}_{1-y}\text{Fe}_{2-z}\text{O}_4$ samples.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Lattice strain (%)</th>
<th>$\rho_{\text{theo}}$ (g/cm$^3$)</th>
<th>$\rho_{\text{exp}}$ (g/cm$^3$)</th>
<th>Porosity (%)</th>
<th>$M_s$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.60</td>
<td>4.41</td>
<td>4.16</td>
<td>5.67</td>
<td>23.41</td>
<td>18</td>
</tr>
<tr>
<td>0.2</td>
<td>15.96</td>
<td>4.83</td>
<td>4.52</td>
<td>6.42</td>
<td>41.79</td>
<td>50</td>
</tr>
<tr>
<td>0.4</td>
<td>16.38</td>
<td>4.87</td>
<td>4.58</td>
<td>5.95</td>
<td>43.11</td>
<td>67</td>
</tr>
<tr>
<td>0.6</td>
<td>16.41</td>
<td>4.95</td>
<td>4.69</td>
<td>5.25</td>
<td>44.13</td>
<td>98</td>
</tr>
<tr>
<td>0.8</td>
<td>16.82</td>
<td>5.13</td>
<td>4.94</td>
<td>3.70</td>
<td>45.37</td>
<td>110</td>
</tr>
<tr>
<td>1.0</td>
<td>18.37</td>
<td>5.10</td>
<td>4.90</td>
<td>3.92</td>
<td>43.52</td>
<td>113</td>
</tr>
</tbody>
</table>
where $\rho_{\text{exp}}$ is the experimental density which is calculated by Archimedes' principle [7,11]. The measured values of these parameters are presented in Table 1. It could be observed that lattice parameter is increased up to $x = 0.8$ and then it decreases by increasing the Co content. This is in a good agreement with the results of previous work [8] for $x$ up to 0.2. The non-linear behavior of lattice parameter might be attributed to replacement of smaller Mg ions by larger Co ions. Moreover, it could be due to the occupation of Co and Mg ions in A and B sites. This change in cation distribution might be responsible for the decrease in lattice parameter at higher content of Co ($x > 0.8$). The crystallite size of the samples is increased initially up to $x = 0.2$ and then it remains almost constant by increasing the Co concentration up to $x = 0.8$ (Fig. 5); however, at $x = 1.0$, both the crystallite size and lattice strain are increased (see Fig. 5 and Table 1). It has already been reported [9] that the variation of crystallite size is a normal trend due to the induced microstrain resulting from the replacement of Mg ions by...
Co ions up to $x = 0.2$; at $x = 0.4-0.8$, it seems that a surface relaxation takes place [9]. Density is increased up to $x = 0.8$ and attains a maximum value of 4.94 g/cm$^3$ at this point (Table 1); this is in a good agreement with the corresponding porosity value, which is a minimum in this specimen (3.70%). In the sample with $x = 1.0$, density is decreased. This behavior of the density at $x = 1.0$ might be due to the difference in atomic weight of Co and Mg ions, which is attributed to the fact that reduction in mass overcomes the decrease in volume of the unit cell [9].

### 3.3. Morphological behavior of the sintered samples

SEM micrographs of the Co$_x$Mg$_{1-x}$Fe$_{2-z}$O$_4$ powder samples, at the same conditions of milling, are exhibited in Fig. 6. It seems that by increasing Co content to $x = 0.2$, the particles grew slightly, but they remained almost constant by increasing the $x$ content up to $x = 0.8$. However, a remarkable particle growth was observed in the sample with $x = 1.0$, which seems to be double in size compared to $x = 0.0$. The average particle size of the samples was measured using lineal intercept method from these images and found to be 0.5 and 1.0 µm in the samples with $x = 0.0$ and $x = 1.0$, respectively. Furthermore, it seems that by increasing Co content, the particle agglomerations are increased. This could be due to replacement of non-magnetic Mg ions by magnetic Co ions in the structure of Mg-ferrite, which results in the occurrence of further attraction between the particles due to Co ions magnetic moments [1,7,33].

### 3.4. Magnetic properties

The magnetic properties of ferrites depend on the chemical composition and cation distributions in the octahedral and tetrahedral sites. Moreover, it was reported that coercivity of these materials depends on several factors such as size distribution, micro strain, anisotropy and temperature [19,33]. Fig. 7 shows hysteresis loops of Co$_x$Mg$_{1-x}$Fe$_{2-z}$O$_4$ ferrites with $x = 0.0-1.0$. By increasing Co content up to $x = 1.0$, the coercivity ($H_c$) of the samples is increased. It might be due to a fact that the cobalt ferrites have greater anisotropy constants compared to the magnesium ferrites. The saturation magnetization ($M_s$) is increased by increasing Co content up to $x = 0.8$ and thereafter, its value decreases by increasing Co to $x = 1.0$ (Fig. 8). Thus, $M_s$ follows the same trend as that of the density which is in general true, and thus the sample with the maximum density, has the highest value of $M_s$. A similar behavior was reported for $x = 0.15$ [11]. A maximum saturation magnetization has been reported for Co content of $x = 0.2$, which was decreased for higher concentration of Co [8]. The variation in saturation magnetization behavior could be described by Neel's two sub-lattice model [8,34]. In this model, the structure of magnetic spinel consists of two sub-lattices of which namely are the tetrahedral (A) and octahedral (B) with metal ions distributed in these two sites. The magnetic moment of sub-lattices acts in opposite direction to each other. The magnetization difference between B and A sites determine the net magnetization of materials, i.e. $M = |M_B - M_A|$ [34,35]. Thus, the initial increase in saturation magnetization could be due to substitution of non-magnetic Mg ions by magnetic Co ions. Both Mg and Fe ions are distributed in tetrahedral and octahedral sites, preferentially. However, by increasing Co content up to $x = 0.8$, the Co ions should occupy most of A sites that cause a fraction of Fe ions to be displaced into B sites; this results in an enhancement in the net magnetic moment. The reduction of $M_s$ in the sample with $x = 1.0$, may be due to simultaneous migration of Mg ions from A to B and Fe ions from B to A sites. The decrease in $M_s$ at higher content of Co ($x = 1.0$) might also be attributed to the formation of (Co,Mg)O secondary phase which has probably a lower value of magnetization. The measured values of $H_c$ and $M_s$ via a permagraph are given in Table 1.
3.5 Microwave transmission behavior

Scattering parameters or S-parameters are coefficients (elements) of a scattering matrix. They are used to describe behavior of linear microwave networks. S-parameters are widely used in microwave measurements as they formulate the transformation properties in terms of incident and reflected waves and can be directly measured with network analyzers [36, 37]. S-parameters are a measurement-friendly alternative to conventional two port network parameters. Indeed, scattering parameters are conveniently extracted in the laboratory, but they are also explicitly useful in design. Because the S-parameters of a linear two-port network interrelate incident and reflected waves of energy at input and output ports, as opposed to intertwining input and output port voltages and currents, they are useful in the design of microwave amplifiers. The reason underlying this design utility is that voltages and currents are more difficult to quantify uniquely at microwave frequencies than are delivered energies and average signal power levels. Additionally, the scattering parameters of lossless two ports have a unique property that enables their judicious exploitation in the design of lossless matching networks serving to average signal power levels. Scattering parameters are used at wide bandwidth at X-band frequency. Furthermore, the wavy nature of the “S21 versus frequency” curves is mainly associated with the ferromagnetic resonance (variation of real and imaginary permeability by changing of EM) state of the Co substituted Mg ferrites. Moreover, since no composite material was used as a matrix for theses samples, it is expected there is no dielectric loss in our samples, according to Ref. [40]. Thus, this suggests that the resonance induced is more probably associated with the magnetic loss characteristics of the samples, i.e., hysteresis loss, eddy current and domain-wall displacement, which are more obvious than that of dielectric losses like conduction loss, dielectric relaxation loss and resonance loss. This simply means that once the Co is added to Mg ferrite, both the saturation magnetization and applied magnetic field vary. Consequently, the resultant resonance would be attributed to the magnetic wall movement as well as domain motion.

By increasing Co content from x = 0.2–1.0, the transmission loss curve is located between 0 and ~10 dB. According to formula (6), it could be concluded that by decreasing S21, transmission loss is decreased. However, the sample with x = 0.8 has the favorable transmission behavior compared to the rest of the samples. With increase in magnetic properties, and in particular Mh, microwave transmission behavior of the samples is improved; thus the sample with a higher density is more suitable for transmission applications. It was reported that the structure and morphology of the samples have complex influences on the microwave properties [19]. Consequently, the sample with x = 0.8 can be used in the range of 8–12 GHz as the best-fitted material with optimal S21.

4. Conclusion

The Co-substituted Mg-ferrites with various contents of Co were successfully synthesized by a standard ceramic technique. Structural, magnetic and microwave transmission properties were investigated as a function of Co content. The XRD analysis showed that a desired single-phase spinel was formed by increasing Co content up to x = 0.8. The maximum value of density (4.94 g/cm³) was obtained for x = 0.8. Particle size distribution, investigated by SEM, revealed that the average particle size increases by increasing Co content to x = 0.2, remains almost unchanged by increasing x up to 0.8, and then increases remarkably at x = 1.0. The coercivity increases to 113 Oe at x = 1.0, whereas saturation magnetization attains a maximum value of ~45.40 emu/g at x = 0.8. Sample with x = 0.8 exhibits the optimal value of transmission loss at X-band frequency. It is observed that cation distribution, morphology, microstructure, density, etc. are important parameters to affect the magnetic and transmission properties.

Therefore, there is a critical value of Co (x = 0.8) substitution in Mg ferrite that enhances the saturation magnetization and microwave transmission.

References

17–21.


