Improvement of the Magnetic Properties of Mn-Ni-Zn Ferrite by the Non-magnetic Al\textsuperscript{3+}-Ion Substitution

A.A. Sattar, H.M. El-Sayed, K.M. El-Shokrofy and M.M. El-Tabey

\textsuperscript{1}Department of Physics, Faculty of Science, Ain Shams University, 11566 Abbasia, Cairo, Egypt
\textsuperscript{2}Department of Physics and Mathematical Engineering, Faculty of Engineering, Menoufia University, Shebin El-Kom, Egypt

Abstract: The effect of Al-substitution on the physical, IR spectra and magnetic properties of Mn\textsubscript{1-x}Ni\textsubscript{x}Zn\textsubscript{y}Al\textsubscript{2-x}Fe\textsubscript{3+2x}O\textsubscript{4} (x=0 to x=0.15, with step= 0.025) ferrites, prepared by conventional ceramic method, has been studied. The analysis of IR spectrum indicated the distribution of Al-ions between both A and B-sites. On Al substitution, the values of saturation magnetization, initial permeability and Curie temperature were increased. The dc resistivity is also increased with increasing Al-content. Such results are promising ones for the high frequency applications.

Key words: Ferrites, IR-spectra, magnetic properties, Mn-Ni-Zn ferrites, Al\textsuperscript{3+}-substituted ferrites

INTRODUCTION

From the applications point of view, both Mn-Zn and Ni-Zn ferrites represent the most important types where they are used in many ferrite devices such as inductor cores, converters, magnetic heads, electromagnetic wave absorbers etc. Mn-Zn ferrites possess high initial permeability and magnetization but these ferrites are not suitable for magnetic applications at high frequency due to their high electrical conductivity and therefore high power losses. Ni-Zn ferrites, on the other hand, have high resistivity, low-dielectric loss and high Curie temperature but they have relatively low initial permeability at high frequencies. Recently many authors studied the combination of these two ferrites in order to obtain favorable magnetic properties with low losses especially at high frequencies. The microstructure, the magnetic properties and the dc resistivity of Mn\textsubscript{1-x}Ni\textsubscript{x}Zn\textsubscript{y}Fe\textsubscript{3+2y}O\textsubscript{4} ferrites, prepared by citrate precursor method, has been investigated\textsuperscript{[1]}\textsuperscript{[2]}. Unfortunately, the resistivity decreased with increasing Mn-content. The effect of sintering and microstructure on the initial permeability for Mn\textsubscript{10-x}Ni\textsubscript{x}Zn\textsubscript{y}Fe\textsubscript{10+2y}O\textsubscript{4} and Mn\textsubscript{12-x}Ni\textsubscript{x}Zn\textsubscript{y}Fe\textsubscript{3+2y}O\textsubscript{4} were studied\textsuperscript{[3]}\textsuperscript{[4]}. It was found that, the sintering temperature has a great effect on the structural and magnetic properties of these ferrites. Finally, the Mn-substitution effect on the conductivity, magnetic properties and dielectric behavior of Ni-Zn ferrites was carried out\textsuperscript{[5]}. It was found that, there was an enhancement in the saturation magnetization. However, the initial permeability, Curie temperature and dc resistivity were decreased with increasing Mn-content. In the present study, the effect of Al-substitution on the physical, IR spectra, the magnetic properties and electrical resistivity of Mn\textsubscript{1-x}Ni\textsubscript{x}Zn\textsubscript{y}Al\textsubscript{2-x}Fe\textsubscript{3+2y}O\textsubscript{4} ferrites will be studied.

MATERIALS AND METHODS

Ferrite samples with chemical formula Mn\textsubscript{12-x}Ni\textsubscript{x}Zn\textsubscript{y}Al\textsubscript{2-x}Fe\textsubscript{3+2x}O\textsubscript{4} (x=0 to x=0.15, with step 0.025) were prepared by conventional ceramic method. High purity oxides, 99.95\%, of NiO, ZnO, Al\textsubscript{2}O\textsubscript{3}, and Fe\textsubscript{2}O\textsubscript{3}, with MnCO\textsubscript{4} were mixed together according to their molecular weights. The mixture of each composition was ground to a very fine powder and presintered at 900\textdegree\textsuperscript{C} for 15 h. The presintered mixture was ground again and pressed at room temperature under a pressure of 3.8\times10\textsuperscript{6} Pa into tablet and toroidal forms. They were finally sintered at 1300\textdegree\textsuperscript{C} for 4 h in two cycles and then slowly cooled in N\textsubscript{2} atmosphere to room temperature at a rate of 1\textdegree\textsuperscript{C}/min.

X-ray diffraction patterns were performed using a diffractometer of type X'Pert Graphics and identify with Cu K\textalpha radiation. The theoretical X-ray density (d\textsubscript{0}) of the samples was calculated using the formula (d\textsubscript{0}=8M/NaN\textsuperscript{2}) where, M is the molecular weight, N is Avogadro's number and a is the lattice parameter. The density d of each composition was measured in toluene using Archimedes principle. The porosity percentage P(\%) was calculated according to the relation P=100 [1-(d/d\textsubscript{0})] %. The FTIR spectra were carried out (using Perkin Elmer

Corresponding Author: A.A. Sattar, Department of Physics, Faculty of Science, Ain Shams University, 11566 Abbasia, Cairo, Egypt E-mail: Adel_Sattar@hotmail.com
spectro-photometer) in the range from 200-600 cm\(^{-1}\). The grain size was obtained by scanning electron microscope (SEM) type (JEOL JSM5600). The magnetization (M\(_{s}\)) was measured using the vibrating sample technique. The magnetizing field ranges from 0.0 up to 1 Tesla. Toroidal shaped samples of inner diameter = 0.75 cm, outer diameter = 1.55 cm and average thickness \(\sim 0.3\) cm were used as transformer cores for measuring the initial permeability. The initial permeability \(\mu\) was measured as a function of temperature at a constant frequency \(f = 10\) KHz of a sinusoidal wave. The magnetizing current in the primary coil \(I_p\) is kept constant at 4 mA. The value of \(\mu\) was calculated using Polymirnov’s formula\(^{[3]}\). According to this formula we have, \(V_p = K \mu I_p\), where, \(V_p\) is the induced voltage in the secondary coil and \(K = 0.4I_pN_pN_A/\omega L\) where, \(N_p\) and \(N_s\) are the number of turns of primary and secondary coils, respectively. (\(N_p = N_s = 15\) turn), \(A\) is the cross-section area of the sample, \(\omega\) is the angular frequency and \(L\) is the average path of the magnetic flux.

**RESULTS AND DISCUSSION**

**Physical properties**

**X-ray analysis:** The formation of single phase of M\(_n\)Fe\(_{2}\) ferrites is confirmed from the XRD patterns of the investigated samples. The values of lattice parameters are determined using Bragg’s law and are plotted as a function of Al-ion concentration in Fig. 1. It is clear that as the Al-concentration increases, the lattice parameter decreases. Similar behavior was observed in Al-substituted both Mn-Zn\(^{[8]}\) and Ni-Zn ferrites\(^{[11]}\). The decrease in lattice parameter with Al-concentration could be easily explained on the basis of the ionic radii where the radius of Al-ion (\(\sim 0.51\) Å) is smaller than that of the iron ion (\(\sim 0.67\) Å).

![Graph showing variation of lattice parameter and porosity with Al-concentration](image)

**Fig. 1:** The variation of the lattice parameter \(a\) (Å) and porosity \(P(\%)\) with Al-Concentration(x)

For the spinel structure, the theoretical lattice parameters \(a_0\) could be calculated using the following equation\(^{[12]}\):

\[
a_0 = \frac{8}{3\sqrt{3}} \sqrt{3}(r_i + r_o)
\]

where, \(r_i\) is the radius of the oxygen ion (1.32 Å), \(r_i\) and \(r_o\) are the ionic radii of tetrahedral (A-site) and octahedral (B-site) sites, respectively. To calculate \(r_i\) and \(r_o\), the following cation distribution is assumed:

\[
\text{Mn}_{1.8}^{2+} \text{Zn}_{0.2}^{2+} \text{Fe}_{0.2}^{3+} \text{Mn}_{0.4}^{2+}\]

\[
\text{Mn}_{1.8}^{2+} \text{Ni}_{0.1}^{2+} \text{Ni}_{0.1}^{2+} \text{Fe}_{1.8}^{3+} \text{Fe}_{0.2}^{3+}\] \(\text{O}_4\)

This cation distribution is based on the following:

1. For the unsubstituted sample, 80% of Mn-ions occupy the tetrahedral position (A-site) and the remaining, 20%, occupy the octahedral position (B-site)\(^{[10]}\). For substituted samples, this ratio is slightly changed due to Al-substitution.
2. Zn ions prefer to occupy the tetrahedral sites while Ni ions occupy the octahedral sites.
3. Concerning Al\(^{3+}\)-ion distribution, there are two points of views. The first one is that the Al\(^{3+}\)-ions in spinel ferrites are distributed on both tetrahedral and octahedral sites, such that, the majority of Al-ions occupy the octahedral position\(^{[16-20]}\). The other one is that the Al\(^{3+}\)-ions occupy completely B-sites\(^{[11,21-22]}\). IR spectroscopic analysis, as it will be discussed later, shows that Al ions are distributed on both A and B-sites.

In this cation distribution, the formation of Fe\(^{3+}\)-ion during the sintering process is taken into consideration. The ionic radius for each site is calculated according to the following equations:

\[ A = (1.1r_{Al}) + 0.4r_{Zn} + 0.2r_{Fe} + 0.4 (1-t) r_{Mn}\]

\[ B = \frac{1}{2} (x-t) r_{Al} + (0.4 + t) r_{Mn} + (0.4 - x - y) r_{Fe} + y r_{Zn}\]

where, \(r_{Al}\), \(r_{Zn}\), \(r_{Fe}\), \(r_{Mn}\), and \(r_{Ni}\), are the ionic radii of aluminum, zinc, manganese, trivalent iron ion, nickel and divalent iron ion, respectively. The values of the ionic shows that the ionic radius depends on the coordination number\(^{[26]}\). The values of \(t\) and \(y\) in the assumed cation distribution, were chosen as fitting parameters such that good fitting between \(a_{01}\) and \(a_{exp}\) is obtained (Table 1).

**Porosity and grain size:** Figure 1 also shows that, as Al-content increases the porosity \(P(\%)\) increases. It is
known that, the porosity of ceramic samples results from two sources, intragranular porosity ($P_{\text{in}}$) and intergranular porosity ($P_{\text{inter}}$). Thus the total porosity $P(\%)$ could be written as the sum of the two types i.e.,

$$P(\%) = (P_{\text{in}} + P_{\text{inter}})$$  \hspace{1cm} (3)

Furthermore, it was reported that the intergranular porosity ($P_{\text{inter}}$) depends on the grain size\textsuperscript{[20,22]}. By studying the scanning electron microscope (SEM) for the samples, it is found that as the Al-concentration increases from $x=0.05$ up to $x=0.15$ there is no considerable change in the grain size. Therefore as Al-content increases the intergranular porosity ($P_{\text{inter}}$) remains almost constant. Thus according to equation (3), the increase of the total porosity $P(\%)$ results mainly from the increase of intragranular porosity ($P_{\text{in}}$) with Al-concentration. Such a conclusion is in agreement with that previously reported in case of Al-substituted of Zn and Cu-Cd ferrites\textsuperscript{[16,21]}.

**IR-spectral analysis:** The study of far-infrared spectrum is an important tool to get information about the positions of the ions in the crystal through the crystal's vibrational modes\textsuperscript{[24]}. It is known that the normal and inverse cubic spinels have four IR bands representing the four fundamentals $v_1$, $v_2$, $v_3$, and $v_4$\textsuperscript{[17]} It has been reported that, the first three IR fundamental bands are due to tetrahedral and octahedral complexes, while the fourth one is due to the lattice vibrations\textsuperscript{[26]}. Figure 2 shows the IR spectra of some studied samples ($x = 0.0, 0.05, 0.1$ and $0.15$). The positions of their bands are given in Table 2. The high frequency bands $v_1$ ($547$-$561$) and $v_2$ ($378$-$409$) are attributed to the vibration of iron ions in both tetrahedral and octahedral positions, respectively. The third vibrational frequency band $v_3$ ($310$-$344$) is associated with the divalent octahedral metal ions and oxygen complexes. Finally, the fourth vibrational band ($v_4$) ($220$-$288$) is attributed to the lattice vibrational frequency\textsuperscript{[23]}.

It is obvious from the Table 2 that as Al-concentration ($x$) increases $v_1$ shifts to higher frequency while $v_3$ shifts to lower frequency. These shifts in the frequencies of the bands could be explained on the basis that the change in the bond length has an inverse relation with the band frequency shift\textsuperscript{[9]}. Figure 3 shows the variation of the radii of tetrahedral site ($r_a$) and octahedral site ($r_b$) with Al-content. It is clear that as Al-concentration increases, $r_a$ decreases while $r_b$ increases, which explain the increase of $v_1$ and the decrease of $v_2$ and $v_3$. The shift of the lattice vibration band $v_4$ to the higher frequency could be attributed to the difference in masses between the substituted and displaced ions. In this composition, Fe$^{3+}$-ions are replaced

| Table 1: The values of $x$ and $y$ with Al-concentration |
|-----------------|-----------------|-----------------|
| Al-Conc. ($x$) | $y$ | Fe$^{3+}$-Conc. ($y$) |
| 0.000 | 0.000 | 0.180 |
| 0.025 | 0.012 | 0.170 |
| 0.050 | 0.020 | 0.162 |
| 0.075 | 0.024 | 0.155 |
| 0.100 | 0.030 | 0.146 |
| 0.125 | 0.037 | 0.126 |
| 0.150 | 0.040 | 0.114 |

| Table 2: Frequency (cm$^{-1}$) of the IR observed bands |
|-----------------|-----------------|-----------------|
| Al-Conc. | Tetra. | Octahedral bands | Lattice |
| $v_1$ | $v_2$ | $v_3$ | $v_4$ | $v_5$ | $v_6$ | $v_7$ |
| 0.00 | 547 | 409 | 344 | 324 | 272 | 240 | 222 |
| 0.05 | 553 | 398 | 346 | 319 | 277 | 249 | 221 |
| 0.10 | 559 | 397 | 343 | 307 | 278 | 248 | 220 |
| 0.15 | 561 | 378 | 344 | 310 | 288 | 240 | 222 |

Fig. 2: IR-spectrum of samples with $x=0.0, 0.05, 0.10$ and $0.15$

Fig. 3: Variation of tetrahedral ($r_a$) and octahedral ($r_b$) radii with Al-content

164
by Al\textsuperscript{3+}-ions which have smaller mass than that of Fe\textsuperscript{3+}. Thus, the total mass of lattice decreases leading to an increase of the frequency band $\nu_c$.

**Magnetic properties**

**Magnetization and coercive field:** The variation of magnetization $M$ (emu g$^{-1}$) with the static applied magnetic field $H$ (up to 1 Tesla) for all investigated samples at room temperature is shown in Fig. 4. As a normal behavior, the magnetization increases with increasing the applied magnetic field and attains its saturation value for fields higher than 0.6 Tesla. The dependence of saturation magnetization $M_s$ determined by extrapolation of the magnetization curve to $H=0$, on the Al-concentration ($x$) is shown in Fig. 5. It is clear that, as the Al-ion concentration increases $M_s$ increases rapidly to have a maximum value at $x=0.05$ and then it decreases with increasing the Al-concentration. This behavior could be explained according to the above assumed cation distribution. It is known that, for Mn-Zn and Ni-Zn ferrites there is a canting angle, Yafet-Kittel angle ($\alpha_{ck}$), between the moments in B-site at Zn-concentration $\approx 0.4$. Such a canting is due to the negative B-B interaction$^{[28,30]}$. Thus the total magnetization $M$ could be expressed as$^{[21]}$

$$M = M_A \cos \alpha_{ck} M_A$$  \hspace{1cm} (4)

where, $M_A$ and $M_B$ are the magnetic moments of A and B-sites, respectively. Using the assumed cation distribution and taking the values of the magnetic moments of Fe\textsuperscript{3+}, Fe\textsuperscript{2+}, Zn\textsuperscript{2+}, Ni\textsuperscript{2+}, Al\textsuperscript{3+} and Mn\textsuperscript{2+} as 5, 4, 0, 2,

**Fig. 4:** The magnetization $M$ (emu g$^{-1}$) versus the applied magnetic field $H$ (T)

**Fig. 5:** The variation of saturation magnetization $M_s$ (emu g$^{-1}$) and coercive Field $H_c$ (A m$^{-1}$) with Al-concentration

0 and 5 $\mu_B$, respectively, the total magnetic moment is written as;

$$M = \mu_0 (9.8 - 5x + 5t - y) \cos \alpha_{ck} + (5t - 3) \mu_0$$ \hspace{1cm} (5)

In view of equation (5) and according to the values of $x$ and $t$, in Table 1, the increase of $M$ with $x$ up to $x=0.05$ can be attributed to the increase of $\cos \alpha_{ck}$, i.e., a decrease of $\alpha_{ck}$. For $x>0.05$, i.e., further replacement of Fe\textsuperscript{3+} ions by non magnetic Al\textsuperscript{3+} ions in B-sites, leads to a decrease of the magnetization of the B-sites and hence the total magnetization should decrease as we found experimentally. In other words, after improving the parallelism at $x=0.05$, further replacement of Fe\textsuperscript{3+} ions by
non-magnetic Al$^{3+}$ ions in B-site leads to decrease the value of $M_s$ and hence the total magnetization $M$ should decrease.

The percentage increase in saturation magnetization ($\Delta M_s, %$) of the Al-substituted samples is listed in Table 3.

It is clear that, for Al-concentration $x=0.05$, the percentage increase of $M_s$ at room temperature, reaches to about 17% greater than that of un-substituted one which is an important result from the technological point of view.

Figure 5 shows the change of the coercive filed ($H_c$) with Al-concentration ($x$) at a magnetizing field $H=300$ A m$^{-1}$. It is obvious that $H_c$ decreases with increasing Al-content. This behavior could be explained through Brown's relation$^{[21]}$ which is given by:

$$H_c \geq \frac{2K_1}{\mu_0 M_s}$$  

(6)

where, $K_1$ is the anisotropy constant. It is known that the anisotropy field in ferrites results mainly from the presence of Fe$^{3+}$ ions$^{[20]}$. According to the above results, for $x=0.05$, $K_1$ decreases (the concentration of Fe$^{3+}$ions decreases) while $M_s$ increases. Thus the two factors enhance the decrease of $H_c$. For $x>0.05$, both $K_1$ and $M_s$ decrease with increasing Al concentration. Thus the decrease of $H_c$ for high Al concentration indicates that $K_1$ is the dominant factor. The decrease of $K_1$ due to Al-substitution in different ferrites was previously reported$^{[20,21]}$.

<table>
<thead>
<tr>
<th>Al-conc. ($x$)</th>
<th>$M_s$ (emu g$^{-1}$)</th>
<th>$\Delta M_s$ (%)</th>
<th>$\mu_s$</th>
<th>$\Delta \mu_s$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>21.03</td>
<td>---</td>
<td>223.5</td>
<td>---</td>
</tr>
<tr>
<td>0.025</td>
<td>23.71</td>
<td>12.77</td>
<td>331.6</td>
<td>48.5</td>
</tr>
<tr>
<td>0.050</td>
<td>24.68</td>
<td>17.34</td>
<td>367.9</td>
<td>64.7</td>
</tr>
<tr>
<td>0.075</td>
<td>23.31</td>
<td>10.84</td>
<td>288.5</td>
<td>29.2</td>
</tr>
<tr>
<td>0.100</td>
<td>21.99</td>
<td>4.578</td>
<td>287.8</td>
<td>28.9</td>
</tr>
<tr>
<td>0.125</td>
<td>21.76</td>
<td>3.493</td>
<td>296.2</td>
<td>32.6</td>
</tr>
<tr>
<td>0.150</td>
<td>21.33</td>
<td>1.419</td>
<td>296.6</td>
<td>32.8</td>
</tr>
</tbody>
</table>

**Initial permeability and Curie temperature:** Figure 6 shows the variation of the initial permeability $\mu_s$ with temperature $T(K)$ for all samples. It is found that the curves are typical of multidomain grains showing a sudden drop in $\mu_s$ at $T_c$. The Curie temperature $T_c$ is determined by drawing a tangent for the curve at the rapid increase of $\mu_s$. The intersection of the tangent with the $T$-axis determines $T_c$. The dependence of both initial permeability $\mu_s$ at room temperature and $T_c$ on the Al-concentration are shown in Fig. 7. It is obvious that, $\mu_s$ follows the same behavior as that of $M_s$ where a maximum is noticed at $x=0.05$. The similarity in behavior of $\mu_s$ and $M_s$ with Al-concentration $x$ arises directly from the approximate equation for the initial permeability$^{[20]}$.

$$\mu_s = (M_s^2 D / \sqrt{K_f})$$  

(7)

where, D is the average grain diameter. The percentage increase of the initial permeability $\Delta \mu_s(\%)$ for the Al-substituted samples are reported in Table 3. The values of $(\Delta \mu_s(\%))$ are in the range (29-64%). It is also

![Fig. 6: The temperature dependence of the initial permeability $\mu_s$ for different Al concentration](image-url)
Fig. 7: The variation of the initial permeability $\mu_i$, (at room temperature) and Curie temperature $T_C$ (K) with the Al-concentration

2. The increase of the intragranular porosity which in turn hinders the motion of charge carriers.

CONCLUSION

- The lattice parameter decreases while the porosity increases with Al-ion substitution in Mn-Ni-Zn ferrites.
- The IR-analysis supports the distribution of Al-ions in both A and B sites.
- Al-ion substitution improves both the saturation magnetization and initial permeability.
- Curie temperatures and the dc resistivity of Mn-Ni-Zn ferrites are increased for all substituted samples. These results are promising in high frequency applications.

REFERENCES


