Effect of Mn-substitution on the structure Co$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$

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Abstract: One Ferrite is a ferromagnetic substance where it is ideally used to manufacture devices such as rectifiers, memory devices, and inductors hearts as well as for various applications of microwave waves. The electrical and structural characterization of ferrites depends on preparation methods, nature of dopant, and dopant concentration. For these reasons, the series samples of Co$_{0.6}$Zn$_{0.4}$MnxFe$_{2-x}$O$_4$ ferrites prepared, using a traditional ceramic process, Mn-Zn ferrites were synthesized and sintered up to 1200 °C for 5 hours. We tested the X Ray diffraction (XRD) for different Mn-substitution (where $x = 0, 0.2,$ and 0.4). XRD studies confirmed that the sample’s structural have a cubic spinel phase. The electrical characterization (such as conductivity, real and imaginary dielectric constant) was measured and discussed, as well.

Keywords: Ferrite, ferromagnetic substance, Co-Zn ferrites, soft magnetic

1. Introduction
Since the discovery of ferrites materials, they have gained much research attention. It has been focused on the intense fundamental and applied research to enhance the physical properties of ferrite. Ferrite materials are extensively used in electronic devices such as memory storing apparatus, sensors, electromagnetic wave absorbers, and actuators. The most significant of these ferrites are soft magnetic like those dependent on oxides [1]. Mn-Zn ferrite is widely used in applications with high frequencies up to 10 MHz [2-4]. Mn-Zn ferrites are also commonly utilized in electronics because of high magnetic density, low core loss, dielectric resistivity, and magnetic permeability [5, 6]. Such ferrites are possible to be synthesized by co-precipitation, hydrothermal methods, sol.-gel techniques, ball milling of high-energy, micro emulsion technique, and traditional methods ceramic technique [7-13]. Ferrite’s magnetic properties of Mn-Zn based on temperature dependence have been studied by several researchers [14], and a function of grain size [15]. The Mn ferrite magnetic moment (MnFe2O4) has much lower resistivity compared to CoFe2O4 and NiFe2O4 [16]. The structural, electrical, and magnetic characterization of ferrites depends on both the preparation method and the dopant concentration. Thus, the sequence samples were prepared using Mn substituted in Co-Zn ferrites (Co0.6Zn0.4MnxFe2−xO4). Therefore, this work focuses on the influence of substitution of Fe$^{3+}$ ions by the Mn$^{3+}$ ions in Co Zn ferrites. The effect of changing Mn substituted will be investigated by characterizing the structure and electrical of the samples. Thus, this work focuses on the structural and electrical properties, to find that the best value of Mn- substitutions for the Co-Zn ferrites.

2. Materials and Preparation Method
In this work, magnetic Co$_{0.6}$Zn$_{0.4}$MnxFe$_2$−xO$_4$ ferrites (where $x = 0, 0.2,$ and 0.4) synthesized using a conventional ceramic method of the double sintering. The used raw material was ferric oxide (Fe$_2$O$_3$), cobalt oxide (CoO), zinc oxide (ZnO). It used as a substitution material which is manganese dioxide (MnO$_2$). To allow homogenous mixing, stoichiometric quantities of raw materials have been blended in a soggy medium. To shape homogeneous slurry, ethanol has been added. Then the samples powders were grinded through hand-mill for hours. The grinded samples were calcined for 4 hours in a furnace at 900 °C and then cooled down gradually to room temperature. The powder was once again balled milled for hours. To investigate the electrical measurements, the samples were pressed into a
tablet shape under a 3-ton pressure after that the samples were sintered up to 1200 °C for 5 hours. The samples were sintered two times at the same used parameters.

3. The Results and Discussion

3.1. XRD characterization

The XRD study of Co0.6 Zn0.4 Mn_x Fe_{2-x}O_4 (x=0, 0.2, 0.4) revealed a single-phase pattern which gives an indication that ferrite with a cubic spinel structure. Gorter [17] has worked extensively with the spinel system. The measured XRD of the different samples is given in Figures 1 and 2. It is shown that all XRD peaks in Fig. 1 (a, b) and Fig. 2 (a) have at (220), (311), (222), (400), (422), (511), and (400) crystal planes. The XRD intensity peaks vary as structural changes. These changes often depend on the position, form, and quantity of the atom in the cell. Furthermore, the grain size and temperature affect the variations in peak intensity. At 2θ = 18.6 appears a weak intensity peak which is a characteristic peak of (111) plane (see, Fig.1 (b)). Furthermore, Fig. 2 (a), shows the XRD pattern of x-substitution =0.4 which displays a strong peak at 2θ = 18.6 that belongs to MnFe2O4. As well as this peak of MnFe2O4 at 2θ = 18.6 is not observable in Fig.1 (a). It can be suggested that due to the existence of Mn-substitution comparison with Fig. 1 (a), and Fig. 2 (a).

![Figure 1. The reaction synthesis of MTH.](image-url)
Debye Scherrer equation is \( D = \frac{0.9 \times \lambda}{\beta \times \cos \theta} \) was used to calculate the grain size. Crystallite average size can be estimated from the (311) peak of diffraction, which shows the maximum strength in all samples. Thus, X-ray wavelength \( \lambda = 1.5406 \, \text{oA} \) used and the Bragg’s angle \( \theta \). The full width at half maximum \( \beta \) values extracted from XRD results, which calculated in radians. The calculated grain size has been found for all samples in range between \((0.697 \, \text{1} \) micron). The cubic samples lattice parameter \( a \) was determined from an equation of d-spacing \( (dhkl) \). Corresponding to the highest intensity peak (311), by the following relation: 

\[
a = \frac{d_{hkl}(h^2 + k^2 + l^2)^{1/2}}{2}
\]

where: \( h, k, \) and \( l \) represent the miller indices of the crystal planes.

3.2 Dielectric measurements

The dielectric constant \( \varepsilon \) is dependent on variation in the frequency. Of all the samples at room temperature, the real and imaginary dielectric constant was measured using LCR meter. Figure 2 (b), 3 (a, b), and 4 (a) indicate the frequency dependence of the dielectric constant. The value of \( \varepsilon \) continuously decreased with rising frequency up to 1 MHz.
Figure 4. a) The real dielectric measurement vs. frequency of Co0.6 Zn0.4 Mnx Fe2-xO4: (a) Mn substitution = 0 and (b) Mn substitution = 0.2.

It is evident from Fig.(4) to Fig.(6), that the dielectric constant changes with the frequency based on the used current and different Mn-substitution. As the real dielectric constant falls very sharply at low frequencies below 0.5 MHz, after which the decrease is gradually with increasing frequency. It can be seen that the dielectric constant values in Fig. 3 (b) and Fig. 5 (a) that the decreasing curve behaviour of the dielectric constant is little bit different. The sample frequency dependence (Co – Zn ferrites) was similar to the usual dielectric behaviour defined by Ravinder [18]. This reduction occurs because of the electronic interaction between Fe2+ and Fe3+ ions that cannot obey the alternating field above a certain frequency of the externally applied electric field. This behaviour is in clear accordance with the results in [19].

Figure 5. (a) The real dielectric constant vs. frequency of Co0.6 Zn0.4 Mnx Fe2-xO4 (where Mn substitution = 0.4). (b) The a.c conductivity vs. frequency of Co0.6 Zn0.4Fe2-xO4 (where Mn substitution = 0).

Based on [20, 21], the ferrite conduction mechanism were closely associated with their dielectric behaviour. For this reason, we present the a.c conductivity with frequency in the dielectric loss is shown in Fig. 5 (b) and Fig. 6.

3.2. Measurements of the A.C. conductivity
In all samples (Fig. 5 (b) and Fig. 6), conductivity increased sequently during the frequency applied increases, resulting in maximum conductivity at Mn-substitution equals 0.4. Thus, the conductivity in response to the frequency showed an interesting characteristic. The theory of Koops, Maxwell [22-23] clarified that the AC conductivity increases with that frequency and this pattern is in line with the experimental findings in this research. The resistivity in the samples was calculated. Therefore, Ferrites have a high resistivity in order of 106 Ω.cm. To transformer core applications of up to a few MHz frequencies, this makes it very useful.
Figure 6. (a) The A.C conductivity measurements of Co_{0.6}Zn_{0.4}Mn_xFe_{2-x}O_4: (a) Mn-substitution = 0.2. (b) Mn-substitution = 0.4

4. Conclusion

In summary, a series of Mn-substitution Co-Zn ferrites system Co_{0.6}Zn_{0.4}Mn_xFe_{2-x}O_4 where x=0.0, 0.2, 0.4 synthesized by ceramic technique and sintered up to 1200 oC for 5 h. We examined the Mn-content influence on the structural parameters. The measurements of electrical properties were studied for all samples. The dielectric constant was calculated in its real (ε) and imaginary (ε') parts using LCR meter. The dielectric constant decreased by two parts, real and imaginary, with increasing frequency. The A.C conductivity was measured for all samples at room temperature. The work is in progress to find the optimal Mn-substitution values.

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