Study on The Influence of Crystal Structure and Grain Size on Dielectric Properties of Manganese Ferrite (MnFe$_2$O$_4$) Nanoparticles

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Abstract. Manganese ferrite (MnFe$_2$O$_4$) has been successfully synthesized by using co-precipitation methods with a various particles size of 13.1, 13.8, 16.2, 18.1, and 18.4 nm. Analysis of crystal structure properties which has been carried out by using XRD (X-Ray Diffraction) method revealed that all samples belong to cubic spinel structure. The measurement used computerized impedance spectroscopy system in the frequency range of 10-120 Hz. The real dielectric constant ($\varepsilon'$), imaginary dielectric constant ($\varepsilon''$), and impedance ($Z$) were determined at room temperature as a function of frequency. The dielectric constant (real and imaginary) and impedance decreased with frequency up to 70 kHz, and then it was constant at a frequency more than 70 kHz. The dielectric properties depending on the crystal structure are also investigated, it consists of the degree of crystallinity, lattice parameter, strain, X-ray density and the impurities of the sample. In the range of grain size of 13.1-18.4 nm, the real ($\varepsilon'$) and imaginary ($\varepsilon''$) dielectric constants, and loss tangent increased with the increase of the grain size. In addition, impedance ($Z$) decreased with increasing grain size. The dielectric constant was found to be the highest for MnFe$_2$O$_4$ with a particle size of 18.1 nm because of low strain value of 0.028 and high X-ray density value of 5.11. Therefore, a sample with the highest dielectric properties is a sample with grain size of 18.1 nm with real dielectric constant of 311; imaginary of 118; and impedance of 328 kΩ at 10 kHz. The frequency variation of ($\varepsilon'$ and $\varepsilon''$) is explained by Knop phenomenological theory and hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ on octahedral sites.

Keywords: MnFe$_2$O$_4$ Nanoparticle, Complex Dielectric Constant, Grain Size, and Crystal structure

1. Introduction

Magnetic nanoparticles such as manganese ferrite possess excellent magnetic and dielectric properties. These spinel ferrite nanoparticles are generally used in magnetic recording media, a microwave device, and magnetic resonance imaging [1]. The major advantages of the ferrite material are that they perform higher efficiency, low cost, and appropriate dielectric loss and hence meet potential applications in microwave device and memory cores [2]. The dielectric properties of the spinel ferrites are generally affected by factors of preparation method, cation distributions, grain size, etc. [3]. Rani [4] studied the dielectric properties of spinel ferrite and reported that the value of dielectric constant increases with increasing particle size. These phenomena may be due to the fact that when the particle size increases, the number of polarizable ferrous ions on the octahedral site increases. Rezlescu and Rezlescu [5] explain the composition dependence of the dielectric constant with the assumption that...
the mechanism of dielectric polarization is similar to that of the conduction. They have observed that the electron exchange between Fe$^{2+}$ and Fe$^{3+}$ which results in local displacement of electrons in the direction of the electric field determines polarization. Narayanasamy [6] reports that the number of Fe ions at the B sites decreases with the grain size reduction. This phenomenon results in a reduction of the number of Fe$^{2+}$↔Fe$^{3+}$ pairs at B sites and therefore the polarization also decreases with the reduction in grain size. However, the dielectric properties of nanocrystalline manganese ferrites have not yet been investigated in detail.

In this paper, the influence of crystal structure and grain size on dielectric properties of manganese ferrite nanoparticles that were prepared through co-precipitation method is investigated. The permittivity and impedance with various frequencies at room temperature of dielectrics are analyzed.

2. Experimental Method

Manganese ferrite has been synthesized by using co-precipitation method with FeCl$_3$·6H$_2$O (Merck, Germany) and MnSO$_4$·H$_2$O (Merck, Germany). The synthesis was started by putting 3.37 mL of HCl (37%) into 0.84 gram of MnSO$_4$·H$_2$O and 2.703 gram of FeCl$_3$·6H$_2$O which were dissolved into 20 mL of distilled water and mixed until homogeneous. The solution was dropped to NaOH and stirred with 770 rpm velocity at a certain temperature. Furthermore, the solution was precipitated by external field (permanent magnet). The precipitation was washed in seven times by using distilled water to obtain a pure MnFe$_2$O$_4$. Samples were dried in a furnace at 80 °C for four hours. The crystal structure and grain size of samples were analyzed by using X-Ray Diffractometer (XRD) Shimadzu model XD-3H (Cu-Kα =1.5406 Å), and Transmission Electron Microscope (TEM) Jeol Jem-1400. In this study, the synthesis parameter of MnFe$_2$O$_4$ performed with NaOH concentration and time centrifugation is shown in Table 1.

| Sample name | Mass of MnSO$_4$·H$_2$O (g) | Mass of FeCl$_3$·6H$_2$O (g) | Volume of HCl (mL) | NaOH (M) | Stirring time (minutes) | Synthesis temperature (°C) |
|------------|-----------------------------|-----------------------------|--------------------|----------|------------------------|--------------------------|
| N5         | 0.84                        | 2.703                       | 3.37               | 1.5      | 120                    | 80                       |
| N3         | 0.84                        | 2.703                       | 3.37               | 5        | 120                    | 80                       |
| N4         | 0.84                        | 2.703                       | 3.37               | 10       | 120                    | 80                       |
| N2         | 0.84                        | 2.703                       | 3.37               | 10       | 90                     | 80                       |
| N1         | 0.84                        | 2.703                       | 3.37               | 10       | 150                    | 80                       |

Dielectric properties were measured by using computerized impedance spectroscopy on a circuit of AC in the frequency range from 10 to 120 kHz. Powder samples were firstly compacted into pellets of 1.23 cm in diameter at the compressive force of 50,000 N. The dielectric properties measured such as complex dielectric and impedance as a function frequency.

3. Results and Discussion

The XRD spectra of the samples are shown in Figure 1. All of the main peaks are indexed as the spinel of MnFe$_2$O$_4$. The average crystalline size of MnFe$_2$O$_4$ samples was calculated from X-Ray line broadening of reflections of (220), (311), (400), (333), and (440) by using Scherer’s equation. The broadening of the reflection peaks indicates that the samples are composed of small particles [1]. Figure 1 shows a sample of N1 with a small grain size that has broadening of the reflection profile. The broadening of the reflection profiles is not only caused by the small particle or the crystallite size but also due to the lattice strain, instrumental errors, dislocation, impurities, etc. [7].
Figure 1. XRD pattern of MnFe$_2$O$_4$: (a) N1; (b) N2; (c) N3; (d) N4 and (e) N5

Table 2. XRD Analysis of MnFe$_2$O$_4$

| Sample name | Grain size (nm) | Lattice parameter (Å) | X-ray Density (g/cm$^3$) | Strain |
|-------------|-----------------|-----------------------|--------------------------|--------|
| N1          | 13.1            | 8.36                  | 5.26                     | 0.034  |
| N2          | 13.8            | 8.48                  | 5.04                     | 0.035  |
| N3          | 16.2            | 8.44                  | 5.11                     | 0.029  |
| N4          | 18.1            | 8.44                  | 5.11                     | 0.028  |
| N5          | 18.4            | 8.48                  | 5.04                     | 0.025  |

The lattice parameter, strain, X-ray density and particle size of different parameter synthesized are compared in Table 2. the average grain size of the nanoparticle is calculated from the highest peak of X-Ray diffraction of (311) by using Scherer’s equation.

\[ t = \frac{k\lambda}{B \cos \theta}, \]  

(1)

where \( t \) is grain size, \( \lambda \) is the wavelength of the Cu-K\( \alpha \) radiation (\( \lambda = 1.5406\text{Å} \)), \( \theta \) is the Bragg’s diffraction angle, and \( B \) is the full width at half maximum (FWHM) of the peak in the X-ray diffraction pattern [2].

X-Ray density depends on the lattice constant and molecular weight of the sample which is calculated by using the relation [2].

\[ d_x = \frac{8M}{N_\alpha^3} \]  

(2)
where \( M \) is the molecular weight of the ferrite sample, \( N \) is the Avogadro number, \( a \) is lattice constant and 8 represents the number of molecules per unit cell. The strain is considered as a crystal defect from nanoparticles MnFe\(_2\)O\(_4\). The presence of this strain weakens the electrical response of the sample.

![Diffraction pattern and morphology of nanoparticles MnFe\(_2\)O\(_4\)](image)

**Figure 2.** (a) Diffraction pattern and (b) Morphology of nanoparticles MnFe\(_2\)O\(_4\)

Ring diffraction patterns are closely related to XRD analysis as shown in Figure 2(a), which corresponds to the crystal plane (440), (333), (400), (311) and (220). Ring discontinuity indicated the polycrystalline structure of nanoparticles and high value of grain size. Morphology of nanoparticles looks more dispersed and distributed relatively homogeneous as shown in Figure 2(b). The dielectric properties of MnFe\(_2\)O\(_4\) as a function of frequency is shown in Figure 2(b).

![Real Permittivity of MnFe\(_2\)O\(_4\)](image)

**Figure 3.** Real Permittivity of MnFe\(_2\)O\(_4\) (a) N1; (b) N2; (c) N3; (d) N4 and (e) N5
Figures 3 and 4, show that dielectric properties (Real and Imaginary) decrease as a function frequency. The highest value of dielectric constant at a lower frequency can be explained by the Maxwell-Wagner interfacial polarization and Koop’s phenomenological theory [8]. The low-frequency dispersion may be due to the inhomogeneous nature of studied dielectric of which compound has two layers [9, 10]. The first layer is the larger ferrite grains of high conducting elements separated by the second thin layer of relatively weak conducting substance (grain boundary). The grain boundaries and grains are more effective at low and high frequencies respectively. As grain boundaries offer high resistance, the electron gets crowded there and thus produces an enhanced space charge polarization. As a result, the material has larger permittivity in the low-frequency region [7]. It is expected that the dielectric constant may decreases with the increase of the frequency until it reaches a nearly constant because beyond a certain frequency of the electric field. Further, the moment dipole on the material may not follow the alternating field, so it reaches a constant value [11]. The real and imaginary dielectric constants tend to increase as the grain size increases. According to the Iwauchi, for a different structure of large particles contains more ferrous ions than the small particles and becomes more conductive. The influence of crystal structure on dielectric properties can be explained by the structure of ferrite.

Ferrite has spinel structure into a cubic close-packed structure of oxygen ions. The ions occupy two types sites. One of them is called tetrahedral sites of which is surrounded by four oxygen ions in tetrahedral sites. The other sites are known as the octahedral of which the cation is coordinated by six oxygen ions in octahedral site. The exchange of Fe$^{2+}$ and Fe$^{3+}$ ions in spinel structure will result in local displacement that is caused by an electric field, so more and more sites in spinel structure can increase the polarization because of increasing the number of Fe ions. Increasing grain size in ferrite causes increasing the number of ion Fe in site octahedral, this phenomenon results in an increasing the number of Fe$^{2+}$ Fe$^{3+}$ pairs in octahedral sites, and therefore the polarization also increases with the increasing grain size [4]. Rezlescu and Rezlescu have studied the dielectric properties of Cu-Mn and Cu-Ni Ferrites by varying the composition, frequency, and temperature. They explained the composition dependence of the dielectric constant with the assumption that the mechanism of dielectric polarization is similar to the conduction process. They have observed that the electron
exchange between Fe$^{2+}$ and Fe$^{3+}$ which results in local displacement of electrons in the directions of the electric field determines the polarization [5]. Figure 5 shows Cole-Cole plot of MnFe$_2$O$_4$ nanoparticles. The Cole-Cole plot is capable to show the relaxation of material and provide information on the kind of electrical processes occurring within the material such as polarization process [6]. It is also observed that relaxation time increases as a grain size increases.

Impedance as a function frequency obtained by the impedance spectroscopy is shown in Figure 6. The impedance decreases as the frequency increases. The impedance at low frequencies is high because the influence of grain boundaries are not conductive. The effect of grain boundaries reduced is due to the increase of electrical energy applied so that conductive grains are more predominant at high frequency. Figure 6 also shows the impedance increases as a grain size decreases. It may be due to the particle surface that poor conductor becomes thicker than the higher grain size [12].

![Figure 5. Cole-Cole plot of MnFe$_2$O$_4$: (a) N1; (b) N2; (c) N3; (d) N4 and (e) N5](image)

![Figure 6. Impedance as a function of frequency of MnFe$_2$O$_4$ (a) N1; (b) N2; (c) N3; (d) N4 and (e) N5](image)
4. Conclusion
MnFe$_2$O$_4$ nanoparticles were successfully prepared by coprecipitation method. The formation of spinel ferrite has been investigated by X-Ray Diffraction method. It is also obtained that dielectric properties increase as the particle size increases. It may be due to the different structure of large particles containing more ferrous ions than the small particles, and becoming more conductive. In addition, relative permittivity decreases as a function of frequency. It is because above a certain frequency of the external field, the dipole is not able to follow the frequency of alternating current.

5. References
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