Preparation of Nano Crystalline Zinc –Ferrite as Material for Micro Waves Absorption by Sol-Gel Methods

Sabah Ibrahim Abbas*, Hussein Taqi John and Ali Jabbar Fraih
Department of Physics, College of Science, University of Wasit, Alrabie, Wasit, Iraq; sabahibo@yahoo.com, hu-seintg@yahoo.com, alijbbar67@yahoo.com

Abstract

Objective: To prepare zinc ferrites materials and study the sintering effect on the structural and microwaves absorption in the X-band rang. Methods/Statistical Analysis: Zinc Ferrite nanoparticles have been prepared by using the sol-gel methods. The samples were sintered at three temperatures (400°C, 600 °C, 800 °C) for two hours. The spinal phase of zinc ferrite structure and crystallite size was examined by XRD spectrum, pattern show that nanoparticles structure exhibit mixed phase of ZnO and ZnFe₂O₄. Atomic force microscopy (AFM) was used to study the surface topography. AFM images reveal a uniform distribution of semispherical shaped nanostructure with average grain sizes ranging between (70.71 nm -92.03 nm). The microwave absorption in X-band rang was examined with a vector network analyzer (VNA). Findings/ Application: The maximum microwave absorbance at 9 GHz for sample sintering at 800 °C with narrow bandwidth (8.5-9.5 GHz). The minimum the attenuation coefficient is less than -15 dB with absorber thickness (1.2 cm) for all samples.

Keywords: Magnetic Materials, Microwave Absorption, Sol-Gel Method

1. Introduction

Magnetic properties of nanoparticles materials have a broad uses in the various scientific and industrial applications. These applications are represented as ferrofluids; surface functionalized nanoparticles for biological sensing application; magnetic storage media; magnetic targeted drug delivery; magnetic resonance imaging. Microwaves absorbing materials were gained a much attention due to the absorb energy from microwaves and can be used in the stealth technology development of aircraft, television image. Zinc ferrite nanoparticles have extremely important in the gas sensor application. Many methods have been used to prepare magnetic ferrite nanomaterials such as sol-gel methods, co-precipitation, mechanochemical, hydrothermal/solvothermal, spray pyrolysis. Nanostructure of zinc ferrites exhibited interesting physical and chemical properties due to extremely small grain size and large surface area. The sol–gel chemical methods have been used to prepare of different mixed metal oxides, nanomaterials, nanoscale, nanoporous oxides. The sol-gel processes have given numerous advantages such as best mixing of the raw materials and excellent homogeneity, ultrafine and reproducible zinc ferrites with small size distribution. The homogeneous microstructure of zinc ferrite indicating the ability to control the electric magnetic properties and heat treatments temperature which decrease the impurities generated during the preparation and variation in the composition. Absorbing materials are classified into electric –loss materials, magnetic – loss materials and the materials that have both mechanisms. The materials which have both mechanisms represented for ferrite materials that have high relative permittivity \( \varepsilon_r \) and relative permeability \( \mu_r \). The frequency dependencies of the complex relative permittivity and permeability, respectively

\[
(\varepsilon_i' = \varepsilon_i + j \varepsilon_i) \quad \text{and} \quad (\mu_i' = \mu_i + j \mu_i) \]

on the absorbing materials. The

*Author for correspondence
control of the relative permittivity and relative permeability of the materials can get a high attenuation of the microwave at the surface of these material\textsuperscript{12,13}. Absorption of electromagnetic waves within the absorber material must be permeate the absorber surface without reflection in this case the impedance of the material must be equal the impedance of free space, the enter electromagnetic waves into radar absorbing materials, a part of energy will be scattered and other part of energy will be absorbed by absorber material\textsuperscript{14}. In our work, zinc ferrites with excellent magnetic properties were prepared by a sol-gel technique and the microwaves absorption properties of these composites were investigated.

2. Experimental Procedure

\text{ZnFe}_2\text{O}_4 nanoparticles were prepared by sol-gel methods. The mixture consist of three solution, 100 ml (0.2M) of iron nitrate \text{Fe(NO}_3\text{)}_3.9\text{H}_2\text{O} (4.837 g), 100 ml (0.2M) of zinc nitrate \text{Zn(NO}_3\text{)}_2.9\text{H}_2\text{O} (3.787 g), were used as a precursor solution and were gelated by adding 100 ml of citric acid (\text{C}_6\text{H}_8\text{O}_7) solution with concentration (0.2M) of (3.842 g) as ligand molecules, and distilled water as the solvent. The control on PH of the solution was fixed at (7) by using many drops of ammonia and the solution was heated on the hot plate at 60 °C for half hour. The temperature is increased to 80 °C for (9) hour the solution was turned into gel. The gel material dried at temperature 120 °C. The burnt ash was calcined at different temperature (400, 600 and 800)°C for (2) hour to get better crystallization and homogenous cation distribution. The powder are mixed with glycerin as a binder and pressed at (102MPa) by the piston oil to obtain samples as parallelogram with dimensions (2.4× 1.2×1.2)cm to fit the waveguide dimensions. The samples were sintered for (2) hour again at three sintering temperature (400, 600 and 800)°C. Figure 1 shows the steps of synthesis of zinc ferrite powders.

The structure and the average grain size of the spinal zinc ferrites nanoparticles were examined by X-Ray diffractometer (6000-Shimadzu) by using CuKα radiation source with a wavelength, \(\lambda=1.54060\text{Å}\). The Atomic Force Microscopy studies for samples is investigated, the surface morphology of the Zinc ferrite nanoparticles produced is studied using Scanning Probe Microscope (type AA3000), supplied by Angstrom Advanced Inc. The attenuation coefficient, absorbance tests and impedance measurement have been carried out by using the Agilent E8362B vector network analyzer in the X-band range of 8-12 GHz. A network analyzer can measure the two forward travelling waves and two reverse travelling waves\textsuperscript{15}.

Figure 1. Schematic of procedure to prepare iron oxide nanoparticles.

3. Results and Discussion

X-ray diffraction analysis of Zinc ferrite samples prepared by sol–gel at various sintering temperature (400, 600 and 800)°C indicates the polycrystalline (ZnFe\textsubscript{2}O\textsubscript{4}) belongs to the phase of face centered spinel cubic structure as shown in Figure 2. The zinc ferrite structure possess the cubic phase may be referred to the different technique of preparation which may be product different structure defects\textsuperscript{16}. There are characteristic intensity peaks at \(2θ=29.89°, 35.21°, 36.857°, 42.81°, 55.09°, 56.597°, 62.12°, and 73.673°\), can be corresponding to (220), (311), (222), (400), (422), (511), (440) and (533) planes of ZnFe\textsubscript{2}O\textsubscript{4} were indexed by comparing with (JCPDS card No. 65-3111). X-ray diffraction pattern shows that nanoparticles structure exhibit mixed phase of ZnO and ZnFe\textsubscript{2}O\textsubscript{4}. The lower intensities of diffraction peaks at \(2θ=31.791°, 36.283°, and 47.573°\) that correspond of (100), (101) and (102) plans that belongs to the primitive hexagonal structure of zinc oxide that comparing with (JCPDS Card no 36-1451). The lower intensities peaks of zinc oxide indicate that there is a small amount of zinc oxide did not turn from the zinc oxide structure to zinc ferrite structure. In order to obtain pure ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles and have to comprehend the thermal characterizations, the as prepared ZnFe\textsubscript{2}O\textsubscript{4} particles is further calcined at (400, 600 and 800)°C respectively the calcined temperature assigned \(T_C\). The high intensity of major diffraction peak of spinel zinc ferrite at the (311) plane
was depended as a measure of its crystalline degree. It is obvious from patterns that all peaks become sharp and high intensities which mean strengthened crystallization when the calcinations temperature increased. The crystalline of ZnFe₂O₄ is accelerated as the calcined temperature \( T_C \) above 600 °C. The nanocrystallite sizes of sintering powder were calculated from diffraction peak broadening (311) of the ZnFe₂O₄ by using Debye-Scherer formula:\(^{12}\)

\[
D = \frac{k \lambda}{\beta \cos \theta}
\]

Where \( D \) is the average crystallite size, \( K = 0.89 \) is a constant to the shape of the crystal, \( \lambda \) is the wavelength of X-RAY diffraction, \( \theta \) is the Bragg angle, \( \beta \) is the full width at the maximum (FWHM). The sintering temperature increased that caused to incases the crystallite size from (26.6)nm at temperature 400°C to (56.23) nm at temperature (800) °C. Generally the sintering process decreases lattice defects and strain\(^{18}\). The broad of XRD peaks indicate that zinc ferrite particles in the nano-sized scale. The lattice constant of \( a = 8.424 \) nm can be calculate by using the relation\(^{19}\).

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

Where \( a \) is the lattice constant, \( d \) is represent the interplanar spacing, and \( h, k, \) and \( l \) indicate the miller indices. The interplanar spacing can be calculated by using bragg law.

![Figure 2. XRD patterns of Zinc Ferrite nanoparticles at different sintering temperatures.](image)

The Atomic Force Microscopy (AFM) images and topographical analysis of ZnFe₂O₄ with resolution is demonstrated about (0.1 - 1 nm), are described in Figure 3a, b, c. The surface morphology of zinc ferrite powder consists of smaller individual and semispherical particles. All images confirm that the grains are uniformly and homogeneous distributed within scanning area (2060 nm×2060 nm). The zinc ferrite powder roughness average and average grains sizes were listed in Table 1. The table shows that smaller grain size of particles is 70.71 nm at sintering temperature 400°C and the grains size increases with the sintering temperature increases. Higher zinc ferrite average particle sizes and cluster sizes are due to the \( \text{Zn}^{2+} \) ion which increases the combustion reaction temperature causing in an intensified individual particle growth\(^{22}\). The surface area of as burnt powder have a mesoporous character, due to the calcinations, the product nanoparticles showed a clear decrease of the surface areas because sub-micrometer primary particles sized have been agglomerated into larger secondary particles. The effects of the nanoparticle size of Zinc ferrite on the microwave absorbing characteristics and electromagnetic properties. High magnetic permeability in the range of the gigahertz frequency due to the maximum value of saturation magnetization and their low eddy current loss and that may be attributed to the effect of grain size and particle shape. The larger \( \varepsilon'' \) and \( \mu'' \) leads to the larger dielectric loss and magnetic loss characteristic to enhancement the absorption of electromagnetic wave.

The real and imaginary parts \( \varepsilon' \), \( \varepsilon'' \) of the complex relative permittivity rises with reduce of the grain size. This may be explained as one is the improvement of the charge polarization between particles because of extending of the grain surface area; the second is the enhancement of metallic particle in the composite by the decrease the grain size. The higher values of \( \varepsilon'' \) for the smaller of grain size correspond to the larger conductivity. The real and imaginary parts \( \mu' \), \( \mu'' \) respectively of the complex relative permeability increase with reducing the grain size. The results can be referred to the decreasing of eddy current loss and the increase of particle volume fraction with decrease of particle size in the composite. The maximum reflection loss increases with decreasing of the grain size, which is referred to the increase of complex relative permittivity and complex relative permeability\(^{21}\).

**Table 1. The Average Crystallite sizes and Roughness average for ZnFe₂O₄ nanoparticles**

<table>
<thead>
<tr>
<th>The sintering Temperature (C)</th>
<th>Roughness Average (nm)</th>
<th>Average grains sizes from AFM (nm)</th>
<th>The average crystallite sizes from XRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>1.21</td>
<td>70.71</td>
<td>26.6</td>
</tr>
<tr>
<td>600</td>
<td>1.76</td>
<td>77.93</td>
<td>30.13</td>
</tr>
<tr>
<td>800</td>
<td>0.591</td>
<td>92.03</td>
<td>56.23</td>
</tr>
</tbody>
</table>
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Figure 3. AFM of Zinc Ferrite nanoparticles sintering at different temperature (a) at 400°C, (b) at 600°C, (c) at 800°C.

The measured values of reflected scattering parameters (S11) and transmitted parameters (S21) were used to determine the absorbance and attenuation coefficient of the microwave were plotted as a function of frequency in the X-band range (8–12 GHz) with increasing 0.5dB of the three samples are shown in Figure 4 and 5. The absorbance is calculated by using these equations:

\[ dB = 10 \log R \]  

Where \( R \) is the reflection coefficient, the transmission coefficient \( T \) is calculated by using the same equation (3). The attenuation coefficient or reflection loss \( R_\text{L} \), of the incident electromagnetic wave can be calculated by applying the following equation:

\[ \text{Re f. loss} = \text{atten. Coeff.} = 20 \log |R| \]  

\[ R^2 + T^2 + A^2 = 1 \]

Figure 3 shows the ZnFe\(_2\)O\(_4\) nanoparticle exhibit a good microwave absorbance properties with smaller frequency indicates the absorbance dependence on the frequency, and also can be seen that absorbance increases with increase the sintering temperature. The maximum microwave absorbance at 9 GHz for sample sintering at 800°C with narrow band width (8.5–9.5 GHz), and broad
band width (9-11 GHz) for samples 600°C. Dielectric constants are lowering with increasing frequency for samples sintered at temperature (400, 600 and 800)°C. The increase in the complex relative permittivity and complex relative permeability is referred to the change in the lattice constant and the grain size. Permittivity and permeability values enhancement after sintered due to the increase of sintered density\(^2\). The interfacial polarization and intrinsic electric dipole polarization that causes to arise dielectric properties of polycrystalline Zinc ferrite. The heterogeneous structure of ferrites with low conductivity between grains that separated by high resistivity of the grain boundaries that causes to create the interfacial polarization. The polarizations in the ferrites have been referred to the existence of \(Fe^{2+}\) ions which increases the heterogeneous spinel ferrite structure. Since \(Fe^{2+}\) ions that cause the higher value of the dielectric constant\(^2\).

Figure 4. Listed the absorbance curves as a function of frequency for samples at all Temp.

Figure 4 shows the variance of the attenuation coefficient with microwaves frequency in which the attenuation coefficient is less than -15 dB with absorber thickness (1.2 cm) for all samples at 9 GHz with broad band for sample that sintered at 600°C. The attenuation coefficient increases with frequency increasing. The multiple microwave absorption which correspond to the multiple dielectric and magnetic resonances in the X-band (8-12 GHz). These materials exhibit the enhancement of the microwave absorption due to their proper electromagnetic wave matching between the magnetic loss and dielectric loss. The enhancement of microwave absorbing of the spinel ferrites can be interpreted by substitution made the crystallite size smaller and distorted the lattice structure which will induce repetition reflection when the microwave propagating in the ferrite, so it stimulates the absorption of the largest amount energy\(^2\). Microwave magnetic losses create from eddy currents, ferromagnetic resonance and hysteresis. The hysteresis loss is not important in the weak field of electromagnetic wave. The contribution of the domain wall resonance can be canceled. The eddy current loss can be ignored due to related to the electric conductivity and thickness, where ferrites are nonconductive materials. The contribution to microwave absorption resulting from the decreases in coercivity due to substitution and from the nanometric particles, which increases the superficial grain area. For a smaller grain size, the phenomenon of polarization interface and multiple reflections become essential factors for the attenuation\(^2\).

4. Conclusion

\(\text{ZnFe}_2\text{O}_4\) nanoparticles were synthesized by the sol-gel method. The measurement results of X-Ray Diffraction confirmed the formation of spinal phase ferrites and the crystallite size of the samples increases with increasing the sintering temperature. AFM images was confirmed the formation of nanoparticles. Zinc ferrite can be considered as a microwave absorbing materials in higher range frequency 8-12 GHz. “The crystallite size” of \(\text{ZnFe}_2\text{O}_4\) has important effects on magnetic properties and microwave absorbing characteristic.

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6. References


