Synthesis and Study of Calcination Effect of Zinc Ferrite on the Structure and Morphology of Nanoparticles.

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Abstract

Three samples of spinel powdered zinc ferrites were successfully fabricated via microwave-assisted combustion method followed by calcination at temperature of 500°C for three hours. Phase purity and surface morphology that estimated via XRD pattern and field emission-scanning electron microscopy images (FE-SEM) showed that the samples have cubic spinel - structure with average crystallite size is increase from 15.8 nm to 26.53 nm and from (23.03nm to 28.16 nm when glycine-to-nitrate ratio is decreased before and after calcination at 500 oC for three hours. However the calcination results is increase in average crystallite size and average lattice constant. FE-SEM image indicated that the particles Zinc ferrite possesses shape symmetry and uniformity. Fourier transform infrared spectroscopy (FT-IR) were us to study vibration mode in synthesized spinel ferrite. As calcination the absorption band of a specific bonds are shifted to a lower wavenumber.

Key words: Ferrite, calcination, microwave-assisted combustion, nanoparticles.

1.Introduction

The compounds that formed by iron oxides and transition metal oxides in order to obtained as powder or ceramic bodies with ferromagnetic-type properties known as ferrites [1]. Various factors can be influence of structural, magnetic, and optical properties of ferrites of which, size of particle, preparation method, type of dopant ions[2], chemical compositions, as well as sintering temperature[3]. Among various ferrites spinel – structure ferrite with the general formula (MFe$_2$O$_4$) became an interesting categories of technological materials due to their an important properties of which, excellence chemical stability, high saturation magnetization, so them suitable for magnetic, mechanical, and catalytic applications[4]. In spinel-structure metal cations are located between A–site (tetrahedral) and B-site (octahedral) formed through the oxygen ions in a unit cell. This distribution influence on the magnetic properties of MFe$_2$O$_4$, that could be controlled by crystallite size and thermal treatment[5] Zinc ferrite is a soft magnetic spinel structure that possesses high resistivity, excellent magnetic properties, as well as high thermal and chemical stabilities [6] [7]. It is one of the iron based cubic spinel space group S.G. Fd3m, [8] Recently, Zinc ferrite has also received great interest because of the magnetic, adsorption, and
photo-catalysis applications [9]. Spinel structure was synthesized with various methods among these, chemical precipitation method [10] hydrothermal methods [11] conventional heating (CHM) method [12] in here zinc ferrite was synthesized via microwave-combustion routes. Several features of this route among those clean, morphology of particles are in control, short time reactions[13]; cost effectiveness of this route is lower than the other wet chemical routes for synthesis ferrites [14].

2. Experimental Part

2.1 Synthesis of Zinc Ferrite

Nitrate salts of Zinc and Iron as metal sources and fuel where (Zn\(^{2+}/Fe^{3+}\)) is taken as a mass ratio (1:2) respectively were mixed and dissolved via stoichiometric amount of distilled water then it stirred by a magnetic stirrer has a maximum temperature (100°C) model manufactured at China for 20 min. Later stoichiometric amount of fuel (glycine) was added within the mixed via continuous stirring until dark brown colour was formed. The mixture was transferred to a microwave oven with microwave irradiation power 1000 Watt. The solution via fuel in to microwave boiled and subjected to dehydration accompanied by decomposition and starting released gases. If the solution reached the combustion point, it became solid. Finally, filter papers were used to resulting compound filtered. Product powder was washed via ethanol and distilled water for (5) times in order to remove the residual initial materials, dried at (70 °C) for two hours and allowed to cool in the oven itself. Finely mortar was used to ground the result powder for (3min.) in order to obtain fine powders, then this fine powders were calcinates at ( 500 °C) for (3hr). Synthesis steps were shown in Figure 1.

![Figure 1. A schematic representation of microwave-assisted combustion route used for the synthesis of spinel ZnFe\(_2\)O\(_4\) ferrite.](image)

2.2 Characterization Techniques

After preparation of samples, Characterization for the synthesized powdered samples is an essential step in order to understand of synthesis protocol and attest the successfulness of them. In this search techniques that used for the characterization of nanoparticles powder are (X-Ray
Diffraction, XRD), (Field Emission Scanning Electron Microscope, FE-SEM) and (Fourier Transform-Infrared Spectroscopy, FT-IR). The phase composition and crystalline structure of ferrites was studied using Shimadzu diffract meter model XRD 6000 (manufactured at Japan) at university of Baghdad / college of education (Ibn- Al.Haitham), Iraq. Device employs Cu Kα (λ =1.1548 Å). The surface morphology of the samples was recorded with various magnification powers by two devices, (1) FE-SEM device kind TESCAN Mira3- France and (2) FE-SEM device kind FEI Nova Nano SEM 450. The detectors at university of Mashhad, Iran and university of Al–Basrah /college of science, Iraq respectively. (FT-IR) spectrum was recorded on a (Shimadzu-8400S spectrometer) at the range of (4000 cm⁻¹ – 450 cm⁻¹) at chemical analysis centre, Iraq.

3. Result and discussion
3.1 Structure and Impurity Phases Characterization
Figure (2I) manifest XRD patterns for as-synthesized spinel powdered ZnFe₂O₄ samples, while Figure(2II) manifest XRD patterns for spinel powdered ZnFe₂O₄ ferrites that followed by calcination at 500 °C for (3hr.). In Figure (2I) for as-synthesized spine ZnFe₂O₄ ferrite when the glycine-to-nitrate ratio 0.66 crystalline phase structure is observed. peaks at 2θ values of 18.31°, 30.04°, 35.37°, 36.89°, 42.94°, 53.24°, 56.72°, 62.33° and 73.61° belong to the (111), (220), (311), (222), (400), (422), (511), (440) and (533) planes of spinel zinc ferrite, respectively that can be referred to the cubic-spinel structured matches via the standard (JCPDS card No. 22-1012) of Zn-ferrite. There are two extra peaks at 31.84°, and 47.61°, which belong to (220), (311), (222), (400), (422), (511), (440) and (533) planes of spinel zinc ferrite, respectively that can be referred to the cubic-spinel structured matches via the standard (JCPDS card No. 22-1012) of Zn-ferrite. There are two extra peaks at 31.84°, and 47.61°, which belong to (220) plane of ZnO. Good crystalline phase structure can be observed for S2 at glycine-to-nitrate ratio 0.5 as shown in the Figure (2I). As glycine-to-nitrate ratio decrease to 0.33, regular variation in the crystalline phase structure can be observed for S3 with tiny trace in phase structure ZnO compared with the other synthesized samples S1 and S2.

![Figure 2I. XRD pattern for as-synthesis powdered spinel Zn-ferrite at various glycine-to-nitrate ratio, (S1): G/N: 0.66, (S2): G/N: 0.50, and (S3): G/N: 0.33.](image-url)
Figure (2II) showed that as calcination at (500°C) for (3hr.) the diffraction peaks become sharper and narrower. This refers to the increase of the crystallinity. The full width half maximum of highest peak decreases with calcination at this temperature this mean that increased in the average particle size of the samples with calcination. Peaks of impurities with high crystallization were observed in the patterns in Figure (2II). The increase in the average crystallite size after calcination is because of the increase in nanoparticles size and/or small nanoparticles merge to form bigger particles. Similar observed in other search [15].

![Figure 2II. XRD pattern for powdered spinel Zn-ferrite at various glycine-to-nitrate ratio, (S1): G/N: 0.66, (S2): G/N: 0.50, and (S3): G/N: 0.33 followed by calcination at 500 °C for (3hr.).]

Structure parameters such as average particle sizes (D) and average lattice constant (a) were calculated from the higher intensity of (311) plane within XRD profile, in accordance with Scherer's equation and Bragg's law respectively [16].

Table 1. Structure parameters for synthesized samples of the spine Zn-ferrite by Microwave – assisted combustion method with different glycine-to-nitrate ratio before and after calcination at 500 °C for (3hr.).

| Sample | G/N ratio | a (Å) | XRDD (nm) |
|--------|-----------|-------|-----------|
| S1     | as-synthesized       | 0.66  | 8.407     | 15.8      |
|        | calcinated           | 0.66  | 8.440     | 23.03     |
|        | as-synthesized       | 0.50  | 8.391     | 23.70     |
| S2     | calcinated           | 0.50  | 8.440     | 27.05     |
|        | as-synthesized       | 0.33  | 8.427     | 26.53     |
| S3     | calcinated           | 0.33  | 8.434     | 28.16     |
From Table 1, it is clear that increase of average particle size as calcination at 500°C for 3hr. According to the study, annealing temperature generally reduced the lattice defects and strains. However, it has also been noted, that the effect of coalescence process of smaller grains, which takes place at elevated annealing temperatures relative to the time results in the increase in the average grain size of the nanoparticles. This is consistent with previous work that reported by P. Sivakumar et.al.[17]. Crystal lattice parameter and average particle size are directly related. Literature stating that, increasing in the particle size resulting in increase or decrease in the crystal lattice parameter [18]. In here we noted that if the average particle size increased the crystal lattice parameter will be decreased from (8.40-8.39)Å at glycine-to-nitrate ratio decrease from (0.66 - 0.50), but this decrease not continues where it is increase at glycine-to-nitrate ratio 0.33 without calcination. However the results in Table 1 indicate that the average particle size and crystal lattice parameter increase as calcination at 500°C for 3 hours. These results shown that there is remarkable change in lattice parameters with the calcination.

3.2. Morphological and Chemical Composition Analysis

The surface morphology and particle sizes for synthesized spinel ZnFe$_2$O$_4$ ferrite before and after calcination via various glycine –to-nitrate ratio were characterized via FE-SEM shown in the Figure (3I) and Figure (3II) respectively.
Figure 3I. FE-SEM images for as-synthesis powdered spinel Zn-ferrite at various glycine-to-nitrate ratio, (S1): G/N: 0.66, (S2): G/N: 0.50, and (S3): G/N: 0.33 followed by calcination at 500°C for (3hr.).

For as-synthesized samples S1 and S2 in Figure (3I) there are voids that can be seen very clearly. Depending on the earlier studies average crystallite size is related to the pH value. When the pH value is too high, there is a lot of gas that products during combustion process into microwave – oven leading to an increase in porosity and a decrease in average crystallite size. In addition to their agglomerated in particles due to the interaction between the magnetic nanoparticles. Similar result were observed by other researchers [17][19]. In contrast to the as-synthesized sample S3 that possess no avoids may be due to the fuel- low ratio. These results indicate that a change in the fuel amount lead to significant changes in the surface morphology of the powders. The FESEM images show that as-synthesized Zinc ferrite possess uniform, symmetry spherical-like particles. In Figure (3II), it is clear that the mentioned samples which are calcinated at 500°C for three hours that represent the homogeneous distribution of grain size in the nanometer region and grain range tend to be spherical in shape. FE-SEM images showed few voids and pores that can be seen very clearly. In addition, it is noted that the ferrite samples have agglomerates. which may be attributed to sintering process as a result of chemical reaction. It may be the duty of magnetic forces or weak Vander Waals bonds to tie these agglomerates together. Among reasons that illustrated morphologies of spherical-like particles:(i) the fuel and preparation route (ii) the lower surface-to-volume ratio for spherical-like particles. Second fact include the effect of morphology and grain boundary mobility on properties of the synthesized ferrites. Similar observed seen in reference [20].
3.3 Fourier Transforms - Infrared (FT-IR) Spectroscopy Characterization

The FT-IR spectra of all synthesized spinel ZnFe₂O₄ ferrite before and after calcination via Microwave–assisted combustion method with different glycine to nitrates ratio presented in Figure (4I) and (4II) respectively. The FTIR spectra of powdered spinel Zn-ferrites were recorded in the range 4000–450 cm⁻¹ (as pellets in KBr). In Figure (4) spinel ferrites structure shows major bands, $\nu_A$ and $\nu_B$. These two vibration bands are related to intrinsic stretching vibration for $\text{M}_{\text{Tet}} \leftrightarrow \text{O}$ and octahedral $\text{M}_{\text{Oct}} \leftrightarrow \text{O}$ sites. The band that appears between ($\nu_A, 500 \text{cm}^{-1}-600 \text{cm}^{-1}$) refers to tetrahedral - site, while the band that appears between ($\nu_B, 400 \text{cm}^{-1}-480 \text{cm}^{-1}$) corresponding to the octahedral - sites. Those bands are features of all ferrites. Peak at 1222 cm⁻¹ that is weak peak could be assigned to the C–O stretching due to adsorbed CO₂. The band between 1400 cm⁻¹-1500 cm⁻¹ is ascribed to a symmetric stretching vibration appearing from the residual nitrate. The peaks that appeared between (1605 cm⁻¹) represent C=O vibrations mode. There appears to be a peak at around at 3742 cm⁻¹ is assignable to O-H band from water, when the product powders were washed with distilled water after synthesis. Compared between Figure (4I) and Figure (4II), it is clear that no new bands appeared around the range of 600 cm⁻¹. Although it is not possible to use FT-IR for measuring particle size, FT-IR spectra will analyse the trend in particle size. As the particle size is raised, the absorption band of a specific band is transferred to a lower wavenumber. The shifting of absorption bands clearly shows, as calcination, the rise in particle size. These findings clearly support the results of the data from XRD. Similar observed seen in reference [2],[21],[22],[23],[24],[25]and [26].

**Figure 4I.** FT-IR spectra for as-synthesis powdered spinel Zn-ferrite at various glycine-to-nitrate ratio, (S1): G/N: 0.66, (S2): G/N: 0.50, and (S3): G/N: 0.33.

**Figure 4II.** FT-IR spectra for powdered spinel Zn- ferrite at various glycine-to-nitrate ratio, (S1): G/N: 0.66, (S2): G/N: 0.50, and (S3): G/N: 0.33 followed by calcination at 500 °C for (3hr.).
4. Conclusion
In summary, the results revealed to three things: (i) microwave-assisted combustion method with glycine as fuel provides a rapid, simple, low cost and environmental friendly route for the synthesis of spinel ferrites using inexpensive precursors. Spinel Zn-ferrite samples which synthesized by this route almost display agglomeration with avoids, (ii) accordingly, present work, the fuel (Glycine) quantity has a major impact on structure and morphology. Results of XRD refereed to cubic spinel-structure with space group Fd3m. average crystallite size is increase when glycine–to-nitrate ratio is decreased 15.8 nm to 26.53 nm, (iii) there are remarkable change in the structure and morphology of Zn-ferrite nanoparticles takes place at calcination of the synthesized powdered spinel ferrites at (500°C) for (3hr.). Average crystallite size is increase with calcination at 500°C for (3hr.) with homogeneous distribution of grain size in the nanometer region. In addition the shifting of absorption bands to a lower wavenumber proved as calcination.

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