Preparation of Nanoparticle Li-Ferrite Materials by Different Chemical Method

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Abstract

Lithium ferrite is one of promising material that has many applications in a civil field. Primarily, there are two chemical methods for preparation Li\textsubscript{0.5}Fe\textsubscript{2.5}O\textsubscript{4} spinal structure were dependent, represented by Low Temperature Solid State Reaction (LTSSR) and Modified Combustion Method (MCM) instead of freeze drying method that was used previously. The purpose of this research concentrated on how to produce nanoparticle of Li\textsubscript{0.5}Fe\textsubscript{2.5}O\textsubscript{4} spinal structure. The analysis those were used to investigate the aim of this research were X-ray Diffraction (XRD), and Transmission Electron Microscope (TEM). The phase and homogeneity of ferrite was proved by X-ray diffraction. The finite and homogenous powder was investigated by Transmission Electron Microscope (TEM). The results showed the MCM method is better than other one, because the first was the presence of pure phase of Li-ferrite whereas the LTSSR-method showed a multiphase. Regarding to TEM analysis, both methods were perfect in producing a fine particle size in the range (46-77 nm).

Keywords: Li-Ferrite, fine particle size, Williamson method, TEM-analysis

Introduction

The microwave properties of ferrites appear to have been first studied by Roberts [1], he observed that the non-reciprocal properties of ferrites as exemplified by the microwave faraday effect. Ferrites are compounds with the chemical formula MFe\textsubscript{2}O\textsubscript{4} where M is a divalent metal such as magnesium, manganese, nickel, zine, cobalt, iron, etc. The common ferrites have high resistivity of order (10^9 ohm.cm), combined with quite high initial permeability and saturation inductions of order (10^3 gauss) in comparable with (10^5 ohm-cm) and (10^4 gauss) for ferromagnetic metals. The properties which have made ferrites useful at radio and television frequencies also provide the key to their use a microwave frequency. Their high resistivity enables an electromagnetic wave to penetrate the martial and the magnetic field component of the wave can
thus interact with the magnetic behavior of the microwave of the microwave permeability of ferrite. The permeability exhibits a pronounced resonance at a frequency which is simply related to the strength of the applied magnetic field within the ferrite.

The spinel magnetic ferrites have been more considerable interest through the unique and versatile properties. The nanosized particles play an important role in the electrical and magnetic behaviors compared to that of the bulk counterparts [2]. Lithium ferrites spinel structure have become important materials for the microwave applications such as circulators, isolators, and phase shifters due to their high resistivity, low dielectric losses, high Curie temperature, square hysteresis loop, and low cost rather than garnets were used for microwave devices[3-7]. The diverse properties of spinel Li-ferrites originate from their ability to incorporate a variety of transition metalcations into their lattice, causing a subsequent change in their structural, optical, magnetic, and electrical properties [8,9]. Lithiumferrite and their properties are found to be strongly dependent on the preparation conditions represented by; method of preparation, sintering time, sintering temperature, pH value

There are many methods used to synthesis nanoparticle size of spinel ferrites such as co-precipitation, sol-gel, microemulsion, hydrothermal, and citrate gel[10, 11]. In the preparation of lithium based ferrites, low temperature sintering is needed to suppress lithium volatility and oxygen loss during sintering. Many researchers proposed that the citrate gel method is a simple route to synthesize materials in the form of nanoparticle by lower sintering temperature, those were investigated by studying the properties of several ferrites [12-14]. This research is a part of huge project concentrated on a spinel Li-ferrite structure; the first stage of this project was concentrated how to produce a nanoparticle of Li-ferrile spinel structure by using two chemical preparation methods. Low Temperature Solid State Reaction (LTSSR) and Modified Combustion Method (MCM) both were used and find the better one through the results of XRD and TEM. The factors those were dependent in the comparison between two methods, the presence of pure Li-ferrile spinel structure and nanoparticle and homogenous particle size.

**Experimental procedure**

The synthesize of Li-ferrite powder by LTSSR-method [15,16], was depends on the chemical reagents, ferric chloride (FeCl$_3$.6H$_2$O), lithium chloride (LiCl$_2$.6H$_2$O) and sodium hydroxide (NaOH), which provided with high purities. Appropriate amounts of above powders were mixed in stoichiometric ratios (1:2:8) by the following chemical equation. The mixture was milled at room temperature for 30 minutes in an aqueous molarity.

\[
\text{LiCl}_2+2\text{FeCl}_3+8\text{NaOH} \rightarrow \text{Li}_0.5\text{Fe}_{2.5}\text{O}_4+4\text{H}_2\text{O}+8\text{NaCl}
\]

The preparation of the powder done by different pH-value, (pH=0,3,10). The reaction started readily during the mixing process, accompanied by release of abundance of heat, and the mixture gradually grew from mushy to colloidal. The drying at room temperature, the mixture was washed by distilled water several times. Finally, the products were collected by filter and the precipitates were dried in an oven at (100 °C) for (3hr). The synthesized Li-ferrite Li$_{0.5}$Fe$_{2.5}$O$_4$ was then annealed at (500°C) for (5hr), and other sample annealed at (700 °C) for (5hr), to produce a final product.

The second method was applied, MCM-method [17], by using citric acid as a fuel for combustion reaction to produce a spinel structure of Li$_{0.5}$Fe$_{2.5}$O$_4$. Li-nitrate and Fe$^{3+}$-nitrate nonahydrate were used as starting materials. An aqueous solution of mixture was applied with additional excess of Li-ions by (3%) in molarity. These excess of Li-cations was happened in order to avoid the formation of hematite that was
found as a second phase with ferrite when the cation molar ratio is stoichiometric. Later, the citric acid was added to the precursor solution with the metal to citric molar ratio by 1: 1. The solution was mixed and then slowly dried in oven at (100°C) for (10 hr) in order to undergo dehydration. After cooling down to room temperature, the dried gel was sintered at (250 °C) for (12 hr) in order to induce gel decomposition. The further annealing was in air at (700 °C) for (5 hr). The synthesized products by two methods were characterized by XRD with CuKα1-line and (λ=1.5405 Å). The range of analysis was (2θ=10-60), and the working voltage was 40 kV and the current was 40 mA. The transmission electron microscopy (TEM) was used also to observe the morphology and the size distribution of the nanoparticles for the spinel structure Li-ferrite produce by two methods. The comparison between two preparation methods was summarized by the results of XRD and TEM.

Results and Discussion

The procedure that was dependent to investigate the nanoparticle of Ferrite phase for both preparation methods was represented by XRD and SEM analysis. The XRD for the samples prepared by LTSSR-method is shown in Fig. 1-3, with different ph-values. The results showed that there were multiphase related to presence a strange peaks or non-coincidence with ASTM date of Li-Ferrite. Whereas, the sample prepared by MCM-method for different ph-values as shown in Fig. 4,5. It was clear that the XRD-patterns exhibited the presence of pure phase for Li-ferrite as spinal structure. That was returned to coincidence the peaks of X-ray patterns, with ASTM data of Li-ferrite. It was clear to expect that the phase might be appeared with slightly variation in the lattice constants. It was clear that the prepared samples exhibited a pure phase of Li-ferrite as cubic spinal structure of Li_{0.5}Fe_{2.5}O_{4} phase. The comparison in the patterns of XRD for the samples was prepared by LTSSR as shown in Figs.1-3. There is a hematite cubic phase with long lattice constants concluded from the analysis of Fig.1, the lattice constant was (a=33.038 Å). While the samples prepared by LTSSR with different ph-values showed impure cubic phase of ferrite, as exhibited in Figs. 2,3, related to presence of undefined peaks within the range (2θ=37-45). The thing was noticed is the decreasing the intensity of those peaks as the ph-value increased, that means the increasing of ph-value tend to produce a single phase of spinel ferrite. In spite of the presence of impure ferrite phase but predominate one was spinal cubic structure with lattice constant (a=8.3260Å), and (a=8.3424Å) concluded from Figs. 2,3 respectively. This variation in the lattice constants return to slightly variation in 2θ. On the other hands, the lattice constant of spinal cubic structure concluded from Fig. 2, is more approaching from the real one which are (a=8.328 Å) with the space group is P4332.

The results of XRD-patterns for the samples prepared by MCM method, as shown in Figs. 4,5. The pure phase of Li-ferrite with cubic spinal structure appeared during the coincidence of the diffracted peaks with ASTM data, and there are no strange peaks as appeared before. The second thing, the calculated values of lattice constants were (a=8.3219Å) for ph-value=3 and (a=8.3372Å) for ph-value=10. Both results are more coincidence with theoretical one. There is another benefit from x-ray analysis represents by using Williamson method to determine the particle size of the powder produced. It was clear that the particle size was (24.08±3.65 nm) it was smaller than the value calculated by Rezlescu et al [18], and strain ratio of about 0.095±0.102, as clear in Fig. 6. The TEM analysis for both LTSSR and MCM methods are shown in Fig. 7a-c, and Fig. 8 a,b respectively. The analyses of the TEM photograph, for both methods, were exhibited the homogeneity of the particle size with the average size in the range (46-77 nm). It was clear that the best sample prepared regarding to the nanoparticle size in the range (46-48 nm) which are nearly twice of the theoretical value calculated Williamson method. It was higher than the values concluded by Amiri et al [15] and Jovic et al [17] with the same procedure respectively. This results is play an important role in producing
this material as a good solvent to get a paint solution for microwave absorption. That is tending to produce a high efficient solvent material for painting.

![Figure 1](image1.png)

**Figure 1:** Indicate the X-ray pattern for the sample prepared by LTSSR method

![Figure 2](image2.png)

**Figure 2:** Indicate the X-ray pattern for the sample prepared by LTSSR method with pH=3

![Figure 3](image3.png)

**Figure 3:** Indicate the X-ray pattern for the sample prepared by LTSSR method with pH=10.
Figure 4: Indicate the X-ray pattern for the sample prepared by MCM method with ph=3.

Figure 5: Indicate the X-ray pattern for the sample prepared by MCM method with ph=10

Figure 6: indicate the application of Williamson method to calculate the particle size
Figure 7; Indicate the analysis TEM photo for the sample prepared by LTSSR, the average particle size is (a) 77.4 nm, (b) 48.1 nm, (c) 46.3 nm.

Figure 8; Indicate the analysis TEM photo for the sample prepared MCM method, the average particle size is (a) 69.7 nm, (b) 57.6 nm.
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