Crystallite Size-Lattice Strain Estimation and Optical Properties of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ Nanoparticles

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Abstract. In the present work, we performed William-Hall plot using uniform deformation model (UDM) to estimate the crystallite size and lattice strain of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ with various calcination temperature. The calculated crystallite sizes are 25.86 nm, 29.55 nm and 24.97 nm for nanoparticles which were calcined at a temperature of 600°C, 800°C and 1000°C, consecutively. The strain of nanoparticles has value in the order of 10$^{-3}$. Controlling the calcination temperature will facilitate a change in crystallinity of nanoparticles and influence their crystallite size and strain of the crystal lattice. The optical band gap energy of samples nanoparticles is in a range of 1.09 eV – 3.30 eV. Increasing calcination temperature increased the direct and indirect band gap energy. The Urbach energy was found to increase with increased of gap energy. These results demonstrated that higher structural and optical properties of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ can be obtained from a higher calcination temperature.

1. Introduction

Ferrite nanocrystalline semiconductor such as Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ has been widely studied because the need for materials which have excellent magnetic and optical properties for data storage media [1]. For this reason, since a decade Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ has gained a great interest of many researchers. The Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrite nanoparticle possesses a cubic close-packed crystal structure with FCC bravais lattice. These cations both divalent and trivalent are distributed in two crystal sites such as tetrahedral and octahedral sites. Specifically, the preferred site of those cations in an entire crystal structure of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ is in accordance with the cation distribution rule of mixed-spinel structure [2]. The cation distribution is practically affected by the preparation method, calcination temperature and addition of proper cations into the spinel structure [3,4,5,6]. Those factors generate a migration of cations between the two sites and possibly cause defect and deformation of a lattice. Lattice defect and deformation can be in form of lattice strain and lattice dislocation. Physically, lattice strain is in connection with the optical properties of nanoparticles as a study reported by Sheena et al [5]. For this reason, studying the lattice strain of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles and the method for its estimation is very important for understanding the electronic structure as well as its optical and magnetic properties. In the previous work, we had performed a study about the effect of calcination temperature on vibrational spectra and magnetic properties of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles [7]. The particle size of nanoparticles was calculated by using Scherrer’s equation. The Scherrer’s equation gives rougher crystallite size estimation because it doesn’t take attention to the contribution of strain and instrumental correction on diffraction peak broadening [8]. In the purpose for addressing the effect of lattice strain on the microstructure of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles, herein we perform a study of crystallite size and lattice strain estimation using William-Hall (W-H) plotting method with uniform
deformation model (UDM). In addition, the crystallite size of nanoparticle obtained by UDM was compared with the Scherrer’s equation. Furthermore, the optical properties of Mn₀.₅Zn₀.₅Fe₂O₄ nanoparticles were also studied in relation to the lattice strain which was tuned by calcination temperature.

2. Experimental Method

2.1 Preparation and Characterization of Mn₀.₅Zn₀.₅Fe₂O₄

Samples of Mn₀.₅Zn₀.₅Fe₂O₄ nanoparticles with difference calcination temperature were synthesized by using coprecipitation method such as reported by [6,7]. The calcination temperatures used in this study were 600°C, 800°C and 1000°C. The samples were characterized by their microstructural parameters using XRD technique. The optical properties of samples were characterized by using diffuse reflectance UV-visible spectrophotometer.

3. Result and Discussion

3.1 XRD Analysis

In a previous study [7], we had performed the diffraction pattern of Mn₀.₅Zn₀.₅Fe₂O₄ nanoparticles with various of calcination temperature. In accordance with those patterns, we can estimate the crystallinity and structural characteristics of Mn₀.₅Zn₀.₅Fe₂O₄ matrix along with the texture coefficient (TC). A study of TC was carried out by considering the grains of nanoparticle which have certain preferred orientations and are diffracted by X-ray as diffraction planes. A single crystalline material possesses a preferred orientation while a polycrystalline material possesses some preferred grain orientations. Physically, TC value informs the distribution of crystallographic orientations. The TC value also informs the degree of crystallinity of samples. Sample with high TC values (TC > 1) has the high degree of crystallinity. Practically, TC determines the comparison between relative intensities of the observed peak with those of the standard powder diffraction intensities of the same compound [9]. The calculation of TC can be carried out by using equation 1 [9],

\[
TC(hkl) = \frac{I(hkl)/I_o(hkl)}{(I/N) \sum_{n=1}^{N} I_n(hkl)/I_{o,n}(hkl)}.
\]

The \(I_o(hkl)\) determines the intensities of standard powder diffraction for the \((hkl)\) diffraction plane. The \(I(hkl)\) is the relative intensity of the observed peak, while \(N\) determines the number of the observed diffraction peak in X-ray diffraction pattern. The TC \((hkl)\) values of sample Mn₀.₅Zn₀.₅Fe₂O₄ with various calcination temperatures can be displayed in Figure 1.

![Figure 1](image-url)
Figure 1 shows the variation of texture coefficient for three system of the planes of the matrix. If the value of TC (hkil) ≈ 1 for all the diffraction planes (hkil), then the sample nanoparticles are randomly oriented crystalline such as the standard powder (JCPDS). The results are shown in Figure 1 confirmed that the diffraction plane of (311) has the highest value of TC (hkil) ascribed that this direction is the highest preference orientation of grains. The peaks of (220), (400), (422) and (511) for samples calcined with 600°C and 800°C have TC (hkil) in range of 0 to 1. This indicates the lack of grains to orient in those directions. As increasing calcination temperature, the TC (311) increases, the preferential growth of crystallites in this direction which is perpendicular to (hkil) plane is greater [9]. Consequently, increasing the calcination temperature will facilitate tuning the crystallinity of nanoparticles.

The estimation of crystallite size and lattice strain have been done by using W-H plot with uniform deformation model (UDM). Mathematically, the UDM can be represented by equation 2 [10],

\[
\beta_{hkil} \cos \theta = \left( \frac{k \lambda}{d} \right) + 4e \sin \theta \tag{2}
\]

where \(d\) is the crystallite size of nanoparticles, \(k\) is the Scherrer’s constant (≈ 0.89); \(e\) is the lattice strain; \(\beta_{hkil}\) is the broadening of the diffraction peak measured at FWHM (in radians); \(\lambda\) is the wavelength of X-Ray (1.5406 Å) and \(\theta\) is the diffraction angle of peak. Plots are drawn between term \(4\sin \theta \) (X-axis) and term \(\beta_{hkil} \cos \theta \) (Y-axis). The results can be displayed in Figure 2 and Table 1.

![Figure 2. W-H plot of Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) calcined at temperature 600°C (a), 800°C (b), 1000°C (c) and the relation between crystallite size-strain nanoparticle and calcination temperature (d).](image)

### Table 1. Crystallite size and strain of Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) with Scherrer and W-H UDM method.

| No. | Calcination Temperature (°C) | Scherrer’ crystallite size (nm) \(^{(a)}\) | W-H UDM Crystallite size (nm) | Strain \((x10^{-5})\) |
|-----|-----------------------------|---------------------------------------------|------------------------------|---------------------|
| 1   | 600                         | 18.30                                       | 25.86                        | 1.2                 |
| 2   | 800                         | 24.80                                       | 29.55                        | 0.4                 |
| 3   | 1000                        | 22.30                                       | 24.97                        | 0.3                 |
Figure 2a – Figure 2c show that all data are poorly linear. These linear trendlines are really poor compared than result reported by [11]. The results reported by [11,12] also show that UDM method give worse linear trendline of the data than Size-Strain Plot (SSP) method. This suggests the use of SSP method to obtain better result. The crystallite sizes of nanoparticle which have been calculated by using the UDM were greater than Scherrer method. These results agree with the calculation reported by [7,9,10]. Nanoparticles size estimated using Scherrer’s equation is quite different from that obtained by WH plotting. This difference due to the strain that can induce a greater broadening in the diffraction peak [11]. Figure 2 shows that there are positive and negative slopes in the plots. The positive and negative slopes indicate the existence of compressive and tensile strain on the lattice of nanoparticles [10]. The crystallite size of nanoparticles decreased with an increase of calcination temperature due to the densification process exhibited by nanoparticles.

3.2 Optical Properties of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$

The optical properties of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles can be represented by the UV-visible absorbance spectra, absorption index and the Urbach energy such as Figure 3. There are two absorbance peaks found in each absorbance spectra. The maximum electronic excitation occurs at a wavelength of 341 nm for sample calcined at a temperature of 600°C. Hence the wavelengths of 348 nm and 327 nm were found to be the maximum electronic excitation for sample calcined at a temperature of 800°C and 1000°C, consecutively. Small absorbance peaks at 493 nm, 446 nm, and 436 nm were found due to scattering effect of photon and surface defect of crystal nanoparticles [9].

By plotting of the absorption index against wavelength as shown in Figure 3(b) indicating that the absorption index of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ is very small (in order of $10^{-5}$). These small values of the absorption index indicate the low and weakly absorption were possessed by the samples [9]. The optical gap energy of nanoparticles is determined by using Tauch’s plot which represented by the equation 3 [9] and displayed in Figure 4,

$$ahv = \left( \frac{A}{t} \right)hv = B(hv - E_g)^n$$

where $a$ represents the absorption coefficient, $hv$ is the photon energy, $A$ is the normalized absorbance, $t$ the sample’s thickness, $E_g$ is the optical gap energy, $B$ is an energy independent constant and $n$ is a constant which represents the optical transitions of electrons in electronic band edge of nanoparticles. The $n = 2$ for the indirect allowed transition and $n = \frac{1}{2}$ for the direct allowed transition. The direct optical band gap energy of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles increased with an increase of calcination temperature. This direct gap energy facilitates electron to excite from valence band to conduction band with the same wavenumber $k$. The Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles show two indirect optical band gap energies. Their values are smaller than direct optical gap energy. These energies are
needed by the electron to excite from valence band to near conduction band edge via phonon with different wavenumber \( k \). Increasing calcination temperature is followed by increase indirect optical band gap energy due to change in the electronic band structure of nanoparticles during calcination. In fact, the \( E_g \) value changed as the \( E_u \) value changes. The \( E_g \) value increased when the \( E_u \) value increased. Therefore, the excited electron preferred to transit from the valence band to the band tailing.

**Figure 4.** Direct optical band gap energy (a) and indirect optical band gap energy (b) of \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles for each calcination temperature of 600°C, 800°C and 1000°C.

4. **Conclusion**

The crystallite size and lattice strain of \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles with different calcination temperature have been successfully estimated by using the W-H plotting with the UDM method. The calculated crystallite size is greater than that obtained by using Scherrer’s formula due to the contribution of strain which facilitates defect and lattice imperfection of nanoparticles. The prepared \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles have weak absorption ability to the UV-visible radiation and low optical band gap energy which depend practically on the calcination temperature.

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6. **References**

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