Study of structural and optical properties of the ferrite films prepared by chemical pyrolysis spray technique

Gh. J. Alyasary¹, H. H. Almarmade² and D. h. Altiee¹

¹University of Al-Qadisiyah College of Education/Dep. of Physics.
²University of Sumer College of basic education.

Ghafran.altiee@gmail.com, sumer55noor@gmail.com

Abstract. Copper-zinc ferrite (CuFe₂O₄) films have been deposited successfully by spray pyrolysis technique. Ferrite films deposited of thickness (450 ± 15nm) at temperature (400 ± 10 °C) and annealing (600 °C) for range of (4h). The compound was doping with zinc at rates (x= 0,0.2,0.4). The crystalline structure of the prepared films was determined Tetragonal a spin Ferrite in peak (211), and when it was doping with zinc, it turned into cubic in peaks (311). The particle size was found to decrease by increasing the concentration of (Zn). The optical properties have been identified of films wavelengths of (300-900) nm. The results showed that the transmittance for all thin films increases as the wavelength increases then saturates at higher wavelengths.

1. Introduction

The Formula AB₂O₄ refers to spinal ferrites are very big class of oxides with very large application in industry from simple permanent magnets to microwave application, magnetic recording, gas sensors[1]. The relative control of the magnetizations of the layers in these devices necessitates to spin the magnetization of the layers this is due to by magnetically coupling this sheet to a hard one[2]. To deposition thin films of ferrite[3], scientist have find a number of methods such as plating ferrite, sol-gel method, Chemical method[4], electro deposition method, sputtering, RF sputtering and spin spray pyrolysis[5]. Microstructure of thin film is an important parameter in determining their magnetic[6]. There are various growth parameters that affect the microstructure of the films like substrate temperature during deposition [7], Thermal expansion coefficient and lattice mismatch between the target and substrate [8].

2. Experiments

ZnₓCu₁₋ₓFe₂O₄ thin films with (x=0.0,0.2,0.4) of thickness (450 ± 15nm) were prepared by spray pyrolysis technique on substrate of SiO₂/Si at (400±10°C) substrate cleaning plays an important aim in the deposition of thin films because for the chemical deposition as the contaminated surface provide nucleation sites facilitating growth resulting into non-homogeneous film with different orientation and impurities ZnₓCu₁₋ₓFe₂O₄ thin film were prepared by spray pyrolysis technique, Analytic reagent grade chemical (Fe(C₂O₄)₂·2H₂O), (ZnCl₂) (Cu(NO₃)₂·3H₂O) were used as raw materials, solutions were dissolved separately in de-ionized water at the concentration of (0.0 2) M for Zn²⁺ final solution were prepared by mixing these three solution in 1:2 with the ration of (x=0.0,0.2,0.4).
\[ \text{ZnCl}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{heat}} \text{ZnO(s)} + \text{Cl}_2(g) + \text{H}_2\text{O(l)} + \text{H}_2(g) \]  \quad \ldots \quad (1)

\[ \text{2Cu (NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O} \xrightarrow{\text{heat}} 2\text{CuO(s)} + 4\text{NO}_2(g) + 3\text{H}_2\text{O(l)} \]  \quad \ldots \quad (2)

\[ \text{Fe(C}_2\text{O}_4)_2 \rightarrow \text{FeO(s)} + \text{CO}_2(g) + \text{CO}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s) + 1/2 \text{O}_2(g) + \text{heat} \rightarrow \gamma \text{-Fe}_2\text{O}_3 \]  \quad \ldots \quad (3)

\[ (1-x)\text{ZnO} + (x)\text{CuO} + \text{Fe}_2\text{O}_3 \xrightarrow{\text{heat}} \text{Zn}_{(1-x)}\text{Cu}_x\text{Fe}_2\text{O}_4 \]  \quad \ldots \quad (4)

3. Results and Discussion

3.1. Structure properties

From figure (1) X-ray diffraction results showed that all films were prepared by chemical pyrolysis spray method were spinal ferrite. The diffraction patterns corresponding after annealing reveal that the film crystallize in polycrystalline preferred orientation along (211) plan type of tetragonal. When it was added (Zn\(^{2+}\)) it turned into (cubic) in peaks (311). The lattice constant was calculated for pure Cu Fe\(_2\)O\(_4\) films. The results in Table (1) were found to have increase value than the deflection ratio. The average size was calculated with the increase in the ratio of fouling and according to the results listed in Table (1) because the radius of the ionic atom of the copper is smaller than the radius of the ionic atom of the zinc of the crystal and thus reduce average size. The lattice constant \(a_o\) calculated from equation [9,10]:

\[ a_o = d \sqrt{h^2 + k^2 + l^2} \]

The average crystallite size (\(D\)) was calculated by using Scherrer’s formula [11,12].

\[ D = (0.9 \times \lambda) / (\beta \times \cos \theta) \]

where, \(\lambda\) the wavelength of X-rays (1.5406 \(\text{Å}\)), \(\beta\) is the full-width at half-maximum in radian and \(\theta\) the angle of diffraction. It is seen that as the Zn content increases the crystallite size decreases from 17.44 to 14.96 nm.

![Figure 1. X-ray diffraction patterns.](image-url)
3.2. Optical properties

3.2.1. Transmission (T)

Figure (2) shows the relation between transmittance and wavelength in the range of (300 - 900) nm for Cu-Zinc Ferrite films. The transmittance for all thin films increases as the wavelength increases in the wavelength range of about (300-600) nm, and then saturates at higher wavelengths. This material is good in absorbance at wavelengths of (300-600) nm so it can be used in the work of reagents or solar cells. The spectrum shows high transmittance in the visible and infrared regions, and low in the ultraviolet region.

### Table 1. Lattice constant (a), crystallite size (D<sub>ave</sub>).

| x-value | Lattice Parameter | D   |
|---------|-------------------|-----|
|         | (A°)              | (nm) |
| 0.0     | a= 5.8005, C=8.5985 | 17.44 |
| 0.2     | 8.39              | 15.92 |
| 0.4     | 8.42              | 14.96 |

3.2.2. Absorbance (A)

The variation of the absorbance spectrum with wavelength is opposite to the transmittance spectrum. The study of absorbance was in the range of (300–900) nm. Figure (3) shows the relation between absorbance (A) and wavelength for Copper-Zinc Ferrite thin films. It is clear that absorbance decreases rapidly the wavelength increases in the wavelength range of about of (300-600) nm, and then decreases slowly at higher wavelengths.
It can be noticed that the absorbance decreases as the concentration of Zinc increases and this can be attributed to the localized conductivity levels introduced by Zn$^{2+}$ cations.

![Absorbance vs Wavelength](image)

**Figure 3.** Absorbance (A) versus wavelength (λ).

### 4. Conclusion

The results obtained from the study of the structural characteristics of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ films and in terms of (0,0.2,0.4) showed that the process of attribution to the variable of the nature of crystalline structure, The prepared films are Tetragonal type the preferred direction(211)When doping with (Zn$^{2+}$) Turned into cubic type the preferred direction (311). From the optical properties found increase in transmittance and decrease in absorbance which meant an improvement in crystalline structure.

### Reference

[1] D. K. Pawara, S. M. Pawarb, P. S. Patil and S. S. Kolekara, "Synthesis of Nanocrystalline Nickel–Zinc Ferrite(Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$) Thin Films by Chemical Bath Deposition Method", Journal of Alloys and Compounds, Vol. 509, pp. 3587-3591, (2011).

[2] Anuj Jain, Ravi Kali, Baranwal, Ajaya Bharti, Z. Vakil and C. S. Prajapati, "Study of Zn-Cu Ferrite nanoparticles for LPG sensing", Journal of the scientific world, NO., PP., (2013).

[3] A. Manikandan, J. Judith, Vijaya, L. John, Kened and M. Bonoudina, "Structural, optical and magnetic properties of Zn$_{1-x}$Cu$_x$Fe$_2$O$_4$ nanoparticles prepared by Microwave combustion method", Journal of Molecular Structure, vol. 1035, pp. 338-340, (2013).

[4] S. S. Kumbhar, M. A. Mahadik, V. S. Mohite, K. Y. Rajpure and C. H. Bhosale, "Synthesis and Characterization of Spray Deposited Nickel-Zinc Ferrite Thin Films", 4th International Conference on Advances in Energy Research, Vol. 54, pp. 599-605, (2014).

[5] P. J. Brown and J. B. Forsyth, "The crystal structure of solid", Arnold, (1973).

[6] M. Caglar, S. Ilican and Y. Caglar, "Influence of substrate temperature on structural and electrical properties of ZnO films", Trakya Univ. J Sci, Vol. 7, No. 2, pp. 153-158, (2006).
[7] A. T. Raghavender, N. H. Hong, E. Chikoidze, Y. Dumont and M. Kurisu, "Effect of Zinc Doping on The Structural and Magnetic Properties of Nickel Ferrite Thin Films Fabricated Pulsed Laser Deposition Technique", Journal of Magnetism and Magnetic Materials, Vol. 378, pp. 358-361, (2015).

[8] M.I. Khan, K.A. Bhatti, Rabia Qindeel, "Characterizations of multilayer ZnO thin films deposited by sol-gel spincoating technique", Journal of Results in Physics, No. 7, pp. 651-655, (2017).

[9] Liao DL, Badour CA, Liao BQ. Preparation of nano sized TiO2/ZnO composite catalyst and its photocatalytic activity for degradation of methyl orange. JPhotochem Photobiol A Chem 2008;194:11.

[10] S.N. Klausen, P.A. Lindgard, K. Lefmann, F. Bodker, S. Moorup, Phys. Status Solidi A, 189 (2002) 1039.

[11] R. Laishram, C. Prakash, Journal of Magnetism and Magnetic Materials, 305 (2006) 35. 24. Cao Jun-gang, Li. Jian-jun, Duan Hai-feng, Lin Ying-jie, Chem. Res. Chinese Universities, 28 (2012) 590.

[12] P. Priyadharsini, A. Pradeep, P. S. Rao, G. Chandrasekaran, Mater. Chem. Phys., 116 (2009) 207.